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# Codoping method for the fabrication of low-resistivity wide band-gap semiconductors in p-type GaN, p-type AlN and n-type diamond: prediction versus experiment

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## Abstract

We review our new valence control method of a co-doping for the fabrication of low-resistivity p-type GaN, p-type AlN and n-type diamond. The co-doping method is proposed based upon *ab initio* electronic structure calculation in order to solve the uni-polarity and the compensation problems in the wide band-gap semiconductors. In the co-doping method, we dope both the acceptors and donors at the same time by forming the meta-stable acceptor–donor–acceptor complexes for the p-type or donor–acceptor–donor complexes for the n-type under thermal non-equilibrium crystal growth conditions. We propose the following co-doping method to fabricate the low-resistivity wide band-gap semiconductors; p-type GaN:[Si + 2Mg (or Be)], [H + 2Mg (or Be)], [O + 2Mg (or Be)], p-type AlN:[O + 2C] and n-type diamond:[B + 2N], [H + S], [H + 2P]. We compare our prediction of the co-doping method with the recent successful experiments to fabricate the low-resistivity p-type GaN, p-type AlN and n-type diamond. We show that the co-doping method is the efficient and universal doping method by which to avoid carrier compensation with an increase of the solubility of the dopant, to increase the activation rate by decreasing the ionization energy of acceptors and donors, and to increase the mobility of the carrier.

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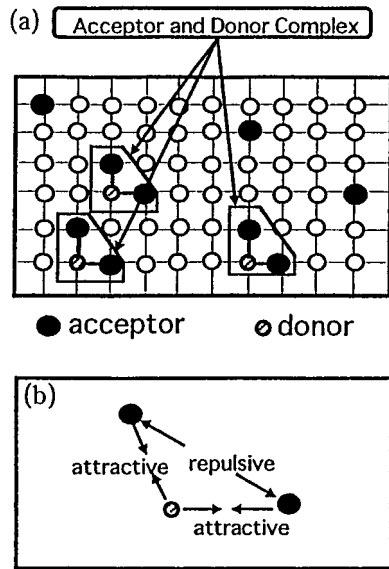
## 1. Introduction

The fabrication of both a low-resistivity p- and n-type wide band-gap ( $E_g$ ) semiconductor is very difficult due to the so-called uni-polarity and the compensation problems in the wide band-gap semiconductors, such as GaN ( $E_g = 3.4$  eV), AlN ( $E_g = 6.2$  eV) and diamond ( $E_g = 5.4$  eV). Blue-ultraviolet laser application and high-power electronics application by using GaN, AlN and diamond have been hampered by the resistivity p-type GaN, p-type AlN and n-type diamond. The origin of the difficulty in the fabrication of the low-resistivity wide band-gap semiconductors is the compensation effect due to the low solubility and the low activation rate which is due to the deep energy level of the acceptor or donor. The acceptor or donor energy level is very deep (about a few hundreds of meV) relative to room temperature ( $\sim 30$  meV) because of the small dielectric constant, for example, GaN:Mg (200 meV), AlN:C (500 meV) and diamond:P (430 meV). If the acceptor energy level is about 500 meV, we can activate the hole densities of less than  $10^{-6}$  of the acceptor concentration at room temperature. In order to fabricate the low-resistivity wide band-gap semiconductor, we should avoid the compensation with the increasing solubility of the dopant, and should increase the activation rate of the carriers by reducing the energy level of the acceptor or donor, and also should increase the mobility of the carriers by reducing the scattering rate of the carriers.

