GRATING COUPLING OF SURFACE PLASMON POLARITONS AT VISIBLE AND MICROWAVE FREQUENCIES

Submitted by

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To the University of Exeter
as a thesis for the degree of
Doctor of Philosophy in Physics

NOVEMBER 1999

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I certify that all material in this thesis which is not my own work has been identified and that no material is included for which a degree has previously been conferred upon me.
The work presented here concerns the electromagnetic response of diffraction gratings, and the rôle they play in the excitation of surface plasmon polaritons (SPPs) at the interface between a metal and a dielectric. The underlying aim of this thesis is to build on the current understanding of the excitation of SPPs in the visible regime, and extend and develop these ideas to microwave wavelengths.

The position and shape of the resonance of the SPP is extremely sensitive to both the interface profile and the properties of the surrounding media and hence, by using a suitable grating modelling theory, this dependence can be utilised to parameterise the profile and optical properties of the media. Indeed, the first two experimental chapters of this thesis present the first characterisations of the dielectric function of titanium nitride, and non-oxidised indium using such a grating-coupled SPP technique.

Experimental reflectivities measured at visible frequencies are normally recorded as a function of the angle measured from the normal to the average plane of the grating surface, however this data becomes cumbersome to record at microwave wavelengths. Hence, a new technique is developed which requires no moving detector and records the reflectivities as a function of the angle between the plane of incidence and the normal to the grating grooves. These reflectivities are initially recorded from a silver-coated grating at visible wavelengths, but are also recorded from non-lossy metallic gratings in the microwave regime. A large amount of beam spread is inherent in microwave experiments, and therefore the apparatus is further developed to collimate the incident beam. Finally, two samples are considered where a dielectric grating is deposited onto a planar metal substrate. The data recorded from the first sample demonstrates that it is possible to couple microwave radiation to SPPs that propagate along the planar metal-dielectric interface. Furthermore, it demonstrates that if the dielectric is lossy, the absorption on resonance of the modes is greatly enhanced. The second study illustrates the novel result that with near-grazing incident radiation and with the dielectric-grating grooves orientated such that they are parallel to the plane of incidence, coupling is possible to SPPs at three different energies.
"He who asks a question is a fool for five minutes; he who does not ask a question remains a fool forever."

Chinese Proverb
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<td>Attenuated Total Reflection</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
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<td>GM</td>
<td>Guided Mode</td>
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<tr>
<td>PSD</td>
<td>Phase Sensitive Detector</td>
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ACKNOWLEDGMENTS

As a member of the Thin Film Photonics Group, a helping hand is never far away. I would like to take this opportunity to thank the many people, all of whom I can also call friends, who have assisted, encouraged and supported me throughout my PhD. The biggest thank you of all must go to my supervisor for the last three-and-a-bit years, Professor Roy Sambles. His enthusiasm for science and its understanding, and his enormous wealth of ideas never ceases to amaze me. Being called a “drongo” took a bit of getting used to, but then I realised that everyone, including academics, are “drongos” from time to time! Another huge thank you must go to my external supervisor at DERA (Farnborough), Dr Chris Lawrence, who secured the funding and provided the necessary equipment in order to undertake the experiments. Well, all the equipment apart from the metallic underpants I’m still waiting for! By the way, if you ever go bowling with him, make sure he plays with normal balls – apparently his have target-seeking mechanisms! Thanks also to Dr Bill Barnes, who acts as an excellent Roy substitute when the Big Man is away. I am also indebted to the work and suggestions of the team of “technicians” who have designed, built, modified and re-modified so many bits and pieces of equipment on my behalf. Particular thanks to Pete Cann (The Man) and Steve Tuckett, but also to Kevin White, Phil Vossler, Melvyn Gear, Dave Jarvis and Ron Clarke. Also thanks to John Meakin for chasing after me when I fill in a form incorrectly, and to Barry “in stores” Elston for the glue that doesn’t stick and the permanent pens that aren’t! The secretarial staff deserve a big acknowledgement too, that’s Margaret, Jennifer, Denise, Shirely and Val. Thanks also to Dr Jefferey Jones (University of Exeter), Hrant Azizbekyan (Engineering Center of the Armenian National Academy of Sciences) and Alex Smout (DERA Malvern) who have helped me with the titanium nitride, indium and azimuthal-angle studies respectively.

But how can I forgive… sorry - forget(!) all the friends I have made within the Thin Film Photonics group. Thanks to old-boy Mikey J (the man with a worse hair-cut than me, but I’ve never told him that!). Your stories never fail to make me chuckle… no matter how many times I hear them! Sorry if I’ve ever annoyed you with all my questions – you really have been a great help. From one veteran to another, Pete “now
with wings” Vukusic, for setting Mike J straight on many of his stories. To my colleagues in that strangely uncivilised end of the lab they call “Group 13”. That’s Piers “Ovinus Worrius” Andrew and Phil “I love JS too” Worthing for helping me to understand what I’m supposed to be doing. Also thanks Martin “it’s not a race” Salt, John “scary but nice” Wasey, and Pete “small but nice” Hobson. May you each flood the basement at least once a year forever more! Moving back into Group 20 land, I would like to say thanks Benny “sandwich boy” Hallam, who when he joined the group was polite and sensible, by lunchtime he was as bad as the rest of us. To Dominic “Quick shot” Mikulin who put up with me sitting opposite him for the first year, and Nathan “XS” Smith for serving time for the last two years. To the Man from Japan, Nobuharu Okazaki, for providing hours of entertainment and to Alan Brady for putting up with his antics! To Mike “the sensible Scotsman” Linehan, and to Ben “nice jumper” Hodder. (Ben, if you ever need someone with good musical tastes in your band then let me know!) To Richard Watts, who, when he wasn’t writing papers found time to teach me how to do an angle scan, again and again and again! To housemate “H” (no, not the one from Steps, but Hazel Went) for putting up with my bad habits, and to Ian Hooper and his many friends! To Nick “the cardboard soldier” Wanstall for helping me with bits of computer code, and to the other theoreticians, the “odd couple” (although now divorced), Binoy Sobnack and Weichao Tan.

To my science teachers at Wells Cathedral School for teaching it so well, and to all my non-physics friends for paying an interest in what I do (and no, I don’t want to go into medicine!)

Also, to the Defence Evaluation and Research Agency (DERA), Farnborough for their financial support of this work, which has been carried out as part of Technology Group 08 of the MoD Corporate Research Programme.

To my girlfriend Helen for her support and love, and for helping me to put everything into perspective. Our six 6 years together have been so enjoyable – long may they continue!

Finally, to my Mum and Dad for financing my education. A huge thank you to them both and my sister for all their love, encouragement and support.
CHAPTER 1

Introduction

The work presented in this thesis concerns the coupling of incident radiation to the surface mode that propagates along the interface between a metal and a dielectric. This mode is known as the surface plasmon polariton (SPP) and its excitation was first experimentally observed in the spectra from ruled diffraction gratings by Wood in 1902. Chapter 2 presents a brief historical overview of the developments in the understanding of the physics describing the SPP. A derivation of the planar-interface dispersion relation of the SPP is presented, and the spatial extent of the fields associated with the mode are examined. This demonstrates that the mode is non-radiative, and consists of longitudinal oscillations of surface charge whose fields are well confined to the interface. Methods for coupling radiation into the mode are described, with particular emphasis on grating-coupling (since this is the method employed in experiments presented here). In addition, the phenomena of SPP mediated polarisation conversion and grating-induced band gaps are discussed.

Chapter 3 describes the influence of the interface profile and properties of the surrounding media on the reflectivity from grating samples. This is achieved by introducing the theoretical model based on the formalism of Chandezon et al. (1982) that is used herein. By modelling the electromagnetic response of gratings samples, it is demonstrated that the propagation of the mode and the shape and position of its resonances are extremely sensitive to the properties of the interface and its surroundings. Since three of the experimental chapters presented here consider the response of metallic samples at very low (microwave) frequencies, particular attention is made to the properties of near-perfectly conducting samples.

Chapters 4 and 5 demonstrate how the sensitivity of the SPP to its surroundings may be exploited to determine the optical properties of metals. By fitting the zero-order, polar-angle dependent reflectivities from metal-coated diffraction gratings (of suitable pitch and depth) to the predictions from the modelling theory described in Chapter 3, the complex dielectric functions of titanium nitride (Chapter 4) and indium (Chapter 5) are determined throughout the visible regime. Since indium is easily oxidised in
air, a sample geometry is used in which the SPPs are excited at a protected silica-
indium boundary. The experimentally determined complex dielectric functions for
both materials are compared with a simple Drude model, and a more sophisticated
Drude-Lorentz model, in order to obtain approximate values for the metals’ relaxation
times and plasma frequencies.

Chapter 6 presents a new technique for recording the zero-order reflectivity from a
sample as a function of the angle of azimuth. This is a generally useful technique
since, unlike the more conventional polar angle of incidence scans used in Chapters 4
and 5, it involves no moving signal detector. The technique is used to record the
response of a silver-coated diffraction grating at a range of polar angles of incidence,
and the data are successfully fitted to the grating modelling theory. The work
presented in the chapter tests the validity of the conical diffraction theory [Elston et
al. (1991 a,b)], and provides an accurate characterisation of the grating profile.

 Chapters 7, 8 and 9 each represent work undertaken in the microwave regime at
frequencies between 26.5 and 40 GHz, and use a scaled up version of the apparatus
developed in Chapter 6. This technique is particularly advantageous at these much
longer wavelengths since polar angle scans are particularly cumbersome due to the
large area swept out by the signal detector. In Chapter 7, the reflectivities from both
singularly and doubly corrugated samples are presented, where the corrugation is
milled directly into a near-perfectly conducting metal substrate. By developing an
apparatus that provides a well-collimated incident beam, excellent agreement is
achieved between the experimentally recorded data and the predictions from the
grating modelling theory.

The responses of corrugated dielectric overlayers deposited upon planar metal
substrates are considered in Chapters 8 and 9. With such samples, the interface that
provides the coupling mechanism, and the interface along which the SPP propagates
are separated. The dielectric material used is petroleum wax, which, in the available
frequency range, is found to have a similar refractive index to glass at visible
frequencies. Due to the ease with which the grating profiles can be cut into the wax
compared to milling them directly into the metal substrate, this coupling technique
presents an advantage over the more conventional geometry. The average thickness
of the dielectric layer studied in Chapter 9 is too small to be able to support guided modes, however such modes, in addition to the SPP, are supported by the thicker sample studied in Chapter 8. The effects of non-zero $\epsilon'$ (where $\epsilon = \epsilon' + i\epsilon''$) in the dielectric are theoretically investigated for the sample used in Chapter 8, and the degree of absorption is shown to be greatly enhanced on resonance of well-coupled modes. Chapter 9 presents the novel result that when a near-grazing beam is incident on the sample with its grooves orientated such that they are parallel to the plane of incidence, coupling to the SPP is possible with both p- and s-polarised radiation at three different energies. The identity of each of the modes excited at the three energies are confirmed as the resonant excitation of the SPP and an explanation is provided for their coupling conditions by modelling their electric field profiles and their dispersion with frequency and in-plane momentum. In both these chapters, good agreement is obtained between the experimentally recorded reflectivities, and the theoretically modelled results.

Finally, Chapter 10 contains a summary of the work presented in this thesis, possible ideas for future work, and a list of publications arising from the studies presented here.
CHAPTER 2

A review of the properties of radiatively coupled surface plasmon polaritons.

2.1. Introduction

In this chapter some of the physics and properties of surface plasmon polaritons (SPPs) propagating on planar and corrugated surfaces are briefly described. The dispersion relation for the propagation of the SPP on a planar metal-dielectric interface is derived and the spatial extent of the electric fields associated with the mode is explored. This demonstrates that the mode is non-radiative in the planar-interface limit, and consists of a longitudinal oscillation of surface charge whose fields are well confined to the interface. An historical overview of the understanding of the Wood’s (SPP) and Rayleigh anomalies (pseudo-critical edge), which were first observed around the turn of the 20th century, is presented and optical coupling to the SPP is discussed with particular emphasis on grating coupling. Finally, the phenomenon of SPP mediated polarisation conversion is discussed, and the creation of grating induced gaps in the SPP dispersion curve is explained.

2.2. Historical Overview

The electromagnetic surface waves discussed throughout this thesis may propagate along a planar interface between two dissimilar media without radiation losses. Surface waves [Barlow and Cullen (1953), and Goubau (1959)] have attracted much scientific attention over the last one hundred years. For example, Zenneck in 1909 realised the possibility of propagation of radio waves around the Earth when one considers the upper half space as a pure dielectric and the lower as a conductor. A similar wave of radiation coupled to oscillating charge density may propagate along a metal-dielectric interface. Today, we often refer to this mode as a surface plasmon polariton (SPP) and it may be considered as a “sound” wave propagating through the free-electron gas of the metal.
CHAPTER 2  A review of the properties of radiatively coupled surface plasmon polaritons.

The work presented in this thesis is concerned with the excitation of the SPP within systems that involve diffraction gratings, and it is perhaps Joseph von Fraunhofer who deserves the credit for the invention of the diffraction grating in 1821 in the form that it is known today. He produced finely ruled reflection gratings with a diamond point in mirrored surfaces which enabled him to conduct a thorough study of their performance and, for the first time, to calculate the wavelength of light. He explained the phenomenon of diffracted orders and verified the grating equation:

\[ \lambda_g (\sin \vartheta_N - \sin \theta) = N \lambda_g \]

where \( \theta \) and \( \vartheta_N \) are the angles of incidence and diffraction of the \( N \)th order respectively, and \( \lambda_g \) is the grating period.

Wood studied the spectra of similar ruled metallic diffraction gratings in 1902. He viewed the spectra of an incandescent lamp reflected from a grating, and observed an uneven and unexpected distribution of light. Dark and bright bands were seen in the spectra of transverse magnetic (TM) light and between these bands the intensity changed over a very narrow spectral region. The theory of diffraction gratings at the time was unable to explain the two anomalies, which are now known to be the result of two different physical processes. The features that he observed are illustrated in Figure 2.2.1, where the reflected intensity has been recorded as a function of the angle of incidence (\( \theta \)), measured from the normal to the average plane of the grating.

Lord Rayleigh correctly predicted the positions of the bright anomalies in the TM spectra in 1907 as part of his Dynamical Theory of Gratings (an extension to his earlier Theory of Sound). He found that the scattered field is singular at wavelengths at which one of the diffracted orders emerges from the grating at grazing angle, which results in a sudden redistribution of the available energy. Hence, the sharp change in reflectivity observed by Wood is generally referred to as the Rayleigh anomaly. His theory also suggested that the anomalies only appear when the incident electric field is polarised perpendicular to the grating grooves – it predicted no anomalies for the orthogonal polarisation. Further experiments over the next three decades again by Wood (1912 and 1935), and also by Ingersoll (1920) and Strong (1935) verified these initial observations.
One of the problems with Rayleigh’s theory was that it only predicted a singularity at the anomaly’s wavelength – it did not yield any information about the shape of the feature. However Fano (1941) presented an alternative treatment. The grating equation (Equation 2.2.1) illustrates that the component of the momentum of the incident radiation parallel to the average plane of the grating surface will be enhanced in integer multiples of $2\pi/\lambda_g$ (where $\lambda_g$ is the grating spacing) and a series of diffracted orders will result. He proposed that when this component is greater than the momentum of the incident beam ($\sin \vartheta > 1$), it becomes evanescent and will be diffracted into a pair of surface waves travelling along the grating surface and exponentially damped in the direction perpendicular to it. These waves are not able to leave the interface since both the dielectric and the metal repeatedly reflect them, and no part of their energy is dispersed outside the surface region. Fano showed that a quasi-stationary state may be set up, where the pairs of surface waves are excited by the impinging incident radiation at the surface of the grating and act as forced oscillators. The waves are considered to be quasi-stationary because in real metals there are losses due to heat production; the width

*Figure 2.2.1* Theoretically-derived angle-dependent reflectivity data from a gold coated grating illustrating the bright (Rayleigh) and dark (Wood’s) anomalies observed by Wood (1902).
of the interval in which the resonance is felt being proportional to the magnitude of this damping.

However, the electrons associated with the surface waves can only be excited at the interface if there is a component of the incident wave polarised with its electric vector perpendicular to the surface. In addition, the electrons will oscillate resonantly only if the tangential momentum of the oscillations approaches a permissible value determined by the real part of the permittivity of the metal ($\varepsilon'$). It is the negative sign of $\varepsilon'$ that inverts the direction of the normal component of the electric field at the interface and allows the possibility of coupling to this quasi-stationary state due to the charge density variations induced on the metallic surface. Since for most materials there is no analogous magnetic property, the correct polarisation of incident radiation is vital.

Wood’s initial publications reported that the anomalies appeared only in the component of the incident light which was polarised with its electric vector perpendicular to the rulings (p-polarised, TM). It was not for another 50 years that “Parallel Diffraction Grating Anomalies” were generally accepted when Palmer (1952) observed them in the s-polarised spectra from gratings with much deeper grooves. He illustrated that with s-polarised incident radiation sharp, bright anomalies occurred at the same angles as the anomalies previously predicted by Rayleigh and observed in the p-polarised spectra by Wood. Rayleigh’s theory did not predict these TE anomalies and neither did Fano’s classical treatment. It eventually became clear that Rayleigh’s Dynamical Theory of Gratings was only valid for shallow grooves (an issue that will be discussed in detail in the following chapter). Hence his theory was unable to predict the bright bands in the s-polarised spectra observed by Palmer, and the dark bands in the p-polarised spectra observed by Wood.

During the mid- and late-1950s, much progress was made in attempting to explain the Wood’s anomaly. The resonance effect proposed by Fano, in conjunction with the developments of treating the electrons in a metal as a plasma [Pines and Bohm (1952)] led Ferrell (1958) to confirm that the density oscillations of these electrons occurred in multiples of a basic quantum of energy, $\hbar\omega_p$. It was therefore interpreted that this plasma oscillation was associated with a basic unit of energy that was termed the
plasmon. When excited by a high-energy incident beam of electrons, these plasma oscillations should emit radiation at the plasma frequency. The experimental evidence for the existence of bulk plasmons was provided by Steinmann (1960), who bombarded metal films with 25 keV electrons. Ferrell also predicted that image forces at the surfaces of a thin metal film should constrain the electrons. This would contribute an uncertainty to the momentum normal to the foil and allow these surface plasmons to radiate transversally. Powell (1958, 1960) detected the decay by radiative emission of both excited surface and bulk plasmons, which were found to have the characteristic energies ($\omega_p/\sqrt{2}$ and $\omega_p$ respectively) that had been earlier predicted by Ritchie (1957) and Ferrell (1958).

Fano (1941) realised that the surface waves that he proposed that propagate along the boundary between a dielectric and a metal were simply a special case of the waves first suggested by Zenneck (1909) and Sommerfeld (1909). Since these waves propagate along the metal boundary with a momentum greater than that of the incident radiation in the dielectric (air) medium, it is impossible for them to radiate or to couple to them on a planar interface. However Teng and Stern (1967) used an optical grating that could impart some additional momentum to the surface plasmon, so that it could couple to a radiating electromagnetic field. The experiment consisted of bombarding the grating with a high-energy electron beam and observing peaks in the out-coupled TM radiation. To verify that the surface plasmon was the cause of these peaks, an additional experiment was carried out. Electromagnetic radiation incident at the emission angle, and of the same frequency as the peaks, should be absorbed as it excites the surface plasmon. This was the case, and as the angle of incidence with respect to the grating normal was varied, troughs appeared at the same position as the peaks in the electron-beam experiment. Using the angular positions of these peaks, the authors were able to determine the wave vector parallel to the surface of the grating of the surface plasmon and hence the dispersion curve could be mapped out. This confirmed the excitation of surface plasmons unequivocally and presaged their direct optical coupling with the use of a grating - confirming Wood’s observations.

Fano’s theory was further verified experimentally by Ritchie et al. (1968), and Beaglehole (1969). They each provided one of first comprehensive experimental
studies of optically excited surface plasmons (known as surface plasmon polaritons, SPPs) on metal gratings. Ritchie et al. were able to experimentally derive the dispersion curve of the SPP by plotting the positions of the peaks in the p-polarised spectra from their grating. Meanwhile Beaglehole was able to illustrate that coupling to the mode is possible for both p- and s-polarised light if the grating grooves are twisted with respect to the plane of incidence, and provided that there is a component of the electric field along the direction of surface plasmon propagation.

2.3. Surface Plasmon Polaritons at the Interface of Semi-infinite Media

The term polariton has evolved to denote the coupling of the electromagnetic photon field to the polar excitations in a solid. Bulk polaritons propagate in an unbounded medium, while surface polaritons may be defined as the coupling of the incident field to surface dipole excitations that propagate along the interface between two dissimilar media. In this section, the dispersion of the polariton that may propagate at the interface of a metal and a dielectric is derived, and the spatial extent of its fields is discussed.

2.3.1. The Dispersion Relation

We restrict ourselves to considering the interface of two semi-infinite, optically isotropic, homogeneous media that are characterised by frequency dependent, complex dielectric constants \( \varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) \). For simplicity both media assumed to be non-magnetic (\( \mu = 1 \)) and the interface is planar. In addition, it is convenient, at least initially, to consider media that are loss-free.
First consider the configuration shown in Figure 2.3.1 with electromagnetic modes propagating in the x-direction along an interface in the xz-plane at y = 0. The surface polariton for this configuration will correspond to solutions of Maxwell’s equations which satisfy the boundary conditions at the interface and whose field magnitude varies in a wave-like manner in the x-direction, but vanishes exponentially in the y-direction. In other words, there exists evanescent, interface modes in both media. The electric fields of these interface modes in each medium take the form,

\[
E_1 = E_i^0 \exp[i(k_{x1}x - \omega t)] \exp(ik_{y1}y); \quad y > 0 \quad \text{Equation 2.3.1}
\]

\[
E_2 = E_r^0 \exp[i(k_{x2}x - \omega t)] \exp(ik_{y2}y); \quad y < 0 \quad \text{Equation 2.3.2}
\]

where \(E_i^0 = (E_{x1}^0, E_{y1}^0, E_{z1}^0)\) and \(E_r^0 = (E_{x2}^0, E_{y2}^0, E_{z2}^0)\) are the vector fields at the interface in medium 1 and 2 respectively; \(k_{y1} = k_{y1}' + ik_{y1}''\) and \(k_{y2} = k_{y2}' + ik_{y2}''\) are the
components of the wave vectors perpendicular to the interface; and
\( k_{x1} = k_{x2} = k_x = k'_x + i k''_x \) and \( \omega_1 = \omega_2 = \omega \) are the components of the wave vectors parallel to the interface and the frequency respectively (which are common to both media).

By deriving the wave equation for \( E_1 \) and \( E_2 \) \( (\nabla^2 E = \mu_0 \varepsilon \partial^2 E / \partial t^2) \), one finds the following expressions for \( k_{y1}^2 \) and \( k_{y2}^2 \):

\[
k_{y1}^2 = \frac{\omega^2}{c^2} \varepsilon_1(\omega) - k_x^2 = \frac{\omega^2}{c^2} n_1^2(\omega) - k_x^2 \tag{Equation 2.3.3}
\]

\[
k_{y2}^2 = \frac{\omega^2}{c^2} \varepsilon_2(\omega) - k_x^2 = \frac{\omega^2}{c^2} n_2^2(\omega) - k_x^2 \tag{Equation 2.3.4}
\]

where \( n(\omega) = \varepsilon(\omega)^{1/2} \) is the frequency dependent refractive index for the corresponding media. Since the two media are neutral, and therefore \( \nabla \cdot D = 0 \) in each medium, we obtain the following relation between the \( x \) and \( y \)-components of \( E_1 \) and \( E_2 \):

\[
E_{y1} = -\frac{k_x}{k_{y1}} E_{x1}; \quad y \geq 0 \tag{Equation 2.3.5}
\]

\[
E_{y2} = -\frac{k_x}{k_{y2}} E_{x2}; \quad y \leq 0 \tag{Equation 2.3.6}
\]

On applying the boundary conditions for the normal components of \( D \left( D_{y1}^0 = D_{y2}^0 \right) \), and also for the tangential components of \( E \left( E_{x1}^0 = E_{x2}^0 \right) \) the following expression is obtained:

\[
\frac{k_{y1}}{k_{y2}} = \frac{\varepsilon_1(\omega)}{\varepsilon_2(\omega)} \tag{Equation 2.3.7}
\]
By combining Equation 2.3.3, Equation 2.3.4 and Equation 2.3.7, the following equation for the dispersion relation for the interface modes is obtained:

\[ k_{p}^2 = \frac{\omega^2}{c^2} \frac{\varepsilon_1(\omega)\varepsilon_2(\omega)}{\varepsilon_1(\omega) + \varepsilon_2(\omega)} = k_{SPP}^2 \]  

Equation 2.3.8

or

\[ k_{SPP}^2 = \frac{\omega^2}{c^2} n_s^2(\omega) \]  

Equation 2.3.9

where \( n_s \) is the “refractive index” of the interface mode which is a function of the dielectric constants of both media.

In addition, by using the expressions for \( E_1 \) and \( E_2 \), and similar expressions for \( H_1 \) and \( H_2 \) in Maxwell’s equation for \( \nabla \times \mathbf{H} \) and applying the boundary conditions for \( \mathbf{B}, \mathbf{H}, \mathbf{E} \) and \( \mathbf{D} \), the results \( H_x = H_y = 0 \) and \( E_z = 0 \) are obtained for both media. Also, the following expression for the z-component of \( \mathbf{H} \) may be derived:

\[ H_{z1} = H_{z1}^0 \exp[i(k_s x - \omega t)] \exp(ik_{y1} y) \]  

Equation 2.3.10

\[ H_{z2} = H_{z2}^0 \exp[i(k_s x - \omega t)] \exp(ik_{y2} y) \]  

Equation 2.3.11

where

\[ H_{z1}^0 = H_{z2}^0 = \frac{\omega}{c} \frac{\varepsilon_1^2(\omega)}{k_{y1}(\omega)} E_{z1}^0 = H_z^0 \]  

Equation 2.3.12.

Thus, the electric field in each medium lies in the \( xy \)-plane, with the magnetic field normal to this plane. Therefore the interface modes are TM in nature.
2.3.2. Brewster and Fano Modes

By combining Equation 2.3.3, Equation 2.3.4 and Equation 2.3.8, the following expressions may be obtained:

\[ k_{y1}^2 = k_x^2 \frac{\varepsilon_1(\omega)}{\varepsilon_2(\omega)} \quad \text{Equation 2.3.13} \]

and

\[ k_{y2}^2 = k_x^2 \frac{\varepsilon_1(\omega)}{\varepsilon_2(\omega)} \quad \text{Equation 2.3.14}. \]

These equations illustrate that in frequency regions where \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) are both purely real and positive, \( k_{y1} \) and \( k_{y2} \) are also real. Whereas when \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) have opposite signs, \( k_{y1} \) and \( k_{y2} \) are imaginary. It is therefore not surprising that different frequency (wave vector) regions support different types of interface modes.

The interface modes that occur when \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) are purely real and have opposite signs correspond to surface electromagnetic modes that propagate without radiation loss along the interface and whose fields decay exponentially to zero in the \( y \)-direction. These modes are known as Fano modes (Section 2.1) and are equivalent to the propagation of the SPP along a planar, non-lossy metal-dielectric interface.

The interface modes that occur when \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) are both positive correspond to Brewster modes, and since \( k_{y1} \) and \( k_{y2} \) are both real and have the same signs, it is clear that the surface mode generated is in fact not bound to the interface. By inspection of Equation 2.3.13 and Equation 2.3.14, we can appreciate that this mode is generated when

\[ \tan \theta = \frac{n_2(\omega)}{n_1(\omega)} = \sqrt{\frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega)}} = \frac{1}{\tan \beta} = \tan \theta_B \quad \text{Equation 2.3.15} \]

which occurs when
\( \theta + \beta = 90^\circ \) \hspace{1cm} \textit{Equation 2.3.16.}

At \( \theta = \theta_B \) (the Brewster angle) there is no re-radiation of p-polarised radiation from medium 2 since there is no component of motion of the induced interface charge in this direction. Note that, although Brewster modes are not bound to the surface (\textit{i.e.} they do not attenuate with distance from the interface like the Fano modes discussed above), they do satisfy the criterion for interface modes that there be only one electromagnetic wave in each medium (\textit{i.e.} they involve an incident wave but no reflected wave in one medium, and a refracted wave in the other).

To demonstrate that the expression derived in \textit{Equation 2.3.8} and the Brewster mode dispersion relation are equivalent, the dispersion relation for the Brewster mode is derived separately below.

\[
\sin \theta_B = \frac{n_2(\omega)}{\left[n_1^2(\omega) + n_2^2(\omega)\right]^{\frac{1}{2}}} = \left[\frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega) + \varepsilon_2(\omega)}\right]^\frac{1}{2} \hspace{1cm} \textit{Equation 2.3.17}
\]

\[
\therefore k_x = n_1k_0 \sin \theta_B = k_0 \frac{n_1(\omega)n_2(\omega)}{\left[n_1^2(\omega) + n_2^2(\omega)\right]^{\frac{1}{2}}} = \left(\frac{\omega}{c}\right) \left(\frac{\varepsilon_1(\omega)\varepsilon_2(\omega)}{\varepsilon_1(\omega) + \varepsilon_2(\omega)}\right)^\frac{1}{2} \hspace{1cm} \textit{Equation 2.3.18}
\]

where \( k_0 = \omega/c \) is the wave vector of the incident radiation in free space.

The equivalence of \textit{Equation 2.3.8} and \textit{Equation 2.3.18} demonstrates that the SPP is a manifestation of the Brewster mode for which the media have purely real permittivities of opposite signs (\textit{e.g.} a non-lossy metal-dielectric system). It is clear that Brewster modes have values of \( k_x \) that are smaller than the wave vector of the bulk polaritons in either medium. However, the opposite is true for Fano modes, which therefore cannot directly couple to bulk polaritons in the dielectric, \textit{i.e.} the SPP is described as non-radiative.

It is also important to note that, in the case of the Brewster modes, the \( x \)- and \( y \)-components of the electric fields are in phase with each other and the \( y \)-components in the two media have the same signs. For Fano modes, the \( x \)- and \( y \)-components are one
quarter of a cycle out of phase with one another, and the $y$-components of the field in
the upper and lower media have opposite signs. Furthermore when $\varepsilon_r(\omega) \to -\varepsilon_i(\omega)$
and in the absence of damping, it is clear that $k_x \to \infty$ ($\lambda_x \to 0$) and $E_{y2}^0 = -E_{y1}^0 = iE_x^0$
($Equations$ 2.3.5, 2.3.6, 2.3.13 and 2.3.14). Hence, at this frequency, the magnitudes of
the $x$- and $y$- electric field components are equal. This frequency corresponds to that of
the uncoupled (or unretarded) surface electric dipole excitation.

Conversely, as $\varepsilon_r(\omega) \to -\infty$ ($i.e.$ a perfectly conducting metal) we find that $k_x \to n_x k_0$
($Equation$ 2.3.8), $i.e.$ the mode becomes more photon-like. In addition, from $Equations$
2.3.5, 2.3.6, 2.3.13, and 2.3.14 it is apparent that $k_y^0 \to 0$, $k_y^\infty \to \infty$ and $E_{y2}^0 / E_{y1}^0 \to 0$,
$i.e.$ the Fano modes reside entirely in medium 1 and are polarised only in the $y$-
direction. Therefore the modes are essentially bulk polaritons propagating in the
dielectric (medium 1) along the $x$-axis.

