THEORETICAL INVESTIGATION OF ELECTRICALLY ACTIVE DEFECTS IN SILICON

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Abstract

First principles methods can provide the structure and electrical properties of defects in silicon. The theory behind these calculations is presented and illustrated for a number of defect systems. In particular, the energy levels of transition metal hydrogen defects are described along with those of radiation induced complexes.

Introduction

Deep level transient spectroscopy (DLTS) is one of the most important means by which defects with deep levels are characterised. However, there have been relatively few studies correlating the results obtained from this technique with other experimental studies and with theoretical calculations. This has resulted in a great deal of speculation and controversy about the identity of defects giving rise to particular transitions. Clearly, the more experimental and theoretical information that can be obtained about a particular defect, reduces the risk of an incorrect assignment.

With radiation defects as well as complexes of transition metal impurities, there are usually several coexisting defects, each producing levels in the band gap, so that the task of assigning levels to specific defects is extremely difficult. This is compounded by the difficulty that DLTS has in identifying the chemical composition and symmetry of the defect. Nevertheless, advances in defect profiling, Laplace transform capacitance spectroscopy, the application of stress to DLTS probes, as well as the correlation of EPR and FTIR studies, has led to considerable progress. Theoretical investigations have also played an important role.

Here we shall mainly discuss transition metal hydrogen (TM–H) defects and only briefly mention radiation defects leaving a more specific investigation to be discussed elsewhere [1].

Si wafers are easily contaminated by transition metal (TM) impurities. This happens, for example, during heat treatments or when metallic contacts are added to devices. The main effect of the TM impurity is to introduce carrier traps and recombination centres. As unintentional contaminants Fe, Cu or Ni are usually found in concentrations of $\sim 10^{12}\,\mathrm{cm}^{-3}$ but, even in these minute amounts, they have measurable effects on minority carrier lifetimes. It is now known that the electrical properties of a TM centre can be greatly modified by interaction with hydrogen. Hydrogenation of substitutional TM centres can shift the position of the deep levels due to the impurity [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12]. Remarkably, the TM impurity can, in some cases, be completely passivated [13, 14, 15]. This, of course, has raised interest in the properties of TM–H defects although the dissociation temperature of the complexes appears to be quite low [16]. For example, the levels of isolated Au and Pt are reactivated by annealing around 200 °C [6] and 330 °C respectively [3].

Moreover, it is becoming apparent that levels reported many years ago are, or could be, due to TM–H defects. For example, DLTS measurements [17, 18, 19, 20] on Pt doped *n*-Si have revealed a deep electron trap, located near the surface, with a level at $\sim E_c - 0.50$ eV and which plays an important part in limiting the lifetime of minority carriers. The assignment of this level has been very controversial and there are several models for the defect responsible for this level: Pt–Pt pairs [21, 22], Pt–O pairs [19, 23, 24] and a Pt-vacancy defect. However, very recently, Sachse *et al.* [16] have argued that this mid-gap level arises from a defect involving Pt and hydrogen. This has created additional interest in the effects of H on the electrical levels of TM defects.

Information in the literature on the activation energies and capture cross-sections of TM impurities determined by DLTS measurements suffers from discrepancies and inconsistencies. Thus the tabulated capture cross-sections of a given defect sometimes differ by orders of magnitude [25]. Capture cross-sections are sometimes thermally activated which imply that the activation energy measured by DLTS is not simply the thermodynamic energy level. This can cause difficulties in reconciling theory with experiment. In addition, the emission of carriers from bistable defects may give information on the levels of a metastable defect configuration and are not directly related to thermodynamic ones. The di-carbon centre in Si is an excellent example of this [26]. Finally, a serious problem confronting theoretical modelling is that the electrical character of the level is not always reported. Thus whether a transition[1] is $(0/+)$ or $(-/0)$ is in many cases unknown. The magnitude of the cross-section can give a guide to the character: those of second acceptors and donors are usually an order of magnitude smaller than the single acceptors or donors because of the Coulomb barrier encountered in the reactions:

$$D^{+} + h^{+} \longrightarrow D^{2+} \quad \text{or} \quad D^{-} + e^{-} \longrightarrow D^{2-} \ .$$