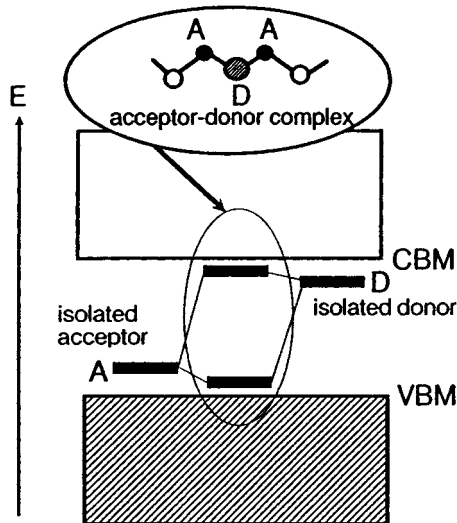
To do so, we propose an effective new valence control method of the co-doping in which we dope both n- and p-type dopants at the same time under thermal non-equilibrium crystal growth conditions by using molecular beam epitaxy (MBE) or metal organic chemical vapour deposition (MOCVD). We find that the co-doping method forms the meta-stable acceptor-donor-acceptor (A-D-A) complexes for the p-type or donor-acceptor-donor (D-A-D) complexes for the n-type in the wide band-gap semiconductors based upon *ab initio* electronic structure calculations. The formation of A-D-A or D-A-D complexes decreases the effective formation energy of the dopants under thermal non-equilibrium conditions by reducing the lattice relaxation energy and the Madelung energy because the two pairs of the attractive acceptor-donor (A-D) interaction overcome the one pair of the repulsive acceptor-acceptor (A-A) interaction (see figure 1). The formation of the A-D-A or D-A-D complex increases the carrier mobility because the scattering mechanism changes from the long-range Coulomb interaction to the short-range interaction with metallic carrier density upon the co-doping. The formation of the A-D-A or D-A-D complexes decreases the ionization energy of acceptors or donors, because a donor level is raised and an acceptor level is lowered in the formation of the bonding and anti-bonding states (see figure 2). When a single acceptor (A) interacts with a single donor (D), the A and D levels will be pushed close to the band edges. Since an additional acceptor upon the co-doping interacts with the anti-bonding donor states with the formation of an A-D-A complex, the acceptor level of an additional A is lowered. Based upon *ab initio* electronic structure calculation, we have designed a realistic co-doping method for the fabrication of low-resistivity p-type GaN, p-type AlN and n-type diamond. Finally, we will compare our predictions of the various co-doping methods and a recent successful co-doping experiment to demonstrate the effectiveness and universality of the co-doping method in the valence control of the wide band-gap semiconductors.

## 2. Calculation method

Our calculations were performed in the framework of the local-density approximation (LDA) with supercells (Kohn and Sham 1965). For GaN and AlN, we used the augmented-spherical-wave (ASW) method (Williams *et al* 1979) in which we used a parametrized form of the exchange-correlation energy of the homogeneous electron gas given by Hedin and Lundquist



**Figure 1.** Co-doping forms: (a) metastable A–D–A complex with (b) attractive A–D interactions and repulsive A–A interactions. In order to make p-type semiconductors, we should freeze in the A–D–A complex using the thermal non-equilibrium crystal growth method.



**Figure 2.** The acceptor (A) level is lowered and the donor (D) level is raised by the formation of the A–D–A complex upon co-doping.

(1971) and von Barth and Hedin (1972). For valence electrons, we employed 3d, 4s and 4p orbitals for the Ga and the outermost s and p orbitals for the other atoms. We studied doped and co-doped p-type GaN and AlN with periodic boundary conditions by generating supercells that contained the object of interest with 32 atoms.

For diamond, we carried out an *ab initio* molecular dynamics simulation (Car and Parrinello 1985) based upon the LDA with the periodic boundary conditions of supercells

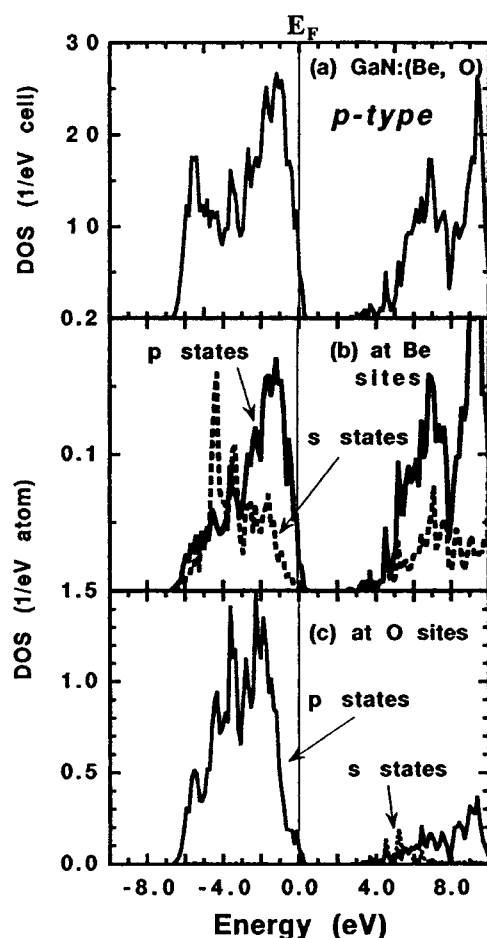
containing 64 atoms of C, P, N, B, S and H. Electron wavefunctions and charge density were expanded into plane waves with cut-off energies of 59 and 118 Ryd, respectively, by using a norm-conserving pseudopotential (Troullier and Martins 1991). Bloch functions were used in the calculations at the  $\Gamma$ -point. For the fabrication of the low-resistivity n-type diamond, we calculated the electronic structure and found a stable atomic configuration of the isolated and co-doped D–A–D complex with fully relaxed atoms in the supercells using *ab initio* molecular dynamics simulation (Car and Parinello 1985).

