The WideGap 2001 workshop (held at the University of Exeter, UK in late March) brought together a diverse international group of multi-disciplinary scientists who are investigating the doping characteristics and materials properties of wide-bandgap semiconductors, including gallium nitride, indium nitride, silicon carbide, zinc oxide and diamond. Many papers related to the achievement of higher levels of p-dopant activity, which is a continuing requirement for wide-gap semiconductor development, particularly for blue and violet lasers as well as high-power electronic devices.

Co-doping wide-bandgap semiconductors

A method of attaining higher doping levels in wide-gap semiconductors is the acceptor-donor co-doping process (applicable to both MOCVD and MBE growth), described in an invited paper at the WideGap 2001 workshop by H Katayama-Yoshida from the University of Osaka. Although co-doping is still somewhat controversial (since the concept has not been accepted by all research groups), a mounting pile of evidence supports it as a viable production technology. As can be seen below, the increasing number of results being presented - including device data and patent applications - supports the concept and the wider commercial application of this technology in the future.

In reality, the attainment of high and activated p-doping levels for gallium nitride and other wide-bandgap semiconductors remains difficult. In part, this is due to the relatively deep acceptor levels allocated for the preferred dopants (e.g. 200 meV for magnesium in gallium nitride). In turn, the energy required for activation restricts the attainable hole carrier densities to the mid-10^17 cm^-3 range, even for doping levels as high as 2x10^20 cm^-3 (e.g. only 1% dopant activation). At these high magnesium doping levels the substitutionally located magnesium atoms are believed to be unstable and to easily migrate to the more stable interstitial sites. This migration leaves behind a gallium vacancy, resulting in the so-called dopant compensation mechanism for wide-gap semiconductors.

The accepted reason for the relatively poor activation of these low-efficiency single-element dopant systems is that their activation energies (200-500 meV) are too high for easy activation at room temperature. In contrast, the purported success of the co-doping complexes is that their activation energies are lower (around 100 meV).

To overcome dopant compensation, the co-doping concept introduces two oppositely polar atoms at the same time in a 2:1 ratio, forming metastable three-atom complexes located at adjacent crystal sites.

The diagram illustrates the co-doping concept, which introduces two oppositely polar atoms at the same time in a 2:1 ratio, forming metastable three-atom complexes located at adjacent crystal sites. An acceptor-donor-acceptor (A-D-A) complex (with a ratio of two acceptor atoms to one donor) is formed for p-doping and a donor-acceptor-donor (D-A-D) complex (with a ratio of two donor atoms to one acceptor) for n-doping.
and a donor-acceptor-donor (D-A-D) complex for p-doping. Their introduction into the epitaxially grown layers raises the dopant activation levels and lowers the layer resistivity from the values obtainable from their respective single acceptor or donor dopants. Thus, the co-doping of either magnesium and silicon or beryllium and silicon is recommended to improve the p-doping of GaN due to the formation of their respective A-D-A complexes [magnesium-silicon-magnesium or beryllium-silicon-beryllium], which occupy the nearest-neighbour sites in the crystal lattice.

Other p-generating complexes which are reported to improve the p-doping of GaN include magnesium-hydrogen-magnesium and magnesium-oxygen-magnesium.

For the development of p-doped AlN layers, the use of a carbon-oxygen-carbon complex is recommended for the highest p-dopant activation levels (covered by a European patent application). For a more efficient n-doping of diamond, D-A-D complexes such as nitrogen-boron-nitrogen have been used. Zinc oxide (another wide-bandgap semiconductor) has also been difficult to p-dope - aluminium, gallium and indium have all been recommended as p-dopants under co-doping conditions. Currently, aluminium or gallium co-doped with nitrogen are recommended dopant systems for zinc oxide, using the N-Ga-N type of complex.