If one of the media is now allowed to become lossy, then clearly from $Equation$ 2.3.8,
$Equation$ 2.3.13 and $Equation$ 2.3.14, $k_x$, $k_{y1}$ and $k_{y2}$ all become complex. It can be
shown that in this system, a surface mode may propagate along the interface which has
attenuated fields in both media [Burstein et al (1972)]. These types of modes are
generally referred to as Zenneck modes [Zenneck (1909)], and have phase velocities
greater than that of bulk polaritons at the same frequency in the loss-free medium.
When $\varepsilon_r^2 < 0$, the Zenneck mode corresponds to lossy Fano mode that is equivalent to
the SPP that propagates along the boundary of a real (lossy) metal and a dielectric.

Let us continue with the previous example of the metal-dielectric interface, where the
metallic media is again assumed to be perfectly conducting. Hence, the electron system
in the metal will behave as a free electron gas where the real part of the metal’s
dielectric constant varies as

$$\varepsilon_r^2(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$$

$Equation$ 2.3.19

where
\[ \omega_p^2 = \frac{\rho \varepsilon^2}{\varepsilon_0 m} \]

defines its plasma frequency, \( \rho \) is the free electron density, \( e \) is the electronic charge, \( m \) is the electronic mass and \( \varepsilon_2 = \varepsilon'_2 \) is the relative permittivity of medium 2.

Substituting the dielectric function for the metal into the dispersion relation (Equation 2.3.18) gives

\[
k^2_x = k_0^2 \left( \frac{\varepsilon_i \left( 1 - \frac{\omega_p^2}{\omega^2} \right)}{\varepsilon_i + \left( 1 - \frac{\omega_p^2}{\omega^2} \right)} \right)
\]

where \( \varepsilon_i = \varepsilon'_i \) is the relative permittivity of medium 1 which is independent of frequency and \( k_0 = \omega/c \). Solving this equation for \( k_x \) as a function of \( \omega \) yields two solutions, one for the positive root and one for the negative root (Figure 2.3.2). The positive root leads to mode solutions of the Brewster type, whose dispersion curve is asymptotic to \( \omega = ck_x \sqrt{1+\varepsilon_i^{-1}} \). Since this mode exists within the light-line (\( \omega = ck_x \sqrt{\varepsilon_i} \)) they can be coupled to at any frequency, given \( \theta \) is correctly chosen, and are hence termed radiative modes. Conversely, the negative solution leads to solutions of the Fano (SPP) type. This mode is clearly seen to asymptotically approach the light-line in the limit \( \omega \ll \omega_p \) confirming the previous result. This means that since \( k_x \) for the Fano mode is always less than the momentum of the incident beam in the dielectric, at no frequency can it be directly excited by an incident photon, i.e. it is non-radiative. As predicted by Ferrell (1958), the frequency of the uncoupled electric dipole oscillation is asymptotic to \( \omega = \omega_p / \sqrt{2} \) (when \( \varepsilon_i = \varepsilon_{air} = 1.0006 \)).
2.3.3. Spatial Extent of the Surface-plasmon Fields

This section discusses the spatial extent of the surface plasmon polariton (SPP), illustrating that its field has its maximum at the interface, decaying exponentially perpendicularly to it (Figure 2.3.3).
A review of the properties of radiatively coupled surface plasmon polaritons.

Figure 2.3.3. The charges and electromagnetic field of surface plasmons propagating in the $x$-direction. The exponential dependence $E_y$ away from the interface is seen on the left.

The skin depth, $L_{ym} = 1/k_{ym}$, (where $m$ is the medium label) at which the amplitude falls to $1/e$ of its initial value is derived below.

From Equation 2.3.3 and Equation 2.3.4 we find

$$k_{ym}^2 = \varepsilon_m k_o^2 - k_x^2$$  \hspace{1cm} \text{Equation 2.3.22}

$$k_{ym}^2 = \frac{\omega^2}{c^2} \left( \frac{\varepsilon_m - \frac{\varepsilon_1 \varepsilon'_2}{\varepsilon_1 + \varepsilon_2}}{\varepsilon_1 + \varepsilon_2} \right) = \frac{\omega^2}{c^2} \left( \frac{\varepsilon_m^2}{\varepsilon_1 + \varepsilon_2} \right)$$  \hspace{1cm} \text{Equation 2.3.23}

For a real metal-dielectric interface, the dielectric has a real part of the complex permittivity, $\varepsilon'_1 > 0$ and the imaginary part, $\varepsilon''_1 = 0$. In the approximation that medium 2 is a good metal, $\varepsilon'_2 << 0$ and $|\varepsilon'_2| > \varepsilon''_2$, Equation 2.3.23 becomes

$$k_{ym}^2 = \frac{\omega^2}{c^2} \left( \frac{\varepsilon_m^2}{\varepsilon_1 + \varepsilon'_2} \right)$$

$$\therefore L_{ym} = \frac{1}{k_{ym}} = \frac{\lambda_0}{2\pi} \left( \frac{\varepsilon_1 + \varepsilon'_2}{\varepsilon_m^2} \right)^{\frac{1}{2}}$$  \hspace{1cm} \text{Equation 2.3.25}

where $\lambda_0$ is the wavelength of the incident radiation.
For example, gold at a wavelength of 630 nm gives $L_{y1} = 314$ nm, and $L_{y2} = 29$ nm, while silver gives $L_{y1} = 408$ nm and $L_{y2} = 23$ nm [6.17, $\varepsilon_{\text{Au}} = -10.8 + 1.47i$, $\varepsilon_{\text{Ag}} = -17.6 + 0.67i$, Schröder (1981)].

It is clear that when medium 2 is an ideal metal ($\varepsilon'_2 \to \infty$), then, as expected there is no penetration of the electric field into the metal ($L_{y2} = 0$). In addition, perhaps surprisingly, $L_{y1}$ becomes infinite as $\varepsilon'_2 \to -\infty$. However this is sensible because as $\varepsilon'_2 \to -\infty$, the dispersion relation (Equation 2.3.8) tends to $\omega = ck$ and becomes more light-like. This confirms the result discussed in the previous section (2.3.2) that the mode is no longer confined to the interface, but behaves more like a bulk polariton propagating in the dielectric.

The absorption of the metal causes the intensity of the SPP propagating along the interface to decay as $\exp(-2k'_s x)$, where $k'_s$ is the imaginary part of the wave vector along the interface. Hence the length $L_s$ at which the intensity decreases by a factor $1/e$ is given by

$$L_s = \frac{1}{2k'_s} \tag{Equation 2.3.26}$$

By substituting $\varepsilon_2$ for $\varepsilon'_2 + i\varepsilon''_2$ in Equation 2.3.8, we have

$$k_s = k_0 \left[ \frac{\varepsilon_1 (\varepsilon'_2 + i\varepsilon''_2)}{\varepsilon_1 + \varepsilon'_2 + i\varepsilon''_2} \right]^{1/2} \tag{Equation 2.3.27}$$

where $k_s = k'_s + ik''_s$ and $k_0 = \frac{2\pi}{\lambda_0}$.

The imaginary part of $k_s$ is given by
CHAPTER 2 A review of the properties of radiatively coupled surface plasmon polaritons.

\[ k_s' = \frac{\pi \varepsilon_2^{*} \varepsilon_1^{3/2}}{\lambda_0 \varepsilon_2'} \] \hspace{1cm} \text{Equation 2.3.28}

\[ \therefore L_s = \frac{\lambda_0}{2\pi} \frac{\varepsilon_2'}{\varepsilon_2\varepsilon_1^{3/2}} \] \hspace{1cm} \text{Equation 2.3.29}

Using the values of the permittivity of gold and silver at a wavelength of 630 nm [determined by Schröder (1981)] we have \( L_s = 8 \ \mu\text{m} \) and \( L_s = 46 \ \mu\text{m} \) respectively.

2.4. Excitation of Surface Plasmons

The excitation and the subsequent possible detection of surface plasmons was first predicted to occur in the characteristic energy loss experiments of fast electrons reflecting from the surface of metals [Pines and Bohm (1952)]. Electrons passing through a solid will transfer some of their momentum and energy to the electrons of the solid. The component of this momentum along the surface of a metal film may be used to excite a surface plasmon at the interface if the amplitude of the momentum available is large enough. As discussed previously, Powell et al. (1958 & 1960) detected the decay of excited surface plasmons after having bombarded a metal film with high-energy electrons. Teng and Stern (1967) used a grating to impart additional momentum to the surface plasmon and mapped the dispersion curve. However, because of the difficulty in obtaining a sufficiently small aperture of the electron beam, it was only possible to determine the dispersion curve for high values of \( k_s \). However, Ritchie et al. (1968) successfully managed to obtain a complete map of the dispersion curve by using a grating surface to couple \textit{optically} into the surface plasmon mode.

As discussed in Section 2.3.2, a photon cannot transform into a SPP without some form of momentum enhancement. There are two ways in which this may be achieved and they as discussed in the following subsections.
2.4.1. **Prism Coupling**

There are two methods of prism coupling light to SPPs. These are the *Otto* (1968) and the *Kretschmann-Raether* (1968) geometries, both of which take place on smooth surfaces [*Figure 2.4.1*]. They use the phenomena of total internal reflection in a high-index prism that has been brought near to a metal interface. The SPP is excited optically via the enhanced momentum of an evanescent wave that will penetrate into the rare medium.

Should light be propagating in a dielectric, and be incident at an angle $\theta$ on a metal interface, a wave of surface charges will be induced with wave vector $n \sin \theta \omega / c$, which for all $\theta$, is less than $n \omega / c$, where $n$ is the refractive index of the dielectric. However, as described previously, the SPP has a wave vector greater than $n \omega / c$, and it is this discrepancy that prevents the SPP from being directly excited. However, a spacer layer with refractive index $n_s$ may be employed between a metal M and a prism (P) [*Figure 2.4.1(a)*]. Medium P has refractive index $n_p > n_s$ and hence the component of momentum along the interface between the media can be increased:

$$k = n_p \sin \theta \left( \frac{\omega}{c} \right)$$ \hspace{1cm} \text{Equation 2.4.1}

*Figure 2.4.1* Two methods of prism-coupling radiation to SPPs; (a) Otto configuration, and (b) Kretschmann-Raether configuration.
If the angle of incidence, $\theta$, at the prism/dielectric(air) interface is greater than the critical angle, such that only an evanescent field penetrates into the spacer layer, the electromagnetic field will be able to couple to the SPP at the metal interface if the increased momentum of the evanescent field is equal to $k_{SPP}$. This is an attenuated total reflection (ATR) technique and was first utilised by Otto (1968). The coupling strength is determined by the width of the air gap and optimum coupling is achieved for a gap width of the order of the incident wavelength. This is difficult to achieve for experiments at visible wavelengths since the dimensions of dust particles are much larger than the width of the spacer layer. However, in the infra-red, the optimum gap width required becomes more practical (Bradberry et al, 1988).

The configuration shown in Figure 2.4.1(b) was first demonstrated by Kretschmann and Raether (1968) and involves evaporating a thin metal film directly on to the surface of the prism. The low index gap is now provided by the metal layer itself. The evanescent fields pass through the film and excite a SPP on the bottom surface of the metal. Since the metal has a much higher optical impedance than air, optimum coupling at visible wavelengths may be achieved for a film thickness of approximately 45 nm.

To summarise, the ATR-coupling technique utilises the higher pseudo-momentum obtainable in a prism, to couple to a SPP on a metal surface via the evanescent wave in a low-index layer. Coupling to the SPP via the ATR technique is therefore only possible in the frequency region that lie between lines (a) and (b) in Figure 2.4.2 below.
2.4.2. Grating Coupling

As discussed previously, SPPs are non-radiative, however coupling between surface and bulk polaritons can take place when the surface is rough. Since a rough surface corresponds to a superposition of a number of different gratings, the physics underlying the coupling of SPPs to bulk polaritons at a rough interface is essentially the same as that via a single corrugation. Therefore only the phenomenon of grating-induced SPP coupling will be discussed.

Wood first observed coupled SPPs using the grating configuration in 1902. Incident radiation at an angle $\theta$ with respect to the normal of the average plane of the surface can scatter from the grating, increasing or decreasing the component of its wave vector by integer multiples of the grating wave vector $k_g$ ($k_g = 2\pi/\lambda_g$). This gives rise to diffracted orders. When a diffracted order has a wave vector greater than that of the incident grazing radiation in medium 1 [$n_1k_0 = \sqrt{\epsilon_1(\omega/c)}$] it will not propagate and will become evanescent. It is the enhanced momentum of these evanescent fields that may couple radiation to the SPP according to the coupling condition.
\[ \mathbf{k}_{\text{SPP}} = n_i \mathbf{k}_o \sin \theta \pm N \mathbf{k}_g \]  

*Equation 2.4.2*

where \( N \) is an integer and \( n_i = \sqrt{\varepsilon_i} \) is the refractive index of medium 1. Hence it is conventional to label the SPP with the diffracted order that provides the coupling mechanism. When the grating is mounted such that the grating wave vector is parallel with the plane of incidence, all three vectors are collinear. For this situation, *Figure 2.4.3* illustrates schematically the effect that corrugating the surface has on the dispersion relation. The periodicity of the surface is represented as a 1-D lattice with spacing \( k_g \), the grating wave vector. The lattice points are scattering centres which may add or subtract momentum from the incident photon in integer multiples of \( k_g \).

Radiative coupling using p-polarised (TM) incident light to the SPP can now be achieved since there exists diffracted regions of the dispersion curve within the light lines (shaded). (Note that by corrugating the surface, strictly the planar dispersion relation can no longer be used. However, in the small amplitude limit, *Equation 2.3.8* is a good approximation.)

*Figure 2.4.3* The dispersion curve for grating coupled SPPs which has been reflected at the Brillouin zone boundaries. Parts of the scattered dispersion curves that fall between the light lines (shaded) can be radiatively coupled. A number of the crossing points of the dispersion relations within the shaded area are labelled in units of \( k_g \) according to the coupling mechanisms involved.
If the azimuthal angle, $\phi$ defined as the angle between the plane of incidence and the grating wave vector, is not equal to zero, then $k_{spp}, k_i$ and $k_g$ are no longer collinear and the scalar equivalent of Equation 2.4.2 becomes

$$k_{spp}^2 = n_i^2 k_0^2 \sin^2 \theta + N^2 k_g^2 \pm 2n_i N k_g k_0 \sin \theta \cos \phi$$

Equation 2.4.3.

The coordinate system used throughout this thesis to describe the orientation of the grating is illustrated in Figure 2.4.4 below. The polar angle, $\theta$, is used to describe the angle of incidence measured from the normal to the average plane of the grating; the azimuthal angle, $\phi$, describes the rotation of the plane of incidence from the positive $x$-axis. The $x$-axis runs perpendicularly to the direction of the grating grooves (parallel to the grating wave vector), and $\phi$ is measured in the $x$-$z$ plane. The polarisation is defined with respect to the plane of incidence, i.e. p-polarised radiation (TM: transverse magnetic) has its electric vector in the plane of incidence, s-polarised radiation (TE: transverse electric) has its electric vector orthogonal to it.

![Figure 2.4.4 Grating geometry and coordinate system used throughout this thesis. The direction of the electric field vector (E) is illustrated for the situation when p-polarised (TM) radiation is incident.](image)
Figure 2.4.5 shows a schematic 2-D $k$-space diagram illustrating the solutions of Equation 2.4.3 for a grating surface where $\lambda_0/n_1\lambda_s = 0.68$. The dashed circle about the origin represents the maximum momentum component available from a grazing photon in the dielectric ($n_1k_0$), i.e. coupling is only possible to modes that fall within its area (shaded). The solid circle about the origin corresponds to the wave vector of the SPP ($k_{spp}$), which is larger than the incident wave vector ($n_1k_0$), preventing incident photons coupling directly to it. The grating allows the wave vector of the SPP to be changed by integer multiple of $k_g$, hence we observe diffracted SPP circles about each scattering centre, the arcs of which occur within the shaded area are shown. A photon incident with momentum component $n_1k_0\sin \theta$ and at an azimuthal angle $\phi$ may now couple to a SPP as illustrated.

Figure 2.4.5. A $k$-space representation of a grating with wavelength-to-pitch ratio, $\lambda_0/n_1\lambda_s = 0.68$. The circle with a thick-dashed radius represents the maximum possible momentum in the plane available from a photon propagating above the grating. The circle with the thick solid radius represents the momentum of the zero-order SPP mode; the arcs of the diffracted SPP modes that fall within the shaded area are also shown (thin solid radii). Hence, coupling to SPPs is only possible in the shaded area. The arrows indicate the coupling between a photon at angle of incidence $\theta$ to a SPP via a grating vector of $2k_g$ at an azimuthal angle of $\phi$, where the mode propagates at an angle $\phi$ with respect to the grating grooves.
2.5. Polarisation Conversion

Since Wood’s first experimental observations of the dark bands in the reflected spectra from ruled gratings in 1902, it has been known that the “anomalies” may only be recorded when the direction of the electric-field vector is perpendicular to the direction of the grating grooves. However, this is only true when the grating grooves are perpendicular to the plane of incidence ($\phi = 0 \pm 180^\circ$) [Beaglehole (1968)]. Recent advances in the modelling techniques (to be discussed in the next chapter) have permitted the exploration of polarisation conversion in geometries where the grating has been rotated. When orientated in this way, the grating is said to be in the conical mount.

Unlike other optical coupling mechanisms, diffraction gratings may couple both orthogonal polarisations to SPPs. Bryan-Brown et al. (1990) demonstrated that for small amplitude, non-blazed gratings, an increase in the azimuthal angle from $\phi = 0^\circ$ to $\phi = 90^\circ$, results in the coupling efficiency to p-polarised radiation being reduced, while at the same time producing some s-polarisation component in the reflected beam. When the grating grooves are at 45° to the plane of incidence, maximum p-to-s conversion is obtained and if the grating is rotated by a further 45° in azimuth, they observed coupling to the SPP via only s-polarised radiation. Generally, the coupling of each polarisation to the SPP follows a $\sin^2 \phi$ dependence, varying between zero and a maximum over an azimuthal angle range of 90°. These results have been reproduced theoretically by Elston et al. (1991a and b). However, the work of Bryan-Brown et al. (1990) considered only a small amplitude grating. Although it has generally been considered that coupling to the SPP with p-polarised radiation at $\phi = 90^\circ$ is not possible, a recent study by Watts et al. (1997c) has shown this to be untrue for sufficiently deep gratings. In addition, Chapter 9 illustrates that coupling to a SPP mode using p-polarised radiation via a grating orientated at $\phi = 90^\circ$ is also possible by using a dielectric grating on a metal substrate.

Polarisation conversion is achieved as a result of breaking the symmetry of the system in which the electric fields of the SPP mode supported at the surface of the grating do not lie in the plane of incidence. In propagating across the grooves, a tilted component
of the surface plasmon electric vector will exist on rising up or dropping down the side of a groove. This component cannot be in the incident plane and hence, although the SPP is always transverse magnetic in character (if excited in isotropic media), we have created ‘s’ character in its radiation field. Hence, in the conical mount, when \( \mathbf{k}_{\text{spp}} \) is no longer collinear with \( \mathbf{k}_g \) the out-coupled SPP will consist of both p- and s-polarised components.

2.6. Photonic Energy Gaps in the Propagation of SPPs on Gratings

In a similar way to the electrons in a crystal, energy gaps open up in the dispersion relation of surface plasmon polaritons propagating along a corrugated metal-dielectric interface. Work by Yablonovitch (1987 and 1993) predicted and demonstrated, in the microwave regime, the existence of photonic band gaps in a three-dimensional structure with refractive index modulations that are periodic on the scale of the wavelength of the incident radiation. Such a material is called a photonic crystal. Likewise, the surface of a diffraction grating may also be regarded as a 1-D (single-grating) or 2-D (bi-grating) photonic crystal. Grating induced photonic bandgaps were first reported by Ritchie et al. in 1968, and later by Chen et al. (1983) who recorded their magnitudes. Photonic crystals are currently attracting much interest due to the potential they offer to control spontaneous emission, for example in laser diodes and light-emitting diodes. [e.g. Kitson et al. (1998)].

Consider a SPP propagating perpendicular to the grooves on a metallic grating with pitch \( k_g = 2\pi/\lambda_g \) and profile given by

\[
A(x) = a_1 \sin(k_g x + \Phi_1) + a_2 \sin(2k_g x + \Phi_2) + \ldots + a_N \sin(Nk_g x + \Phi_N) + \ldots
\]

Equation 2.6.1

where \( a_1, a_2, \ldots, a_N \) are the amplitudes of the harmonic components of the corrugation, and \( \Phi_1, \Phi_2, \ldots, \Phi_N \) are the relative phases (this presentation will be discussed in more detail in Chapter 3). When radiation is incident upon such a distorted grating with a finite first harmonic component, the \( 2k_g \) wave vector will result in the forward and
backward travelling waves \( \exp(\pm ik_g x) \) interfering constructively to set up a standing wave. Using simple symmetry arguments, we expect two different standing waves to arise

\[
\Psi_1 = \exp(ik_g x) + \exp(-ik_g x) = 2\cos(k_g x) \quad \text{Equation 2.6.2}
\]

\[
\Psi_2 = \exp(ik_g x) - \exp(-ik_g x) = 2i\sin(k_g x) \quad \text{Equation 2.6.3}.
\]

The nodes for one of these standing waves coincide with the peaks of the grating, the other has its nodes aligning with the troughs. The field distributions and hence the energies of the two waves are different and thus an energy gap occurs at the point of intersection of the \(-1\) and the \(+1\) dispersion curves. Figure 2.6.1 illustrates the \( R_{pp} \) response (where the subscripts refer to the incident and detected polarisations respectively) from a grating orientated at \( \varphi = 0^\circ \) with \( \lambda_g = 634 \text{ nm} \), \( a_1 = 5 \text{ nm} \), \( a_2 = 2 \text{ nm} \), \( \Phi_1 = \Phi_2 = 0 \), \( \varepsilon'_2 = -17.5 \) and \( \varepsilon''_2 = 0.7 \).

*Figure 2.6.1* Numerically modelled \( R_{pp} \) response of a periodically modulating surface with two Fourier components. The second grating component allows an energy gap to open up at the intersection of the two dispersion relation branches \((-1, 1)\). The parameters used in the modelling were \( \lambda_g = 634 \text{ nm} \), \( a_1 = 5 \text{ nm} \), \( a_2 = 2 \text{ nm} \), \( \Phi_1 = \Phi_2 = 0 \), \( \varepsilon'_2 = -17.5 \) and \( \varepsilon''_2 = 0.7 \).
By deriving the field distribution around the interface, it can be shown that the extrema of the normal field component and surface charge distribution for the high energy standing-wave solution occur at the troughs of the grating profile, whereas for the low energy solution, they occur at the peaks \([Barnes\ et\ al.\ (1996)]\). These distributions are illustrated in Figure 2.6.2. It is clear that due to the relative distortion of the fields between the two solutions, a different energy will be associated with the two standing waves. The grating perturbs the field distributions associated with the surface charges so that when the charges are located at the troughs of the profile, the field lines are compressed together increasing the stored energy associated with the mode \((\omega_+)\). The opposite occurs at the peaks \((\omega_-)\).

In the absence of a first harmonic in the grating profile, coupling is still possible between the two counter-propagating modes via two consecutive \(k_g\) scatters. However, this second-order process is much less probable than a direct \(2k_g\) scatter, and hence the size of the induced photonic bandgap is comparatively small for small amplitude gratings. Clearly, the higher harmonics of the grating profile will allow further photonic
band gaps to open up. For example Chen et al, (1983) studied the gaps that open up at the crossing of the (-1,2), (-2,2), (-1,3), (-2,3) and (-1,4) diffracted dispersion curves requiring scatters of up to $5k_g$.

### 2.6.1. **False Momentum Gaps**

Work by Heitmann et al., (1987) and Celli et al. (1988) amongst others suggested the existence of momentum gaps in addition to the energy gaps described above. However it has since been established that there are no momentum gaps for the propagation of SPPs and the false $k$-gaps are actually due to an over-coupled mode [Weber and Mills (1996)]. The zeroth order reflected beam from a grating comprises a component due to specular reflection and one due to re-radiated SPP emission. When the SPP is optimally coupled, the reflected and re-radiated components are equal in magnitude and exactly in anti-phase, hence they interfere resulting in a zero in the net reflectivity. Suppose that an experimental geometry is chosen such that two perfectly coupled modes exist on either side of a crossing point. As they are brought closer together in frequency the two 100% coupled modes will overlap. Clearly in the region where they coalesce, the reflectivity minimum cannot become deeper, and instead the re-radiated SPP component becomes greater than the specularly reflected component, and the reflectivity is seen to rise. There now appears to be a reflectivity maximum between the two weaker minima and a “momentum gap” has appeared.

### 2.6.2. **Coupling to the high and low energy branches**

The strength of coupling to the SPP modes at the centre of the band gap (i.e. at the Brillouin zone edge) is determined by the relative phase, compared with the fundamental, of the Fourier coefficient involved in setting up the standing wave. For example, in the region of the (1,-1) gap, the relative phase of the first harmonic component ($\Phi_2$) is important. When the surface is blazed (i.e. $\Phi_2 = 0$) there is equal coupling between the two SPP branches. However when the surface profile is non-blazed ($\Phi_2 = \pm90^\circ$) the coupling strengths of one of the branches is reduced to zero in the proximity of the centre of the gap (Weber and Mills, 1985; Nash et al., 1995; Barnes
et al., 1996.) This is illustrated in Figure 2.6.3 below for $\Phi_2 = -90^\circ$ (top) and $\Phi_2 = +90^\circ$ (bottom).

Figure 2.6.3 Numerically modelled reflectivity plots showing the influence of the phase component $\Phi_2$ between the fundamental and first harmonic.
In order to experimentally demonstrate these results, Nash et al., (1995) manufactured a non-blazed, distorted sinusoid, 800 nm pitch, gold coated grating and recorded angle dependent data at a number of different wavelengths. The symmetry of the surface ($\Phi_2 = +90^\circ$) resulted in the high-energy branch of the dispersion curve exhibiting zero coupling in the gap region. A replica of this grating was made by pressing the warmed original substrate into Perspex, producing a profile with $\Phi_2 = -90^\circ$. The replica was shown to have the opposite response, showing no coupling to the low energy branch of the split dispersion curve.

For coupling to occur at the (1,-1) crossing point between incident photons at $\theta = 0^\circ$, and the standing wave, there must be a component of the incident E-field normal to the surface at the required points of the profile to generate the necessary surface charge. When $\Phi_2 = -90^\circ$, [Figure 2.6.4(a)] the peaks of the $2k_g$ component (dashed line) of the Fourier series correspond to flat regions of the grating profile and hence coupling to the branch whose field maxima occur at the peaks of the profile of the first harmonic is impossible. Similarly, when $\Phi_2 = +90^\circ$, it will be the branch with field maxima at the troughs that is uncoupled [Figure 2.6.4(b)]. However, when $\varphi_2 = 0^\circ$ the peaks and troughs of the $2k_g$ component occur at equivalent points with respect to the grating profile and hence the coupling is the same for both branches [Figure 2.6.4(c)]

% Figure 2.6.4 The $k_g$ (solid) and $2k_g$ (dotted) components of a distorted sinusoidal grating with relative phases $\Phi_2 = -90^\circ, +90^\circ$ and $0^\circ$.\n
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_6_4.png}
\caption{The $k_g$ (solid) and $2k_g$ (dotted) components of a distorted sinusoidal grating with relative phases $\Phi_2 = -90^\circ, +90^\circ$ and $0^\circ$.
\end{figure}
2.7. Summary

The work presented in this chapter has introduced the surface plasmon polariton (SPP) as a longitudinal oscillation of surface charge density at the interface of a metal and a dielectric. By deriving the dispersion of the mode on a planar interface, it is shown that the mode is non-radiative with exponentially decaying fields into the surrounding media. Methods of enhancing the momentum of the incident field in order to achieve radiative coupling to the SPP have been discussed, with particular attention to grating coupling. This strong confinement of the mode at the interface results in the dispersion of the mode being extremely sensitive to the boundary along which it propagates and the media surrounding it; this characteristic will be discussed in the following chapter. Finally, the phenomenon of SPP induced polarisation conversion has been briefly discussed and the existence of energy gaps in the dispersion of grating coupled SPPs has been explained.
CHAPTER 3
The influence of the interface profile and properties of the surrounding media on the reflectivity from a grating sample.

3.1. Introduction

The strong confinement of the SPP at the interface of a metal and a dielectric has been discussed in the previous chapter. The propagation of the mode, and therefore the shape and position of its resonance, are extremely sensitive to the properties of the interface and its surroundings, and it is for this reason that over the last 30 years this has been exploited for uses in many applications. These have included gas and bio-sensing [e.g. Nylander et al. (1982) and Jory et al. (1994)], optical switching and more generally, the characterisation of media, overlayers and the functional form of the grating profile [e.g. Rosengart and Pockrand (1977), Bryan Brown et al. (1993) and Watts et al. (1997a)]. In general, these parameters may be obtained by recording the reflectivity from the sample as a function of angle of incidence and/or wavelength, and “fitting” the data to a suitable modelling theory.

The work presented in this thesis describes experiments undertaken both at visible frequencies and in the microwave regime. Surface relief gratings for use at visible frequencies (including those used in the studies presented in Chapters 4, 5 and 6) are commonly manufactured by the interferographic exposure of photoresist [Hutley (1982)]. The chemical is spun down onto a glass substrate and the grating is written by exposing the layer to two expanded, collimated beams of coherent ultra-violet radiation. As a result of the exposure, the chemical composition of the photoactive compound changes. Regions of the layer illuminated by the beam are rendered more soluble in a developer and hence the variation may be converted into a spatial profile on the substrate. Exposing the developed sample to 254 nm radiation cross-links the polymer, and baking of the substrate completes the hardening process. A more robust sample may then be prepared by ion- or atom-beam etching the profile through from the
photoresist into the silica-glass beneath. Finally, in order to actually excite the SPP with incident electromagnetic radiation, and observe its resonance, it is necessary to coat the grating with a metal.

Although the interfering beams create a perfect sinusoidal image in the photoresist, the final gratings are significantly distorted from this ideal profile. This is associated with the non-linear response of photoresist to exposure as a function of time, and the difficulty in fully removing the exposed photoresist at the bottom and sides of the grooves in the development process. In addition, the etching rate of photoresist is known to vary with the angle of incidence and therefore the grating’s profile, and the sputtering or thermal evaporation of metal onto the grating will introduce further deviations. It is therefore vital, that in order to accurately predict the reflectivity from a grating, any modelling theory must be able to represent the deviation from the purely sinusoidal case. A significant part of this chapter is therefore dedicated to the discussion of such distortions of the surface profile.

The experiments described in this thesis are not only undertaken at visible wavelengths, but also in the microwave regime. For these wavelengths, it is much easier to manufacture a perfect sample via computer-aided design techniques. However, metals become much more ideal in the microwave regime, and hence the response from a near-perfectly-conducting sample is considered. Such modelling experiments illustrate the need to increase the depth-to-pitch ratio of the grating to observe the resonance of the SPP, and hence the effects of increasing the fundamental amplitude of the corrugation are described. In addition the use of dielectric overlayers are discussed.