### 3. Co-doping method for the p-type GaN:[2Mg+O], [2Be+O], [2Mg+Si], [2Be+Si], [2Mg+H], [2Be+H] and [2C+O]

Since we form the meta-stable A–D–A complex by using the co-doping method under thermal non-equilibrium crystal growth conditions, we could not use the total energy or formation energy, which is based on the thermal equilibrium thermodynamics. In order to form the meta-stable A–D–A complex, we assumed that the kinetics of the formation of the A–D–A complex is dominated by the long-range Coulomb interaction when diffusion is limited under the thermal non-equilibrium conditions.

The *ab initio* electronic structure calculations showed a small increase in the Madelung energy of Mg-doped GaN compared with that of Be-doped GaN (Yamamoto and Katayama-Yoshida 1997a). We found that the Mg acceptor wavefunction was more localized on the neighbouring N atoms than the Be acceptor (Yamamoto and Katayama-Yoshida 1997b). We found a strong Coulomb repulsive interaction between Be acceptors, resulting in the low solubility and instability of Be impurities in GaN (Yamamoto and Katayama-Yoshida 1997c). These findings suggest that the Mg acceptor level is deeper than the Be acceptor level. The acceptor energy of the Mg is very deep at about 200 meV. Therefore, the high-density doping of Mg ( $\sim 2 \times 10^{20} \text{ cm}^{-3}$ ) can only achieve hole carrier densities in the mid- $10^{17} \text{ cm}^{-3}$  range at room temperature ( $\sim 30 \text{ meV}$ ) because of the low activation rate of the deep Mg acceptor. High Mg acceptor doping ( $\sim 2 \times 10^{20} \text{ cm}^{-3}$ ) causes a very low hole mobility due to the long-range Coulomb scattering mechanism of the isolated Mg impurities. If we increased the Mg concentration up to  $\sim 2 \times 10^{20} \text{ cm}^{-3}$ , the compensation was observed in the experiment. In order to avoid the compensation, to reduce the acceptor energy level and to increase the solubility of the dopant, we propose a co-doping method by using the reactive donors, O, Si and H, which play an important role in lowering the Mg acceptor level due to the strong hybridization between the reactive donor and the Mg acceptor wavefunctions (Yamamoto and Katayama-Yoshida 1997).

We applied the concept of reactive co-doping to p-type GaN doped with Be: the reactive donor will enhance the incorporation of Be acceptors due to the strong attractive interaction between the reactive donor and the acceptor. We found that the co-doping of the n- and p-type dopants (the best ratio of their concentrations is 1:2) enhanced the incorporation of the acceptors in p-type GaN crystals due to a deduction of the Madelung energy, resulting in the formation of an A–D–A complex which occupies nearest-neighbour sites (Yamamoto and Katayama-Yoshida 1997a, 1998, Katayama-Yoshida and Yamamoto 1997, Katayama-Yoshida *et al* 1996). We show total and site-decomposed density of states (DOS) of p-type GaN:[2Be+O] in figure 3, which shows a strong interaction between the reactive O donor and Be acceptor. More details are given elsewhere (Yamamoto and Katayama-Yoshida 1997, 1998, Katayama-Yoshida and Yamamoto 1997). Considering the above variation of the impurity levels in the band gap and a change in the scattering mechanism from the long-range Coulomb interactions to the short-range dipole-like ones with the formation of the A–D–A complex, this increases not only the net carrier densities but also the hole mobility. Thus, p-type GaN with



**Figure 3.** (a) Total and (b), (c) site-decomposed DOS of the co-doped p-type GaN:[2Be + O] crystals. Energy is measured to the Fermi level ( $E_F$ ).

the simultaneous co-doping exhibits low resistivity and high crystallinity.