Additional support for the co-doping concept now comes from many other sources and includes several Japanese patents from Katayama-Yoshida and Nichia which claim higher hole densities (see Tables 1 and 2), as well as related reports of higher acceptor levels. Significant evidence for co-doping includes the SIMS analysis of the InGaN layers in a Nichia white LED supporting the co-doping of 2Mg plus O, where the oxygen concentration is higher in the p-region than in the n-regions of the device. The latter process is also supported by a Japanese patent showing the presence of magnesium together with oxygen (see Figure 2) and, in a different patent, magnesium co-doped with silicon (see Figure 3), both atom pairs being respectively present in the approximate atomic ratios of 2:1.

Additional conceptual support is provided by the fabrication by K H Ploog and O J Brandt (J Vac. Sci Technol. A 16, 1609) of p-type cubic GaN, using Be-O-Be co-doping to get high hole concentrations of $5 \times 10^{19}$ cm$^{-3}$ (with high mobility $[150 \text{ cm}^2/\text{V} \cdot \text{s}]$ and high conductivity), and recent work by Wessels' group where co-doping reduced the acceptor level to 135 meV (at the same time increasing the p-carrier density from $1 \times 10^{17}$ cm$^{-3}$ to $2 \times 10^{18}$ cm$^{-3}$ and lowering the resistivity from 8 to 0.2 Ωcm). According to Katayama-Yoshida, this resistivity can be lowered to 0.01 Ωcm by optimal co-doping. Aoyagi from Riken has also reported Mg-Si-Mg co-doping in an atomic layer epitaxy (ALE) process where carrier densities in excess of $10^{19}$ cm$^{-3}$ and a reduced acceptor energy level of 90 meV were obtained. In this ALE process one layer receives the acceptor dopant and the next layer receives the donor co-dopant, providing one to two orders of magnitude increase in dopant activation, or as much as 80% acceptor activation. However, this layer growth process needs to be optimised to obtain higher layer mobilities. A recent Nichia paper [Yasahito Zohta, Jpn. J. Appl. Phys. 40 (2001) ppL423 -L425] defines several acceptor levels for magnesium co-doped GaN, with one energy level as low as 14 meV, which is believed to be due to a Mg-Si-Mg co-doping complex.

**Figure 2.** Net hole concentrations versus co-donor concentrations for (a) 2Mg:O and (b) 2Mg:Si.

*The Mg concentration is fixed at about $10^{20}$ cm$^{-3}$.**

Significant evidence for co-doping includes the SIMS analysis of the InGaN layers in a Nichia white LED supporting the co-doping of 2Mg plus O, where the oxygen concentration is higher in the p-region than in the n-regions of the device.
The concept of co-doping (apparently used by Nichia for LED production) should become more widely accepted and used to improve the doping levels of nitride semiconductor materials in other labs around the world.

ZnO appears to be poised for rapid development as a compound semiconductor material, since the initial problems associated with both p- and n-doping have now been solved and blue LEDs have already been made...It is also being considered as a replacement for indium tin oxide (ITO) conductive coatings.

Table 1. Comparison of net hole densities (a) between co-doped p-type GaN:[2Mg+Si] and GaN:Mg, and (b) between co-doped p-type GaN:[2Be+Si] and GaN:Be (H Katayama-Yoshida et al, Application made for Japanese Patent: Fabrication method of the low-resistivity p-type GaN: JP HB-258054 [Published in JP H10-101496]). Courtesy of Katayama-Yoshida.

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>Net hole densities in co-doped p-type GaN:[2Mg+Si] (cm⁻²)</th>
<th>Net hole densities in p-type GaN:Mg (cm⁻²)</th>
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<tbody>
<tr>
<td>250</td>
<td>5.3x10¹⁷</td>
<td>1.2x10¹⁷</td>
</tr>
<tr>
<td>300</td>
<td>8.2x10¹⁷</td>
<td>2.1x10¹⁷</td>
</tr>
<tr>
<td>350</td>
<td>1.2x10¹⁸</td>
<td>3.2x10¹⁷</td>
</tr>
<tr>
<td>400</td>
<td>8.2x10¹⁹</td>
<td>1.1x10¹⁸</td>
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<tr>
<td>350</td>
<td>1.2x10¹⁸</td>
<td>3.5x10¹⁷</td>
</tr>
<tr>
<td>400</td>
<td>9.5x10¹⁹</td>
<td>1.0x10¹⁸</td>
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</tbody>
</table>