3.2. Grating modelling theories

In Chapter 2, a historical overview of experimental observations of the SPP is provided. Here, we briefly discuss some of the developments made in theoretically reproducing these “anomalous” results. However, it should be appreciated that, even today, predicting the reflectivity from gratings often requires much computing time. Hence the rigorous fitting of the theory to the experimental data in order to obtain the surface parameters has only really become practical within the last ten years.
In order to rigorously model the electromagnetic response of an interface Maxwell’s equations must be solved in both the upper and lower media, and the appropriate boundary conditions must be satisfied. These are:

1. The continuity of the tangential $\mathbf{E}$- and $\mathbf{H}$-fields at any interface.
2. The outgoing wave equation, i.e. all fields remain finite as $y \to \infty$.

The modelling theory used to predict the electromagnetic response from the sample in this work is based on an approach developed by Chandezon et al. in 1982. However it was Lord Rayleigh (1907) who proposed the first rigorous approach. He assumed that the various diffracted orders were coupled together by a boundary condition on the surface of a perfectly conducting grating. Rayleigh expresses the field far away from the grating as a series of outgoing plane waves of constant amplitude, while close to the surface he also takes account of evanescent waves whose amplitudes decrease exponentially with distance away from the interface.

Rayleigh’s theory was able to correctly predict the point at which a diffracted order passes from being real and propagating in the dielectric, to being evanescent in the metal. However, it fails to predict the surface plasmon resonances observed by Wood and the Rayleigh anomalies observed in the reflected TE-spectra from deep metallic diffraction gratings by Palmer (1952). This is because his method is only valid for shallow gratings with pitch-to-depth ratios of up to 0.07 [Petit and Cadilhac (1966)]. His theory does not take into account the effect of the incident field in the space within the grating grooves. This will act as to induce circulating currents at the surface of the grating and these in turn generate travelling electromagnetic waves. Clearly this problem becomes more significant as the grating grooves are made deeper. In addition, since his theory makes the assumption that the metal is perfectly conducting, the surface plasmon resonances would have been very difficult to observe since they will occur at the same angular position as the Rayleigh anomaly (Section 3.7). Restricting the system to shallow grooves will result in modes that are under-coupled and extremely narrow. It was perhaps for this reason that the two anomalies were often considered to be artefacts of the same physical phenomenon at this time.
In fact, up until the mid-1960s all grating theories generally assumed the metal to be perfectly conducting. In order to correct the results for the effects of finite conductivity, the theoretical results were simply multiplied by the reflectance from a planar slab of the same material. Of course, this assumption is not always valid, as indicated by Häglund and Sellberg in 1966 who showed that in the region of the resonance of a SPP, a significant proportion of the radiation incident upon a metallic grating does not leave the surface. Hence the dark bands, similar to those first observed in the TM reflectivity spectrum from ruled speculum metal gratings by Wood in 1902, were not obviously apparent in theories up to this time.

However, in 1965 Hessel and Oliner presented the first theory that confirmed that there are in fact two distinct types of anomaly. They successfully predicted the Wood’s anomaly by describing it as a resonance effect where a guided wave propagates along the surface. In addition, their theory predicted the existence of the Rayleigh anomaly (pseudo-critical edge - due to the passing off of higher diffracted orders) for both incident polarisations. Since it employs a surface reactance boundary condition that takes into account the standing waves within the grooves, it is valid for all types of media, and for shallow and deep gratings alike.

The results of Häglund and Sellberg described above were later reproduced in a new integral formalism developed by Maystre (1973), based on the Rayleigh expansion and also taking into account forward scattering within the grooves and the finite conductivity of the metal. In addition, Hutley and Bird (1973) and McPhedran and Maystre (1974) confirmed the results in comprehensive experimental and theoretical studies. However, in the microwave regime, it is adequate to assume the metal is ideal and a discussion of the propagation of SPPs on perfectly conducting gratings and the possible observation of the surface plasmon resonance will be presented later in this chapter. Regardless of whether lossy, or perfectly conducting gratings are being considered, a theory based on the formalism of Chandezon et al. (1982) is utilised throughout this thesis, and is outlined in the section below.
3.3. The Differential Formalism of Chandezon et al.

The limitation imposed by Rayleigh’s theory is not encountered in the Chandezon method as this approach uses a co-ordinate transformation to effectively flatten the surface, thus allowing the exact matching of the boundary conditions at the interface. The translation used is

\[ \begin{align*}
    v &= x \\
    u &= y - A(x) \\
    w &= z.
\end{align*} \]

where \( A(x) \) represents the interface profile. Despite easing the application of the boundary conditions, the expression of Maxwell’s equations in this non-orthogonal co-ordinate system \((u, v, w)\) is more complex. Hence Fourier expansions are used to describe Maxwell’s equations and the incident and scattered fields. Clearly, in order to solve the problem numerically, it is necessary that these infinite series are truncated and therefore a limit must be placed on the number of scattered orders in the system. Hence a compromise must be reached between adequately describing the system and obtaining convergence in the routine, and minimising the necessary computation time. For most of the modelling work undertaken in this thesis, the number of scattered orders was limited to 6, however an increase in the pitch-to-depth ratio would require this truncation parameter to be suitably increased.

Chandezon’s original theory is able to model several interfaces each of the same singularly periodic relief profile, with the plane of incidence parallel to the grating vector \( (\varphi = 0^\circ) \). However there have been a number of recent advances made which permit the modelling of:

- Gratings in the conical mount \( (\varphi \neq 0 \ i.e. \ the \ plane \ of \ incidence \ is \ not \ parallel \ to \ the \ grating \ wave \ vector, \ k_g) \ [Elston et al. (1991a,b)].\)
- Conical diffraction from corrugated multilayered isotropic media [Li (1994)].
- Multilayer gratings of arbitrary shape. [Preist et al. (1995) and Granet et al. (1995a)].
- Improvement of numerical stability (Scattering matrix technique) [Cotter et al. (1995)].
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- Conical diffraction from corrugated multilayered uniaxial media [Harris et al. (1996a)].

- Response of bi-grating structures (an interface corrugated in two different directions) [Granet et al. (1995b), Harris et al (1996b)]

- Response of blazed (non-symmetric) and overhanging gratings by using an oblique transformation. [Granet et al. (1997) and Preist et al. (1997)].

A useful overview of the original formalism of Chandezon et al. and its recent developments is provided in the PhD thesis of Wantall (1999).

As discussed above, all calculations based on the differential formalism of Chandezon et al. give only approximate solutions to the problem as they rely on an infinite Fourier series that must be truncated. However the most rigorous method for modelling gratings is perhaps that of Maystre (1978) who uses an integral technique and which permits the modelling of multi-layered and multi-shaped gratings of any depth-to-pitch ratio. The downfall of this technique is its numerical and conceptual complexity compared to the differential formalism described above.

3.4.  Representation of the surface profile

As previously discussed, the excitation of the SPP on a metal-dielectric interface allows one to characterise the surrounding media. However to achieve this accurately, the profile of the surface must first be correctly quantified since it is usually impossible to manufacture a purely sinusoidal interface. Many workers have approached this representation in a number of different ways. For example, Bryan Brown et al. (1993) proposed to distort the sine wave by raising it to a power:

\[ A(x) = h \left( \left( \frac{\sin(k_g x) + 1}{2} \right)^\gamma - \frac{1}{2} \right) \]

Equation 3.4.1

where \( k_g \) is the grating wave vector and \( h \) is the grating groove depth.
Wood et al. (1995) demonstrated the failure of Bryan-Brown’s model (Equation 3.4.1) in its inability to accurately represent a grating profile manufactured by interferometry and fast-atom etching. Instead they illustrated that their experimentally derived data could be fitted to a model based on a Fourier series representation of the surface. The amount of distortion was small and was consistent across a number of different wavelengths in the visible regime. This Fourier Series approach was suggested by Rosengart and Pockrand (1977), and later used by Pipino and Schatz (1994) to model angle-dependent reflectivities from distorted-sinusoidal metallic gratings. This is a sensible parameterisation to use as the individual Fourier amplitudes $a_1, a_2, \ldots, a_N$ govern the strength of the direct coupling mechanisms to the $\pm 1, \pm 2, \ldots, \pm N$ diffracted orders and associated SPPs respectively. Hence, throughout this work, a truncated Fourier series representation of the surface profile, $A(x)$, is also used:

$$A(x) = a_1 \sin(k_g x + \Phi_1) + a_2 \sin(2k_g x + \Phi_2) + \ldots + a_N \sin(Nk_g x + \Phi_N)$$

Equation 3.4.2

For non-blazed (symmetric) profiles the phases $\Phi_1, \Phi_2, \ldots, \Phi_N$ are each set to $\pi/2$ and Equation 3.4.2 reduces to a simple cosine series

$$A(x) = a_1 \cos(k_g x) + a_2 \cos(2k_g x) + \ldots + a_N \cos(Nk_g x)$$

Equation 3.4.3

However, unlike Rosengart and Pockrand who expressed the grating distortion using only the $2k_g$ ($a_2$) term, Wood et al. found it necessary to include a term in $3k_g$ ($a_3$). The pitch of the grating was chosen to allow the excitation of the $\pm 1, \pm 2$ and $\pm 3$ real diffracted orders and associated SPPs, and hence higher Fourier amplitudes could be ignored. As an example, Figure 3.4.1 illustrates the distortion arising from the introduction of a first and second harmonic ($a_2$ and $a_3$). Similarly, Figure 3.4.2 shows the effects of changing the relative phase of the first harmonic ($\Phi_2$). The electromagnetic response from all of the profiles shown can quickly and easily be modelled using the Chandezon method.
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Figure 3.4.1 The distortion arising from the introduction of a first harmonic, \( a_2 \) (---) compared to an undistorted sinusoid (—). The distortion caused by the addition of a further harmonic, \( a_3 \), is also shown (•••). The relative amplitudes of the Fourier coefficients are \( 0.1a_1 = 0.5a_2 = a_3 \), with \( \Phi_1 = \Phi_2 = \Phi_3 = \frac{\pi}{2} \) (using Equation 3.4.2).

Figure 3.4.2 Illustration of the effect of changing the relative phases of the fundamental and first harmonic with \( a_2 = 0.2a_1 \), \( a_3 \) and higher harmonics set to zero, \( \Phi_1 = 0 \) and (a) \( \Phi_2 = 0 \) (b) \( \Phi_2 = \frac{\pi}{2} \) (c) \( \Phi_2 = \pi \) and (d) \( \Phi_2 = \frac{3\pi}{2} \) (using Equation 3.4.2).
The addition of a first harmonic, \( a_2 \) with a suitable phase with respect to the fundamental (i.e. either use \( \Phi_1 = \Phi_2 = \pi/2 \) \([Figure 3.4.1]\), or \( \Phi_1 = 0, \Phi_2 = 3\pi/2 \) \([Figure 3.4.2]\)) clearly flattens the bottom of the trough and sharpens the peaks compared to the undistorted sinusoidal profile. Gratings manufactured using the interferographic technique often demonstrate profiles of this form due to the non-linear response of the exposed photoresist.

Note the symmetry of the profiles in \( Figure 3.4.2 \). Profiles (b) and (d) with \( \Phi_1 = 0 \) and \( \Phi_2 = p\pi/2 \) (where \( p \) is an integer) possess the symmetry \( A(x) = -A(x) \). On the other hand, profiles (b) and (d) with \( \Phi_2 = p\pi \) are not symmetric about \( x = 0 \) and are said to be \textit{blazed} and begin to resemble a sawtooth structure.

By increasing the number of Fourier coefficients, it is possible to accurately represent more complicated profiles. For example the profile shown in \( Figure 3.4.3 \) has been represented using fourteen Fourier coefficients. \( Figure 3.4.4 \) shows a square grating represented with the same number of Fourier coefficients and the undesirable oscillation illustrates the difficulty in modelling a profile with vertical edges using this technique.

\[Figure 3.4.3 \text{ (a): Fourier series representation using fourteen coefficients of the profile shown in (b).}\]
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Figure 3.4.4 (a): Fourier representation using fourteen coefficients of a square wave grating (b).

3.5. The reflectivity features and the Littrow angle

It is often helpful to use the concept of $k$-space to predict the number and position of reflectivity features in an angle scan. This representation is particularly useful when choosing the optimum angle of incidence and wavelength at which to carry out an experiment. Clearly, before attempting to construct a $k$-space diagram, or produce fits to experimental data, the pitch of the grating ($\lambda_g$) must be accurately determined. The point at which Equation 3.5.1 is satisfied provides an excellent method for doing this. A Rayleigh anomaly is observed when a real diffracted order ceases to propagate in the dielectric and becomes evanescent in the metallic media (or vice-versa). The resulting redistribution of energy is experimentally observed as a sharp step in the detected reflectivity.

$$k_0 = n_k k_0 \sin \theta \pm N \lambda_g$$  \hspace{1cm} Equation 3.5.1

The height of the step depends only on the amount of radiation diffracted into the order in question, and hence the shape of the feature is dependent on the grating depth.
However there is a large degree of degeneracy associated with fitting only to this feature, and no information about the dielectric properties of the media surrounding the interface can be extracted.

As described in Section 2.4.2, it is possible to resonantly excite SPPs at a metal-dielectric interface for a number of different angles of incidence and wavelengths when the following coupling condition is satisfied,

\[ \mathbf{k}_{\text{SPP}} = n_1 \mathbf{k}_0 \sin \theta \pm N \mathbf{k}_g \]

Equation 3.5.2.

Since \( \mathbf{k}_{\text{SPP}} \) is strongly dependent on the interface profile and the media surrounding the boundary, one may successfully parameterise the profile and dielectric properties by fitting the theoretical model to the shape and position of the surface plasmon resonances (SPRs). However, more than one resonance condition is often observed in a typical momentum scan, therefore it is convenient to label the SPRs with the sign and number of the diffracted order which is providing the coupling via its evanescent field.

*Figure 3.5.1 (top)* illustrates the reciprocal space for a non-blazed metallic grating (\( \varepsilon = -17.5 + 0.7i \)) with \( a_1/\lambda_g = 0.050 \), \( a_2 = 0.1a_1 \), \( a_3 = 0.02a_1 \) and \( \lambda_0/\lambda_g = 0.575 \).

The light circles have radius \( k_0 \) and are spaced by the grating wave vector \( k_g = 2\pi/\lambda_g \).

For clarity, the SPP circles have not been shown, but as discussed in Section 2.4.2, they exist at a slightly higher momentum than the incident photon (for example, *Equation 2.3.8* gives \( k_{\text{SPP}} \approx 1.03k_0 \) for a planar silver interface at 632.8 nm). The white arrow represents a momentum scan along the direction perpendicular to the orientation of the grating grooves (\( \varphi = 0 \)), and hence one may predict the order of features that may be observed in the specular beam (zeroth order): +2 SPP, +2 Rayleigh anomaly, -1 SPP, -1 Rayleigh anomaly, +3 SPP, +3 Rayleigh anomaly.
Below the reciprocal space diagram are the theoretically modelled $R_{pp}$ responses of the zeroth, minus 1, plus 2 and plus 3 orders (where the subscripts refer to the incident and detected polarisations respectively. The reflectivities are plotted on a logarithmic scale and as a function of scaled in-plane momentum ($k_x/k_0$). These traces are best realised experimentally by scanning the polar angle of incidence ($\theta$) where $k_x = k_0 \sin \theta$. The

Figure 3.5.1 (top) The $k$-space diagram for a grating with $k_0/k_g = 0.575$. The white arrow corresponds to a momenta scan $0 < k/k_0 < 1$ in the direction of $k_x$ ($\phi = 0$). The theoretically modelled $R_{pp}$ response of the zeroth, minus 1, plus 2 and plus 3 orders are shown beneath the $k$-space diagram. The respective Littrow angles (black dashed lines) and Rayleigh anomalies (white dashed lines) are also illustrated.
white dashed lines indicate the positions of the Rayleigh anomalies, and the black dashed lines show the symmetry lines for each of the orders illustrated. These symmetry points correspond to their Littrow mounting angle, defined as the angle of incidence that coincides with the relevant diffracted order having exactly the reversed momentum of the incident beam. Hence, the Littrow condition is satisfied when

$$k_x = k_0 \sin \theta_L^N = Nk_g - k_0 \sin \theta_L^N$$

Equation 3.5.3

and so

$$\sin \theta_L^N = \frac{k_x}{k_0} = \frac{Nk_g}{2k_0}$$

Equation 3.5.4

where $k_0$ is the momentum of the incident photon, $k_g$ is the grating wave vector and $\theta_L^N$ is the Littrow mounting angle for the $N$th diffracted order. Hence, for the system described above, $\sin \theta_L^0 = 0$, $\sin \theta_L^{-1} = -0.288$, $\sin \theta_L^{+2} = 0.575$ and $\sin \theta_L^{+3} = 0.863$. Notice how the two SPRs in the +2 order trace (i.e. the resonances associated with the –1 and +3 diffracted orders) are symmetric in both position and coupling strength about their Littrow angle. Note that the –1 and +3 SPRs do not share the same symmetry in the zeroth order trace, since this order must be symmetric about $\sin \theta_L^0 = 0$. These and other similar symmetries must be present in order for reciprocity to be satisfied.

The theoretically predicted response from the grating shown in Figure 3.5.1 is illustrated as a function of in-plane scaled momentum. Clearly it is not possible to experimentally record data in this way directly, instead the reflectivity from the grating may be recorded as a function of angle of incidence (polar, $\theta$ or azimuthal, $\phi$) or incident wavelength. If the data in Figure 3.5.1 is instead plotted as a function of angle of incidence, the width of the resonances would vary depending on the angle at which they occur. Hence, it is often useful to plot the predicted reflectivities as a function of incident momentum so that the symmetry of the diffracted orders about their respective Littrow angles may be observed.
Generally all metals behave as near-perfect conductors in the microwave regime since the electrons in the metal may respond almost perfectly to the incident-oscillating field. Therefore the effect of any small variation in the frequency-dependent dielectric function of the metal is insignificant. An apparatus has been developed that allows the response of such a sample to be recorded as a function of both wavelength and azimuth angle-of-incidence simultaneously. This is achieved in the microwave regime using a rotating table and continuous-wave source (Chapter 7). However when the reflectivity is recorded from a similar, scaled-down sample in the visible regime, the dielectric response of the metal is no longer wavelength-independent and hence it becomes more difficult to characterise the profile. In addition, only at the frequency of SPP resonance is it possible to gather enough information to determine the dielectric response of the substrate and hence the accurate measurement of a metal’s dielectric function across a range of wavelengths is very difficult. Therefore, the dielectric functions of metals in the visible regime are normally determined by fitting to a number of angle-scans ($\theta$ or $\varphi$) each at a different incident wavelength. Traditionally scans are carried out as a function of the polar angle ($\theta$) (Chapters 4 and 5), however an azimuthal angle ($\varphi$) scan has a number of advantages, principally that it involves no moving detectors (Chapter 6).

### 3.6. The profile of the grating

The grating modelled in the previous section has a distorted profile of the form of Equation 3.4.2. For the remainder of this chapter, the studies are limited to similar non-blazed surfaces, where the cosine series may be used to represent the profile.

As was briefly discussed earlier in this chapter, the use of a Fourier Series representation of the interface is convenient since it effectively allows one to introduce extra low amplitude periodicities into the grating profile. This introduces the grating wave vectors $2k_g$, $3k_g$ *etc* into the system, where the wave vector, $Nk_g$, is responsible for the direct coupling mechanism to the $\pm N$ SPP. Thus the size and relative phase of each of the Fourier amplitudes has a profound effect on the width, depth and position of the associated SPR. It is this sensitivity that allows the functional form of the grating
profile to be accurately determined by fitting the predictions from the grating modelling theory to the experimental results.

### 3.6.1. Variation of $a_1$, the fundamental amplitude

*Figure 3.6.1* shows the effect on the $R_{pp}$ specular response of the grating similar to that studied in *Section 3.5*, in the region of the +1 SPR of varying the fundamental amplitude of the profile. The off-resonance signal decreases as the fundamental amplitude is increased and more energy is channelled into diffracted orders. Notice also that the depth of the resonance initially increases with increasing amplitude and reaches a maximum, where the reflectivity falls to zero, at approximately $a_1 = 0.02\lambda_g$. At this point, the radiation reflected directly from the surface (the zeroth diffracted order) and the radiation out-coupled from the SPP are equal and exactly out of phase. With values of $a_1$ less than approximately $0.02\lambda_g$, the two components do not sum to zero, and the resonance is said to be under-coupled. As $a_1$ is increased above the optimal coupling condition, again the phase and magnitude of the components will vary, and the depth of the resonance will decrease. Eventually the resonance minimum becomes a peak for $a_1 > 0.06\lambda_g$ (approximately) since the sum of the two components of the specular beam is now greater than the fraction of energy remaining in the specular order. It is also clear that the width of the resonance and the distance of the SPR from its corresponding Rayleigh anomaly both increase as the grating grooves are deepened. This perturbation of the SPR dispersion has been discussed by *McPhedran and Waterworth* (1972), *Pockrand* (1976) and *Raether* (1988). They illustrated that the half-width and distance of the resonance from its associated Rayleigh anomaly both increase linearly, to a first-order approximation, with the square of the grating amplitude. Similar phenomena can be observed in the region of the −2 SPR (*Figure 3.6.2*), where the mode is excited via two successive $k_g$ scatters. These relationships are illustrated in *Figure 3.6.3* for the theoretical data presented here.
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Figure 3.6.1  The effect of varying the fundamental amplitude on the $R_{pp}$ specular response in the region of the +1 SPR. The grating parameters used in the modelling are $k_0/k_g = 0.575$ and $\varepsilon_2 = -17.8 + 0.7i$, and $a_i$ is varied from $0.01\lambda_g$ to $0.07\lambda_g$.

Figure 3.6.2  The effect of varying the fundamental amplitude on the $R_{pp}$ specular response from the same grating as studied in Figure 3.6.1 in the region of the –2 SPR.

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Consider once again the grating represented in Figure 3.5.1 and in particular the predicted zero order response. As the in-plane momentum is increased from $k_x/k_0 = 0$ a SPR associated with the $+2$ diffracted order is observed, followed by its Rayleigh anomaly, and then a Rayleigh anomaly associated with the $-1$ diffracted order and its SPR. The third order SPP at higher values of $k_x/k_0$ is only weakly coupled by the purely sinusoidal profile and hence its resonance is difficult to observe in Figure 3.5.1.
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Figure 3.6.4 The effect on the specular $R_{pp}$ response from the grating ($\varepsilon_2 = -17.8 + 0.7i$) of increasing the magnitude of the first harmonic ($a_2$) of the surface profile. The solid line illustrates the undistorted sinusoidal profile ($a_1/\lambda_g = 0.050$) where $\lambda_0/\lambda_g = 0.575$. The dashed line is the predicted response from a profile with the addition of $a_2 = 0.1a_1$ and the dotted line shows the modelled reflectivity when $a_2 = 0.2a_1$.

Figure 3.6.4 illustrates that a change in shape and a deepening of all these resonances may be observed as the magnitude of $a_2$ is increased.

The distortion of a purely sinusoidal interface by a first harmonic introduces the possibility of scattering of radiation by the wave vector $\pm 2k_g$ in addition to $\pm k_g$ provided by the fundamental component. Therefore the first harmonic and its associated wave vector now provide a direct coupling mechanism into the second diffracted orders and excite the associated SPP by an alternative and more probable process than the double $k_g$ process from the fundamental. As this alternative mechanism begins to dominate, rapid changes in the diffracted efficiencies and the shape of the SPR are observed. However, as Figure 3.6.4 illustrates, the 2nd order SPP
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is not the only feature affected, as a substantial change in the shape of the 1st order resonance is also observed. This is because the first-order SPR may now be excited by a \((\pm 2k_g, \mp k_g)\) scattering process, in addition to the direct \(\pm k_g\) mechanism.

It is clear that the third-order SPP is not well manifested in the specular reflectivity from an undistorted grating (solid line). The lack of harmonics distorting the profile from a sinusoid, in addition to the small depth to pitch ratio means that the percentage of radiation being scattered into the +3 diffracted order is not great enough to easily observe the resonance experimentally. However, as demonstrated in Figure 3.6.4, the introduction of a first harmonic into the gating profile increases the coupling of incident radiation to the third order SPP since radiation may now be diffracted by the more probable double scattering event \(\{\pm 2k_g, \pm k_g\}\).

3.6.3.  Variation of \(a_3\), the second harmonic

*Figure 3.6.5* illustrates the effect of increasing the magnitude of the second harmonic \(a_3\) on the +3 SPP observed in the specular reflectivity from a metallic grating \((\varepsilon_2 = -17.8, 0.7i)\) with \(a_1/\lambda_g = 0.050\) and \(a_2 = 0.1a_1\), where \(\lambda_0/\lambda_g = 0.575\). Similarly, *Figure 3.6.6* shows the effect on the specular \(R_{pp}\) response of the grating in the regions of the +1 and -2 SPRs. It is important to note that the +3 SPP excited by radiation incident on a profile that contains only the fundamental and first harmonic components is manifested as a maximum in reflectivity rather than a minimum (*Figure 3.6.4*). The +3 SPP is coupled to by radiation diffracted by either the \((\pm k_g, \pm k_g, \pm k_g)\) or \((\pm 2k_g, \pm k_g)\) scattering events, where the latter is the more probable. A maximum reflectivity is observed because the dominant scattering event introduces a phase difference between the radiation out-coupled from the SPP and that specularly reflected from the interface such that they add, rather than interfere destructively as observed with the +2 and –1 resonances. However, on the introduction of a second harmonic and the associated \(3k_g\) wave vector, the +3 SPP may be excited directly by a single \(\pm 3k_g\) scattering event. This direct coupling mechanism will dominate over the other two alternative events, and results in a phase difference such that a minimum reflectivity is
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\[ \text{Figure 3.6.5} \] The effect on the specular \( R_{pp} \) response from the metallic grating \( (\varepsilon_z = -17.8, 0.7i) \) in the region of the \(-3\) SPR of varying the magnitude of the second harmonic \( (a_3) \) of the grating profile. The solid line illustrates the profile with \( a_1/\lambda_g = 0.050, \ a_2 = 0.1a_1, \ a_3 = 0 \) where \( \lambda_0/\lambda_g = 0.575 \). The other lines show the predicted responses when \( a_3 = 0.02a_1 \) (dashed), \( a_3 = 0.04a_1 \) (dotted), \( a_3 = 0.06a_1 \) (dot-dash) and \( a_3 = 0.08a_1 \) (dot-dot-dash).

observed. Therefore as the magnitude of \( a_3 \) is increased, the resonance anomaly changes from a maximum to a minimum (Figure 3.6.5).

The significant change in shape and position of the SPRs in Figure 3.6.4, Figure 3.6.5 and Figure 3.6.6 clearly illustrates the serious problems that may be encountered in the fitting of experimental data to the theoretical model if the grating profile is not represented by a sufficient number of Fourier components. Clearly, such a restriction on the surface parameters may lead to an incorrect characterisation of the dielectric functions of the surrounding media. However the flexibility of the grating modelling procedure used in this thesis allows, in theory, for an infinite number of Fourier profile components to be introduced. Since it is sensible to keep computation times to a minimum, the series is truncated at the point at which the reflectivity from the sample

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In this way, one may accurately determine the permittivities of the media surrounding the interface.

3.7.   The permittivity of the grating substrate

The work described in this thesis may be divided into two sections. The first three experimental chapters are concerned with the characterisation of the interface and the dielectric properties of the metallic substrate at visible frequencies. The remaining chapters investigate the response of periodic and corrugated structures at much longer wavelengths when real metals generally become near-perfectly conducting. However in order to observe the resonance of the surface mode at microwave frequencies, it will be demonstrated that the pitch-to-depth ratio of the grating must often be greater than that normally used in the visible regime. This increase in perturbation results in reflectivity
features that are quite different to those normally associated with SPPs. Therefore this section considers a series of gratings of varying depth and illustrates the change in reflectivity as the metal is made near-perfectly conducting. Hence, by using a rigorous grating modelling theory, it is possible to design a surface from which the resonance of a SPP may be observed in the reflected intensity.

First consider a diffraction grating that is able to diffract radiation into the ±1 and ±2 orders, and excite the corresponding SPPs. For the sake of simplicity, only purely sinusoidal gratings will be considered in this section, however it is important to realise that it is generally difficult to manufacture such an ideal profile. In addition, the predicted responses are plotted as a function of angle of azimuth since such a study is easily undertaken at microwave frequencies. Clearly there is no need to examine more than 90° of azimuthal dependent data unless the grating is non-symmetric (blazed). Each of the reflectivity scans has been modelled at a fixed polar angle of incidence \( \theta = 30^\circ \), with a wavelength-to-pitch ratio, \( \lambda_0/\lambda_g = 0.707 \). The white arrow on the \( k \)-space diagram below \((Figure 3.7.1)\) represents this system, and hence first- and second-order Rayleigh anomalies and SPRs are expected.

![Figure 3.7.1 k-space diagram of the grating modelled in this study \((\lambda_0/\lambda_g = 0.707)\). The white arrow represents an azimuthal angle scan \((\varphi = 0 \rightarrow 90^\circ)\) at a fixed polar angle of incidence \( \theta = 30^\circ \).](image)
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Figure 3.7.2 (a) shows the $R_{pp}$ response from this grating with $a_i/\lambda_s = 0.033$ and a metal permittivity typical of silver at $\lambda_0 = 632.8$ nm (where $\varepsilon_{2(\text{Ag})} = -17.8 + 0.7i$). Notice how the +2 SPP is inverted in nature. As previously discussed, this is because a second order feature can only be excited by two successive $k_g$ scattering events. The phase change associated with this double scatter causes the out-coupled beam to constructively interfere with the specularly reflected beam and a maximum in intensity results. Figure 3.7.2 (b) shows a similar system, but the silver grating is now replaced with a near-perfectly conducting one of the same surface profile.

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Figure 3.7.2 The predicted $R_{pp}$ reflectivity as a function of azimuthal angle ($\phi$) from a grating with the following parameters: $\lambda_0/\lambda_s = 0.707$, $a_i/\lambda_s = 0.033$, $\theta = 30^\circ$, and (a) $\varepsilon_2 = -17.8 + 0.7i$, (b) $\varepsilon_2 = -10^6 + 10^9i$. The dotted lines show the angular positions of the Rayleigh anomalies.

It is immediately obvious that in effectively making the substrate more metallic the resonances have become much narrower and have moved in angular position towards their respective Rayleigh anomaly, to such an extent that the two features are difficult to distinguish from each other. The SPP dispersion relation for a planar interface (Chapter 2) provides an estimate of the difference in momentum between that of the Rayleigh anomaly and the SPP:

$$k_{spp} = k_0 \frac{\varepsilon'_1 \varepsilon'_2}{\sqrt{\varepsilon'_1 + \varepsilon'_2}}$$

*Equation 3.7.1*
where \( k_0 \) and \( k_{\text{SPP}} \) are the momenta of the incident photon and SPP, and \( \varepsilon'_1 \) and \( \varepsilon'_2 \) are the real parts of the permittivity of the dielectric and metal respectively. Hence, it is clear that \( (k_{\text{SPP}} - k_0) \to 0 \) as \( \varepsilon'_2 \to -\infty \).