However, there appear to some exceptions to this as in the cross-sections for the $(=/-)$ and $(-/0)$ transitions in V_2 [27]. Additional help in the assignment of the

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[1] We adopt the customary notation for solid state physics. The levels are labelled (i/j), where i is the charge state of the defect when it is occupied and j when empty.

character of the transition comes from the field dependence of the emission rate. Emission of electrons from single acceptor levels in the upper half of the band gap is not expected to be sensitive to a electrical field because the final state is neutral. This, however, is not the case when the transition arises from a donor where a large Poole-Frenkel effect is to be expected. A smaller effect occurs for double acceptors. Analogous arguments can be given for hole transitions to donors in the lower half of the band gap. These aspects show that the analysis of a DLTS spectrum is rarely ever straightforward. DLTS can also provide information on defect concentration as a function of depth. If two different transitions have the same depth profile, it is tempting to argue that they arise from the same defect. This is particularly important as it is rarely the case that theoretical modelling is able to give sufficiently precise information to assign a defect based on a single DLTS transition. If several transitions have been assigned then the possibility for error is reduced. However, if one transition is masked by another defect, then the method may be misleading. An example of this are the $(-/0)$ levels of AuH_2 and AuH_1 (as well as the Ag analogues) which are particularly close and whose profiles have caused confusion. Another example is an early DLTS study of Au_s by Lang *et al.* [28] in which the traps at $E_c - 0.56$ and $E_v + 0.35$ eV were incorrectly assigned to different defects [29]. Unfortunately, DLTS does not provide any direct information about the structure or chemical composition of the defect.

The application of uniaxial stress can lead to information on the symmetry of the defect which is extremely useful in its identification. This technique has been applied [30] to the *A*-centre, or V–O centre in Si, which is known to have C_{2v} symmetry [31]. To our knowledge, this technique has only been applied to investigate the symmetry of one TM-related centre in silicon [32].

A serious problem at the present time are the difficulties that first principle modelling methods using density functional theory or Hartree-Fock theory have in reproducing energy levels of defects. These modelling methods give information on formation energies, equilibrium defect concentrations, structural details, vibrational modes, diffusion energies, hyperfine parameters all of which can be compared directly with the results of experiments. However, it is not clear whether they will prove so useful for deep defects if their electronic levels are the prime focus. For example, Au appears to form at least two defects with hydrogen, and Au, AuH_1 and AuH_2 have acceptor $(-/0)$ levels, which differ only by 0.04 eV, while their donor levels differ by about 0.2 eV. *Ab initio* methods cannot calculate these levels to this precision: there are even difficulties in describing the band gap correctly. Thus there is a need to develop new theoretical methods, probably involving some empirical ingredient, which can address these issues. One approach is discussed below.

Method

The donor level with respect to E_v is the difference between the ionisation energy of the defect and that of bulk Si. To circumvent the evaluation of the later, we compare the ionisation energy of the defect with that of a standard one. If the ionisation energy of defect d is greater than that of the standard s, then the donor level of the defect d lies below that of s. Now, if the wavefunction of the defect is localised within the cluster and does not overlap the surface, then in principle the ionisation energy of the defect can be calculated by the cluster method. However, as the valence band wavefunctions are always extended throughout the cluster and affected by the surface, the bulk ionisation energy cannot be calculated by the method. This is the reason why we compare the ionisation energy of the defect, I_d, with that of the standard defect, I_s. The position of the donor level, $E(0/+)_d$, is then given by

$$E(0/+)_d = E(0/+)_s + I_s - I_d \ , \tag{1}$$

where the donor level of the standard defect, $E(0/+)_s$, is taken from experiment. In the same way, electron affinities can be used to determine the acceptor levels. The electron affinity is the work done in taking a electron from infinity and placing it in the defect. It is then the energy difference between the neutral and negatively charged defects and if A_d is greater than A_s, then the acceptor level of the defect lies below that of the standard.

