Deep thoughts on shallow dopants

The application of novel techniques, both theoretical and experimental, to the problems of doping wide bandgap semiconductors was the theme of the recent WideGap2001 workshop. ***Caspar Fall*** *and* ***Robert Jones*** *report.*

The WideGap2001 workshop held at the University of Exeter, UK, on 21–23 March, brought together 75 experimentalists and theoreticians from across the world to discuss the successes and current problems of doping a variety of wide bandgap semiconductors. The organization of this event was made possible by a grant from the European Science Foundation and the financial support of several industrial partners. Contrary to many conferences that are limited to one specific semiconductor material, WideGap2001 crossed material boundaries and focussed on defects and impurities in gallium nitride (GaN), silicon carbide (SiC), zinc oxide (ZnO) and diamond.

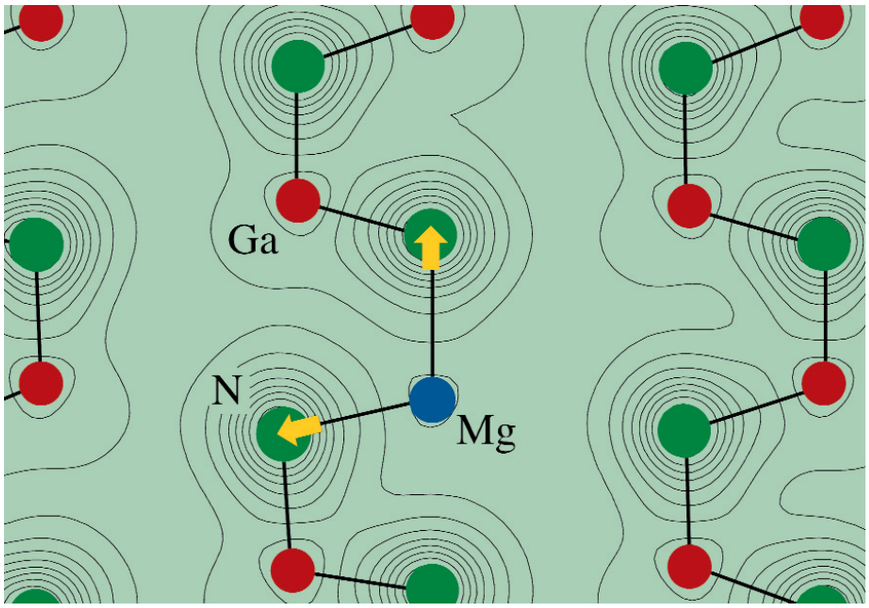

Fig. 1. Electronic charge density around a single negatively charged magnesium atom (blue disk) on a gallium lattice site in wurtzite GaN. The wurtzite c-axis is in the vertical direction. The gallium and nitrogen atoms are represented as red and green disks, respectively. The nitrogen atoms near the magnesium impurity are found to relax outwards with respect to their ideal lattice sites (yellow arrows).

Some common problems

There is a great deal of interest in overcoming problems relating to shallow dopants in wide bandgap materials. For example, in GaN oxygen and silicon are known to be shallow donors but there are difficulties in finding efficient shallow acceptor dopants for creating p-type material. Magnesium and beryllium are favored but have high activation energies. In ZnO, an effective method to achieve p-type conduction is still eluding current researchers. In diamond, boron is a shallow acceptor but there are difficulties finding suitable shallow donors. Phosphorus and sulfur are key candidates and there is intense interest in optimizing their activity. Nevertheless, dopants in all these materials suffer from problems relating to solubility and the formation of complexes, for example with hydrogen which is a common impurity, or with native interstitials and vacancies.

Modeling methods

A striking characteristic of the WideGap 2001 workshop was the large number of theoretical groups represented. Physicists are well aware that modeling from first principles is a very effective way in which dopant activity can be predicted. Combined with leading-edge computational resources, the so-called *ab-initio* codes can determine theoretically, amongst other properties, the structural, electrical, optical and vibrational characteristics of crystalline defects. The computed formation energies, equilibrium concentrations, diffusion paths, and behavior under applied stress of a variety of defects are often in excellent agreement with experiment, as are the calculated results of electron paramagnetic resonance experiments. Such valuable information helps to understand a wide variety of experimental observations and aims to predict the results of new ones. It is significant that the shallow oxygen donor in GaN was first suggested from theoretical results.