Clearly, it would be difficult to experimentally observe the reflectivity features shown in Figure 3.7.2(b), particularly at microwave frequencies where at least a 1° beam spread is inherent in the system. Therefore it is necessary to manufacture a grating profile that supports the SPP over a wider range of momentum. As previously discussed (Section 3.6) this may be achieved by increasing the amplitude of the grating, the effects of which are illustrated for this near-perfectly-conducting substrate in Figure 3.7.3.

![Figure 3.7.3](image)

*Figure 3.7.3* The effect on the specular \( R_{pp} \) response of the sample of increasing the amplitude of the profile formed in a near-perfectly-conducting substrate where \( \lambda_0/\lambda_g = 0.707 \), \( \theta = 30^\circ \) and \( \varepsilon_2 = -10^6 + 10^6 i \).
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It will be discussed in Chapter 7 that the width of the SPP is governed by two damping parameters [Pockrand (1976) and Raether (1988)]: the imaginary part of the dielectric functions of the media surrounding the interface ($\varepsilon''$), and the depth of the grating profile ($2a_i$ for a purely sinusoidal profile). For relatively shallow gratings, such as the one modelled in Figure 3.7.2, it is the primarily the imaginary part of the dielectric function of the metal substrate that determines the width of the SPR. Clearly the penetration of the field into a near-perfectly-conducting material with such a large, negative, real part of the permittivity will be very small compared to, for example, the skin depth of silver at 632.8 nm. Hence direct Joule heating of the substrate is largely insignificant and therefore the choice of $\varepsilon''$ has very little effect on the response from the grating. This insensitivity is illustrated in Figure 3.7.4.

Figure 3.7.4  Theoretically modelled reflectivity data from the grating discussed in Figure 3.7.1 with $a_i/\lambda_y = 0.033$ and $\varepsilon'_2 = -10^6$ around the (a) +2 and (b) −1 SPR. The solid line represents the electromagnetic response of the surface when $\varepsilon''_2 = 10^9$ (also shown in Figure 3.7.2(b)). Similarly, the squares represent the response when $\varepsilon''_2 = 10^0$ and the triangles when $\varepsilon''_2 = 10^{12}$.
3.8. The use of overlayers

Since SPPs are surface modes, their fields are strongly localised at the surface of the metal, and therefore they are sensitive to any changes that may occur around the interface. Hence deposition of a dielectric overlayer increases the momentum of the surface mode and shifts the position of the resonant angle, where the size of the shift depends on the thickness and refractive index of the overlayer [Raether (1988)]. In addition, if the overlayer is lossy, then the width of the resonance is also increased. The sensitivity of the SPP to changes in its surrounding environment can therefore be used to characterise the properties of an overlayer. An obvious application of this sensitivity is to employ SPPs as sensors. Molecules can be designed that absorb a particular chemical species from their environment and as they do so, their optical constants change. If a thin layer of such a molecule is deposited on to the surface of a metallic grating, then the SPP resonance position can be used to monitor these small changes [e.g. Jory et al. (1994)]

Figure 3.7.2(b) illustrates the specular $R_{pp}$ response from a grating with $a_g/\lambda_s = 0.033$ formed in a near-perfectly-conducting substrate. This resonance of the SPP may be widened by either increasing the corrugation amplitude (as previously discussed), or by depositing an absorbing overlayer. Figure 3.8.1 illustrates the effect on the $–1$ SPR of depositing a slightly absorbing dielectric overlayer ($\varepsilon_d = 2.29 + 0.05i$) on top of a near-perfectly-conducting grating such that both the air-dielectric and dielectric-metal interfaces have the same profiles. As expected, the half-width of the resonance increases, and the resonant condition moves away from its associated Rayleigh anomaly.
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Figure 3.8.1  Graphs showing the effect on the specular $R_{pp}$ response of depositing a series of lossy overlayers of different thicknesses on top of a grating formed in a near-perfectly-conducting substrate. Both interfaces have the same profile, $a_i/\lambda_g = 0.033$, where $\lambda_0/\lambda_g = 0.707$, $\theta = 30^\circ$, $\varepsilon_d = 2.29 + 0.05i$ and $\varepsilon_2 = -10^6 + 10^9i$. The vertical grey line corresponds to the position of the $-1$ Rayleigh anomaly.

The use of overlayers in this thesis is restricted to the microwave regime (Chapters 7, 8 and 9), where a corrugated dielectric overlayer is deposited on top of a planar metal substrate (Figure 3.8.2). Figure 3.8.3 illustrates the predicted response from a similar sample for each of the cases where the average thickness of the dielectric overlayer is varied between $a_i < t < 2.5a_i$ in steps of 0.25$a_i$. The corrugation amplitude used is $a_i = 0.033\lambda_g$ where $\lambda_0/\lambda_g = 0.707$ (i.e. the same profile as used in the previous figures), the dielectric and metal permittivities are $\varepsilon_d = 2.29 + 0.05i$ and $\varepsilon_2 = -10^6 + 10^9i$ respectively. Also shown for comparison purposes is the predicted response from a grating formed directly into a near-perfectly conducting metal substrate of the same surface profile.
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Figure 3.8.2 Schematic diagram illustrating the sample used in the modelling to demonstrate the change in response with varying dielectric thickness \( t \). Clearly the corrugation amplitude, \( a_i \), must be less than the dielectric thickness, \( t \).

Figure 3.8.3 The predicted specular \( R_{pp} \) response from the sample shown in Figure 3.8.2 (planar substrate) at a number of different dielectric thicknesses \( t \) in the region of the –1 SPR. The parameters used are \( \lambda_0/\lambda_s = 0.707 \), \( a_i = 0.033\lambda_s \), \( \theta = 30^\circ \), \( \varepsilon_d = 2.29 + 0.05i \) and \( \varepsilon_2 = -10^6 + 10^9i \). Also shown for comparison is the response from a sample where the corrugation is produced directly into the near-perfectly conducting substrate \( (i.e.\ no\ overlayer) \). The vertical grey line corresponds to the position of the –1 Rayleigh anomaly.
Again, the resonance widens and moves away from its associated Rayleigh anomaly as the average thickness of the overlayer is increased. Clearly, the minimum average thickness of the dielectric obtainable is when it is equal to the grating amplitude \( t = a_1 \), however even with these parameters, the resonance has shifted by \( 3^\circ \) of azimuth, deepened and significantly widened compared to the predicted results with no overlayer.

### 3.9. Summary

The work presented in this chapter has introduced the rigorous grating modelling theory that is used throughout this thesis, which is based on the formalism of Chandezon et al.. An examination of the effect on the reflectivity from a metallic diffraction grating of varying its depth and degree of distortion has been undertaken. Such distortions from the sinusoidal case are often introduced in the manufacturing processes, particularly in the production of gratings for use at visible frequencies via interferographic techniques. These distortions are seen to dramatically affect the response from a grating in the region of SPP excitation, hence highlighting the need to accurately determine the profile before attempting to characterise the permittivities of the surrounding media. It has been demonstrated that it is useful to describe the distorted profile as a truncated Fourier Series since each harmonic has a wave vector associated with it which provides the direct scattering mechanism to a corresponding diffracted order. For example, the amplitude of the first harmonic \( a_2 \) provides the direct scattering mechanism to the second diffracted order, which in turn provides the necessary enhanced momentum to directly excite the second-order SPP. Consequently, distortion alters the distribution of the incident energy among the diffracted orders and hence changes the coupling conditions to the SPPs. Hence the effect on the reflectivity of the grating of varying the first three terms of the Fourier Series is closely examined.

The effect of changing the permittivity of the substrate is also investigated, and in particular, the response from a near-perfectly-conducting metal is compared to a lossy one. The problems associated with observing SPRs on such metals at microwave frequencies are highlighted and the solutions discussed. These involve a deepening of the grating grooves and/or the use of an absorbing overlayer.
CHAPTER 4

Surface plasmon polariton study of the optical dielectric function of titanium nitride.

4.1. Introduction

The first experimental study in this thesis provides a practical example of the way in which grating-coupled surface plasmon polaritons (SPP) may be used to characterise the dielectric properties of metallic materials. It presents the first detailed study of the coupling of incident visible radiation to the SPP that propagates along a corrugated air-TiN interface. Some of the useful properties of TiN are initially listed, and a few of its many potential applications are described. It is for this reason that many previous workers have already determined its optical properties using other characterisation techniques (e.g. ellipsometry), and these are discussed in Section 4.3. The grating-coupled SPP technique provides an alternative to traditional characterisation techniques (e.g. Kramers–Kronig analysis) that may require additional information about film thickness, or the sample’s optical properties in other parts of the electromagnetic spectrum. The experimental apparatus required to record the angle-dependent reflectivities from a diffraction grating at visible frequencies, and hence observe the resonances, is introduced in Section 4.4. Angle-dependent reflectivities are obtained in the wavelength range 500–875 nm and by comparison with the grating modelling theory, both the imaginary and real parts of the dielectric function have been determined. The dielectric function derived is fitted to a model based on a combination of interband absorptions and free-electron response evaluating both the plasma energy and relaxation time (Section 4.6).
4.2. TiN$_x$ properties and applications

Titanium nitride (TiN$_x$) belongs to a group of transition metal compounds that are of considerable interest because they have a variety of properties that lend themselves to many potential applications. For example, TiN$_x$ has become widely used as a wear-resistant coating on tools because of its mechanical resistance, low friction coefficient and high melting point [Munz et al. (1986)]. Its high chemical stability and low resistivity also make it a good candidate as a diffusion barrier in semiconductor metallization systems [Kanamori (1986), and Gagnon et al. (1996)]. TiN$_x$ is also fascinating in that it appears gold in colour owing to the displacement of the plasma edge into the visible range by the onset of interband transitions [Karlsson et al. (1982), and Schlegel et al. (1977)]. Hence it is often used as a scratch-resistant alternative to gold on decorative jewellery. Its high Drude-like reflectance in the infra-red and high absorptivity in the visible and near infra-red have encouraged its use as a selective absorber and heat mirror. Unfortunately the plasma edge is located at too high an energy to make it an efficient solar absorber in its stoichiometric form [Karlsson et al. (1982), Rivory et al. (1981), and François et al. (1985)]. However it is well known that the plasma energy and the optical and electrical properties of TiN$_x$ films are strongly dependent on the deposition conditions, film thickness and titanium-nitrogen ratio [Rivory et al. (1981), François et al. (1985), Böhm et al. (1972), Kurtz et al. (1986), Szczyrbowski et al. (1988), Pascual et al. (1991) and Valkonen et al. (1986)]. This present study is concerned with exploring these interesting optical characteristics in the visible part of the spectrum using the optical excitation of surface plasmons.

4.3. Previous measurements of $\varepsilon(\omega)$ of TiN$_x$.

The first multi-wavelength study of the optical constants of TiN$_x$ appears to have been carried out by Böhm et al. (1972). They calculated the optical dispersion and absorption parameters of Ti(C,N) solid solutions by means of ellipsometric measurements between energies of 0.6 and 5.5 eV. Their results illustrate the Drude-like response of TiN$_{0.94}$ at low energies and its disturbance by the onset of interband transitions as the photon energy is increased. Schlegel et al. (1977) characterised TiN$_x$ samples using Kramers-Kronig analysis [Wooten (1972)] of reflectivity measurements carried out between 0.3
and 12 eV. Their samples were prepared by chemical vapour deposition (CVD) on to heated crystals of TiN$_x$. Karlsson et al. (1982) and Rivory et al. (1981) both obtained the dielectric function of opaque (thickness, $d > 100$ nm), stoichiometric TiN$_x$ samples prepared by reactive sputtering on to fused-silica and glass substrates respectively. Kramers-Kronig analysis was again used to determine the optical permittivities between 0.02 and 6.2 eV (Karlsson) and 0.5 and 6 eV (Rivory). Szczyrbowski et al. (1988) and Valkonen et al. (1986) determined the optical constants of sputtered TiN$_x$ films in the visible and near infrared spectral regions from measurements of transmission, reflectance and film thickness ($d < 31$ nm). Pascual et al. (1991) deposited opaque TiN$_x$ films by plasma-assisted chemical vapour deposition (PACVD) and determined its dielectric function by means of spectroscopic ellipsometry in the UV–visible range.

The use of grating-coupled surface plasmon polaritons (SPP) in the study of the profile and permittivity of metal surfaces provides an alternative method to the techniques described above. As described in Chapter 2, the reversal of the normal component of the electric field at the surface results in the SPP being very strongly localised at the interface and so it is extremely sensitive to the dielectric properties of the media either side of the boundary. However, on a flat surface the SPP can neither be directly coupled to, nor can it radiate. The enhanced wave vector required to couple into the mode may be provided by using an optical diffraction grating, where the in-plane wave vector enhancement is in multiples of the grating wave vector $k_g$. By varying the magnitude of the incident wave vector in the plane of the grating, wave vector values are found at which incident radiation may couple resonantly to the SPP mode. Experimentally, the excitation of a SPP is observed as a dip in the angle-dependent reflectivity.

Previously, the grating-coupled SPP method has successfully been used to characterise metals including copper [Nash et al. (1995)] and silver [Nash et al. (1996)], and Steinmüller–Nethl et al. (1994) have reported the excitation of SPPs on a thin TiN$_x$ film sputtered onto an approximately sinusoidally-modulated substrate. They recorded angle-dependent reflectivities at four incident wavelengths in the visible regime and compared them with those predicted from a rather simplistic treatment of the interaction of radiation with the surface. This allowed them to estimate the dielectric function of
TiNₓ at these discrete wavelengths. The grating-coupled SPP method presents many advantages over the other techniques described previously. For example, it does not require transmittivity data or the determination of film thickness, hence permitting the use of optically opaque metallic films. It can also be used to calculate the permittivity of a material over a limited wavelength range without the knowledge of its optical response elsewhere in the electromagnetic spectrum - there is no Kramers-Kronig based interpretation.

This present study uses grating coupling of radiation to SPPs on a TiNₓ surface to obtain the dispersion relation of the TiNₓ film. Values of the complex dielectric function are determined at visible wavelengths by comparison of the in-plane reflectance from the corrugated TiNₓ-air interface as a function of the angle of incidence, to the predictions from a rigorous grating theory model which uses the differential formalism of Chandezon et al. (1982). By varying the grating parameters used to generate a theoretical reflectivity trace in the way demonstrated in the previous chapter, it is possible to obtain a good quality fit to the experimental data and hence determine the shape [Wood et al. (1995)] and optical permittivity [Nash et al. (1995 and 1996)] of the TiNₓ surface.

4.4. Experimental

4.4.1. Sample preparation

The corrugated surface used in this work was prepared in silica by standard interferographic techniques [Hutley (1982)]. The method of preparation involves the exposure of spin-coated photoresist on a silica disc to the interference pattern produced by first splitting and then recombining an argon-ion laser beam. After exposure, the photoresist is chemically developed and the resulting profile transferred into the silica by fast atom etching. This produces a robust and large area diffraction grating with a well-defined pitch (in this case \( \lambda_s = 930 \text{ nm} \)) and a uniform surface profile that is somewhat distorted from a pure sinusoid. Subsequent deposition of an optically thick \( (d \approx 600 \text{ nm}) \) layer of titanium nitride produces a metallic-air interface that may support SPPs (Figure 4.4.1).
The TiN$_x$ film was deposited by TEER Coatings Ltd (Kidderminster, UK) using the closed field unbalanced magnetron sputter ion plating system [Monaghan et al. (1993)]. The substrate is ion-cleaned before deposition that ensures a high degree of adherence to the silica surface. Initial sputtering is from a pure titanium target which is “poisoned” by bleeding nitrogen into the coating chamber. In order to attempt to control the titanium/nitrogen ratio of the sputtered sample, the intensity of 501 nm radiation emitted from the target is monitored. From past experience, it is thought that approximately stoichiometric TiN$_x$ may be deposited on the substrate when the intensity of radiation falls to 60% of the original value. The coating pressure in the chamber, back filled with Ar gas, was $4 \times 10^{-3}$ Torr and the substrate bias voltage and temperature were 30 V and approximately 150 °C respectively.

Figure 4.4.1  SEM image the of TiN$_x$-coated diffraction grating used in this study. The contrast of the image is not as high as one would expect from a similar gold-coated sample due to the lower electrical conductivity of TiN$_x$. 

The TiN$_x$ film was deposited by TEER Coatings Ltd (Kidderminster, UK) using the closed field unbalanced magnetron sputter ion plating system [Monaghan et al. (1993)]. The substrate is ion-cleaned before deposition that ensures a high degree of adherence to the silica surface. Initial sputtering is from a pure titanium target which is “poisoned” by bleeding nitrogen into the coating chamber. In order to attempt to control the titanium/nitrogen ratio of the sputtered sample, the intensity of 501 nm radiation emitted from the target is monitored. From past experience, it is thought that approximately stoichiometric TiN$_x$ may be deposited on the substrate when the intensity of radiation falls to 60% of the original value. The coating pressure in the chamber, back filled with Ar gas, was $4 \times 10^{-3}$ Torr and the substrate bias voltage and temperature were 30 V and approximately 150 °C respectively.
4.4.2. Reflectivity Measurements

Previous workers, for example Pascual et al. (1991), have shown the real part of the dielectric function of TiN to be negative, and therefore able to support interface modes, at wavelengths in excess of approximately 500 nm. The wave vector of the incident radiation in the dielectric is \( n_1 k_0 \) (where \( k_0 = \omega/c = 2\pi/\lambda_0 \) and \( n_1 = 1.0003 \) is the refractive index of air) and it is only possible to couple to the SPP when the in-plane component of this has been suitably enhanced. As previously discussed in Chapter 2, this mechanism is provided by the grating’s periodicity, which may increase or decrease the in-plane component of \( n_1 k_0 \) by integer multiples of the grating wave vector, \( k_g \) \((k_g = 2\pi/\lambda_g)\). Hence, the enhanced wave vector of evanescent fields associated with non-propagating diffracted orders allows incident radiation to couple to the SPP when the following condition is satisfied

\[
k_{SPP} = n_1 k_0 \sin \theta \pm N k_g
\]  

Equation 4.4.1.

Here \( N \) is an integer, \( k_{SPP} \) is the wave vector of the SPP and \( n_1 k_0 \sin \theta \) is the projection of the wave vector of the incident radiation parallel to \( k_g \).

The SPP resonances were monitored by recording the specularly reflected intensity from the TiN–air interface as a function of the angle of incidence using the apparatus shown in Figure 4.4.2.
A monochromator is used to illuminate the sample, which has a working range of approximately $450 < \lambda_0 < 900$ nm. Passing the beam through two apertures produces a well collimated beam with an area of $\sim 1$ mm$^2$. The incident light is mechanically chopped with a frequency of approximately 1200 Hz and a graduated polariser sets the polarisation of the beam to an accuracy of $\pm 0.1^\circ$. The beam splitter is used to reflect about 4% of the incident radiation into a reference detector, the output from which is later used to normalise the main signal to correct for small changes in beam intensity. The detectors are large area silicon photomultipliers that have had their casings removed so that the beam is incident directly on the silicon wafer. This minimises the problems associated with detector function should the beam move a small distance across the detector during an experiment.

The sample is mounted on a x-z stage that is fixed to a rotating table, allowing the accurate positioning of the grating over the centre of rotation. The signal detector is mounted on the table such that it rotates at twice the speed of the sample allowing it to
accurately track the zeroth-order-reflected beam. The outputs from both the signal and reference detectors are fed into individual phase sensitive detectors (PSDs) which extract the component of the signal that is modulated at the chopper frequency. The outputs from the PSDs are connected to a computer that also controls the rotating table. It divides the main signal by the reference signal and stores the result as a function of angle on the hard disk. The angular scan rate is carefully set so that it is always significantly slower than the PSD time constant.

In order to obtain absolute reflectivity data, a normalisation scan is taken by removing the sample and directly measuring the signal from the light source (with appropriate filters added in its path). When the signal is divided by the reference, this yields the normalisation constant by which the reflectivity data from the grating is divided.

In order to calibrate the angular position of the table, the zero angle is set by sending the reflected beam from the grating back down the incident beam path and through both apertures. Although the table may be rotated with a precision of $\pm 0.01^\circ$, normal incidence can be set to an accuracy of $\pm 0.03^\circ$. The azimuthal angle ($\phi$) of the grating is set to zero with an accuracy of $\pm 0.05^\circ$ by ensuring all the diffracted orders lie in the plane of incidence. This may be achieved by ensuring that at the Littrow angles, the respective diffracted beams pass back down the incident path and through both the apertures.

In this study, a number of angle-dependent scans have been undertaken using monochromatic, p-polarised (TM) radiation. The incident wavelengths range from 500 to 875 nm in 25 nm steps and are incident upon the sample in a plane parallel to the grating wave vector ($\phi = 0^\circ$).
4.4.3. Using the grating modelling theory

Each of the normalised experimental angle-dependent reflectivity scans were fitted by a least-squares procedure using the scattering matrix [Cotter et al. (1995)] technique based on the differential formalism of Chandezon et al. (1982) which was discussed in Chapter 3. The grating profile is described by a Fourier series

\[ A(x) = a_1 \cos(k_g x) + a_2 \cos(2k_g x) + \ldots + a_N \cos(Nk_g x) + \ldots \]  

Equation 4.4.2

Hence by fitting the reflectivity data to the modelling theory, it is possible to parameterise the grating profile and characterise the dielectric function of the metallic material.

In order to provide an accurate description of the complex dielectric function of TiN, it is first necessary to be confident of the surface profile. In the visible regime, it is well documented [for example, Nash et al. (1996)] that the real part of the dielectric function of silver is more negative, and the imaginary part much smaller than the corresponding values for TiN. Hence the surface plasmon resonances on a silver/air interface are far better defined, consequently giving more sensitivity to the grating profile. Therefore, in order to obtain a good first approximation to the profile of the TiN-coated surface, an optically thick layer of silver is thermally evaporated on top of the TiN. The pitch of the grating was chosen so that when \( \phi = 0^\circ \), incident light of wavelength, \( \lambda_0 = 590 \, \text{nm} \) will excite first, second and third order SPP resonances \( (N = 1,2,3) \) which may be observed as resonant features in an angle of incidence scan. By fitting the optical data from the silver surface to the predicted optical response using the theory described previously, it is possible to obtain a good estimate of the three Fourier amplitudes of the corrugated surface that provide the direct coupling mechanism for the three SPP resonances. This truncated Fourier series can then be used in the fitting of data obtained from the TiN-coated surface over the whole spectral regime. Subsequently, after further fitting, allowing all the surface parameters to vary, a new profile for the TiN surface is obtained by averaging the Fourier components over all wavelengths. This new average profile is then held constant at all wavelengths and the data finally refitted in order to obtain the complex dielectric constant at each of the wavelengths studied.
CHAPTER 4  Surface plasmon polariton study of the optical dielectric function of titanium nitride.

4.5. Results

Figure 4.5.1 shows three sets of typical reflectivity data at incident wavelengths of 650 nm, 725 nm and 800 nm. The solid lines are the theoretical fits, which are in very good agreement with the data (circles). The optical properties of TiN are often likened to those of gold, but the off-resonance reflectivity of less than 50% is clearly less than the ~90% to be expected from gold [Watts et al. (1997a)]. In addition, the resonances themselves are broad and shallow. This indicates that TiN, compared to gold, has an increased \( \varepsilon' \) and probably a less negative \( \varepsilon'' \).

As indicated above, the profile of the grating is initially estimated from the optical characterisation of the silver surface, and then improved by fitting to the TiN data. The pitch, as defined by the angular positions of the Rayleigh anomalies in the experimental reflectivity data was calculated to be \( \lambda_x = 930.1 \pm 0.5 \text{ nm} \) with the permittivity of the dielectric (air) set as \( \varepsilon_i = n_i^2 = 1.0006 \). The grating profile used in the final fits to determine the dielectric function of TiN at each of the wavelengths studied is \( a_1 = 34.4 \text{ nm}, a_2 = 9.2 \text{ nm} \) and \( a_3 = 1.0 \text{ nm} \), and the values of the complex dielectric constants of the TiN determined from these fits are listed in Table 4.5.1 \( (\varepsilon_{TiN} = \varepsilon' + i\varepsilon'') \). The errors in these values are dominated by an uncertainty in the Fourier coefficients of the grating profile. This is attributed to the low sensitivity of the broad and shallow resonance features to the various Fourier coefficients. There is also a variation in the uncertainty over the wavelength range due to a change in the number of SPP resonances observable at different wavelengths in the angle of incidence scans. In addition, there is an increase in the uncertainty when two reflectivity minima overlap, and also as the coupling strength to the resonances decrease as the limit \( \varepsilon' = 0 \) is approached. The results presented in this work, along with those of Karlsson et al. (1982), Rivory et al. (1981), Szczyrbowski et al. (1988), Pascual et al. (1981), Valkonen et al. (1986) and Steinmüller-Nethl et al. (1994) are illustrated in Figure 4.5.2.
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Figure 4.5.1 The experimental angle-dependent reflectivities (○, one point in five plotted for clarity) compared with the theoretically-modelled reflectivities (—) created from a single set of parameters describing the grating profile. (a), (b) and (c) show $R_{pp}$ reflectivity measurements (i.e. p-polarised (TM) radiation was incident and detected) at incident wavelengths of 650 nm, 725 nm and 800 nm respectively. The values of the dielectric constants at these wavelengths that were obtained by fitting the model to the experimental data are shown in Table 4.5.1 below.
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Surface plasmon polariton study of the optical dielectric function of titanium nitride.

Table 4.5.1 The optical dielectric function of titanium nitride experimentally determined in this work, together with estimated errors.

<table>
<thead>
<tr>
<th>$\lambda_0$ (nm)</th>
<th>$\varepsilon_r$</th>
<th>$\delta\varepsilon_r$</th>
<th>$\varepsilon_i$</th>
<th>$\delta\varepsilon_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>-0.20</td>
<td>±0.05</td>
<td>2.41</td>
<td>±0.15</td>
</tr>
<tr>
<td>525</td>
<td>-0.64</td>
<td>±0.10</td>
<td>3.12</td>
<td>±0.25</td>
</tr>
<tr>
<td>550</td>
<td>-1.07</td>
<td>±0.10</td>
<td>3.37</td>
<td>±0.10</td>
</tr>
<tr>
<td>575</td>
<td>-1.43</td>
<td>±0.10</td>
<td>3.79</td>
<td>±0.10</td>
</tr>
<tr>
<td>600</td>
<td>-1.91</td>
<td>±0.10</td>
<td>4.17</td>
<td>±0.10</td>
</tr>
<tr>
<td>625</td>
<td>-2.35</td>
<td>±0.05</td>
<td>4.30</td>
<td>±0.30</td>
</tr>
<tr>
<td>632.8</td>
<td>-2.61</td>
<td>±0.05</td>
<td>4.36</td>
<td>±0.30</td>
</tr>
<tr>
<td>650</td>
<td>-2.88</td>
<td>±0.25</td>
<td>4.75</td>
<td>±0.30</td>
</tr>
<tr>
<td>675</td>
<td>-3.02</td>
<td>±0.15</td>
<td>5.18</td>
<td>±0.10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\lambda_0$ (nm)</th>
<th>$\varepsilon_r$</th>
<th>$\delta\varepsilon_r$</th>
<th>$\varepsilon_i$</th>
<th>$\delta\varepsilon_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>-3.58</td>
<td>±0.10</td>
<td>5.36</td>
<td>±0.10</td>
</tr>
<tr>
<td>725</td>
<td>-4.23</td>
<td>±0.10</td>
<td>5.74</td>
<td>±0.20</td>
</tr>
<tr>
<td>750</td>
<td>-4.84</td>
<td>±0.10</td>
<td>6.07</td>
<td>±0.20</td>
</tr>
<tr>
<td>775</td>
<td>-5.19</td>
<td>±0.05</td>
<td>6.24</td>
<td>±0.20</td>
</tr>
<tr>
<td>800</td>
<td>-5.89</td>
<td>±0.05</td>
<td>6.64</td>
<td>±0.20</td>
</tr>
<tr>
<td>825</td>
<td>-6.03</td>
<td>±0.10</td>
<td>6.96</td>
<td>±0.25</td>
</tr>
<tr>
<td>850</td>
<td>-6.67</td>
<td>±0.10</td>
<td>7.60</td>
<td>±0.25</td>
</tr>
<tr>
<td>875</td>
<td>-7.51</td>
<td>±0.20</td>
<td>8.15</td>
<td>±0.30</td>
</tr>
</tbody>
</table>

Figure 4.5.2 A comparison of the values of the dielectric function of TiN, determined in this work (○), with the results of Karlsson et al. (1982) (+), Rivory et al. (1981) (···), Szczyrbowski et al. (1988) (- - -), Pascual et al. (1991) (◊), Valkonen et al. (1986) (×) and Steinmüller-Nethl et al. (1994) (—).
4.6. Discussion

It is well known that the optical properties of TiN$_x$ films are strongly dependent on the deposition conditions, film thickness and the titanium-to-nitrogen ratio. Therefore, the variation in the values of $\epsilon'$ and $\epsilon''$, as illustrated in Figure 4.5.2 is not surprising. The works of Karlsson et al. (1982) and Rivory et al. (1981) both consider opaque samples ($d > 100$ nm) of similar stoichiometries ($x = 1$), and use identical characterisation techniques in order to obtain the optical constants. As a result, the dielectric function of their respective samples compare favourably. Szczyrbowski et al. (1988) and Valkonen et al. (1986) have both sputtered much thinner films ($d < 31$ nm) and although their values of $\epsilon'$ are comparable to those of other workers, their values of $\epsilon''$ are considerably higher due to increased electron scattering. The “thin” films obtained by PACVD and investigated over visible wavelengths by Pascual et al. (1981) show the most anomalous results. It is not clear why their results give values for both parts of the complex dielectric function which are smaller in magnitude than other studies. Steinmüller-Nethl et al. (1994) used a grating-coupled SPP technique to characterise the optical properties of their magnetron-sputtered film at four wavelengths. They appear to have been the first to record SPP excitation on TiN$_x$. Their films were of comparable thickness to those of Szczyrbowski et al. (1988) and Valkonen et al. (1986) [$d = 50$ nm], however they do not show the associated increase in $\epsilon''$. It should be noted that their data fitting technique is based on a pertubative approach to Fresnel equations, and they assume shallow (depth/pitch $< 0.07$), purely sinusoidal gratings. In view of the fact that their grating is produced by interferographic exposure, followed by ion-etching, then the profile is likely to be distorted significantly from the assumed shape. This results in poor quality fits and the errors associated with their deduced values of $\epsilon'$ and $\epsilon''$ will be large.

To summarise, this chapter has provided a comprehensive study of the SPP on a TiN$_x$ sample using a rigorous model of the optical response of metallic gratings to fit the experimental reflectivity data from an optically thick ($d \approx 600$ nm) sputtered film. The grating profile is accurately modelled as a distorted sinusoidal surface by representing it as a truncated Fourier Series and using the theoretical model described previously. From this, fits may be produced that show excellent agreement with the experimental
CHAPTER 4  Surface plasmon polariton study of the optical dielectric function of titanium nitride.

reflectivities (Figure 4.5.1). The experimentally determined dielectric function (Figure 4.5.2) illustrates that $\varepsilon'$ is slightly smaller in magnitude than deduced by other workers for similar films [Karlsson et al. (1982) and Rivory et al. (1981)] however $\varepsilon''$ shows good agreement with these other studies.