The ionisation energies and electron affinities are calculated by applying Slater's transition state argument [33, 34]. Using the relaxed geometry appropriate to the transition state takes into account, to first order, the difference in structures between the neutral and ionised clusters. This method is remarkably accurate. For example, by comparing the total energies of relaxed neutral and ionised molecules, the ionisation energy of the water molecule is found to be 13.37 eV. The Slater method applied to the molecule relaxed with a net charge of $+\frac{1}{2}$ is 13.31 eV while the experimental value is 12.59 eV [35].

An important point is that by comparing the ionisation energies of defects calculated in the same sized cluster, we can reduce a systematic shift in the calculated levels caused by overlap of the wavefunction with the cluster surface. The shift in the level position caused by the surface, to first order, depends only on the asymptotic part of the wavefunction, Ψ_λ, and is given by

$$\int \Psi_\lambda^2(\mathbf{r}) \, V(\mathbf{r}) \, d\mathbf{r} \ . \tag{2}$$

Here, V is the difference between the potential for an infinite solid and a finite cluster and is the same for the defect and the standard if each were embedded in identical clusters. Now, if the energy level of the defect is close to that of the standard then the asymptotic decay of the highest occupied wavefunctions will be similar as these decays are related to the distance between the levels and the band edges. Moreover, as the total charge of the defects are the same, *i.e.*, $+\frac{1}{2}e$ for donor levels, then the amplitudes of the wavefunctions outside the defect cores are expected to be the same if the wavefunctions possess the same symmetry. Hence the first order shift in ionisation energy of the defect will be the same as that as the standard.

The electronic levels are found by embedding the defect in either large hydrogen terminated clusters. For example. tetrahedral 131 ($Si_{71}H_{60}$), or trigonal 134 ($Si_{68}H_{66}$), H-terminated atom clusters have been used. The wavefunction basis consists linear combinations of Gaussian orbitals sited at nuclei and at bond centres, while the charge density is fitted to Gaussian functions also sited at these places.

There are several stages involved in the calculations [36, 37]:

1. The geometrical position of the atoms in the defect are taken from the best available model. For example, four of the atoms bordering the divacancy are rebonded in pairs leaving two Si atoms with dangling bonds, or a H atom in a TM–H defect is placed either next to the TM impurity or attached to a Si neighbour at an anti-bonding site.
2. The initial spin density is found from overlapping the atomic spin densities constructed from atomic wavefunctions. The total charge density is the sum of the spin-up and down densities and is then derived from neutral atoms. These spin densities are used to construct an electronic Hartree potential as well as the exchange correlation potentials for spin-up and down electrons.
3. The electron-ion potential is constructed from pseudopotentials which eliminate the need to consider the core electrons.
4. The Schrödinger equations (or strictly the Kohn-Sham equations) are then solved for the spin-up and down wavefunctions, as well as the orbital energy levels E_λ.
5. The spin densities of all the electrons in the cluster (which can be charged) are then found and these, of course, are not the same spin densities as those initially found from overlapping neutral atoms. The difference reflects the fact that the cluster might be ionised, or more generally, that charge has flowed between atoms so that, for example, the *d*-levels of the TM impurity have filled up while the Si dangling bonds surrounding the impurity have lost electrons.
6. The new spin densities are then used to generate new potentials and the process recycled until the output spin densities are equal to the input ones. This is called the self-consistent cycle and during this process, the energy decreases until it reaches a minimum.
7. The energy, E_T, found here corresponds to the adiabatic energy of a set of fixed ions. If one of the ions is now displaced by a finite amount, and the new spin-densities and energy found, then the energy corresponding to the new position of the ion will in general be different from the previous one. Clearly the adiabatic force on the ion is related to this energy change but it can be shown that these forces can be found very easily from the derivative in the total energy with respect to an infinitesimal change in the position of the ion. To lowest order, there is no contribution from the change in spin-densities.
8. Once the forces on the atoms have been found, the atoms can be moved until the energy is a minimum and these forces vanish. This is called relaxing the assembly of atoms.
9. To find the donor and acceptor levels of a defect we need to calculate its electron affinity and ionisation energy. The electron affinity A_d is the difference in energies between a charged and neutral defect. For definiteness, consider a substitutional TM impurity which gives rise to a three fold degenerate level —