We propose various co-doping methods for the fabrication of the low-resistivity p-type GaN as follows: GaN:[Si+2Mg (or 2Be)] and [O+2Mg (or 2Be)] (Yamamoto and Katayama-Yoshida 1997, Katayama-Yoshida *et al* 1996) We show the effect of co-doping for [2Mg + Si] in GaN (table 1 [12] and figure 4). We compare our co-doping data (tables 1 and 2) (Katayama-Yoshida patent 1996) with the co-doping experiment by Nichia Chemicals Co Ltd (figures 5 and 6) (Nakamura patent 1996). We have performed the SIMS measurement for the commercial white LED from Nichia Chemicals Co Ltd and found a high concentration of the Mg ( $\sim 2 \times 10^{20} \text{ cm}^{-3}$ ) acceptor and O ( $\sim 1 \times 10^{20} \text{ cm}^{-3}$ ) donor at the p-type AlGaIn ( $E_g = 4.1 \text{ eV}$ ) region, which shows the co-doping with formation of the Mg–O–Mg complexes. The enhancement of the hole concentration by co-doping with [2Mg + Si] and [2Mg + O] (Yamamoto and Katayama-Yoshida 1997, Katayama-Yoshida patent 1996) is almost two orders of magnitude. The co-doping shows a strong interaction between the reactive donors, Si (or O) donor and Mg (or Be) acceptor. More details are given elsewhere (Yamamoto and Katayama-Yoshida 1997, 1998, Katayama-Yoshida and Yamamoto 1997). Considering the

above variation of the impurity levels in the band gap and a change of the scattering mechanism from the long-range Coulomb interaction to the short-range dipole-like interaction, we can increase the net carrier densities and the hole mobility. Thus, p-type GaN with simultaneous co-doping exhibits low resistivity with high crystallinity.

**Table 1.** Comparison of net hole densities between co-doped p-type GaN:[2Mg + Si] and GaN:Mg (Katayama-Yoshida *et al* 1996).

Substrate temperature (°C)	Net hole densities in co-doped p-type GaN:[2Mg + Si] (cm <sup>-3</sup> )	Net hole densities in p-type GaN:Mg (cm <sup>-3</sup> )
250	$5.3 \times 10^{17}$	$1.2 \times 10^{17}$
300	$8.2 \times 10^{17}$	$2.1 \times 10^{17}$
350	$1.2 \times 10^{18}$	$3.2 \times 10^{17}$
400	$8.2 \times 10^{19}$	$1.1 \times 10^{18}$

**Table 2.** Comparison of net hole densities between co-doped p-type GaN:[2Be + Si] and GaN:Be (Katayama-Yoshida *et al* 1996).

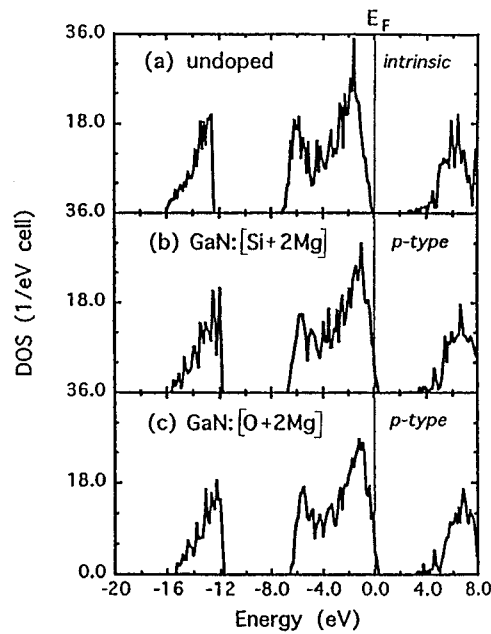
Substrate temperature (°C)	Net hole densities in co-doped p-type GaN:[2Be + Si] (cm <sup>-3</sup> )	Net hole densities in p-type GaN:Be (cm <sup>-3</sup> )
250	$5.2 \times 10^{17}$	$1.2 \times 10^{17}$
300	$8.6 \times 10^{17}$	$2.1 \times 10^{17}$
350	$1.2 \times 10^{18}$	$3.5 \times 10^{17}$
400	$9.5 \times 10^{19}$	$1.0 \times 10^{18}$