4.6.1.  The free-electron behaviour of TiN, and its interband transitions

If the dielectric function of TiN is dominated by a free-electron behaviour at the wavelengths studied in this work, the data presented here would be expected to conform to the Drude model, i.e.

$$
\varepsilon'(\omega) = \varepsilon(\infty) - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2}
$$

*Equation 4.6.1*

$$
\varepsilon''(\omega) = \frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)}
$$

*Equation 4.6.2*

where $\tau$ is the relaxation time, $\omega_p$ is the plasma frequency and $\varepsilon(\infty)$ is the residual dielectric constant (conventionally assumed to be unity). Therefore, as a first-order approximation, linear relationships should be expected by plotting $\varepsilon'$ against $\lambda^2$ and $\varepsilon''$ against $\lambda^2$. Plotting the data in this way gives the curves of Figure 4.6.1(a) and (b) respectively.

*Figure 4.6.1 (a)* shows a high degree of linearity, the $y$-intercept indicating a residual dielectric constant greater than unity. This can be attributed to a positive contribution to $\varepsilon'$ from the occurrence of interband transitions as predicted by a number of previous workers [Karlsson et al. (1982), Schlegel et al. (1977), Rivory et al. (1981), François et al. (1985) and Böhm et al. (1972)]. The linear fit to $\varepsilon''$ is less convincing and hence also suggests that the optical response of TiN is not purely Drude-like in nature. In addition, previous workers have illustrated that the point at which $\varepsilon' = 0$ is situated at a much lower energy than the predicted plasma resonance. The crossing of the $\varepsilon' = 0$ axis is associated with a screened plasma resonance which has been shifted to lower energies by the onset of interband transitions at photon energies above 2.5 eV.
Consequently, any treatment of the complex dielectric constant close to this region must involve splitting it into two parts, one part corresponding to intraband excitations described by the Drude model, and an interband part corresponding to resonant absorptions based on a Lorentz oscillator model, i.e.

\[ \varepsilon'(\omega) = \varepsilon'_D(\omega) + \varepsilon'_I(\omega) \quad \text{Equation 4.6.3} \]

and

\[ \varepsilon''(\omega) = \varepsilon''_D(\omega) + \varepsilon''_I(\omega) \quad \text{Equation 4.6.4} \]

Figure 4.6.1 A plot of (a) \(\varepsilon'\) against \(\lambda_0^2/\mu m^2\) and (b) \(\varepsilon''\) against \(\lambda_0^3/\mu m^3\) for the data presented in this work. A high degree of linearity suggests that the TiN\(_x\) sample is free-electron like. However the \(y\)-intercept of (a) is greater than \(\varepsilon(\infty)=1\), attributable to a positive contribution to \(\varepsilon'\) from the occurrence of interband transitions. The errors illustrated in the values of the dielectric constants are dominated by an uncertainty in the grating profile.
4.6.2. The Drude-Lorentz model

The experimental data is fitted to a model that assumes only one resonant interband transition. This is a reasonable assumption to make since peaks in $\varepsilon'(\omega)$ are expected corresponding to strong interband transitions at approximately 3.7 eV and 5.2 eV [Karlsson et al. (1982), Rivory et al. (1981), and Karlsson et al. (1983)], but the dielectric function has only been determined at energies up to 2.5 eV. Hence only the effects of the wing of the lower energy resonance will be experienced. The two parts of the complex dielectric function are therefore

$$
\varepsilon'(\omega) = \varepsilon(\infty) - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2} + \frac{\tau^2 \omega_p^2 (\omega_0^2 - \omega^2)}{\tau^2 (\omega_0^2 - \omega^2)^2 + \omega^2}
$$

\text{Equation 4.6.5}

and

$$
\varepsilon''(\omega) = \frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)} + \frac{\omega_p^2 \omega \tau}{\tau^2 (\omega_0^2 - \omega^2)^2 + \omega^2}
$$

\text{Equation 4.6.6}

By rearranging these equations and putting $\varepsilon(\infty) = 1$, $\omega_p$ may be eliminated such that

$$
\frac{\varepsilon'(\omega) - 1}{\varepsilon''(\omega)} = \omega \tau \left[ \frac{\omega_0^2 (\omega^2 \tau^2 + 1)}{\omega^2 (\omega_0^2 \tau^2 + 1) + \tau^2 (\omega_0^2 - \omega^2)^2 + \omega^2} \right] - 1
$$

\text{Equation 4.6.7}

From this it is possible to obtain the constants $\hbar \omega_0 = 3.9$ eV and $\hbar / \tau = 1.1$ eV by fitting the functional form of Equation 4.6.7 to experimentally derived data (Figure 4.6.2). The fit to the experimental data illustrated in Figure 4.6.2 is rather poor, but it is important to note that reflectivity measurements were carried out over a very limited frequency range. However the general upward trend in the experimental data is apparent in the model, and the value of $\omega_0$ compares favourably with the energy of the first peak in $\varepsilon''(\omega)$ determined by previous workers (3.8 ± 0.1 eV [Karlsson et al. (1982 and 1983) and Rivory et al. (1981)]). It is then possible to fit to $\omega_p$ by using Equation 4.6.5 and Equation 4.6.6 [Figure 4.6.3 (a) and (b)]. A comparison of the values of $\omega_p$ and $\tau$ determined here to those of previous workers is shown in Table 4.6.1.

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Table 4.6.1  A comparison of the values of $\hbar\omega_p$ and $\hbar/\tau$ of TiN$_x$ experimentally determined in this work, along with the values obtained by a number of previous workers. The nitrogen/titanium ratio ($x$) and deposition method is also listed for comparison.
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Figure 4.6.3 The (a) real part, (b) imaginary part, and the associated uncertainties in the dielectric function of TiN$_x$ determined in the present work. The experimental data (error bars) has been modelled using Equation 4.6.5 and Equation 4.6.6 in order to obtain the plasma frequency, $\omega_p$. The resulting fit is shown as a solid line.

On examination of Table 4.6.1, it is apparent that there is a large spread of values of both $\omega_p$ and $\tau$, dependent on the deposition conditions and stoichiometry of the sample. The plasma frequency and relaxation time calculated in the present study are among the lowest observed, indicating a sample of reduced metallic nature which can at least in part be attributed to a large nitrogen/titanium ratio ($x$). Indeed, this is confirmed by electron energy dispersive spectroscopy measurements which indicate that $x$ is well in excess of unity.
4.7. Summary

In this chapter the dielectric function of TiN$_x$ has been determined throughout the visible regime using a grating-coupled SPP resonance technique. This technique presents a number of advantages over more conventional characterisation methods. For it is only necessary to take reflectivity data at the individual wavelengths at which one wishes to calculate the dielectric function, and no measurement of the film thickness is required. An excellent agreement between the differential formalism of Chandezon et al. (1982) and experimental reflectivities has been obtained, and the resulting dielectric function compares favourably with that determined by previous workers. By making the assumption that TiN$_x$ is only free-electron like in its optical response, it has been demonstrated that the Drude model alone is too simplistic. Instead, a Drude-Lorentz model is more appropriate that assumes a single resonant interband transition, in order to obtain the plasma frequency and relaxation time. A comparison of constants determined from this work and previous studies shows a large spread of results, illustrating the dependence on the stoichiometry and deposition conditions of the sample.
CHAPTER 5
The plasmon study of the optical dielectric function of indium

5.1. Introduction

The last chapter demonstrated how the optical excitation of SPPs may be used to characterise the complex dielectric function of titanium nitride. In this chapter, a similar technique is used to optically characterise indium for a range of wavelengths in the visible region of the spectrum. By exciting the SPPs at a buried indium/grating interface, the indium surface that supports the SPP is kept free from oxidation. Comparison of angle-dependent reflectivities with a grating modelling theory gives both the real and imaginary parts of the dielectric function of indium. These results are compared with free-electron models to obtain an estimate of the plasma frequency and relaxation time.

5.2. Background

Metals that have negative real parts to their dielectric response function in the visible region of the spectrum are able to support optically excited surface plasmon polaritons (SPPs). The best known, and most commonly utilised, are silver [e.g. Pockrand (1974) and Nash et al. (1996)] and gold [e.g. Ritchie et al. (1968) and Nash et al. (1995)] with which a variety of experimental studies have been undertaken. These two metals have received considerable attention for three primary reasons. Firstly they are considered relatively inert and so are not rapidly contaminated allowing ‘free’ surfaces to be explored in air. Secondly they are quite readily deposited by vacuum evaporation as thin films, which is advantageous for many studies. Thirdly, they have optical permittivities \((\varepsilon = \varepsilon' + i\varepsilon'')\) that for silver for the whole visible spectrum, and for gold above 550 nm, satisfy \(|\varepsilon'| >> \varepsilon''\) and \(\varepsilon' << 1\). This leads to relatively narrow surface plasmon
resonances that may be readily observed optically. Other materials that are more easily oxidised have been studied using SPPs at buried interfaces using prism coupling. These include aluminium [Tillin and Sambles (1988)], magnesium [Tillin and Sambles (1989)] and recently zinc [Nash and Sambles (1998)]. This last study also employs grating coupling to a buried interface, a technique previously used by Nash and Sambles to characterise silver (1996). Here this optical excitation of SPPs at a buried grating interface is extended to an exploration of the dielectric response function of indium.

There are good reasons for supposing that indium will support SPRs since its optical response function, as deduced from Théye and Devant’s work (1969), is such as to satisfy $\varepsilon' << 1$ although $|\varepsilon'|$ is only just larger than $\varepsilon''$. This latter fact suggests rather broad resonances. In addition Kovacs (1969) recorded surface plasmon resonances from indium films encapsulated by MgF$_2$ layers. He explored 19 nm, 27 nm and 42 nm thick indium layers and obtained data with 540 nm light, which gave results consistent with the permittivity given by Théye and Devant ($\varepsilon = -29.011 + 9.773i$).

Examination of the literature reveals that the values given by Théye and Devant, deduced from optical reflectance and transmittance of thin films of indium, are probably the most reliable since they have carefully taken into account the oxide layer which inevitably forms when the films are exposed to air. Other results [Ageev and Shklyarevskii (1968), Golvashtik et al. (1967) and Burtin (1964)], presented also by Théye and Devant for the real, $n$, and imaginary, $k$, parts of the refractive index of thicker indium, are substantially different. For example, at 2 eV, while Théye and Devant give $\varepsilon = -38.4 + 14.3i$, Ageev and Shklyarevskii find $\varepsilon = -20.4 + 5.0i$ and Glovashkia et al. find $\varepsilon = -27.2 + 9.0i$ [A further study by Oker et al. (1982) on thin films shows disturbing variations of $\varepsilon$ with wavelength, having unreasonably small values of $|\varepsilon'|$, and should be discounted]. It is in view of these differences, which may in part be due to the lack of correct treatment of the indium oxidation, but may also be associated with the difference in film character, that this study has been undertaken. It presents an exploration of the dielectric response function of indium over the visible spectrum by resonant excitation of the SPP at a buried grating interface of a very thick, effectively bulk film.
5.3. Experimental

There are two essential requirements for optically exciting SPPs at a clean indium interface. Firstly, the interface needs to be protected from oxidation - it needs to be a buried interface. Secondly, and as described in Chapter 2, there has to be a method for providing sufficient in-plane additional momentum to allow coupling of incident photons to the SPP. Both of these requirements are met by depositing, in vacuum, the indium film onto a silica grating.

A grating of pitch of order 800 nm is fabricated in silica by interferographic exposure of a suitable photoresist on a flat silica substrate, followed by chemical development and atom etching. This produces a high quality grating with well-defined, uniform, pitch having a profile which is slightly distorted from a pure sinusoid. On this cleaned silica grating was deposited, by thermal evaporation in a vacuum of $< 10^{-4}$ Pa, a layer of 99.99\% pure indium, to a thickness of order 500 nm (fully optically opaque). On removal from the vacuum this layer was overcoated with a thin lacquer layer to limit progressive oxidation of the indium.

The excitation of the SPPs were recorded as minima in the angle dependent reflectivity of p-polarised (transverse magnetic) light incident in a plane normal to the grating groove direction. To allow access to a wide range of in-plane momenta, a 45\°, 45\°, 90\° silica prism was attached to the flat face of the silica grating substrate by means of a fluid of matching index (Figure 5.3.1). Light incident upon the prism passes through the matching fluid and silica substrate arriving undeflected at the silica/indium grating interface. Angle dependent reflectivities were corrected for reflections at the air/prism entrance face and the prism/air exit face, and normalised to the incident beam intensity before being fitted by modelling theory.
Data, which were recorded over the wavelength range 400 to 900 nm, in 25 nm steps were fitted by an iterative least-squares minimisation procedure using rigorous grating modelling theory based on the formalism of Chandezon et al. (1982) described in Chapter 3. By use of the most noise-free data taken at the centre of the wavelength range studied it is possible to obtain in detail the grating pitch and the first three Fourier coefficients of its amplitude profile. With this information established, all the remaining data is fitted using these profile parameters to yield $\varepsilon'$ and $\varepsilon''$ of the indium layer. Typical fitted data are shown in Figure 5.3.2.

*Figure 5.3.1* Schematic diagram illustrating the sample used in this study. To allow access to a wide range of in-plane momenta a 45°, 45°, 90° silica prism is attached to the flat face of the silica grating substrate by means of a fluid of matching index. Light incident upon the prism passes through the matching fluid and silica substrate and arrives undeflected at the buried silica/indium grating interface. A thin lacquer layer deposited on top of the indium prevents progressive oxidisation through the film.
Figure 5.3.2 Typical experimental angle-dependent reflectivities (□, only one point in five plotted for clarity) compared with the theoretically-modelled reflectivities (—) created from a single set of grating profile parameters. (a), (b) and (c) show the $R_{pp}$ reflectivity measurements (i.e. p-polarised [TM] radiation was incident and detected) at incident wavelengths of 500 nm, 700 nm and 900 nm respectively. The values of the dielectric constants that were obtained by fitting the model to the experimental data for each wavelength studied are shown in Table 5.4.1.
5.4. Results

The optical permittivity values found from the fits to the angle-dependent reflectivity data are listed in Table 5.4.1 and presented graphically in Figure 5.4.1. Also given for comparison are some of the results of Théye and Devant over the same region of the spectrum. There are clearly systematic discrepancies between the two sets of data with the real permittivities deduced here being less negative and the imaginary permittivities being less positive. However the data show similar overall trends with $\varepsilon'$ becoming more negative in an almost linear fashion with wavelength while $\varepsilon''$ rises more rapidly. The simplest explanation for the differences between the data rests with the form of the sample. The sample used here is much thicker, it is protected from oxidation and will correspondingly have a different grain structure and a different relaxation time.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon''$</th>
<th>Reference</th>
<th>Wavelength (nm)</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon''$</th>
<th>Reference</th>
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<tr>
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<td>4.3</td>
<td>Théye &amp; Devant</td>
<td>600</td>
<td>-26.8</td>
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<td>Théye &amp; Devant</td>
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</tbody>
</table>

*Table 5.4.1* The optical dielectric function of indium experimentally determined in this work, together with the results determined by Théye and Devant (1969).
5.5. Discussion

Because of the simple functional dependence of $\varepsilon'$ on wavelength seen in Figure 5.4.1(a), it is tempting to use a Drude model to interpret the data. From Equations 4.6.1 and 4.6.2, note that $-\varepsilon''/(\varepsilon' - 1)$ should vary linearly with $\lambda_0$, with a slope of $1/2\pi\varepsilon\tau$.

Such a plot is shown in Figure 5.5.1 giving a straight line from 625 to 900 nm, indicating that indium illustrates free-electron-like behaviour in this range. The gradient from this figure gives a relaxation time of $(1.01\pm0.04)\times10^{-15}$ s. In addition, Figure 5.5.2 shows a graph of $(1-\varepsilon')^{-1}$ plotted against $\lambda^2$ (from Equation 4.6.1), the gradient of such a plot yields a $\hbar\omega_p$ value of $12.8\pm1.0$ eV. The errors in all of the above values have been calculated by making a comparison between a straight-line fit to all the data.

Figure 5.4.1 A comparison of the values of the dielectric function of indium determined in this work (■), compared with those determined by Théye and Devant (○). Top: real component ($\varepsilon'$). Bottom: imaginary component ($\varepsilon''$).
available, and the reduced set of points that form the linear part of the curves. The large error in the value of the plasma frequency is attributable to the deviation away from a linear relationship at low wavelengths. It is therefore clear that the optical response of indium over the wavelength range studied in this work is not purely Drude-like in nature. In fact, such behaviour is not unexpected since previous workers have shown there to be a number of absorption peaks associated with interband transitions [e.g. Théye and Devant (1969), Oker et al. (1982)].

Figure 5.5.1 A plot of \(-\varepsilon''/(\varepsilon' - 1)\) against \(\lambda_0\) for the values of the dielectric function determined in this work. A high degree of linearity suggests that the indium film is free-electron like. The relaxation time, \(\tau\), is determined from the gradient of the line of best-fit which also passes through the origin. However, since the sample only appears free-electron like at wavelengths in excess of approximately 600 nm, the straight-line plotted is a best-fit to just the high wavelength data.
Consequently, any accurate representation of the complex dielectric function of indium must involve splitting it into two parts: one part corresponding to the intraband excitations described by the Drude model, and an interband part corresponding to resonant absorptions based on a Lorentz-oscillator model. In order to provide a more satisfactory fit to the dielectric function of indium than provided by a simple Drude theory, the experimental data are compared to a model that assumes one absorption peak at frequency $\omega_{\text{p}}$. The two parts of the complex dielectric function based on such a Drude-Lorentz model are given in Chapter 4 (Equations 4.6.5 and 4.6.6). By rearranging these equations, and setting $\varepsilon(\infty) = 1$, a function is obtained which is independent of $\omega_{\text{p}}$ (Equation 4.6.7). By fitting the functional form of this equation to

Figure 5.5.2 A plot of $(1 - \varepsilon')^{-1}$ against $\lambda_{\text{p}}^{-2}$ for the values of the dielectric function determined in this work. The plasma energy, $\omega_{\text{p}}$, is determined from the gradient of the line of best-fit and using the value of $\tau$ previously determined. Once again, since the sample appears free-electron like at wavelengths only in excess of approximately 600 nm [$\lambda_{\text{p}}^{-2} > 2.8(\mu\text{m})^{-2}$], the straight-line plotted is a best-fit to only the high wavelength data.
By assuming a one-resonance Drude-Lorentz model, a function relating the real and imaginary parts of the dielectric function may be obtained. By fitting this function to the experimental data, values of $\tau$ and $\omega_0$ are obtained.

The experimental data, the constants $\tau = (1.08 \pm 0.02) \times 10^{-15}$ s and $\hbar \omega_0 = 6.82 \pm 0.14$ eV are obtained (Figure 5.5.3). Both the real and imaginary parts of the experimentally determined dielectric function may then be fitted to Equations 4.6.5 and 4.6.6, and by using the values of $\tau$ and $\omega_0$ determined above to give $\hbar \omega_p = 11.4 \pm 0.2$ eV (Figure 5.5.4).

There are clear systematic discrepancies between the theoretical fits and the experimental data shown in Figure 5.5.4. It should be noted that even though the reflectivity measurements were carried out over a very limited frequency range, the general trends in the model are clear in the experimentally determined results. Furthermore, the two values of $\hbar \omega_p$ determined by fitting the real and imaginary parts of the dielectric function individually differ only by 0.1 eV. The discrepancy at low
frequencies, particularly in the $\varepsilon'$ data, may be due to the effect of a second absorption band. In fact, an interband transition in the region of $2.0 \times 10^{15}$ rad s$^{-1}$ (1.3 eV) has been previously experimentally observed [Théye and Devant (1969)], and would agree with the results presented here.

However, it is clear, that neither the simple Drude model, nor the one-resonance Drude-Lorentz model describe indium accurately over the frequency range studied. A more sophisticated model is therefore required, but such a multiple-resonance model would have many degenerate solutions to the limited range of experimental data presented here.
5.6. Summary

The complex dielectric function of non-oxidised indium has been experimentally determined throughout the visible regime using a grating-coupled SPP technique. This has been achieved by fitting the reflectivity measurements from a metal-dielectric interface to the predictions from a rigorous grating-modelling theory, using the grating profile, and the complex dielectric constants of indium as fitting parameters. A comparison of the constants determined from this work, with those from a previous study suggests a strong dependence of the dielectric function on the film thickness and deposition conditions.

The plasma frequency and relaxation time have been calculated by fitting the measured dielectric function to a simple Drude model. However, the free-electron model has been demonstrated to be inadequate, and a more sophisticated one-resonance model has also been used. Systematic discrepancies between the modelled and measured dielectric functions illustrate that this model is also mostly too simplistic. However, the values of the relaxation time determined from both models are consistent, and the values of the plasma frequency obtained by fitting the second model to both $\varepsilon'$ and $\varepsilon''$ show excellent agreement.
CHAPTER 6
Azimuthal dependent reflectivity data from metallic gratings

6.1. Introduction

In the previous two chapters, the reflectivity from corrugated metal interfaces were recorded as a function of the polar angle of incidence ($\theta$). The complex dielectric functions of the metallic films were derived by making a comparison between the predictions of the theoretical model, and the response of the sample in the regions of coupling to surface plasmon polaritons (SPPs). However, one does not have to be constrained to this in-plane geometry that is often used. Recent developments to Chandezon’s original theory have permitted the modelling of systems in the conical mount, when the Bragg vector of the grating ($\mathbf{k}_x$) is not in the plane of incidence ($\phi \neq 0$) [Elston et al. (1991a,b)]. In this geometry, polarisation conversion is induced [Bryan-Brown et al. (1990)] and as a result, the reflectivity features have an increased sensitivity to the profile of the grating surface. Watts et al. (1997a) have successfully demonstrated that a surface may be confidently characterised using polar angle-dependent fits to reflectivity recorded for different azimuths. Therefore, in this chapter a new technique is presented that instead involves the measurement of the azimuthal-dependent specular reflectivity to optically characterise a periodically modulated metal-dielectric interface. This method presents advantages over the conventional polar angle scan experiment since it requires no moving signal detector. The data recorded has been fitted to a conical version of Chandezon’s differential formalism using a single set of parameters describing the grating profile and metal permittivity.

The system chosen to study this new technique and to test the conical diffraction model is a periodically modulated gold-air interface. Experimental reflectivities have been recorded from the same grating surface for both s- (TE) and p- (TM) polarised incident
light, and for in-plane and conical geometries. We test the conical diffraction theory by showing that one set of parameters representing the grating profile and dielectric function of the two media at a constant wavelength may produce theoretically modelled reflectivities which agree with all the experimental data sets. In addition, the surface profile obtained by this optical characterisation method is verified by comparison with the profile obtained from an atomic force microscope (AFM) scan of the surface.

6.2. Experimental

6.2.1. Experimental Geometry

Figure 2.4.4 illustrates the experimental geometry and the co-ordinate system being considered in this chapter.

As previously discussed, the grating’s periodicity provides a mechanism via which the incident radiation may increase or decrease the component of its wave vector by integer multiples of the grating wave vector, \( k_g \). This gives rise to diffracted orders that become evanescent when their in-plane momentum is increased such that the magnitude of their wave vector, \( k \), becomes greater than that of the wave vector of the incident radiation, \( n_1 k_0 \). It is the enhanced wave vector of these evanescent fields that allows incident radiation to couple to the SPP according to the condition

\[
k_{SPP} = n_1 k_0 \sin \theta \pm N k_g
\]

Equation 6.2.1

If the azimuthal angle is equal to zero then all the diffracted beams lie in the plane of measurement and Equation 6.2.1 reduces to a scalar equation.

However, it was shown in Section 2.4.2, that for a particular grating, all the solutions of Equation 6.2.1 can be illustrated using a reciprocal space map and the schematic diagram presented there (Figure 2.4.5) also represents the grating studied here. The dashed circle about the origin represents the maximum wave vector available to the incident photon \( (n_1 k_0) \) and the fainter dashed circles within this radius represent the
positions of the observable Rayleigh anomalies that have been scattered by the grating. This illustrates that coupling to the SPPs (solid lines) that exist at a slightly higher momentum is only possible via scattering by ±1, ±2 or ±3 grating wave vectors. The diagram also shows that a photon with wave vector component \( n_i k_0 \sin \theta \) at an azimuthal angle \( \phi \) may couple directly to a SPP, and that \( \theta \) must vary as \( \phi \) changes for coupling to be maintained. When \( \phi \neq 0 \), by simple geometry, we find the scalar equivalent of Equation 6.2.1 is

\[
k_{\text{SPP}}^2 = n_i^2 k_0^2 \sin^2 \theta + N^2 k_g^2 \pm 2 n_i N k_g k_0 \sin \theta \cos \phi \tag{Equation 6.2.2}
\]

### 6.2.2. Experimental Procedure

The grating studied in this work was prepared in a silica substrate by standard interferographic techniques discussed in Section 3.1, which resulted in a grating of pitch, \( \lambda_g = 930 \text{ nm} \). An optically thick gold layer was evaporated onto the surface to produce an interface that supports SPPs in the visible region of the spectrum. Gold was chosen in preference to silver because its optical properties will not vary over the time scale of the experiment. Incident radiation of wavelength 632.8 nm on a grating of this pitch permits momentum enhancement such that coupling to six surface plasmon resonances (SPRs) is possible. These are the ±1, ±2 and ±3 resonances (Figure 2.4.5), where the number and sign refer to the diffracted order that provides the resonant coupling to the SPP.

With conventional studies previously undertaken (e.g. Chapters 4 and 5), the intensity of the specularly reflected beam from the grating is recorded as a function of the polar angle of incidence, generally at fixed wavelength. A schematic diagram illustrating the apparatus required to record such data is shown in Figure 4.4.2. The grating is rotated about the z-axis and the signal detector moves such that it tracks the specularly-reflected beam. If the grating grooves are orientated at the azimuthal angle \( \phi \) depicted in Figure 2.4.5, the order of features for the 930 nm grating with increasing \( \theta \) (black dotted line)
would be: Rayleigh anomaly associated with the point at which the -1 diffracted order becomes evanescent, SPP (±1), SPP (±2) and Rayleigh anomaly (±1).

Previous workers have also recorded reflectivity scans as a function of the incident wavelength $\lambda_0$. This method has been used to directly observe the SPP dispersion curve both on a planar metal-air interface [Swalen et al. (1980)], and on a corrugated interface where an energy gap may open up [Weber et al. (1986) and Kitson et al. (1996)]. This method is not particularly suitable for the characterisation of metallic gratings since the optical properties of metallic films vary strongly with wavelength, which makes the fitting of data increasingly difficult.

In the present work, the majority of experimental data is recorded as a function of the azimuthal angle, $\phi$. Figure 6.2.1 illustrates the experimental arrangement used to record the azimuthal-dependent data. Unlike the apparatus shown in Figure 4.4.2 for deriving the polar-dependent data, this method does not require a moving detector. The polar angle, $\theta$, is set using the mirror and the grating placed directly on the rotating table. It is apparent from Equation 6.2.2 and Figure 6.2.2 that if $\theta$ is fixed and $\phi$ varied, a circle in $k$-space inside the light circle will be mapped out which will cut the SPP and Rayleigh anomaly arcs that are associated with the diffracted orders. Clearly from Figure 6.2.2, if $\theta$ is too small then there will be no reflectivity features, and hence a suitable choice of $\theta$ is required to produce useful data. With the polar angle of incidence chosen in Figure 6.2.2, the order of reflectivity features will be SPP (±1), Rayleigh anomaly (±2), SPP (±2) and Rayleigh anomaly (±1).
In both polar- and azimuthal-angle scans undertaken in this study, polarisers are used to set the polarisation of the incident and detected beams. This permits the measurement of the $R_{pp}$, $R_{ss}$, $R_{sp}$ and $R_{ps}$ reflectivities, where the subscripts refer to the setting of the incident and detector polarisers respectively. The latter two reflectivities allow the polarisation conversion signal found when the grating is in the conical mount to be monitored. However, it should be noted that they are identical for non-blazed profiles. It is critically important to ensure that the polarisers are set correctly with respect to the true plane of incidence as p-to-s conversion is acutely sensitive to errors in this alignment.

Polar-angle scans are undertaken with $\varphi = 0^\circ$ and $\varphi = 50^\circ$, and azimuthal-dependent data are recorded at $\theta = 20, 30, 45, 60$ and $75^\circ$. For each scan, 632.8 nm He-Ne radiation is incident on the sample and the $R_{pp}$ and $R_{ss}$ responses are measured. In addition, the polarisation signal ($R_{ps}$ or $R_{sp}$) is also recorded.
It is clear that the choice of an azimuthal-angle scan and the more traditional polar-angle scan allows the experimentalist to sample different widths of the reflectivity features. For example, at the crossing point of the azimuthal scan and the -1 SPP coupling condition shown in Figure 6.2.2 ( \( \varphi = 0 \rightarrow 90^\circ \) ), the angle between the two curves is much smaller than the angle between the trajectory of the polar-angle scan (not shown) and the -1 SPP coupling condition curve at the same point. Hence, the “width” of the mode recorded in an azimuthal-angle scan will be significantly larger than that perceived in a polar angle scan. This effective widening of the resonances may be useful especially when experimenting with metals with \( \varepsilon' \ll 0 \) (e.g. aluminium), whose modes may otherwise be too narrow from which to deduce the optical parameters of the media.
6.3. Results

In order to deduce the grating profile and optical properties of the metal-dielectric interface, the reflectivities obtained from a conic al version of Chandezon’s original differential formalism [Elston et al. (1991b)] have been matched with those recorded experimentally. The theoretical model, described in Chapter 3, uses a truncated Fourier sum of sine waves to represent the shape of the interface,

\[ A(x) = a_1 \cos k_g x + a_2 \cos 2k_g x + a_3 \cos 3k_g x \]

Equation 6.3.1

where \( a_1, a_2 \) and \( a_3 \) are the fundamental, first and second Fourier harmonics which provide the first order scattering mechanisms to the \( \pm 1, \pm 2 \) and \( \pm 3 \) SPPs respectively. The series is truncated at the second harmonic because the components that provide the \( 4k_g \) and higher scattering vectors are found to be insignificant and have little effect on the reflectivity from the grating used in this study.

Experimental reflectivities were recorded as functions of both the polar and azimuthal incident angles. The predictions from the theoretical model were then fitted to the experimental data by using an iterative least squares fitting routine which used the functional form of the grating profile (Equation 6.3.1) and the optical permittivity of the metal layer as fitting parameters. The parameters obtained from the optical characterisation were: \( a_1 = 31.0 \pm 0.4 \) nm, \( a_2 = 8.0 \pm 0.5 \) nm, and \( a_3 = 3.0 \pm 0.4 \) nm. The pitch, as defined by the angular position of the Rayleigh anomalies in the experimental reflectivity data, was calculated to be \( \lambda_g = 930.1 \pm 0.5 \) nm with the permittivity of the dielectric (air) set as \( \varepsilon_1 = n_1^2 = 1.0006 \). The permittivity of the metal (gold) which provided the most accurate fits was \( \varepsilon_2 = -9.62 + 1.25i \). Figure 6.3.1(a), (b) and (c) show a selection of fits to the experimental azimuthal angle-dependent reflectivities, and for comparison, Figure 6.3.1(d) shows a fit to the conventional polar angle-dependent reflectivity. Figure 6.3.1(a) illustrates the polarisation conversion that is induced when the grating is in the conical mount. Clearly, the above parameters provide good fits to the experimental data, although the real part of \( \varepsilon_2 \) is slightly smaller in magnitude than expected for gold at this wavelength.
CHAPTER 6  Azimuthal dependent reflectivity data from metallic gratings.