In the fast evolving field of wide bandgap semiconductors, the experimental techniques employed to probe dopant activity are becoming more and more sophisticated. Not only are photoluminescence and photoconductivity studies routinely applied, but new methods such as positron annihilation, photoluminescence microscopy, and muon spin resonance can now provide equally valuable information.

Silicon carbide

The conference opened with a theoretical talk by Friedhelm Bechstedt (Jena, Germany) on deep level defects in several

SiC polytypes, focusing particularly on vacancies and complexes with boron. This was followed by other theoretical talks on SiC by Risto Nieminen (Helsinki, Finland) and Peter Deak (Budapest, Hungary), all of which highlighted the problems of doping and the formation of compensation centers such as vacancies. Nitrogen and boron incorporated on the silicon site are currently the best donors available. Hydrogen was also singled out as an important passivating impurity. By comparing the computed energetics of hydrogen interstitials with those of complexes containing hydrogen, for example, the tendency of hydrogen to form complex aggregates can be predicted.

John Steeds (Bristol, UK) emphasized the likely role of carbon interstitials in SiC luminescence by combining a transmission electron microscope to produce spatially localized controlled electron irradiation with photoluminescence microscopy. Bengt Svensson (Oslo, Norway) reported on the status of current ion implantation in SiC and showed that ion implantation was the method of choice for selective area nitrogen doping of SiC. However, unknown compensation centers are created which are at present difficult to anneal out.

Gallium nitride

In common with other wide bandgap semiconductors, gallium nitride is difficult to dope with good acceptors. James Speck (Santa Barbara, US) impressed the conference with MBE growth studies of GaN under gallium and nitrogen rich conditions and the success of introducing p-type dopants, such as magnesium, with resulting high hole densities and mobilities. Donat As (Paderborn, Germany) gave a talk on carbon doping of MBE-grown cubic GaN. This impurity was demonstrated to behave as a shallower acceptor than magnesium in cubic GaN. Incorporation of 10^{20} cm^{-3} carbon atoms has been achieved, although the activation efficiency is only about 1%.

Sergei Kucheyev (Canberra, Australia) highlighted the difficulties of eliminating lattice damage from ion implantation in GaN. The importance of dislocations in GaN thin layers was emphasized by Trevor Martin (DERA, UK), who reported experiments on high-power AlGaN/GaN HFETs. Conduction parallel and perpendicular to the growth axis is found to be quite different.

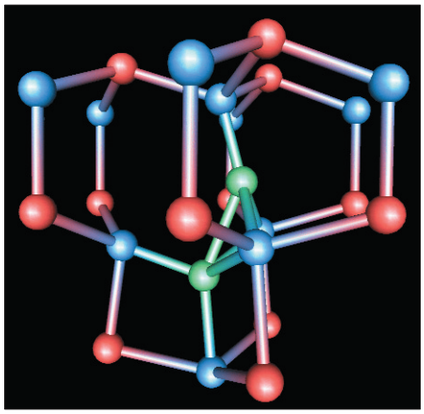

Fig. 2. Beryllium pair defect at a gallium atom substitutional site in wurtzite gallium nitride (red = Ga, blue = N, green = Be). The geometry of this structure was optimized using state-of-the-art first-principles techniques, and corresponds to the lowest energy complex containing two Be atoms. The local vibrational modes of this defect have been computed and a comparison with experimental data is under way. Courtesy of C Latham, Helsinki, Finland.

Photoluminescence

Bo Monemar (Linkoping, Sweden) gave an instructive talk on what has been learned from the photoluminescence of common dopants, such as the shallow donors silicon and oxygen. Progress in identifying the optical signatures of these impurities was reported. Kimmo Saarinen (Helsinki, Finland) highlighted the use of positron spectroscopy in identifying vacancies. Baiba Berzina (Riga, Latvia) discussed optical centers in aluminum nitride, demonstrating the importance of vacancies and oxygen impurities with a view to using this material in dosimetric applications.