Brandt *et al* (1996) and Ploog and Brandt (1998) fabricated the low-resistivity p-type cubic GaN using the Be acceptor and O donor co-doping, with high hole concentrations ( $5 \times 10^{18} \text{ cm}^{-3}$ ), high mobility ( $150 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) and high conductivities ( $50 (\Omega \text{ cm})^{-1}$ ). Their result clearly shows evidence of co-doping with the formation of the Be–O–Be complex, because the ratio of Be and O is 2:1 in the SIMS measurements. Recently, Ploog and Brandt (1998) used H<sub>2</sub>O and Be as the co-dopants and succeeded in fabricating the low-resistivity p-type GaN:[2Be + O] under the control of the O and Be vapour pressure.

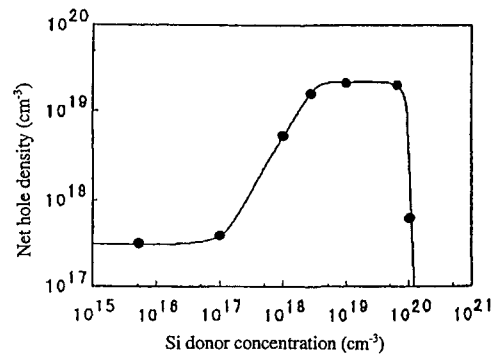
Recently, Wessels's group reported Mg and O co-doping in GaN (Karotkov *et al* 2001). The co-doping reduced the resistivity from  $8 \Omega \text{ cm}$  to  $0.2 \Omega \text{ cm}$  and increased the p-type carrier density from  $1 \times 10^{17} \text{ cm}^{-3}$  to  $2 \times 10^{18} \text{ cm}^{-3}$ , while reducing the acceptor level to 135 meV. This justifies the effect of the co-doping by using the Mg acceptor and O donor; however, we can reduce the resistivity to  $0.01 \Omega \text{ cm}$  based upon our design of the co-doping, if they can optimize the co-doping condition.

Recently, Aoyagi's group (Iwai *et al* 2000) from Riken reported the Mg and Si co-doping using atomic layering epitaxy (ALE). They reduced the acceptor energy level to 90 meV and increased the p-type carrier density to more than  $10^{19} \text{ cm}^{-3}$ . They have not yet optimized the crystal growth conditions because the mobility of the co-doped p-type GaN:[2Mg + Si] is not enhanced and is still low.

Morishima *et al* from the Hitachi Cable group (Morishima *et al* 2001) reported that the number of very shallow acceptor levels at about 10 meV increased with increasing Si donor concentration when Mg acceptors and Si donors are co-doped in the p-type GaN by the MOCVD method.



**Figure 4.** Total DOS of: (a) undoped GaN; (b) co-doped GaN:[2Mg + Si]; and (c) co-doped GaN:[2Mg + O].

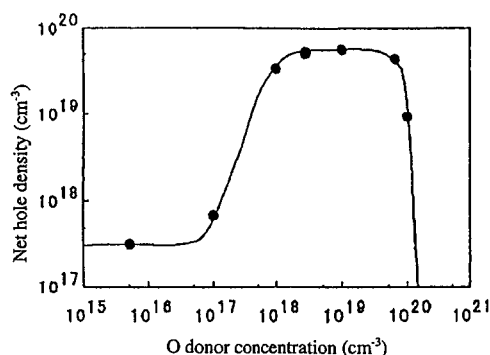


**Figure 5.** Donor (Si) concentration dependence of the net acceptor density upon Mg and Si co-doping. The concentration of Mg is fixed around  $10^{20} \text{ cm}^{-3}$  (Nakamura *et al* 1996).

We have performed SIMS measurements on Nichia's commercially available high-efficiency white LED and found almost the same order of Mg and O concentrations ( $\sim 10^{20} \text{ cm}^{-3}$ ) at the p-type clad layer of  $\text{Al}_{0.25}\text{Ga}_{0.75}\text{N}$  ( $E_g = 4.1 \text{ eV}$ ) (Katayama-Yoshida 2001). This is consistent with the co-doping method. Zohta *et al* (2001) reported the extremely shallow acceptor levels of 14 meV from the valence band maximum in the Nichia's p-type AlGaIn. These results are consistent with the co-doping method of 2Mg + O in the p-type GaN.