Figure 6.3.1 The experimental angle-dependent reflectivities (—) compared with the theoretically-modelled reflectivities (+) created from a single set of fitting parameters. (a), (b) and (c) illustrate the fits to azimuthal angle-dependent scans at $\theta = 30^\circ$, $\theta = 45^\circ$ and $\theta = 75^\circ$ for $R_{sp}$ (polarisation conversion), $R_{ss}$ and $R_{pp}$ reflectivities respectively. (d) shows a fit to a polar angle-dependent $R_{pp}$ reflectivity at a fixed azimuthal angle of $\varphi = 50^\circ$.

($\varepsilon_{Au} = -10.77 + 1.07i$ [Bryan-Brown et al. (1991)].)

To confirm that the fitted parameters are indeed a true representation of the grating’s profile, an atomic force microscope (AFM) was employed to verify the optical characterisation technique. The profile was determined by scanning an AFM stylus over a 20 $\mu$m$^2$ area of the grating. A quarter of this scan has been reconstructed from the raw data recorded by the AFM and is shown in Figure 6.3.2(a). Fourier analysis of the data gives the functional form of the surface to be $a_1 = 30.0 \pm 0.5$ nm, $a_2 = 8.0 \pm 0.5$ nm and $a_3 = 2.8 \pm 0.4$ nm. Figure 6.3.2(b) compares this form with the profile obtained by fitting the optical data.
The profile recorded by the AFM stylus shows an apparent reduction in the grating depth. This may be attributed to the stylus being unable to probe the bottom of the troughs due to its finite width, however with this relatively shallow grating this is unlikely. More simply the difference is due to a calibration error in the height scale of the AFM since scaling by a factor of 1.05 gives an almost perfect agreement.

Figure 6.3.2 (a) 10 µm² AFM image (computer-reconstructed) of the surface of the grating. (b) Fourier analysis of this data yields an average grating profile profile (•••) and a comparison is made with that deduced from the fitting of optical data (—).
6.4. Summary

This chapter has illustrated that the new technique of experimentally recording the azimuthally-dependent reflectivities can be successfully used for the characterisation of the surface profile and optical permittivities of metallic diffraction gratings.

The experimental procedure to monitor azimuthally-dependent reflectivity data presents a number of advantages over the conventional method of monitoring polar angle-dependent reflectivities, primarily because the technique does not involve a moving signal detector. This simplifies the apparatus required for such an experiment (Figure 6.2.1), and eliminates the possibility of experimental errors arising from detector function. In addition, the azimuth scanning method is more favourable for studying gratings at longer incident wavelengths when the conventional polar angle scans become cumbersome due to the large area swept out by the signal detector. Hence, we employ this technique for use in the experiments carried out in the microwave regime detailed in the next three chapters. Furthermore the level of background noise remains constant throughout the experimental scan since only the sample is moving and hence the use of this technique improves the quality of the resulting fits. An azimuthal-angle dependent scan will also allow the experimentalist to record resonance widths that are different to those perceived in a polar-angle scan. This may be useful, for example, when studying a metal with an $\varepsilon'$ which is highly negative so that the SPR may be prohibitively narrow to allow accurate parameterisation of the optical constants of the media either side of the interface.

In addition, this work provides a convincing test of conical diffraction theory producing excellent agreement between the differential formalism of Chandezon and azimuthal angle-dependent reflectivity experiments (Figure 6.3.1). The shape of the surface derived from the fitting process has been shown to be representative of the true profile by comparison with that determined from AFM measurements (Figure 6.3.2)
CHAPTER 7

An experimental study of grating-coupled surface plasmon polaritons at microwave frequencies.

7.1. Introduction

Microwaves belong to the intermediate range of the electromagnetic spectrum that have frequencies lying between 1 GHz and 300 GHz with corresponding free-space wavelengths ranging between 300 mm and 1 mm. It is interesting to note that the initial search for the electromagnetic waves predicted from Maxwell’s equations were carried out using waves of these wavelengths.

The development of microwaves during the war for communications and radar uses led to resurgence in their popularity during the 1950s and 1960s. Radar was initially developed as a passive sensor (i.e. it emits its own energy and does not rely on the illumination of the target by other sources) to replace visual target detection. Work at these frequencies was particularly popular as a number of the experimental problems of optical diffraction could be investigated more easily at much longer wavelengths. *Tremblay and Boivin* (1966), or more recently the book by *Knott, Scheffer and Tuley* (1993) provide a useful summary of the concepts and techniques used in radar applications and experiments undertaken in the microwave regime.

Much work in the literature is concerned with structures that reduce reflections from an interface. The earliest form of absorber was the Salisbury screen, a narrow-band device which consists of a sheet of porous material impregnated with graphite and spaced a
quarter of a wavelength from a metallic backing plate. This effectively creates an “open
circuit”, and the incident wave “sees” free space and there is no reflection (all the power
is delivered to the resistive sheet). An anti-reflection surface may also be achieved by
producing a material that avoids any sudden changes in the refractive index of the media
surrounding the interface. Such an impedance transformer was discovered in parts of
the eyes of nocturnal insects and was investigated in a much scaled-up system by
Bernhard in 1967. These anti-reflection surfaces are further discussed by Raguin et al.
(1993). Research into radar absorbing materials has also been very active over the last
40 years, and it is summarised by Vinoy and Jha (1994).

Another way in which incident radiation on a surface may be absorbed is by coupling it
into a wave that propagates along an interface, and dissipates its energy via Joule
heating of the surrounding media. A surface plasmon polariton (SPP) is an example of
such a mode and a detailed investigation of electromagnetic coupling to it at microwave
frequencies is discussed in this and the following two chapters.

The work undertaken in this chapter illustrates the resonant coupling to the SPP on
metallic diffraction gratings using wavelengths of the order of 10 mm. The wavelength-
and angle-dependent reflectivities have been recorded from purely sinusoidal mono- and
bi-gratings each of pitch 15 mm where the periodicity of the corrugation provides the
necessary momentum enhancement to couple to the surface mode. In order to minimise
the problems associated with non-planar incident wavefronts, an apparatus that
collimates the incident beam has been developed. The experimentally recorded
reflectivities have been successfully fitted to the predictions from the grating modelling
theory described in Chapter 3 with a single set of grating parameters describing the
grating profile and metal permittivity.
CHAPTER 7  An experimental study of grating-coupled surface plasmon polaritons at microwave frequencies.

7.2. Background

Many workers have studied extensively the grating-coupled SPP mode at visible \[\text{e.g. Raether (1988), Watts et al. (1997a) and Nash et al. (1996)}\] and infra-red \[\text{e.g. Zhizhin et al. (1982)}\] wavelengths on corrugated surfaces produced by standard interferographic techniques \[\text{Hutley (1982)}\]. Before this method of grating manufacture was established, gratings had to be manufactured by ruling \[\text{Wood (1902)}\], hence experimentalists often made use of the larger scale of systems available in the microwave regime. For example, \text{Meecham and Peters (1957)} studied the reflection of radiation of wavelength \(\lambda_0 = 32\) mm from a grating with the electric field of the radiation parallel to the grooves. As they scanned the angle of incidence, they observed a redistribution of energy among the diffracted beams at the point at which an order begins, or ceases to propagate - the \textit{Rayleigh anomaly}. They compared their experimental reflectivities from a finite grating (15 grooves) to a theory based on a formalism which, like many other diffraction theories developed around this time, assumed the surface to be of infinite extent and perfectly conducting \(\varepsilon_2 = -\infty\). As discussed in \textit{Chapter 3}, this is a reasonably valid assumption to make since the frequency of the impinging microwave radiation is many orders of magnitude less than the plasma frequency, and the effect of any absorption in the metal will be insignificant due to the negligible skin-depth. Hence at these wavelengths, all metals may be treated as near-perfectly conducting.

It is well known that the propagation length of the SPP along the interface, and hence the width of the resonance is governed by two damping processes \[\text{Raether (1988) and Pockrand (1976)}\]: the absorption of energy in the metal substrate (which is proportional to the imaginary part of the dielectric function of the metal, \(\varepsilon^\prime\) for a given \(\varepsilon^\prime\), and therefore frequency) and scattered radiative losses into the dielectric media (which is proportional to \(a^2\) to first order, where \(a\) is the amplitude of the grating \[\text{McPhedran et al. (1972)}\]). Note that the existence of this radiation loss does not invalidate the previous definition of the surface wave \(\text{Section 2.2}\) since it is dependent only on the surface profile and not the properties of the adjacent media. Hence, for shallow gratings with almost no scattering of radiation into diffracted orders, experimental observation of the SPR is only possible if the metallic medium is lossy.
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(e.g. a corrugated gold surface [Watts et al. (1997a)], $a/\lambda_0 \approx 0.05$, $\varepsilon_{\lambda_0=632.8 \text{ nm}} = -10.8 + 1.3i$). As previously discussed, at microwave frequencies, all metals behave as near-perfect conductors and hence the direct Joule-heating loss is insignificant. However, as the amplitude of the corrugation is increased, the probability of the surface wave being scattered into a diffracted order also grows. In other words, the propagation length of the SPP on a highly corrugated surface will be less than that on a shallow grating. Hence, a propagating surface wave on a highly perturbed surface will not sample an infinite number of grooves, instead it will be scattered by a range of grating wave vectors determined by the Fourier transform of such a finite set of corrugations. This will introduce a range of angles over which the SPP may reradiate into the specular or one of the diffracted orders, and hence an angular width will be associated with the resonance as measured by the loss of reflectivity in the zero order beam. In addition to the widening of the SPR, one also expects the momentum of the resonance to increase due to perturbation of the surface away from the planar case [Raether (1988), Pockrand (1974 and 1976) and McPhedran et al. (1972 and 1973)].

The work of Palmer et al. (1965) shows such a change in the shape of a resonance, and we believe that that work provided the first experimental evidence of the propagation of an electromagnetic surface mode, the SPP, on a near-perfectly conducting surface. They reported measurements for the spectral distribution of radiation of wavelength 4 mm from metal gratings of rectangular profile. When the wave propagation vector is lying in a plane normal to the grating grooves, with the electric field vector perpendicular to the grooves, they observe dark anomalies that become wider as the groove depth is increased. An attempt is made to explain this phenomenon using a theory based on “surface wave modes which are supported by the rectangular periodic structure of the grating”, however no illustration of these results is presented.

It is important to note, however, that the resonance of the mode may only be observed when there is another channel into which energy may be transferred. There are up to three ways in which this may occur. Firstly, Joule heating of any absorbing media in the system will take place. Secondly, energy from the mode may be re-radiated into any propagating diffracted orders in the system. This is a similar effect to that modelled by Kitson et al. (1995) who observed an increase in the width of the resonance when the SPP mode is able to couple to a propagating diffracted order. The diffracted order
provides a strong radiative decay channel for the mode which contributes to its damping, and hence width. Finally, re-radiation of energy from the mode back into the specular beam may occur. If the grating grooves are neither parallel nor perpendicular to the plane of incidence ($\varphi \neq 0^\circ, 90^\circ$), the polarisation of this radiation will be rotated with respect to the incident beam and a polarisation conversion signal may be detected [Bryan-Brown et al. (1990) and Watts et al. (1997b)].

7.3. Experimental

The two gratings studied in this work have been manufactured from approximately 500 mm square aluminium alloy sheets, using a computer-aided design and manufacture technique with a 6 mm diameter ball-ended slot drill. The mill was programmed to produce a purely sinusoidal profile, with a pitch of $\lambda_g = 15$ mm. The first grating (sample #1) has an amplitude of $a_1 = 2$ mm and is shown in Figure 7.3.1 below.

![Figure 7.3.1](image-url)  
*Figure 7.3.1* Photograph of sample #1 studied in this chapter where $\lambda_g = 15$ mm and $a = 2.0$ mm.
The second grating studied is corrugated in both the x- and z-directions (Figure 7.3.2) and its surface profile is represented by the following Fourier Series:

\[
A(x, z) = a_1^x \cos k_g^x x + a_2^x \cos 2k_g^x x + \ldots + a_n^x \cos Nk_g^x x + \ldots \\
+ a_1^z \cos k_g^z z + a_2^z \cos 2k_g^z z + \ldots a_n^z \cos Mk_g^z z + \ldots
\]

*Equation 7.3.1.*

where \( a_i^x = a_i^z = 1.5 \) mm and \( k_g^x = k_g^z = 2\pi/15 \) mm\(^{-1}\).

Undertaking reflectivity measurements in the microwave regime clearly requires a completely different apparatus to the experiments carried out at visible frequencies that were discussed in previous chapters. The equipment used in this, and the following two chapters for use in the 26.5 – 40 GHz frequency range is illustrated schematically in *Figure 7.3.3* below.

Originally, the experimental technique used to record the reflectivity from the samples was based on the NRL arch method of absorber testing. It is a vertical semicircular framework that allows the transmitting and receiving antennae to be aimed at a test.
panel at constant distance (Figure 7.3.4). This allows the reflectivity from the test panel to be measured at virtually any angle of incidence. The addition of a rotating grating ($\phi$) allows the measurement of any non-isotropic response of the sample.

*Figure 7.3.3* Schematic representation of the interconnecting components used to record reflectivities in the 26.5 – 40 GHz frequency range.

*Figure 7.3.4* Diagram of original apparatus based on the NRL arch that was used to record the wavelength- and azimuthal-angle-dependent reflectivities from the sample.
However, after a number of initial experiments were carried out, it became clear that the NRL arrangement is not suitable for the measurement of reflectivities from diffraction gratings. This is due to a number of reasons. Firstly, the standard gain horns emit spherical wavefronts that will introduce the possibility of excitation of the SPP even without the grating. In addition, since the beam divergence of the horns is some 20°, the incident beam will be larger than the sample and the system will suffer from a degree of cross talk between the transmitting and receiving antennae. The introduction of metallic apertures and a dagger board may improve the situation, but these create further spurious artefacts in the measured signal due to diffraction effects at their edges. It is not convenient to use dagger boards or apertures made from microwave absorbing materials since these are typically 9 cm thick, and are therefore cumbersome to use.

The arrangement shown in Figure 7.3.5 is similar to that of the Czerny-Turner spectrometer [James et al. (1969)] and has been developed in order to reduce the aforementioned beam spread and the associated effects of spherical wavefronts and cross talk. By placing the transmitting horn at the focus of a 2 m focal length mirror (with a diameter greater than that of the beam incident upon it), the beam is well collimated. An identical mirror is positioned to collect the specularly reflected beam from the grating and focus it into the detector. In addition, a circular, metallic aperture may also be used to align, and reduce the width of the beam. Clearly, in order to avoid the introduction of aberrations in to the reflected beam, these mirrors should be parabolic, but these are difficult to manufacture. However, spherical mirrors can be manufactured relatively easily, and provide a good approximation to a parabolic mirror for beams of radius much less than the mirror’s radius of curvature.

The spherical mirrors are manufactured by mounting the slab of metal to be worked on a rotary table in a vertical mill (Figure 7.3.6). A flycutter of diameter \( D \), which must be larger than that of the work diameter, and tip radius \( r \) are mounted on the head of the mill tilted at an angle, \( \Theta \), determined by the formula

\[
\sin \Theta = \frac{D}{2(R+r)}
\]

*Equation 7.3.2.*
The arrangement shown in Figure 7.3.5 was used to record the specular reflectivity from sample #1 as a function of wavelength between 7.5 and 11.3 mm at a polar angle of incidence of approximately $\theta = 31^\circ$, and a series of azimuthal angles ($\phi$) every 15° between 0 and 90°. These angles are set to a precision of ±1°. The apparatus is
arranged in a horizontal plane on a series of laboratory benches, with the mirrors and sample held in position with clamp stands. Unfortunately, mounting the sample on the rotating table is difficult in this geometry making azimuthal-angle-dependent data impossible to record. In addition, the alignment of the apparatus is susceptible to disturbance. Therefore, the apparatus was reconstructed in a vertical plane, built on concrete benches, where the sample is placed on the rotating table underneath the two mirrors (Figure 7.3.7). The reflectivity data from sample #2 (bi-grating) and all subsequent microwave data were recorded using this apparatus.

*Figure 7.3.7* Photograph of experimental apparatus used to measure the specular reflectivity from grating #2 (bi-grating), and all subsequent samples studied in this thesis.

The mirrors are bolted on to structures that are able to slide on rails along the concrete bench and, in order to avoid the undesirable effects of diffraction and scattering, they have been manufactured from wood. The mirrors may be twisted to change the angle of incidence ($\theta$), and their height may be changed in order to maintain a source-mirror(1), and mirror(2)-detector distance of 2 m. In addition, the source antenna and detector may also be moved along the bench, rotated, and raised or lowered in height.
For both experimental arrangements described above, the source antenna and detector may be set to pass either p- (transverse magnetic, TM), or s- (transverse electric, TE) polarisations, defined with respect to the plane of incidence. This enables the measurement of $R_{pp}$, and $R_{ss}$, and polarisation conversion $R_{sp}$, and $R_{ps}$ reflectivities where the subscripts refer to the incident and detected polarisations in that order. To account for any fluctuations in the power of the source, the output from the signal detector is divided by that of the reference, and the resulting wavelength- and azimuthal angle-dependent data were normalised by comparison with the reflected intensity from a flat metal plate.

Variation of the magnitude of the incident wave vector in the plane of the grating may generally be achieved by scanning either wavelength ($\lambda_0$), or angle of incidence ($\theta$ or $\phi$). The technique described above keeps the polar angle of incidence constant, in contrast to the conventional method of polar angle scans that are often used for experiments at visible and infra-red wavelengths. It therefore avoids the difficulty of scanning the detector and focusing mirror. In addition, by keeping the system fixed, and only rotating the sample, the possibility of experimental errors arising from detector function is eliminated.

7.4. Results

7.4.1. Sample #1 (mono-grating)

Figure 7.4.1 shows four typical sets of experimental data (+) at azimuthal angles of $\phi = 30^\circ$, $45^\circ$, $60^\circ$ and $75^\circ$ showing the selected reflectivities $R_{pp}$, $R_{sp}$, $R_{ps}$ and $R_{ss}$ respectively. The solid curves are the theoretical fits, which are in excellent agreement with the experimental data.

In an ideal system the wavefronts incident on the sample using the collimated beam apparatus would be completely planar. However, the radiation source is finite and the source antenna and aperture diffract the beam. Hence, in order to achieve this quality of fits, a degree of Gaussian beam spread has to be introduced into the theoretical
modelling. A simple linear relationship is assumed between wavelength and incident-angle spread since the diffraction effects will clearly increase with wavelength. It is also found that the angle spread is dependent on the orientation, \(i.e.\) polarisation of the rectangular transmitting and receiving antennae. Typically, at the centre of the wavelength range, the standard deviation of Gaussian angle spread is \(\sigma(\theta) \approx 0.9^\circ\). This represents a dramatic improvement over the uncollimated system \(\Delta\theta \sim 20^\circ\), but it is still large enough to significantly affect the measured reflectivities.

Figure 7.4.1 The normalised (a) \(R_{pp}\), (b) \(R_{sp}\), (c) \(R_{ps}\) and (d) \(R_{ss}\) experimental wavelength-dependent signals (+) compared with the theoretically modelled results (—) created from a single set of profile and metal-permittivity parameters. Radiation is incident on the test sample at a polar angle, \(\theta = 31^\circ\), and at azimuth angles of (a) \(\phi = 30^\circ\), (b) \(\phi = 45^\circ\), (c) \(\phi = 60^\circ\), and (d) \(\phi = 75^\circ\). The angles quoted are approximate \((\pm 1^\circ)\), and only one point in four is shown for clarity.
The theoretically modelled data were fitted to the experimental reflectivities using the angles of incidence ($\theta$ and $\phi$), the above linear variation of beam spread ($\sigma(\theta)$), and the grating profile ($a_1$, $a_2$, $a_3$ and $a_4$) as fitting parameters. The profile of the grating is initially assumed to be purely sinusoidal, and the angles of incidence are allowed to vary in each scan by up to 1$^\circ$ from their measured values. A small amount of distortion is introduced in the profile to further improve the fits, finally adjusting the degree of beam spread to account for the finite source size and diffraction in the system. The grating profiles determined for each wavelength scan are averaged and the error about the mean calculated. The final fits shown are then all generated from this averaged set of profile parameters: $a_1 = 2.01 \pm 0.01$ mm, $a_2 = -0.02 \pm 0.02$ mm, $a_3 = 0.02 \pm 0.01$ mm, and $a_4 = -0.01 \pm 0.01$ mm with a grating pitch of $\lambda_g = 14.95$ mm.

The permittivities were assumed to be $\varepsilon_1 = n_1^2 = 1.0$ and $\varepsilon_2 = \varepsilon'_2 + i\varepsilon''_2 = -10^6 + 10^9 i$ for the air and metal respectively.

### 7.4.2. Sample #2 (bi-grating)

*Figure 7.4.2* shows the specular $R_{pp}$, $R_{ss}$ and $R_{sp}$ signals (□) from sample #2 (*Figure 7.3.2*) recorded using the apparatus illustrated in *Figure 7.3.7*. They have been measured as a function of azimuthal angle of incidence ($\phi$) between 0$^\circ$ and 90$^\circ$. The wavelength and polar angle of incidence have been fixed at $\lambda_g = 10.0$ mm and $\theta = 46.5^\circ$ respectively. The solid lines illustrate the predictions from a bi-grating version of Chandezon’s theory ([Harris et al. (1996b)])$, the predictions from which were first experimentally verified in a study partly undertaken by the author, and published by Watts et al. (1996). In order to represent the periodicity in two directions, the surface profile is parameterised by using a sum of two Fourier Series, one in the $x$-direction and the other in the $z$-direction (*Equation 7.3.1*). The theoretical predictions shown in *Figure 7.4.2*, have been calculated using the following parameters: $a_1^z = a_1^x = 1.5$ mm (with all higher Fourier coefficients set to zero), $k_g^z = k_g^x = \frac{2\pi}{\lambda_g}$, where $\lambda_g = 15.0$ mm, $\varepsilon_1 = 1.0$ and $\varepsilon_2 = \varepsilon'_2 + i\varepsilon''_2 = -10^6 + 10^9 i$. 

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Figure 7.4.2 The normalised (a) $R_{pp}$, (b) $R_{ss}$ and (c) $R_{sp}$ experimental azimuthal-angle-dependent signals (□) from the bi-grating (sample #2) compared with the theoretically modelled results (—). Radiation of wavelength $\lambda_0 = 10.0$ mm is incident on the sample at $\theta = 46.5^\circ$. Only one experimental data point in five is shown for clarity.
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Each corrugation is assumed to be purely sinusoidal since computation times are at least an order of magnitude longer for a doubly corrugated interface, and become longer still on the introduction of higher harmonics. For the same reason, beam spread is not accounted for in the modelled data due to the multiple calculations this requires.

7.5. Discussion

7.5.1. Sample #1 (mono-grating)

Figure 7.4.1 illustrates that by using the rigorous diffraction modelling theory it is possible to produce high-quality fits to the experimental data allowing the grating profile to be characterised. The grating profile is also determined by scanning a dial-gauge, sensitive to 0.025 mm, across the metallic surface. The profile is fitted to the function $A(x) = a_i \sin(2\pi/\lambda_g)$, where $\lambda_g = 14.99$ mm and $a_i = 2.01$ mm provided the best fit. Clearly these values compare favourably with those determined via reflectivity measurements ($a_1 = 2.01 \pm 0.01$ mm, $a_2 = -0.02 \pm 0.02$ mm, $a_3 = 0.02 \pm 0.01$ mm, and $a_4 = -0.01 \pm 0.01$ mm, $\lambda_g = 14.95$ mm.). During the process of fitting the reflectivity measurements, in addition to the surface profile parameters, both the grating pitch and incident polar angle were used as fitting parameters. Since degeneracy exists between $\theta$ and $\lambda_g$, the small deviation between the values of the pitch is not surprising.

Virtually all of the previous experimental studies of SPPs propagating along metal–dielectric interfaces have been undertaken at visible or infrared wavelengths [e.g. Raether (1988) and Watts et al. (1997a)]. At these frequencies the electromagnetic response of the metallic sample is dependent on both the real and imaginary parts of the dielectric function of the substrate, in addition to the interface profile. However, at microwave wavelengths, all metals behave as near-perfect conductors and hence the penetration of the electric field into the substrate is small compared to the radiation wavelength. In effect, the electromagnetic response of metal gratings at microwave frequencies is largely independent of the imaginary part of their permittivities ($\varepsilon'_2$).
The reflectivity is only dependent on the surface profile of the sample, defined in the modelling theory as the sum of a truncated Fourier series, $A(x)$ (Equation 6.3.1).

The resonant coupling to the SPP is clearly illustrated in Figure 7.4.1. Consider, for example, graph (a). The two peaks correspond to two different coupling mechanisms to the surface mode. The peak at just over 10.5 mm corresponds to a first order coupling to the -1 SPP (via one grating wave vector, $k_g$), whilst the peak at around 8 mm represents a second order coupling to the +2 SPP via two successive $k_g$ scatterings. Coupling to the +2 SPP is also possible via a single $+2k_g$ interaction. However since the profile of the interface has been milled, and shown above, to be very closely sinusoidal, (i.e. the magnitude of the surface profile Fourier coefficients $a_2$ and higher, are small compared to the fundamental amplitude, $a_1$), the aforementioned second order interaction dominates. As the azimuthal angle is increased the resonances move towards each other and coalesce at $\phi = 60^\circ$, having separated again at $\phi = 75^\circ$. Note also the corresponding Rayleigh anomalies, normally visible in momentum scans undertaken on real metals at visible frequencies ($-\infty \ll \epsilon' < 0$), are not visible in these results. This is attributed to two differences between these microwave experiments and those conducted in the visible regime. Firstly, as the frequency is reduced, the SPP dispersion approaches the light-line (Figure 2.3.2) and hence the momentum difference between the critical edge and the resonance condition is much less than for the visible, making the critical edge difficult to experimentally separate from the SPR. One also suffers from a reduced resolution in momentum due the angle of incidence spread that is associated with the nature of the source and distances involved in the experiment.

It is important to verify that the resonances shown in Figure 7.4.1 are indeed those associated with the SPP. It has been demonstrated in the modelling presented in Chapter 3 that the SPR position moves away from its associated Rayleigh anomaly with increasing grating depth (Figures 3.6.1-3.6.3). A similar behaviour is exhibited when the $R_{pp}$ signal from a grating similar to sample #1 is modelled with radiation incident at
\[ \theta = 31^\circ \text{ and } \phi = 30^\circ . \] As expected, the two resonances widen, and move away from their associated Rayleigh anomalies with increasing depth of the grooves (Figure 7.5.1).

As the azimuthal angle is increased, the two resonances visible in Figure 7.4.1(a) move together, coalesce, and then move apart. Clearly, the resonances will move in the opposite sense when the azimuthal angle is decreased, and at \[ \phi = 0^\circ \] the SPPs are resonant at, or just outside the experimental wavelength range (7.5 < \[ \lambda_0 < 11.3 \text{ mm} \]). At \[ \phi = 0^\circ \], the grating grooves are perpendicular to the plane of incidence, and it is well known that in this orientation, coupling to the SPP is possible only with incident radiation with a TM component (p-polarised). The theoretically modelled \( R_{pp} \) response from sample #1 in this orientation is illustrated in Figure 7.5.2 and now a third SPR

Figure 7.5.1 The effect on the \( R_{pp} \) modelled response from a purely-sinusoidal sample of varying its corrugation amplitude between \( a_i = 0.4 \text{ mm} \) and 2.0 mm. It has a pitch, \[ \lambda_g = 15.0 \text{ mm} \], with radiation incident upon in at \( \theta = 31^\circ \) and \( \phi = 30^\circ \). The modelled response with \( a_i = 2.0 \text{ mm} \) corresponds to the predicted reflectivity in the absence of beam spread from sample #1 studied in this chapter. The vertical lines correspond to the point at which a diffracted order (labelled) ceases to propagate and becomes evanescent (Rayleigh anomaly).

As the azimuthal angle is increased the two resonances visible in Figure 7.4.1(a) move together, coalesce, and then move apart. Clearly, the resonances will move in the opposite sense when the azimuthal angle is decreased, and at \( \phi = 0^\circ \) the SPPs are resonant at, or just outside the experimental wavelength range (7.5 < \( \lambda_0 < 11.3 \text{ mm} \)). At \( \phi = 0^\circ \), the grating grooves are perpendicular to the plane of incidence, and it is well known that in this orientation, coupling to the SPP is possible only with incident radiation with a TM component (p-polarised). The theoretically modelled \( R_{pp} \) response from sample #1 in this orientation is illustrated in Figure 7.5.2 and now a third SPR
associated with the +3 diffracted order is also visible. In comparison to Figure 7.4.1(a), the –1 and +2 SPRs have moved to lower and higher resonant wavelengths respectively. In addition, the resonance associated with the +3 diffracted order actually exists at a higher wavelength than the –1 SPR. As expected, the resonances have finite width, and each occur at a slightly higher wavelength than their corresponding Rayleigh anomaly.

In contrast to the $R_{pp}$ response, the $R_{ss}$ signal from the same sample shows no such resonances. This provides further verification that the experimentally and theoretically observed reflectivity features are indeed those associated with the coupling of incident radiation to the SPP. A final confirmation of the above results may be obtained by modelling the electric field above the metal surface. On resonance of a SPP, there must be a component of the electric field normal to the interface to create the necessary surface charge. The modelling theory described in Chapter 3 has been used to predict these fields on resonance of the +2 SPP at (a) $\phi = 0^\circ$ and (b) $\phi = 30^\circ$, and also the off-resonance fields are shown for comparison purposes (c) [$\phi = 30^\circ$, $\lambda_0 = 9.4$ mm]. These field plots which are shown in Figure 7.5.3 clearly demonstrate the enhancement.
of the electric field close to the interface on resonance of the SPP (a and b) compared to the off-resonance system (c). Note that the fields are not symmetric with the grating surface since the SPP is a travelling wave propagating at an angle of \( \phi \) with respect to \( k_g \) (Figure 2.4.5).

![Figure 7.5.3](image)

**Figure 7.5.3** The predicted \( E_{xy} \) instantaneous vector fields above a purely-sinusoidal sample with \( \lambda_g = 15.0 \text{ mm} \) and \( a = 2.0 \text{ mm} \) with radiation incident at \( \theta = 31^\circ \). The three diagrams correspond to (a) \( \varphi = 0^\circ, \lambda_0 = 11.4 \text{ mm} \ [+2 \text{ SPR in Figure 7.5.2}], (b) \varphi = 30^\circ, \lambda_0 = 10.6 \text{ mm} \ [+2 \text{ SPR in Figure 7.4.1(a)] and (c) \varphi = 30^\circ, \lambda_0 = 9.4 \text{ mm} \text{ [off-resonance].} \)
7.5.2. Sample #2 (bi-grating)

The work of Watts et al. (1996) describes a study that is concerned with the experimental and theoretical response of bi-gratings at visible frequencies. It demonstrates that a doubly-periodic grating structure may be illustrated as a two-dimensional $k$-space diagram. Figure 7.5.4 illustrates such a diagram for the bi-grating (sample #2) of pitch $\lambda_y^i = \lambda_x^r = 15.0$ mm studied in this chapter, with radiation of wavelength $\lambda_0 = 10.0$ mm incident upon it at a polar angle of incidence of $\theta = 46.5^\circ$.