called a t_2 level — lying deep in the gap. We suppose this contains n electrons in the neutral case.

If the equilibrium structures of the neutral and charged states are denoted by $\mathbf{R}^0$, and $\mathbf{R}^-$ respectively, then

$$A_d = E_T(t_2^n, \mathbf{R}^0) - E_T(t_2^{n+1}, \mathbf{R}^-) \tag{3}$$

To calculate this, we follow Slater and introduce a transition state defined by an electronic configuration where an extra half a electron is added to the t_2 manifold. Let the relaxed structure corresponding to this be $\mathbf{R}^t$. We then Taylor expand each of the energies of the neutral and ionised defects about the transition state configuration. Thus

$$A_d \approx -E_{t_2} - \frac{\partial^2 E_T(t_2^{n+1/2}, \mathbf{R}^t)}{\partial n\, \partial \mathbf{R}^t} \cdot (\mathbf{R}^- - \mathbf{R}^0). \tag{4}$$

Here E_{t_2} is the Kohn-Sham eigenvalue associated with the t_2-manifold in the transition state. The second term can be ignored if the difference in the structures of the neutral and charged states of the defect are small. The affinity is then related to the Kohn-Sham level of the defect in a transition state. However, the calculation of this quantity is subject to considerable difficulties. For example, the electron affinity of bulk Si is related to the band gap which cannot be calculated with sufficient precision. This is because the extended states of the valence and conduction bands overlap the cluster surface and local density functional theory is well known to lead to incorrect band gaps. However, we can compare the electron affinities for two defects having localised states within the band gap. Their difference being total energy differences, are simply their relative acceptor levels. In practice, the carbon interstitial defect, C_i, which possesses $(-/0)$ and $(0/+)$ levels at $E_c - 0.1$ and $E_v + 0.28$ eV respectively [26] is used as a standard. For second acceptor levels, the $(=/-)$ level of PtH_2 is used (which is taken to lie at $E_c - 0.15$ eV [38]). The acceptor and donor levels of the defect, are then given by:

$$(-/0)_d = (-/0)_s + A_s - A_d \quad \text{and} \quad (0/+)_d = (0/+)_s + I_s - I_d\,,$$

where I_d and I_s are the calculated ionisation energies of the defect and the standard.

Radiation Defects

Table 1 gives the calculated acceptor (relative to E_c) and donor levels (relative to E_v) of several deep level defects as well as the experimental activation energies. The agreement is within about 0.2 eV. The ionisation energy of the vacancy-oxygen pair (A-centre), VO, falls more than 0.28 eV below that of C_i and thus the defect does not possess a $(0/+)$ level consistent with experiment. However, the calculated donor level of VP lies at $E_v + 0.2$ eV and probably is to deep by this amount as no donor level has been reported for this defect. The H–C_i–C_s defect gives a prominent luminescent line (the T-line) and is known to possess an acceptor level at $E_c - 0.2$ eV [39] but the donor level is unknown. The calculated levels for both C_i–P and the divacancy, V_2, lie within 0.2 eV of those observed. Remarkably, the theory gives a donor level of H_{BC} to be close to that observed even though the level is well separated from that of the standard defect C_i. H_{AB} is a deep acceptor at midgap consistent with the inverted ordering of H related levels. It is of interest to note that the $(-/0)$ levels of V_2O and V_2 are very similar and highlights a problem with deep level transient capacitance spectroscopy, DLTS, in being able to distinguish levels of such similar defects.