With all this evidence becoming available and the increasing examples of successful co-doping being reported for p-type gallium, for other nitrides and for n-type diamond, the concept of co-doping (apparently used by Nichia for LED production) should become more widely accepted and used to improve the doping levels of nitride semiconductor materials in other labs around the world.

(For additional reading on this topic see H Katayama-Yoshida et al, J. Phys: Condens. Mat. 13 (2001) 1-14.)

Zinc oxide

There is increasing interest in single-crystal zinc oxide, another wide-bandgap material and assumed to be a versatile semiconductor. ZnO has a bandgap similar to GaN at 3.4 eV and a high thermal conductivity, and was referred to by more than one speaker at the Widegap 2001 meeting.

Bulk crystals of ZnO are available and it is already being used to make varistors and for surge protection devices. ZnO appears to be poised for rapid development as a compound semiconductor material, since the initial problems associated with both p- and n-doping have now been solved and blue LEDs have already been made. Zinc oxide and indium nitride also share a unique property - reported by Chris Van de Walle of Xerox PARC (Palo Alto, CA, USA) - in that hydrogen is a donor dopant for both these materials.

In some application areas, it is being considered as a replacement for indium tin oxide (ITO) conductive coatings. Some evidence for this change in status is the development of highly conductive co-doped p- and n-layers for transparent conductive ZnO oxide uses. Both types of doped layers provide clear window contacts for solar cells as well as providing photovoltaic current collection. Co-ion-implantation of ZnO dopants has been achieved in Japan.

Ion implantation

Ion implantation has always been considered as a viable alternative doping process for GaN. To develop ion implantation parameters for a range of dopant atoms, S Kucheyev of the Australian National University investigated the implantation of 15 elemental ions over a wide range of dosage levels and temperatures.

Unfortunately, GaN appears to have an implantation behaviour radically different from that of either GaAs or silicon. Under ion bombardment, the nitride surface layers swell and become porous as nitrogen is lost, with the concurrent formation of extended defects and voids, and it is difficult to re-crystallise the amorhised layers. As these changes occur, planar defects are formed, the GaN loses mechanical strength, and contact resistance increases, completely nullifying the benefits of doping by ion implantation.
Therefore, with surface erosion occurring at high implantation dosages, the achievement of low activation levels and the inability to anneal away defects, GaN becomes an unlikely candidate for ion implantation doping processes. This leaves device isolation as the only useful nitride application for ion implantation, where electrical isolation is good and stable up to 900°C.

Diamond

The doping of diamond continues to be a challenge and co-doping is again being recommended as the solution.

For n-doping the N-B-N complex has been suggested (Katayama-Yoshida). Also, a presumed P-H-P phosphorus hydrogen complex provided an activation energy of 120 meV in results reported by Koizumi et al (1997 Appl. Phys. Lett. 71 945).

The hydrogenation of diamond is known to produce a surface conductive layer with a lateral hole density of $10^{12} - 10^{13}$ cm$^{-2}$. Current flow can be controlled by a gate electrode and field effect transistors can be made. This property can be eliminated by thermal annealing, but returns after exposure to air.

Jürgen Ristein of the University of Erlangen has performed extensive measurements on the surface conductivity in this system and now appears to have solved this mysterious diamond behaviour. It is now postulated that the surface layer needed to balance the hydrogen-induced hole concentration is the aqueous bicarbonate anion (monolayer). The electrochemical potential of this reaction at pH 6 is about 4.2 eV below the vacuum level and in the range needed to allow electron transfer from the hydrogenated diamond to the surface electrolyte layer.

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