*Figure 7.5.4* $k$-space diagram of the bi-grating studied in this chapter. The shaded circle represents the incident light circle of radius $k_0$. The diffracted light circles that fall within this shaded area represent the positions of the Rayleigh anomalies. Only SPPs, which may be represented by similar circles of slightly greater radius (not shown) that fall within this area, may be coupled to with incident radiation. The dashed arc represents the azimuthal angle scan at a fixed polar angle of incidence ($\theta = 46.5^\circ$) undertaken here.
A comparison of Figure 7.5.4 with Figure 7.4.2 allows one to label the reflectivity features observed in the azimuthal-angle scan (dotted line) shown. The order of the features expected in the reflectivity scan as $\phi$ is increased from 0 to 45° is therefore:

(0,-1), (2,-1), (1,-1), (1,2), (0,2), (2,1), (-1,1), (-1,2), (-1,0).

Here, the Rayleigh anomalies, and associated SPRs, are labelled according to the scattering event(s) they experience, i.e. the (1,-2) diffracted order has been scattered by $k_g$ in the $x$-direction and $-2k_g$ in the $z$-direction.

Since the grating possesses four-fold rotation symmetry, the reflectivity scans are expected to be symmetrical about $\phi = 45°$. This is clearly illustrated in the experimental data shown in Figure 7.4.2 above. However, it is important to note that since there are so many diffracted orders propagating in the system at any chosen angle, only a small proportion of the incident energy is available to be transferred between the orders. It is for this reason that the reflectivity features are much less pronounced in the response from this grating compared to the mono-grating studied above.

Note that the theoretical predictions shown in Figure 7.4.2 have not been “fitted” to the experimental data since this would require unreasonable periods of computation time. Instead, the predicted reflectivities have been calculated by using the pitch and amplitude parameters stated in the original design of the sample. For the same reason, beam spread has not been included in the model. However, the theoretical model agrees well with the experimental data, although the result of neglecting beam spread in the region of sharp features leads to obvious discrepancies.
7.6. Summary

In this chapter, a thorough experimental investigation of the coupling of microwave energy to a surface mode propagating on a corrugated metal-dielectric interface has been presented. This surface wave has been identified as the surface plasmon polariton, the dispersion of which is determined by the surface profile and the dielectric characteristics of the media either side of the interface. Many previous workers have investigated the experimental excitation of the mode on lossy-metallic gratings at visible and infrared wavelengths. However there is little experimental evidence in the literature regarding the resonant coupling to the SPPs that propagate on near-perfectly conducting metals using radiation of microwave wavelengths. At these frequencies, it is only possible to experimentally observe the resonance of the mode if the corrugation is made sufficiently deep such that the mode’s propagation length is reduced.

Experiments at microwave frequencies often suffer from a large amount of beam spread [Khan et al. (1993)]. Here an experimental arrangement has been devised that reduces this problem by collimating the incident beam. By placing the sample on a rotating table, data may be recorded as a function of azimuthal angle of incidence and wavelength. Reflectivities from both a mono- and a bi-grating have been recorded, and a comparison of the experimental results with the predictions from the grating modelling theory shows very good agreement. However, it is clear that a degree of beam spread is still present even in a collimated beam system.
8.1. Introduction

In the previous chapter, the coupling of incident microwave radiation to a SPP that propagates along the surface of a near-perfectly conducting corrugated metal substrate was demonstrated. In such a system, the incident energy is simply redistributed into propagating diffracted orders, or undergoes polarisation conversion, i.e. no power is absorbed by the sample. However, in the work presented in this chapter, it is shown that excitation of the SPP is also possible by depositing an absorbing dielectric layer, sinusoidally-modulated in height, on top of a planar metal substrate. The study is carried out using paraffin wax as the dielectric material on an aluminium-alloy plate, the wax being sufficiently thick to also support a guided mode. Once again, the redistribution of energy is recorded by monitoring the specular beam reflectivity as a function of wavelength ($7.5 < \lambda_0 < 11.3$ mm) and azimuthal angle of incidence ($0^\circ < \varphi < 90^\circ$). The azimuthal-angle-dependent reflectivity scans are fitted to the grating modelling theory described in Section 3.3, with a single set of parameters describing the grating profile, and the permittivity and thickness of the wax layer.

8.2. Background

In previous chapters the coupling of incident energy into SPPs by using corrugated metal surfaces has been discussed, where the grating periodicity provides the required
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in-plane wave vector enhancement. This “classical” grating coupling geometry uses a single corrugated interface, and when grating-coupled in this way, the SPP propagates along the *corrugated* boundary. Since the periodic surface may diffract energy associated with the mode into diffracted orders, the propagation length of the mode is reduced. Other workers have shown that the radiative damping of the mode is proportional to the square of the grating amplitude [McPhedran and Waterworth (1972), Pockrand (1976) and Raether (1988)].

In this, and the following chapter, an alternative grating geometry is utilised (Figure 8.2.1), where the metallic surface is planar. Deposited on top of the metallic substrate is a corrugated dielectric overlayer of mean thickness, \( t \). The dielectric overlayer used is petroleum wax, which has a refractive index at the microwave wavelengths studied here similar to that of glass at visible frequencies (~ 1.5). The upper, semi-infinite dielectric is air and it is the corrugated air-dielectric boundary that excites diffracted orders and provides the required enhanced momentum to couple the incident radiation to the surface mode. This geometry is similar in some respects to the Otto (1968) arrangement (Section 2.4.1) that uses a high-index prism to create an evanescent field across an air gap and couple the field to a SPP on the planar metal-air interface. Here, the prism is replaced by a corrugated overlayer. This coupling geometry for the excitation of SPPs appears to have been first utilised by Müller *et al.*(1997) who successfully coupled 632.8 nm radiation to the SPP mode. Their sample consisted of an evaporated silver substrate, on top of which was a 5 nm layer of gold and a photoresist layer containing an interferographically produced grating.
It is important to note that if the thickness of the overlayer is great enough, the film may support TM and TE-polarised “leaky” guided modes in addition to the SPP. Consider, for example, the planar asymmetrically clad waveguide shown in Figure 8.2.2. The sample may support a series of guided modes, where the minimum thickness, $t$, required to support the $m$th order mode is given by the following inequalities [Yariv (1991)].
For TE\(_m\) modes,

\[
t_m \geq \frac{2m+1}{4} \frac{\lambda_0}{\sqrt{n_d^2 - n_1^2}}
\]

*Equation 8.2.1*

and for TM\(_m\) modes,

\[
t_m \geq \frac{m}{2} \frac{\lambda_0}{\sqrt{n_d^2 - n_1^2}}
\]

*Equation 8.2.2.*

Here, the integer \(m\) is known as the order of the mode, and denotes the number of nodes in the \(E_z\) or \(H_z\) field profiles within the guide for the TE\(_m\) or TM\(_m\) modes respectively. Also \(\lambda_0\) is the vacuum wavelength of the radiation impinging from the air side and, \(n_d\) and \(n_1\) are the refractive indices of the guiding material and air respectively.

*Figure 8.2.2* A planar dielectric slab waveguide, clad asymmetrically with air and metal. The metal and air regions are considered to extend to infinity away from the slab in the \(y\)-direction.
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From *Equation 8.2.1*, it is clear that every TE$_m$ mode has a thickness cut-off below which it cannot propagate. Furthermore, in the limit $t \to 0$, the structure will support no TE guided modes at all. In contrast, the asymmetric waveguide will always support the zero-order TM$_m$ mode even with vanishing thickness of the high index overlayer. The TM$_0$ mode is in fact identical to the SPP that is guided along the interface of a metal and a dielectric. Hence, the SPP may also be considered as the lowest order mode of a metal-clad waveguide. It has no nodes in its $H_z$-field within the high index dielectric and, as described in Chapter 2, its fields decay exponentially away into the metal and air semi-infinite media. *Figure 8.2.3* schematically illustrates the fields associated with the SPP (TM$_0$ mode) associated with a free-electron metal surface at three different frequencies, together with those associated with the first truly guided mode (TE$_0$). In the low frequency limit the metal behaves like a perfect conductor and the optical electric field is excluded from the substrate with an infinite decay length into the media above (*Equation 2.3.25*). Effectively, the mode is a grazing photon, “guided” along the boundary between the air and overlayer. As the frequency of the mode is increased the mode becomes less photon like with exponentially decaying fields both into the metal and air [*Figure 8.2.3(a,b)*]. Eventually, the mode becomes localised at the overlayer-metal interface, with exponentially decaying fields into each medium (c) and the system effectively reduces to a one-interface problem (*i.e* semi-infinite metal and dielectric, $n_0$). However, regardless of frequency, the TM$_0$ mode is always associated with the resonant excitation of the polarisation charge induced at the surface of a metal. Therefore, in this thesis, the mode will continue to be referred to as the surface plasmon polariton (SPP) – even in the two-interface geometry.

The simple description of the system provided above assumes that the waveguide is planar, however in the work presented in this chapter the upper interface of the sample is sinusoidally modulated in height. A demonstration of the change in the dispersion of the modes propagating in a similar sample at visible frequencies on corrugating the top interface is provided by *Salt and Barnes* (1999).
It has previously been discussed that, in contrast to the optical wavelengths where absorption in the metal damps the SPP, metals at microwave frequencies behave as near-perfect conductors. Hence the surface mode that is launched directly along a simple planar interface between semi-infinite air and a metal substrate will have an almost infinite propagation distance. However, in the grating geometry studied in this chapter, there are two independent damping processes that may act on the SPP. Firstly, the mechanism that allows radiation to couple into the SPP (i.e., the grating) will also allow the mode to radiatively decay. This damping process was exploited in Chapter 7 to sufficiently widen the resonances so that they may be experimentally observed. Secondly, although the top and bottom semi-infinite media (air and metal respectively) are effectively non-absorbing at these frequencies, this may not be true for the wax. Since the fields associated with the SPP mode penetrate the overlayer, any loss mechanisms within it ($\varepsilon''_d$) will contribute a term to the damping of the mode. Both of these damping terms will contribute to the width of the surface plasmon resonance (SPR) and will also have a similar effect on any guided modes propagating in the system.

*Figure 8.2.3 (a)-(c) Schematic representation of the electric field ($H_z$) profiles of the SPP (TM$_0$ mode) propagating in an asymmetric, free-electron-metal clad waveguide with increasing frequency. The frequency of the mode shown in (c) is so great that the system behaves effectively like a one-interface system. Also shown for comparison, is the field profile ($E_z$) of the lowest order TE guided mode (TE$_0$) supported by a system with a perfectly-conducting metal substrate (d).*
However, it should be appreciated that a grating may be effectively “zero-order” at certain wavelengths and angles of incidence, *i.e.* there are no propagating diffracted orders in the system. For example, the shaded areas in the reciprocal space diagram representing a grating with $\lambda_0 / \lambda_g = 0.733$ shown in Figure 8.2.4 highlight the momentum space in which the only order propagating is the zero-order beam. Hence, the energy associated with surface or guided modes that exist at values of momentum within these regions can only be radiated back into the specular beam, or absorbed by the wax. In the absence of the latter loss mechanism, re-radiation of energy from the mode back into the specular beam will not give an observable resonance in the reflected signal, unless the grating is orientated such that the grooves are neither parallel nor perpendicular to the plane of incidence ($\varphi \neq 0, \pm 90^\circ, 180^\circ$). In this twisted geometry, the polarisation of the reradiated signal will be different to that of the incident beam, and a polarisation conversion signal may be detected [Bryan-Brown et al. (1990)]. A dip (peak) in the specular $R_{pp}$ and $R_{ss}$ reflectivities will be observed around the resonance condition, together with an associated peak (dip) in the $R_{ps}$ and $R_{sp}$ responses. Clearly, if a non-absorbing grating sample is orientated at $\varphi = 0, \pm 90^\circ$ or $180^\circ$, modes propagating in the “zero-order” region, although having a finite width (associated with their radiative decay $\alpha a^2$), will not be experimentally observed in the reflected signal.

*Figure 8.2.4* Reciprocal space map of a grating of pitch $\lambda_g = 15$ mm with radiation incident of wavelength $\lambda_0 = 11$ mm. The shaded region indicates the values of momentum accessible to incident photons for which no diffracted orders propagate in the system.
8.3. Experimental

By utilising the grating modelling theory introduced in Chapter 3, it is possible to design a sample with wax-grating pitch, amplitude, and thickness to give easily identified and experimentally observed SPRs in the available wavelength range ($7.5 < \lambda_0 < 11.3$ mm). The system chosen for this study has a purely sinusoidal top interface profile $A(x) = a_i \cos \frac{2\pi x}{\lambda_g}$, where $t \approx 2.6$ mm, $a_i \approx 1.5$ mm and $\lambda_g = 15$ mm (Figure 8.2.1).

First it is necessary to determine the permittivity of petroleum wax in the 26.5-40.0 GHz frequency range. This is achieved by completely filling a metallic tray of depth $h$ with wax and recording its wavelength-dependent response at a fixed angle of incidence (Figure 8.3.1). Since the dimensions of the tray are of the same order as the diameter of the incident beam, reflections may take place from the top of the metallic sides of the tray, in addition to the metallic base. The position of the resulting interference fringes allow the permittivity of the wax to be calculated according to the equation

$$m\lambda^m_{\text{min}} = 2h(\varepsilon'_d - \sin^2 \theta)^{1/2}$$

Equation 8.3.1.

where $\lambda^m_{\text{min}}$ is the wavelength corresponding to the $m$th order interference maximum.

The permittivity of the petroleum wax was determined to be $\varepsilon'_d = 2.29$ and constant over the wavelength range studied in this chapter. However the imaginary (damping) term is difficult to determine accurately by this method and is therefore used as a fitting parameter in the subsequent theoretical modelling.
The grating sample itself is prepared by filling a metallic, square tray of side approximately 400 mm and depth 5 mm with hot wax and allowing it to cool. A metallic “comb” of the desired sinusoidal interface profile is manufactured using a computer-aided design and manufacture technique. It is used to remove unwanted wax from the sample by carefully dragging it across the surface until the required grating profile is obtained. The sides of the tray are then removed.

*Figure 8.3.1* Production of interference fringes used to determine the permittivity of the petroleum wax used in this study

*Figure 8.3.2* illustrates schematically the experimental arrangement used to record the reflectivity from the sample, which is identical to that used to measure the response of the bi-grating in the last chapter. The reflectivity data are recorded as a function of wavelength between 7.5 and 11.3 mm, over the azimuthal angle (φ) range from 0 to 90° at a fixed polar angle of incidence, θ ≈ 47°. The source and receiving horn antennae are set to pass either p- (transverse magnetic, TM), or s- (transverse electric, TE) polarisations, defined with respect to the plane of incidence. This enables the
measurement of $R_{pp}$, $R_{ps}$, $R_{ss}$ and $R_{sp}$ reflectivities. To account for any fluctuations in
the emitted power from the source, the output from the signal detector is divided by that
from the reference. The normalised reflectivities over the entire frequency range are
downloaded from a scalar network analyser to a computer and are saved to disk. The
resulting wavelength- and angle-dependent reflectivities from the sample are normalised
by comparison with the reflected signal from a flat metal plate.

Figure 8.3.2  Schematic diagram illustrating the apparatus used to measure the
wavelength- and azimuthal-angle-dependent response from the sample studied in this
work.

8.4.  Results

Figure 8.4.1 illustrates a series of polar grey-scale maps of the normalised $R_{pp}$, $R_{ps}$ and
$R_{ss}$ signals from the sample as a function of frequency and azimuthal angle of incidence.
Since the profile of the grating is non-blazed, the $R_{sp}$ response (which will be identical
to the $R_{ps}$ response) is not illustrated.
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Figure 8.4.1 Normalised (a) $R_{pp}$, (b) $R_{ps}$ and (c) $R_{ss}$ response of the sample as a function of frequency between 26.5 and 40 GHz (11.3 and 7.5 mm), and azimuthal angle of incidence with $\theta \approx 47^\circ$. Data has been recorded between $\varphi = 0^\circ$ and $\varphi = 90^\circ$, and reflected to produce full 360° polar maps.
In Chapter 2 a planar air-metal interface, with photons incident from the air side, was shown to be represented as a single lattice point in $k$-space, based upon which is a light circle of radius $n_k k_0$. The area bounded by this circle represents the range of wave vectors that may be accessed by an incident photon. SPPs and guided modes supported by a high-index dielectric (wax) layer deposited on top of a metal substrate both exist at higher wave vectors than that available from an incident photon ($k_{\text{SPP}} \geq k_{\text{GM}} > n_k k_0$), hence it is impossible to couple directly to either mode via a planar interface. However, the periodic modulation of the wax overlayer may scatter the incident radiation by integer multiples of $k_g$. This results in a series of diffracted light, SPP and guided-mode circles about each reciprocal lattice point. The sections of these diffracted SPP and guided-mode circles that fall within the light circle based upon the origin corresponding to a photon incident from the air side may now be coupled to by the incident radiation (Figure 8.4.2). However, the work presented in this chapter is a multi-wavelength study and so the idea has to be extended by considering a series of light cones about each grating lattice point, as illustrated in Figure 8.4.3. However for clarity, only the specular light cone is illustrated together with cross-sections through the cones for frequencies 26.5 GHz and 40.0 GHz ($\lambda_0 = 11.3$ mm and 7.5 mm respectively). Incident radiation on the sample may be represented by a cone of radius $n_k k_0 \sin \theta$ (dashed line). By viewing from a location above the cones, one may visualise the ellipses mapped out by the intersections of the experimental angle scan with the diffracted light cones, where the points on these curves correspond to the occurrence of a Rayleigh anomaly. These are difficult to observe in the reflectivity data due to the angle spread associated with the experiment. However the ellipses of greater radius corresponding to the coupling of radiation to SPPs and guided modes are clearly evident.
During the fitting process, it is useful to be able to differentiate SPPs from guided modes, and recognise which diffracted order provides the coupling mechanism to each mode. However, from the data illustrated in this study so far, this is not immediately obvious. One way in which each of the modes may be identified is to use the rigorous grating theory described in Chapter 3 to model their dependence on the thickness of the wax overlayer.
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Figure 8.4.4 illustrates, at \( \lambda = 11 \) mm, the predicted \( R_{ss} \) reflectivities from samples with wax thicknesses (a) \( t = 2.1 \) mm, (b) \( t = 2.6 \) mm, (c) \( t = 3.1 \) mm and (d) \( t = 3.6 \) mm, and \( a = 1.5 \) mm, \( \lambda_g = 15 \) mm, \( \varepsilon_g = 2.29 + 0.00i \) and \( \varepsilon_z = -10^6 + 10^9i \). The theoretical data is plotted in the form of a series of reciprocal space maps where \( k_x = k_0 \sin \theta \cos \varphi \) and \( k_z = k_0 \sin \theta \sin \varphi \). The imaginary component of permittivity of the wax overlayer (\( \varepsilon_g^* \)) has been set to zero in order to provide maximum contrast in the diagrams. (An illustration that a variation of \( \varepsilon_g^* \) does not affect the position of the modes in \( k \)-space will be provided later.)
It is interesting to note that the coupling strengths of all the modes appear to fall to zero as $\varphi \rightarrow 90^\circ$. This is because there are no diffracted orders propagating, polarisation conversion is not possible and there is no absorption in the system (Section 8.2). Hence, although coupling to the mode is still possible and its resonance has finite width, it cannot be experimentally observed, as there is no channel into which energy may be transferred.
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The modes visible in Figure 8.4.4(a) are the diffracted SPP (TM_0) modes which propagate along the metal-wax interface. Note that the coupling strength to the SPP also decreases to zero as \( \phi = 0^\circ \) is approached. This is because the incident TE field has no component perpendicular to the grating surface and hence cannot create the necessary surface charge. Clearly, the fields associated with the SPP will sample the wax layer and will penetrate into the air half-space, as shown in Figure 8.2.3. Therefore, the dispersion of the SPP will be dependent on an effective refractive index \( n_d^{\text{eff}} \) since the degree of penetration into the air is governed by the thickness of the wax overlayer. Hence \( k_{\text{SPP}} \sim n_d^{\text{eff}} k_0 \), where \( n_1 \leq n(t)^{\text{eff}} \leq n_d \) with the SPP moving to higher momentum values with increasing thickness, as is clear in Figure 8.4.4. In addition the excitation of guided modes also becomes possible if the dielectric overlayer is sufficiently thick (Equation 8.2.1 and Equation 8.2.2). The lowest order guided mode may be observed in Figure 8.4.4 (b), (c) and (d), however at \( t = 2.6 \) mm the mode is almost coincident with the Rayleigh anomaly. In a similar manner to the SPP, the guided mode also moves away from the Rayleigh anomaly as the wax thickness is increased.

The white dashed circle superimposed on Figure 8.4.4(b) illustrates the equivalent momentum scan undertaken in this study with radiation of wavelength \( \lambda_0 = 11.0 \) mm incident at \( \theta = 47^\circ \). Hence, by comparison of Figure 8.4.4(b) with the experimental study at this fixed wavelength it is possible to identify the guided mode (GM) and SPP, and label the modes according to the diffracted order which provides the coupling mechanism (Figure 8.4.5). Having identified the modes supported by the sample, the reflectivity data are fitted to the grating modelling theory for a series of different wavelengths. By fitting the reflectivity data using a single set of parameters, it is possible to accurately parameterise the grating profile, thickness and permittivity of the wax overlayer. Figure 8.4.6 shows a series of experimental data sets (□) at wavelengths of (a) 7.5 mm, (b) 8.5 mm, (c) 9.5 mm and (d) 10.5 mm, showing the \( R_{pp} \), \( R_{ss} \), \( R_{ps} \) and \( R_{ss} \) signals respectively. The solid curves are the theoretical fits, which are in good agreement with the experimental data. During the fitting process, the amplitude of the corrugation, thickness and real part of the permittivity of the wax, and the polar angle of incidence are all allowed to vary within uncertainty bounds.
from their measured values. The imaginary part of the permittivity of the wax is initially assumed to be zero, the pitch of the grating is $\lambda_g = 15\,\text{mm}$ and the permittivities of the air and metal are assumed to be $\varepsilon_1 = 1.0 + 0.0i$ and $\varepsilon_2 = -10^6 + 10^9i$ respectively. Distortion of the grating profile ($a_2, a_3$) is also introduced, however it does not improve the average quality of the fits. It was shown in Chapter 7 that a beam spread of approximately $\theta_{1/2} = 1^\circ$ is required to account for finite source size and diffraction in the system, therefore a small amount of beam spread is introduced into the theoretical modelling illustrated here. The grating profile, polar angle of incidence and properties of the wax overlayer determined for each azimuthal scan are averaged, and the error about the mean calculated. The final fits shown are then each generated from this averaged set: $a_i = 1.50 \pm 0.02\,\text{mm}$, $t = 2.62 \pm 0.01\,\text{mm}$, $\varepsilon'_d = 2.29 \pm 0.01$, $\varepsilon''_d = 0.04 \pm 0.01$ and $\theta = 46.8 \pm 0.1^\circ$. To confirm the validity of the theoretical model, it is necessary to independently measure the profile of the grating. By scanning a dial-gauge across the wax surface, the grating amplitude and the thickness of the wax layer are determined to be $a_i = 1.48 \pm 0.01\,\text{mm}$ and $t = 2.63 \pm 0.08\,\text{mm}$ respectively. Clearly, these values are within the uncertainties of those determined via the fitting process.

Figure 8.4.5 The experimental $R_{\text{ss}}$ azimuth-angle scan corresponding to the white, dashed line shown in Figure 8.4.4(b)($\lambda_0 = 11\,\text{mm}$). The resonances are identified and labelled according to the diffracted order that provides the coupling mechanism.
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Discussion

This work has demonstrated that it is possible to couple incident microwave radiation to guided and SPP modes via an alternative geometry that does not require forming the grating profile directly in to the metal substrate. Coupling to the SPP in this way is advantageous over the “classical” one-interface grating-coupling geometry since complicated shapes can easily be carved into a wax layer, rather than using expensive machine time to mill the shape directly into a metal. In addition, the SPP that propagates in the single-interface system may only be radiatively damped since the media either side of the boundary are usually non-absorbing. Therefore, a sufficiently

Figure 8.4.6 Typical normalised azimuthal-angle dependent reflectivities (□) compared with the theoretically modelled results (—) created from a single set of fitting parameters. Radiation is incident on the sample at fixed polar angle of incidence of $\theta = 47^\circ$ with wavelengths of (a) $\lambda_0 = 7.5$ mm, (b) $\lambda_0 = 8.5$ mm, (c) $\lambda_0 = 9.5$ mm and (d) $\lambda_0 = 10.5$ mm impinging on the sample. The signals recorded are (a) $R_{pp}$, (b) $R_{ss}$, (c) $R_{ps}$ and (d) $R_{sp}$. The azimuthal-angle scans shown have been extracted from the experimental data sets illustrated in Figure 8.4.1

8.5.  Discussion

This work has demonstrated that it is possible to couple incident microwave radiation to guided and SPP modes via an alternative geometry that does not require forming the grating profile directly in to the metal substrate. Coupling to the SPP in this way is advantageous over the “classical” one-interface grating-coupling geometry since complicated shapes can easily be carved into a wax layer, rather than using expensive machine time to mill the shape directly into a metal. In addition, the SPP that propagates in the single-interface system may only be radiatively damped since the media either side of the boundary are usually non-absorbing. Therefore, a sufficiently
large grating depth is required to shorten the lifetime of the mode and sufficiently widen the resonance so that it may be easily experimentally observed. However by using a corrugated dielectric overlayer with non-zero $\varepsilon'_d$ deposited on a planar metal surface, a second damping mechanism is introduced by which the SPP may decay. Hence the need for such large corrugation amplitudes is decreased.

Figure 8.5.1 and Figure 8.5.2 illustrate at $\lambda_0=11\text{ mm}$, the effect on the modelled $R_{ss}$ response and degree of absorption of the sample, of increasing the imaginary part of the permittivity of the dielectric layer ($\varepsilon''_d$). The diagrams demonstrate that the position of the modes in momentum-space do not change, but the width of these resonances is increased. In addition, an absorbing overlayer will decrease the coupling strength to the SPP since the magnitude of the fields at the metal surface will be reduced. Clearly, the introduction of a non-zero $\varepsilon''_d$ decreases the background reflectivity level, however the degree of absorption on-resonance of a well-coupled mode is greatly enhanced. For comparison, Figure 8.5.2 also illustrates the degree of absorption of a planar sample of the same mean thickness.

![Graph illustrating the effects of increasing $\varepsilon'_d$ (absorption in the wax layer) on the predicted $R_{ss}$ signal with radiation of wavelength $\lambda_0 = 11\text{ mm}$ incident at a polar angle of $47^\circ$, with wax thickness $t = 2.6\text{ mm}$ and grating amplitude $a_t = 1.5\text{ mm}$.](image-url)
In this chapter, the coupling of microwave radiation via a dielectric grating to a SPP that propagates on a planar near-perfectly conducting metal surface has been illustrated. The dielectric material used in this study is petroleum wax and is sufficiently thick such that it is also able to support the lowest order “leaky” guided mode. Due to the ease with which the required grating profile may be shaped from the wax compared to milling the profile directly into a metal substrate, this coupling mechanism may be advantageous over the “classical” geometry. The technique of recording the response of the sample as a function of the azimuthal angle of incidence has been demonstrated. It is particularly useful at these wavelengths because by simply rotating the sample, it is possible to
quickly gather large amounts of data by simultaneously scanning the incident wavelength. Furthermore, the incident beam has been collimated to reduce the undesirable effects of beam spread. Hence good agreement theoretical models based on the differential formalism of Chandezon et al. and the experimental reflectivities have been obtained. The fitting process has enabled the characterisation of the dielectric constants of the wax, which has shown it to be slightly absorbing at these frequencies ($\varepsilon''_a = 0.04i$). In addition, the real part of the wax permittivity derived in the fitting process agrees with the value obtained via interferographic measurements. The effect of a non-zero $\varepsilon''_a$ is to change the coupling strengths of the diffracted SPP and guided mode resonances, and increase the range of momentum values over which energy may be coupled into the modes. The degree of absorption of the sample is also greatly enhanced on resonance of a well-coupled mode.
CHAPTER 9
The coupling of near-grazing microwave photons to surface plasmon polaritons via a dielectric grating.

9.1. Introduction

In this study, a dielectric grating, similar to that discussed in the last chapter, is used to couple near-grazing microwave photons to surface plasmon polaritons (SPPs). The novel result presented here is that when the grating grooves are orientated such that they are parallel to the plane of incidence \( \phi = \pm 90^\circ \), coupling to SPPs with both s- and p-polarised photons is possible at three different energies. It is demonstrated that one mode is coupled to via p-polarised radiation, the other two modes are both coupled to via s-polarised radiation. The multi-layer, multi-shape differential grating theory discussed in Chapter 3 allows the identities of each of the modes to be confirmed by modelling the electromagnetic fields above the metal substrate. In addition, a comparison between the experimentally derived reflectivity scans and the theoretical model is made.

9.2. Background

Of the two orthogonal linear polarisations, it has generally been considered possible to couple only incident s-polarised (TE) radiation to the SPP when the grating grooves are orientated such that they are parallel to the plane of incidence \( \phi = \pm 90^\circ \). However, recent work [Watts et al. (1997)] has shown that for sufficiently deep grooves, coupling is also possible with incident p-polarised (TM) radiation. Here, a similar mechanism for coupling p-polarised radiation to the SPP when the grating grooves are orientated in this way is established. A two-interface geometry is utilised where the corrugated boundary, which provides the coupling mechanism to the SPP, is separated from the planar one.
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along which the mode propagates. A similar geometry appears to have been first used by Müller et al. (1997) who successfully coupled visible (632.8 nm) radiation to the SPP mode. Their sample consisted of an evaporated silver substrate, overcoated with a 5 nm layer of gold and a photoresist layer containing an interferographically produced grating. Other recent studies involving dielectric grating samples include that of Salakhutdinov et al. (1998). They provided a theoretical and experimental study of a metal-dielectric grating that shows increased diffraction efficiency over a conventional metallic grating due to the excitation of “leaky” guided modes in the dielectric layer. In addition, Seshadri (1999) have theoretically investigated the reflection of radiation from a dielectric grating sample with a metallic substrate as a function of the angle of incidence. On excitation of SPPs and guided modes in the dielectric film, they observe peaks in the calculated absorption spectra, and they illustrate that the angular response of the experimentally-determined reflection coefficient may be used to obtain estimates of the average thickness of the film and amplitude of the grating.

In previous chapters, it has been shown that one may couple incident microwave radiation into a SPP (TM$_0$ mode) propagating along a metal-dielectric interface by using a diffraction grating of suitable pitch. If this grating profile is formed in the metal substrate (Chapter 7) then the width of the observed resonances will depend only on the radiative decay of the mode and hence the amplitude of the grating [McPhedran and Waterworth (1972), and Pockrand (1976)]. This is because no energy may be dissipated into the substrate since metals behave as near-perfect conductors at microwave frequencies. However it has been shown in Chapter 8 that it is also possible to couple radiation into the SPP by depositing a corrugated wax overlay on top of a planar metal substrate. The grating again provides the mechanism for radiative decay, but as the wax is slightly absorbing, the SPP may also decay via loss into the wax. In this situation, both damping terms will contribute to the width of the surface plasmon resonance (SPR). In addition, if the grating grooves are neither parallel nor perpendicular to the plane of incidence ($\phi \neq 0, \pm 90, 180^\circ$), then the polarisation of the reradiated signal will be different to that of the incident beam and a polarisation conversion [Bryan-Brown and Sambles (1990)] signal may be detected. If one chooses to detect linearly polarised radiation, then this mechanism provides a third channel into
which energy may be transferred from the detected beam – it is “absorbed” by the polarisation setting of the detector.