Table 1. Electrical levels, eV, of deep centers. $(0/+)$ is referred to E_v and $(-/0)$ to E_c.

Defect	$(0/+)$		$(-/0)$		
	Calc.	Obs.	Calc.	Obs.	Refs.
VO	0.00	···	0.13	0.18	[31]
VP	0.20	···	0.58	0.43	[40]
V_2 (C_{2h})	0.42	0.23	0.51	0.43	[27]
HC_iC_s	0.24	···	0.20	0.20	[39]
C_iP	0.36	0.48	0.60	0.38	[41]
H_{BC}	0.94	1.00	···	···	[42]
H_{AB}	···	···	0.78	0.56*	[43, 44]
V_2O	···	···	0.47	···	

* Muon spin-resonance experiments.

To describe second acceptor levels, the electron affinities of negatively charged defects must be compared with each other. We use as a standard the PtH_2 defect which was once thought to possess a second acceptor level lying between the P donor level at $E_c - 0.043$ eV and the $(-/0)$ level of C_i [45]. However, more recent work has pushed this downwards to be lie at $E_c - 0.15$ eV [38].

Transition Metal Defects

We first consider Au and Ag defects. Neutral Au and Ag have a electronic configuration t_2^3 and are slightly distorted T_d defects with the impurity moving 0.03 Å along [100] for Au and 0.01 Å for Ag. The resulting C_{2v} symmetry is consistent with EPR experiments on Ag [46, 47] and optical absorption studies on Au [48, 49]. The Au–Si and Ag–Si lengths are all between 2.6 and 2.7 Å. We also find a small adiabatic reorientation barriers of 0.11 eV for Au_s^0, and 0.14 eV for Ag_s^0. These are upper limits to the barrier and tunnelling probably plays an important role as reorientation can occur at cryogenic temperatures [48]. The donor and acceptor levels are given in Table 2 and again are within 0.2 eV of those found by DLTS [29].

We now apply this theory to the complexes of substitutional TM impurities with hydrogen. There are three likely positions for the H atom. These are (a) when H

Table 2. Electrical levels, eV, of Au– and Ag–hydrogen defects. (0/+) is referred to E_v and (−/0) to E_c.

	(0/+)		(−/0)		
	Calc.	Obs.	Calc.	Obs.	Refs.
Au	0.21	0.35	0.66	0.56	[29, 6]
AuH_1	0.36	0.21 (G2)	0.62	0.54 (G4)	[6, 4, 10]
AuH_2	0.28	0.47 (G3)	0.62	0.58 (G4′)	[6, 4, 10]
AuH_3	0.00	···	0.26	0.28	[11]
AuH_4	···	···	1.40	···	
Ag	0.46	0.37	0.60	0.56	[5]
AgH_1	0.36	0.28 (H2)	0.45	0.45 (E2)	[5]
AgH_2	0.33	0.38 (H3)	0.50	0.5 (E6)	[5]
AgH_3	0.00	···	0.13	···	
AgH_4	0.00	···	0.97	···	

sits at an anti-bonding, AB, site to a Si neighbour of the TM impurity, (*b*) AB sited to the TM impurity, and (*c*) bond centred, BC, sited between the impurity and Si. For the AuH_1 defect, configurations (*b*) and (*c*) are less stable than (*a*) by 0.23 and 0.47 eV respectively. This result is sensitive to basis size and a smaller basis reverses this ordering [50].

Table 3. Hydrogen stretch modes, cm^{-1}, for three configurations (see text) of AuH_1. Deuterium values in parenthesis. Observed values from [51].