Vibrational spectroscopy

Bernard Clerjaud (Paris, France) showed what could be extracted from local vibrational mode (LVM) spectroscopy of impurities in GaN, finding vibrational modes of magnesium and beryllium complexes possibly linked with oxygen. Hydrogen is known to play a crucial role in the common passivation of magnesium acceptors in GaN, requiring annealing to be performed before p-type conduction is observed. A local vibrational mode at 3125 cm^{-1} has been attributed to a magnesium–hydrogen complex. Crucially, the orientation of the electric dipole induced by this vibration has also been measured, challenging conventional wisdom about the atomic structure of this defect, and allowing comparisons with theoretical models of hydrogen–magnesium complexes to be tested. Chris Van de Walle (Xerox, US) and Caspar Fall (Exeter, UK) reported theoretical models seeking to reconcile the experimental observation with the results of simulations.

A typical result from a first principles calculation is shown in figure 1, where the electronic charge density around a single magnesium atom in GaN is shown. The stronger electronegativity of nitrogen is seen to lead to a strong localization of the electron density around the nitrogen atoms. This information can lead, for example, to predictions of the preferred positions of a supplementary H^+ atom, which is expected to reside in regions of high electronic density. Conversely, H^- interstitials may be expected to diffuse down the c-axis channels in the wurtzite structure, where the electronic density is low.

The high-pressure, high-temperature growth of bulk GaN was discussed by Stanislaw Krukowski (Warsaw, Poland). Using such conditions, oxygen can easily be incorporated as a donor. Magnesium acceptors are also readily introduced but beryllium doping has remained elusive using this growth technique. Chris Van de Walle and Risto Nieminen independently argued from first principles calculations that beryllium doping of GaN might be hindered by the tendency of beryllium atoms to form compensating interstitials rather than substitutional acceptors. Beryllium might favor an interstitial site, with pairs of impurities readily formed, as shown in figure 2. This may explain the low observed doping efficiency of beryllium.

Zinc oxide

Chris Van de Walle reviewed his new theoretical results on native defects in zinc oxide. With a bandgap and lattice parameter similar to those of GaN, ZnO is being seen as a material for future applications. The origin of n-type conduction in ZnO was examined and, contrary to GaN, hydrogen was singled out as a shallow donor in this material. This talk was followed by one from Philip King (ISIS Facility, UK) who experimentally confirmed this result. Indeed, muon spin

spectroscopy has confirmed the prediction of a donor level at 0.019 eV below the conduction band, associated with hydrogen. Danie Auret (Pretoria, South Africa) reported on deep level transient spectroscopy studies of other levels in ZnO induced by proton irradiation. Zinc oxide is found to be remarkably radiation hard compared to GaAs or GaN.

Co-doping

There is current interest in co-doping wide bandgap semiconductors. This involves including two or more impurities (sometimes both donors and acceptors) in the crystal, with the aim of increasing the electrical activity of the dopants. Hiroshi Katayama-Yoshida (Osaka, Japan) gave an interesting talk on his theory of co-doping to produce effective acceptors in wide bandgap materials. Shallow level defects might be made by complexes such as N–Al–N defects in ZnO, and Mg–O–Mg defects in GaN. There is experimental evidence that magnesium and oxygen co-doping increases the hole concentration in GaN. A striking feature of Katayama-Yoshida's talk was the number of patents secured for the effect, a first in this field for a theoretical physicist.

Jörg Neugebauer (Berlin, Germany) gave the results of an impressive set of calculations on the interaction between dopants and crystal growth surfaces, explaining why rough and smooth crystal faces occur under different growth conditions. These calculations may pave the way to an alternative theory of co-doping magnesium and oxygen in GaN, where the presence of surface oxygen may encourage the incorporation of magnesium. This would be especially true if oxygen and magnesium had surfactant and anti-surfactant roles, respectively.

Summary

Chris Van de Walle summed up the meeting in this fast evolving field as one which had successfully brought together groups having interests in different materials and experience with different techniques of doping. It will be judged successful if the methods used in one area are used in others. Certainly, co-doping should be tried in silicon carbide and theorists encouraged to analyze the difficult problems of dopant incorporation and surface effects. These obstacles will need to be overcome in the drive towards nanostructures built from wide bandgap materials.

Further information about this research can be found in the conference proceedings, which will be published by Institute of Physics Publishing in a special issue of *Journal of Physics: Condensed Matter*. The conference Web site at http://widegap2001.ex.ac.uk features a full list of abstracts and some three-dimensional interactive graphics of atomic structures of defects similar to that shown in figure 2.

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