In this study, the reflectivity of near-grazing microwave radiation is recorded as a function of wavelength and azimuthal angle of incidence from a sample consisting of a slightly absorbing, thin dielectric (wax) grating on top of a near-perfectly conducting metallic (aluminium-alloy) substrate. Such a sample enables the coupling of both p- (TM) and s- (TE) polarised incident photons to the SPP at all orientations other than \( \varphi = 0^\circ \), and according to the condition

\[
k_{SPP}^2 = \varepsilon_d^{\text{eff}} k_0^2 \sin^2 \theta + N^2 k_y^2 \pm 2(\varepsilon_d^{\text{eff}})^{\frac{1}{2}} N k_y k_0 \sin \theta \cos \varphi
\]

\text{Equation 9.2.1}

(With incident s-polarised radiation at \( \varphi = 0^\circ \) there is no local normal component of electric field at either the flat or corrugated interfaces to create the necessary surface charge). In \text{Equation 9.2.1}, \( \varepsilon_d^{\text{eff}}(t) \) is an effective complex permittivity of the dielectric that is dependent on the thickness of the overlayer (\( \varepsilon_d^{\text{eff}} \to \varepsilon_d \) as \( t \to \infty \)). The grating pitch and wavelength-range are chosen so that at \( \varphi = \pm 90^\circ \) the grating is effectively “zero-order”, \textit{i.e.} the only order propagating is the specularly reflected beam (see \text{Section 8.2}). Hence any detected losses on excitation of any modes propagating in the system recorded at \( \varphi = \pm 90^\circ \) are solely due to absorption of energy into the dielectric layer (since there is no polarisation conversion at this angle). Wavelength dependent reflectivity scans are fitted to the rigorous grating modelling theory using the corrugation amplitude, wax thickness, polar angle of incidence and the absorption of the wax (\( \varepsilon_d^* \)) as fitting parameters. As grazing incidence is approached, one observes an evolution of the s-coupled SPP into two different modes. Utilisation of the modelling theory to predict the field distribution throughout the sample provides an explanation of this phenomenon.
9.3. Experimental

It is necessary to design a sample whose grating pitch \( \lambda_g \), amplitude \( a_i \) and wax thickness \( t \) will permit the resonant coupling to the SPP using near-grazing photons within the available wavelength range \( 7.5 \text{ mm} < \lambda_0 < 11.3 \text{ mm} \). By utilising the grating modelling theory, the optimum parameters required in order to achieve these results are deduced. The sample chosen has a purely sinusoidal top interface profile, 
\[
A(x) = a_i \cos \frac{2\pi x}{\lambda_g}
\]
where \( a_i = 1.50 \text{ mm} \) and \( \lambda_g = 15.00 \text{ mm} \), with mean thickness of wax, \( t = 1.60 \text{ mm} \). The real part of the complex permittivity of the wax has been determined in the last chapter via interferographic reflectivity measurements from a planar slab of known thickness, and the imaginary part has been measured by fitting the predictions from the grating modelling theory to reflectivity measurements.

The sample is prepared by filling a metallic, square tray of side approximately 400 mm and depth 5 mm with hot wax and allowing it to cool. A sinusoidal template is manufactured with a pitch of \( \lambda_g = 15.00 \text{ mm} \) and fundamental amplitude of \( a_i = 1.50 \text{ mm} \). It is used to remove unwanted wax from the sample by carefully dragging it across the surface until the required grating profile is obtained (Figure 9.3.1).

The experimental arrangement described in the last chapter was again used to record the reflectivity from the sample in order to reduce the undesirable effects of spherical wavefronts (Figure 8.3.2). Variation of the magnitude of the incident wave-vector in the plane of the grating may be achieved by scanning either wavelength \( \lambda_0 \), or angle of incidence \( \theta \) or \( \phi \). In this study the reflectivity data are taken both as a function of wavelength \( 7.5 \text{ mm} < \lambda_0 < 11.3 \text{ mm} \) and azimuthal angle of incidence \( 0 < \phi < 90^\circ \), fixing the polar angle of incidence at \( \theta = 80^\circ \). Figure 9.3.1 illustrates the co-ordinate system used to describe the geometry of the sample.
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The source and receiving horn antennae are set to pass either p- (TM), or s- (TE) polarisations which enables the measurement of $R_{pp}$, $R_{ps}$, $R_{ss}$ and $R_{sp}$ reflectivities, where the subscripts refer to the incident and detected polarisations in that order. To account for any fluctuations in the emitted power from the source, the analyser divides the output from the signal detector by that from the reference. The normalised reflectivities over the entire frequency range are downloaded from a scalar network analyser to a computer and are saved to disk. The resulting wavelength- and angle-dependent reflectivities from the sample are normalised by comparison with the reflected signal from a flat metal plate.

The high polar angle of incidence introduces a problem associated with the effective beam spot size on the sample. A beam spot that is larger than the sample itself will clearly diffract from its edges and surrounding obstacles and results in interference oscillations in the detected signal. By aperturing the two mirrors with microwave

Figure 9.3.1 Photograph of sample used in this chapter, also illustrating the coordinate system and experimental geometry, where $\lambda_g$ is the grating pitch. The direction of the electric field vector $\mathbf{E}$ is illustrated for the situation when p-polarised (transverse magnetic, TM) radiation is incident. The two lower corners of the sample were damaged after the experimental results had been obtained.
absorbing material, it is possible to restrict the size of the incident beam on the grating
and remove these artefacts. In addition, placing randomly angled reflecting material on
the exposed areas of the metal base ensures that only radiation striking the wax surface
will reach the collecting mirror and detector.

9.4. Results

Figure 9.4.1 illustrates two polar grey-scale maps of the normalised experimental $R_{ss}$
and $R_{pp}$ signals from the sample. These are illustrated as a function of frequency
between 26.5 and 40 GHz ($\lambda_0 = 11.3$ and 7.5 mm) and azimuthal angle, at $\theta = 80^\circ$. The
azimuth-angle dependent data has been recorded between 0 and 90° and simply
reflected about the axes to produce a full 360° plot. Similar figures were produced in
the previous chapter and an explanation is provided there of the dispersion of the
reflectivity features they illustrate.

The band labelled $\cdot$ corresponds to the SPP which is coupled to via the second order
diffracted beam ($N = \pm 2$) and is observed as a slight dip in the $R_{pp}$ signal, and a peak in
the $R_{ss}$ response. The Rayleigh anomaly that corresponds to this diffracted order occurs
at a slightly lower angle of azimuth than the SPP, but is not visible in the experimental
data. However, the Rayleigh anomaly corresponding to the point at which the 1st order
diffracted beam ceases to propagate is clearly visible in the $R_{pp}$ data as a dramatic
change in reflected intensity in the specular order response (indicated by the arrow).
The bands labelled $\cdot$, $\blacklozenge$ and $\bigdiamond$ all correspond to the SPP excited by the evanescent
fields associated with this diffracted order ($N = \pm 1$).
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**Figure 9.4.1** Normalised $R_{ss}$ and $R_{pp}$ response of the sample as a function of frequency and azimuthal angle of incidence. Data has been recorded between $\varphi = 0^\circ$ and $\varphi = 90^\circ$, and reflected about the axes to produce full $360^\circ$ polar maps. The band labelled $\bullet$ corresponds to the ±2 SPP, and the bands labelled $\circ$, $\heartsuit$ and $\diamondsuit$ all correspond to the ±1 SPP. The arrow on the upper diagram identifies the corresponding ±1 Rayleigh anomaly.
Figure 9.4.2 illustrates the $R_{ss}$ and $R_{pp}$ response of the sample with the grating orientated so that $\phi = 90^\circ$, which is equivalent to taking a slice through the respective plots shown in Figure 9.4.1. It is important to note that at this azimuthal angle of incidence, the grating wave vector, $k_g$, is perpendicular to the plane of incidence, and hence no polarisation conversion may occur. The reflectivity data recorded at $\phi = 90^\circ$ were fitted to the grating modelling theory using the same parameters for both $R_{ss}$ and $R_{pp}$ scans. During the fitting process, the amplitude of the corrugation, thickness of the wax and the polar angle of incidence are all allowed to vary from their estimated values. The permittivity of the wax is initially assumed to be identical to that determined in the previous study ($\varepsilon_d = 2.29 + 0.04i$), however the imaginary part is allowed to vary in the fitting procedure. The azimuthal angle is set to $\phi = 90^\circ$ and the permittivities of the metal and air are assumed to be $\varepsilon_2 = -10^6 + 10^9i$ and $\varepsilon_1 = 1.0 + 0.0i$ respectively. In addition, the pitch of the grating is independently measured to be $\lambda_g = 15.01 \pm 0.03$ mm. Distortion of the grating profile $(a_2, a_3)$ is also introduced, however it does not improve the average quality of the fits confirming the sinusoidal nature of the corrugation.

The best comparison between the model and the experimentally derived reflectivities is achieved when the following fitting parameters are used: $a_i = 1.49 \pm 0.01$ mm, $t = 1.59 \pm 0.01$ mm, $\theta = 80.0 \pm 0.5^\circ$ and $\varepsilon_d' = 0.061 \pm 0.004$. Comparisons between the predictions using these parameters (solid line) and the experimental data (squares) are shown in Figure 9.4.2.
Figure 9.4.2 The normalised $R_{ss}$ and $R_{pp}$ frequency-dependent response (□) of the sample orientated at $\varphi = 90^\circ$. The solid lines on each of the graphs correspond to the theoretically modelled results that have been created from the same set of fitting parameters. The two experimental data sets shown have been extracted from the data shown in Figure 9.4.1.
The fitted $R_{pp}$ and $R_{ss}$ reflectivity data recorded at $\phi = 90^\circ$ and shown above illustrates good agreement between the theory and the experimental results. The reflectivity data appears more “noisy” than the microwave data presented in earlier chapters at least in part due the large beam spot size associated with the high polar angle used in this study. Clearly the known amplitude of the grating template agrees with the amplitude determined via the fitting procedure. However, the value of the imaginary part of the dielectric constant of the wax determined here ($\varepsilon'' = 0.061\pm0.004$) is slightly greater than that measured in the previous chapter ($\varepsilon'' = 0.04\pm0.01$) when a thicker layer was used. The may be attributed to a difference in deposition conditions of the wax and impurities on the surface of the metal.

*Figure 9.4.1* illustrates the dispersion of modes that are supported by the sample and are excited using near-grazing microwave radiation in the 26.5 to 40 GHz frequency range ($11.3\ \text{mm} > \lambda_0 > 7.5\ \text{mm}$). This section will demonstrate that these modes correspond to the resonance condition of the SPP.

The experimentally measured response of the sample in the special case when the grooves are orientated so that they are parallel to the plane of incidence ($\phi = \pm90^\circ$) is shown in *Figure 9.4.2*. In this situation, polarisation conversion is not possible, and since no orders are propagating in the system other than the specular beam, any energy loss in the reflected signal on resonance of the SPP can only be lost into the media surrounding the interface. It is possible to verify the resonance condition of the SPP by using the grating modelling theory to plot the vector electric fields in the $xy$-plane. A strong local component of the electric field vector normal to the metal-wax interface ($E_y$) induces a periodic oscillation of polarisation charge along the boundary showing the coupling of incident radiation to a surface mode. *Figure 9.5.1* illustrates the predicted $E_{xy}$ instantaneous vector fields at $\phi = \pm90^\circ$ for the three resonance
wavelengths (calculated using the grating theory described in Section 3.3) and it is clear in each case that there is a strong normal component. These graphs have been calculated at an instant in time at which the coupling strength to the SPP is strongest (maximum $E_y$).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.5.1.png}
\caption{The predicted $E_{xy}$ vector fields corresponding to each of the three resonances shown in Figure 9.4.2 at the instant in time of strongest coupling. Diagram (a) corresponds to the low frequency $s$-coupled mode, $\star$; (b) the high energy $s$-coupled mode, $\blacklozenge$, and (c) the $p$-coupled mode, $\lozenge$.}
\end{figure}
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It is important to consider how the SPP is created along the metal boundary in each of the resonance conditions described above, remembering that it is only the local normal component of the electric field which induces surface charge and thus couples to a SPP. When s-polarised radiation at near-grazing incidence impinges on the sample, there is no component of the electric field vector normal to the metal interface to directly create the required surface charge. However, there is always a component of $E$ normal to the profile of the dielectric grating, which is at a maximum at the point of steepest gradient. Hence polarisation charge is induced at these points on the wax-air boundary, which in turn induces charge at points on the metal surface below (approximately at $k_g x = \frac{\pi}{2} (2p + 1)$, where $p$ is an integer). In the p-polarised case, there is clearly a component of $E$ normal to the metal-wax interface. However since it is a plane wave, one may initially think that all the charges induced should be in phase, yet a surface charge density oscillation at the metal boundary is induced. This is because of the difference in path length experienced by a photon striking the top of the high-index wax groove compared with one impinging near the trough. Hence we find that the charge centres are located symmetrically along the metal boundary with respect to the grating profile (at $k_g x = p\pi$), immediately below the peaks and troughs of the dielectric grating.

Of course at $\varphi = \pm 90^\circ$, and on excitation of the SPP, there will be two surface waves propagating in opposite directions along the metal surface. These two counter-propagating eigenmodes may be coupled together via two successive $k_g$ scattering events, setting up a standing wave in the $x$-direction, where the period of the standing wave is the same as the grating pitch ($\lambda_{SPP} = \lambda_g$). The standing wave associated with the p-coupled mode will have a different charge distribution on the surface of the metal to the charge distribution associated with the s-coupled mode, and hence two quite distinct field profiles will result. One field profile has maxima in $E_y$ below the peaks and troughs of the grating surface (coupled to via p-polarised incident radiation), the other with its extrema underneath the points of steepest gradient (coupled to via s-polarised radiation). These correspond to a low and a high energy mode respectively, and hence an energy gap is seen to open up at $\varphi = \pm 90^\circ$. 

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The situation described above is further complicated since at the polar angle of incidence studied in this work ($\theta = 80^\circ$), there may be coupling to the s-coupled SPP at two different energies (Figure 9.4.1), both of which exist at lower energies than that needed to coupled to the p-mode. Therefore, it is interesting to theoretically model the dispersion of the SPP mode as a function of frequency and polar angle of incidence (Figure 9.5.2). The boundary between the areas of low and high reflectivity which forms an arc in the top left corner of Figure 9.5.2 is associated with the $\pm 2$ Rayleigh anomaly, and the dark band that extends from the bottom left corner of both the graphs corresponds to the excitation of the $\pm 2$ SPP. This figure illustrates that one may only couple s-polarised radiation to SPP mode at two different energies when $\sin \theta = k_z/k_0 > 0.9$ (approximately). Notice also that an equivalent “splitting” of the p-coupled mode at high polar angles does not occur. To explain this result, it is useful to refer back to the vector field illustrations of Figure 9.5.1.

First consider the p-coupled mode, where the standing wave in the $x$-direction has its charge centres on the metal surface beneath the peaks and troughs of the dielectric grating. For $\theta \neq 0^\circ$, there are two loops of $E_{xy}$ within each grating period where neighbouring loops are in anti-phase. Now consider the s-polarised case. When $\sin \theta \approx 0.75$, there is only one coupling condition to the SPP and again two loops of $E_{xy}$ are seen in Figure 9.5.1(c). However since the standing wave at the metal interface is out of phase by $\lambda_e/4$ with respect to the grating profile, one loop exists primarily within the wax, the other samples the air. As grazing incidence is approached ($k_z \rightarrow k_0$), one of the field loops becomes dominant at the expense of the other. Eventually one of the loops almost disappears and now neighbouring loops of $E$ are in phase with each other and two quite distinct bands are observed. Band • corresponds to the mode whose loops of $E_{xy}$ are almost entirely contained within the wax of the grating, and by contrast the field loops associated with band ♦ are concentrated within the air. Since a mode whose field loops are concentrated in the wax samples a higher effective refractive index than one whose fields may penetrate into the air, modes associated with band • exist at a lower energy than those of band ♦. This is also clear from the experimental scan shown in Figure 9.4.2 which corresponds to the black dashed line superimposed on Figure 9.5.2. Also evident from these figures is that band • appears
to be the dominant one, and modes associated with it are more strongly coupled to than modes associated with band \( \bullet \). However one may change the relative coupling strengths of the two modes by varying the thickness of the corrugated overlayer. Figure 9.5.3 illustrates the dispersion of the modes with \( \theta \) and frequency when, (a) each of the two bands are equally well coupled \((t = 2.10 \text{ mm})\), and (b) band \( \bullet \) becomes dominant \((t = 2.50 \text{ mm})\).

![Figure 9.5.2](image)

Figure 9.5.2 Theoretical prediction of the \( R_{ss} \) and \( R_{pp} \) response of the sample illustrating the dispersion of the SPP mode as a function of incident momentum \((k_z/k_0 = \sin \theta)\) and frequency. The data has been calculated using the fitting parameters derived earlier in the work where the vertical black dashed lines represents the experimental scans undertaken.
It is important to note that although s-polarised radiation is able to induce surface charge beneath the points of greatest gradient of the air-wax interface at $\varphi = \pm 90^\circ$ and hence couple strongly to modes $/\text{rhombus}^3$ and $/\text{rhombus}^5$, there is no coupling in the $R_{pp}$ response and only weak coupling away from this orientation (Figure 9.4.1). This is because incident p-polarised radiation is not able to induce the necessary surface charge when the grating is at $\varphi = \pm 90^\circ$. In a similar manner, but for all grating orientations, it is impossible for s-polarised radiation to create surface charge beneath the peaks and troughs of the wax-air interface; hence mode $/\text{rhombus}^6$ may only be excited with p-polarised radiation.

**Figure 9.5.3** Theoretical predictions of the $R_{ss}$ response of a similar sample to that used in this study but with thicker wax overlayers: (a) $t = 2.10$ mm and (b) $t = 2.50$ mm.
9.6. Summary

In this work near-grazing microwave radiation has been coupled via a dielectric grating, to SPPs that propagate along a planar metal surface. The reflectivity of the sample is recorded as a function of azimuthal angle and incident wavelength in the microwave regime, using petroleum wax as the high-index dielectric. Good agreement between the predictions from a rigorous grating modelling theory and the experimental reflectivities has been obtained, and the fitting process enables the verification of the profile of the grating and the dielectric constants of the wax at these frequencies.

It is shown that when the grating is orientated with its grooves parallel to the plane of incidence, coupling to a SPP via both incident p- and s-polarised radiation is observed with an energy gap appearing between the two modes. Furthermore, at high polar angles of incidence, the s-coupled mode splits into two bands with different energies. The identity of each of the modes is confirmed as the excitation of the SPP, and an explanation is provided for their coupling conditions by modelling their resonant electric field profiles and their dispersion with frequency and in-plane momentum.
10.1. Summary of Thesis

The work presented in this thesis concerns the coupling of incident radiation to the surface plasmon polariton (SPP) at visible and microwave frequencies. In Chapters 2 and 3, an introduction to the SPP is presented. Chapter 2 provides a brief historical overview of the principal developments in the understanding of the physics of the mode over the past 100 years. By deriving its dispersion relation and exploring the spatial extent of its electric fields, the properties of the SPP are described. In addition, the methods for coupling radiation into the mode are discussed, with particular emphasis on the technique of corrugating a metal-dielectric interface.

Chapter 3 concerns the grating modelling theory used throughout the thesis. Considerations are presented of the effects on the specular reflectivity from the sample of changing the profile of the metal-dielectric interface. The influence of lossy overlayers deposited on top of the metal substrate is also theoretically studied.

The experimental section of this thesis may be divided into two subsections. Chapters 4, 5 and 6 are concerned with work conducted in the visible regime, while Chapters 7, 8 and 9 present studies undertaken at microwave frequencies. More specifically, Chapters 4 and 5 show how the surface plasmon resonance (SPR) technique may be used to characterise the complex dielectric function of metallic materials at visible wavelengths by depositing the metal onto a sinusoidally height-modulated substrate. Chapter 4 provides an optical characterisation of titanium nitride – an extremely hard-wearing material that appears gold-like in colour. Similarly, Chapter 5 presents a study of the optical dielectric function of pure indium. Since indium is easily oxidised in air, the interface along which the surface modes are excited is protected from the atmosphere. In both experiments, excellent agreements are obtained between the results from the grating modelling theory and the experimental reflectivities. In addition, the experimentally determined dielectric functions are compared with a simple Drude, free-
electron model, and then a more sophisticated Drude-Lorentz model, in order to obtain an approximate value of each of the metal’s relaxation times and plasma frequencies.

Chapter 6 illustrates a new technique for recording the angle-dependent reflectivities from grating samples at visible frequencies. The response from a silver-coated grating is recorded as a function of the angle of azimuth, at a number of different polar angles. The data is then successfully fitted to the grating modelling theory in order to characterise the optical permittivities of the silver and accurately determine the profile of the surface. It is shown that this is generally a useful technique since, unlike the more conventional polar angle of incidence scans, it involves no moving signal detector.

The apparatus described in Chapter 6 is scaled up and developed for use at microwave frequencies. In Chapter 7 it is shown how this technique is particularly advantageous since polar-angle scans become cumbersome at these longer wavelengths. It presents a thorough investigation of the coupling of microwave radiation to the SPP that propagates along a corrugated, near-perfectly conducting metal substrate. Both singularly and doubly corrugated (bi-grating) substrates are considered, and the experimental reflectivities show excellent agreement with the predictions from the grating modelling theory. However, it is clearly shown that high quality fits could only be achieved by collimating the incident beam to reduce the effects of beam-spread.

Chapters 8 and 9 are concerned with dielectric gratings that are deposited on near-perfectly conducting, planar metal substrates. With such samples, the interface that provides the coupling mechanism, and the interface along which the SPP propagates are separated. The dielectric material used is petroleum wax, which in the available frequency range, is found to have a similar refractive index to glass at visible frequencies. Due to the ease in which the profiles can be shaped into the wax, compared to milling them directly into the metal substrate, this coupling technique presents an advantage over the more conventional geometry. While the average thickness of the dielectric layer studied in Chapter 9 is always less than one-fifth of the wavelength, the sample studied in Chapter 8 is thick enough to be able to support not just SPPs, but also the first guided mode. The effects of non-zero $\varepsilon''$ in the dielectric are theoretically investigated for the sample used in Chapter 8, and the degree of absorption is shown to be greatly enhanced on resonance of a well-coupled mode.
Chapter 9 presents the novel result that when a near-grazing beam is incident on the sample with its grooves orientated such that they are parallel to the plane of incidence, coupling to the SPP is possible with both p- and s-polarised radiation at three different energies. The identity of each of the modes are confirmed as the resonant excitation of the SPP and an explanation is provided for their coupling conditions by modelling their electric field profiles and their dispersion with frequency and in-plane momentum. In both these chapters, good agreement is obtained between the experimentally recorded reflectivities, and the theoretically modelled results.

10.2. Future Work

The Thin Film Photonics research group, of which the author is a member, has amassed over 15 years of scientific experience in the area of diffractive optics. Without such a knowledge base, many of the results presented here would have been very difficult to achieve. The microwave studies carried out as part of this thesis represent the group’s first steps into a completely different region of the electromagnetic spectrum. The possibility of undertaking experiments at much longer wavelengths has allowed us to consider an enormous range of studies that are impractical, or simply much harder to investigate in the visible regime. Hence the list of potentially interesting future work is huge, and just a small selection of ideas are listed here.

In Chapters 7 and 8, a dielectric grating was deposited on top of a planar metal substrate, which at microwave frequencies, behaves like a near-perfect conductor. On excitation of SPPs that propagate along the dielectric-metal interface, energy is lost into the dielectric if it is lossy (i.e. \( \varepsilon'' > 0 \)). A thorough investigation of lossy dielectrics should be undertaken, with the aim of finding a material, which, when combined with a suitably shaped grating, will absorb a large proportion of the microwave radiation incident upon it. It may be advantageous, certainly for practical applications, to form the diffraction grating in the metallic substrate, and fill the grooves with the dielectric, so that the upper surface is planar (Figure 10.2.1).
The spectral response of such samples will be sensitive to the polar and azimuthal angles of incidence. However, Sobnack et al. (1998) and Tan et al. (1999) have recently theoretically calculated the dispersion curves of SPPs on short-pitch metal gratings consisting of narrow grooves. Such structures establish very large band gaps in the dispersion of the mode, so much so that the SPP bands become almost flat. Hence the resonance positions of the modes are effectively insensitive to the polar angle of incidence ($\theta$) of the radiation. In addition, the shape and separation of the grooves control the frequency and width of these modes. The resonances are the result of the excitation of a standing SPP mode in the grooves, and the excitation of the mode may result in strong resonant absorption of incident p-polarised radiation. Clearly such a deep structure is difficult to manufacture for use at visible wavelengths via traditional interferographic techniques, but it is relatively simple to produce on the microwave scale. However metals at microwave frequencies are normally considered to be perfect conductors and hence the resonances observed on zero-order structures may be infinitely sharp since there is no loss mechanism available in to which the mode may decay. In the visible regime, Sobnack et al. calculated field enhancements on resonance of the SPP of up to a factor of 50 within the grooves. However, at microwave frequencies this enhancement is likely to be at least an order of magnitude higher, which, with a finite $\varepsilon''$ in the metal may cause widening of the modes so that they become experimentally observable. Alternatively, filling the grooves with a slightly lossy dielectric (e.g. petroleum wax) should provide a much greater loss mechanism.

The SPPs described above are extremely localised in the grating grooves of deep, zero-order gratings. However similar flat banded modes should also be apparent on corrugated surfaces that are represented by a Fourier Series with only a fundamental and one high harmonic component. The two corrugations may be formed in the same surface, which may be the dielectric overlayer (Figure 10.2.2) or the substrate, or one
may be formed at each interface (Figure 10.2.3). The fundamental (long pitch) component provides the coupling mechanism to the SPP that propagates along the dielectric-metal interface. The high harmonic (zero-order) component repeatedly folds the dispersion curve and induces the band gaps at the Brilloin zone edges. Hence with a sufficiently short-pitch grating, the bands will become almost flat within the incident light cone.

As discussed in Section 2.5 and illustrated in Chapter 8, a sample corrugated in just one direction is unable to support modes for all angles of azimuth and incident polarisations. However, bigrating structures [where a second corrugation is formed either at 60º or 90º to the original, see Chapter 6 and Watts et al. (1996)] could yield samples that support modes that are insensitive to both the polar ($\theta$) and azimuthal ($\varphi$) angles of incidence. Additionally, the use of random, pseudo-random or mosaic grating structures should be investigated, perhaps combined with a zero order corrugation in the way described above. Such “random” profiles may permit the coupling of incident radiation to SPP modes over a large range of angles and wavelengths due to the range of scattering wave vectors available.

Another structure that should be investigated is one similar to that shown in Figure 10.2.1, but with an additional corrugation formed in the upper interface which is in a
different direction to the original. If the dielectric is sufficiently thick, then one of the
corrugations will permit coupling to guided modes within the layer. Due to the effect of
the second corrugation, these modes will sample a range of dielectric thicknesses and if
the dielectric is slightly lossy, multi-frequency absorption may result.

Another area of interest is the enhanced transmission of microwave radiation through
non-diffracting hole arrays, similar to the very recent work presented by Ebbesen et al.
(1999) and Porto et al. (1999). The explanation of the response of such structures is
still not fully developed. However, it is thought to be similar to that previously
discussed for the zero-order narrow-groove gratings [Sobnack et al. (1998) and Tan et
al. (1999)], with the SPP standing waves now established within the holes.

A series of new experiments could be undertaken to monitor the phase change of the
reflected radiation in the region of the resonance of the SPP. Figure 10.2.4 shows a
modified experimental set up that could be used to study this effect, where the reflected
signal from the sample is combined with the reflection from a perfect mirror. Other
areas of interesting research include the use of focussed incident beams, whereby the
SPP will be excited on a planar interface without the need of a corrugation at all, and the
use of samples that contain defects [e.g. Figure 10.3.1(a)], or consist of only a finite
number of grooves [e.g Figure 10.3.1(b)]. Finally, the possibility of excitation of
surface magneto-plasmons in the microwave regime should be considered.

Figure 10.2.4 Modified microwave-experiment apparatus to record the change in phase
of the reflected signal from the sample in the region of surface plasmon resonances.
10.3. List of Publications

Optical excitation of surface plasmon polaritons on 90° and 60° bi-gratings.
R. A. Watts, J. B. Harris, A. P. Hibbins, T. W. Preist and J. R. Sambles.

Azimuth-angle-dependent reflectivity data from metallic gratings.
A. P. Hibbins, J. R. Sambles and C. R. Lawrence.

Surface plasmon-polariton study of the optical dielectric function of titanium nitride.
A. P. Hibbins, J. R. Sambles and C. R. Lawrence.

Grating-coupled surface plasmons at microwave frequencies.
A. P. Hibbins, J. R. Sambles and C. R. Lawrence.

The influence of grating profile on SPP resonances recorded in different diffracted orders
R. A. Watts, A. P. Hibbins and J. R. Sambles.
The coupling of microwave radiation to surface plasmon polaritons and guided modes via dielectric gratings.
A. P. Hibbins, J. R. Sambles and C. R. Lawrence
Accepted for publication in Journal of Applied Physics, 14th December 1999.
Scheduled for publication in the 15th March 2000 issue (JR99-2335)

The coupling of near-grazing microwave photons to surface plasmon polaritons via a dielectric grating.
A. P. Hibbins, J. R. Sambles and C. R. Lawrence
Recommended for publication in Physical Review E, 14th January 2000 (EL7142).

The plasmon study of the optical dielectric function of indium.
J. R. Sambles, A. P. Hibbins, M. J. Jory and H. Azizbekyan
Accepted for publication in Journal of Modern Optics 8th December 1999 (9.11/25)
REFERENCES

Bernhard, C. G. 1967 {	extit{Endeavour}},{	extbf{26}}, 79.
Boardman, A. D. 1978 {	extit{Electromagnetic Surface Modes}} (Wiley).
REFERENCES

G. Goubau 1959  *IRE Trans. on Ant. and Prop.* **7**, S140.
James, J. F. and Sternberg, R. S. 1969  *The Design of Optical Spectrometers* (London: Chapman and Hall)


REFERENCES

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Year</th>
<th>Journal or Book Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raether, H.</td>
<td>1988</td>
<td>Surface Plasmons on Smooth and Rough Surfaces and on Gratings, (Berlin: Springer).</td>
</tr>
<tr>
<td>Rayleigh, Lord</td>
<td>1907</td>
<td><em>Phil. Mag.</em> <strong>14</strong>, 213.</td>
</tr>
</tbody>
</table>
REFERENCES

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood, R. W.</td>
<td>1902</td>
<td><em>Phil. Mag. 4</em>, 396.</td>
</tr>
<tr>
<td>Zhizhin, G. N., Moskalova, M. A., Shomina, E. V. and Yakovlev, V. A.</td>
<td>1982</td>
<td><em>Surface Polaritons: Electromagnetic Waves at Surfaces and Interfaces</em> (North-Holland, Amsterdam)</td>
</tr>
</tbody>
</table>