$(AuH_1)^q$	$q = 0$	$q = -1$	$q = -2$
Expt.	1787.7 (1292.9)	1813.3 (1310.9)	1827.1 (1319.4)
Config. (*a*)	1947.4 (1401.1)	1890.5 (1359.6)	1893.2 (1361.4)
Config. (*b*)	2014.5 (1427.3)	1980.0 (1402.8)	2118.0 (1500.2)
Config. (*c*)	2419.0 (1726.2)	2500.8 (1783.5)	2454.3 (1748.9)

The H stretch vibrational frequencies for the three configurations are given in Table 3 along with experimental results [51]. Agreement is best for the configuration (*a*) but the sense of the small shifts arising with different charge states are not reproduced. The H-reorientation barrier among the equivalent <111> directions is 0.41 eV for (*a*) and 0.23 eV for (*b*). The observed barrier is athermal and presumably must proceed by a tunnelling mechanism. Local density functional calculations usually overestimate barrier energies [52]. For structures (*a*) and (*c*), the shift in frequency on replacing ^{28}Si with ^{29}Si is $\lesssim 1$ cm^{-1} for each charge state. For configuration (*b*) where H is bonded to the impurity, the shift is negligible. Thus, although the energy and vibrational mode calculations favour configuration (*a*), the observed low reorientation barrier favours configuration (*b*).

For AuH$_2$ and AgH$_2$ defects with C_{2v} symmetry, configuration (a) is more stable than (b) or (c). This structure is the same as that suggested by magnetic resonance on PtH$_2$ defects [45]. AuH$_2$ defects have been detected by infra-red (IR) absorption studies [53, 51]. For the configuration (a), Table 4 shows that the separation in frequencies between the symmetric (A_1) and antisymmetric (B_1) modes is much closer to experiment than the separations in configurations (b) and (c).

Table 4. Hydrogen stretch modes, cm^{-1}, for three configurations (see text) of AuH$_2$ (C_{2v}) complexes. Observed values from [51].

	AuH$_2$		AuHD		AuD$_2$	
	(A_1)	(B_1)			(A_1)	(B_1)
Expt.	1803.3	1785.6	1792.5	1298.6	1304.4	1292.1
Config. (a)	1974.7	1970.5	1972.6	1419.2	1420.6	1417.8
Config. (b)	1988.4	1743.0	1884.6	1303.6	1406.2	1237.5
Config. (c)	2060.6	2013.6	2037.6	1461.9	1475.5	1449.2

The electrical levels are determined assuming that a low spin state results from the addition of each H atom. The addition of one H atom lowers and splits the t_2 level into a filled a_1 level lying below a half-filled e level. The lowering of the t_2 manifold is off-set by the splitting so that the differences in the donor and acceptor levels from those of the TM impurity are quite small. Table 2 gives these levels for configuration (a). The $(=/-)$ levels of AuH$_1$ and AgH$_1$ lie at $E_c - 0.22$ and $E_c - 0.36$ eV respectively. The levels found for configuration (b) are very similar. For example, the $(0/+)$, $(-/0)$ and $(=/-)$ levels of AuH$_1$ lie at $E_v + 0.37$, $E_c - 0.76$ and $E_c - 0.36$ eV respectively.

A second H atom, added in configuration (a), results in an additional electron occupying the e manifold which is pushed downward and splits with the upper level being occupied. Thus once again there are only small shifts in the donor and acceptor levels on going from say AgH$_1$ to AgH$_2$. The e-manifold is filled for AuH$_2^-$ and AgH$_2^-$, and a second acceptor level can only arise from a new state entering the gap. The calculations give no hint for such states and hence the di-hydrogen defects do not possess $(=/-)$ levels.

Adding a third H fills the e-manifold which is now pushed below E_v. Thus AgH$_3$ and AuH$_3$ do not possess any donor levels. However, it appears that an empty level, due to the 5s and 6s levels of Ag and Au respectively, creeps into the band gap. We place the resulting $(-/0)$ levels of AgH$_3$ and AuH$_3$ at 0.13 and 0.26 eV below E_c.

In conclusion, the calculations show that AuH$_n$ and AgH$_n$, $n = 1, 2$ defects, possess $(0/+)$ and $(-/0)$ levels close to Au and Ag, while only the mono-hydrides possess $(=/-)$ levels. The tri-hydride defects possess shallow acceptor levels.

DLTS studies have led to a number of levels assigned to AuH$_n$ and AgH$_n$ defects. There are two uncertainties in identifying these levels. Firstly, the number of H atoms associated with each level and secondly its character. Annealing and defect profiling studies have shown that the G1 (at $E_c - 0.19$ eV), G4 and G2 levels due to Au-hydrogen arise from the same defect [6]. The location of the levels (see Table 2) and their emission cross-sections suggest that they correspond to $(=/-)$, $(-/0)$ and $(0/+)$ respectively. This has been supported by minority carrier transient spectroscopic measurements [53]. The deep penetration of these defects is taken to imply that they possess one H atom. Similar considerations show that in the Ag case the E3 (at $E_c - 0.09$ eV), E2 and H2 levels are due to $(=/-)$, $(-/0)$ and $(0/+)$ levels of AgH_1 [5]. Such assignments agree with our calculations (Table 2). We can exclude AuH_2 and AgH_2 as being responsible for these levels as these defects do not possess a $(=/-)$ level.

Table 2 shows that the levels of the Au– and Ag–hydrogen defects G3 and H3 are close to the calculated donor levels of AuH_2 and AgH_2 respectively. Using a model for the depth dependence of the concentration of the defects [54], Yarykin *et al.* [5] argue that these levels should be assigned to AuH_2 and AgH_2. There has been some changes of view as to their character [4] but the most recent opinion [5] is that they are donor $(0/+)$ levels. This agrees with our calculations. Our results also imply that the corresponding $(-/0)$ levels are very close to those of AuH_1 and AgH_1 respectively. Evidence for these $(-/0)$ levels has been more difficult to obtain. However, an early DLTS [55] and a recent Laplace-DLTS study [10] on Au-doped Si, show a level G4′ at $E_c - 0.58$ eV while the difference in the concentrations of E2 and E3 in the surface region is taken to imply the existence of the $(-/0)$ level of AgH_2 labelled E6 [5]. The G4′ and E6 levels are close to the calculated $(-/0)$ levels.

Both Au and Ag can be passivated by hydrogen [13, 15] and our calculations suggest that AgH_3 and AuH_3 are candidates given our errors can be around 0.2 eV. However, in the case of gold, a level at $\approx E_c - 0.28$ eV [56] arises after a long room temperature anneal [11] and this is close to the calculated $(-/0)$ level of AuH_3. If this level arises from this defect, then the passive defect cannot be due to substitutional Au complexed with H atoms.

Molecular hydrides AuH or AgH are chemically stable with dissociation energies ≈ 3.1 eV and large ionisation energies. If these formed within a void whose surface is passivated by H, then the defects would be electrically inactive. Calculations were carried out on a deca-vacancy, containing AuH and AgH, and whose inner surface was passivated by H [57]. The resulting ionisation and electron affinity were such that no gap levels are present and such defects are then passive. However, whereas it is known that voids form in plasma treated or H-implanted material, it is unclear whether they, or a multivacancy complex containing Au and Ag, can be produced by wet chemical etching.

Conclusions

In summary, the calculations have allowed us to determine the structure and electrical activity of TM–hydrogen defects. This has allowed us to assign the observed DLTS levels to specific defects. AuH_3 and AgH_3 defects have filled t_2-manifolds lying in the valence band and lack donor activity. They possess shallow $6s$ and $5s$ acceptor levels. Molecular hydrides of the metal impurities are passive when inserted into voids or passivated multi-vacancy centres.

The important point is that we can use similar methods to explore the properties of radiation defects such as di-vacancies complexed with hydrogen, phosphorus, carbon or oxygen and this will be reported in a subsequent paper.

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