We have verified the effect of the co-doping of the C acceptor and O donor as the reactive dopant for the fabrication of the low-resistivity p-type GaN:[2C + O] as those for p-type GaN:[2Mg + O] (Yamamoto and Katayama-Yoshida 2001). The impurity level of the C acceptor, N-substituting species, is lowered with the formation of the C–O–C complexes and the solubility of the dopants is enhanced due to a reduction of the lattice relaxation and the





**Figure 6.** Donor (O) concentration dependence of the net acceptor density upon the Mg and O co-doping. The concentration of Mg is fixed around  $10^{20} \text{ cm}^{-3}$  (Nakamura *et al* 1996).

Madelung energy.

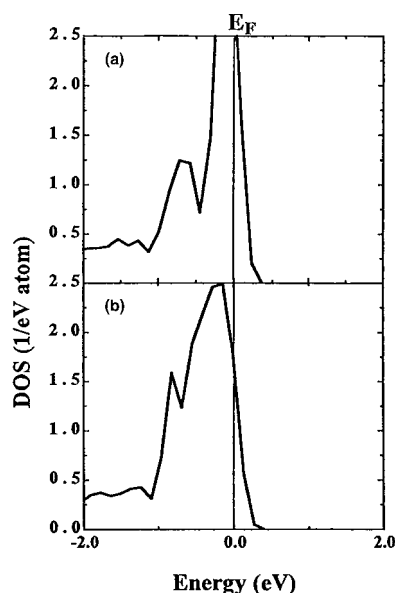
We also propose a co-doping method with Be (or Mg) acceptor and H donor in GaN:[2Mg (or 2Be) + H] in which the acceptor energy level of Mg or Be is lowered by the formation of the Mg–H–Mg or Be–H–Be complex in GaN upon co-doping. This can happen in real materials for the fabrication of low-resistivity p-type GaN using the MOCVD or hydrogen-contained MBE method. Since the Mg-doped as-grown sample by MOCVD is highly passivated by the H donor, then we should remove the hydrogen by thermal annealing in order to activate the Mg acceptor. However, when we remove the hydrogen completely from the as-grown sample, we can only obtain the p-type carrier density up to a mid- $10^{17} \text{ cm}^{-3}$  value even if the Mg concentration is higher than  $10^{20} \text{ cm}^{-3}$ , because of the deep Mg acceptor levels (200 meV). In order to obtain the low-resistivity p-type GaN, we should hold some of the H donor with the formation of the Mg–H–Mg complexes by decreasing the ionization energy of the acceptor due to the strong hybridization. This can be justified because the conductivity of the co-doped sample becomes low when the H donor is completely removed from the Mg–H–Mg complexes by the high-temperature annealing up to  $1400^\circ\text{C}$  (Nakamura 1998, Akasaki 1998).

#### 4. Co-doping method for the p-type AlN:[2C+O]

We have verified the effects of the co-doping of O, as the reactive donors, on the electronic structures for p-type AlN:[2C + O] (Yamamoto and Katayama-Yoshida 1999) as those for p-type GaN:[2C + O]: the ionization energy of C acceptors, N-substituting species, is lowered with the formation of the C–O–C complexes and the solubility of the dopants is increased with decreasing the Madelung energy upon co-doping. Figure 7 shows the comparison of C doping alone and [2C+O] co-doping in the local DOS, indicating shallower acceptor levels and the lighter effective mass of acceptors upon the co-doping (Katayama-Yoshida *et al* JP patent 1997, 1999a, Yamamoto and Katayama-Yoshida 1999). We predict that the co-doping of C, as the acceptor, and O, as the reactive donor, will be an effective method for the fabrication of low-resistivity p-type AlN crystals by using MOCVD and MBE.

#### 5. Co-doping method for the n-type diamond: [B+2N], [H+2P] and [H+S]

The calculated donor levels measured from the conduction band minimum (CBM) are 470 meV for P, 1.63 eV for S and 1.92 eV for N, in our *ab initio* calculations. These values are too large to activate enough donor electrons to the conduction band as carriers for the low-resistivity



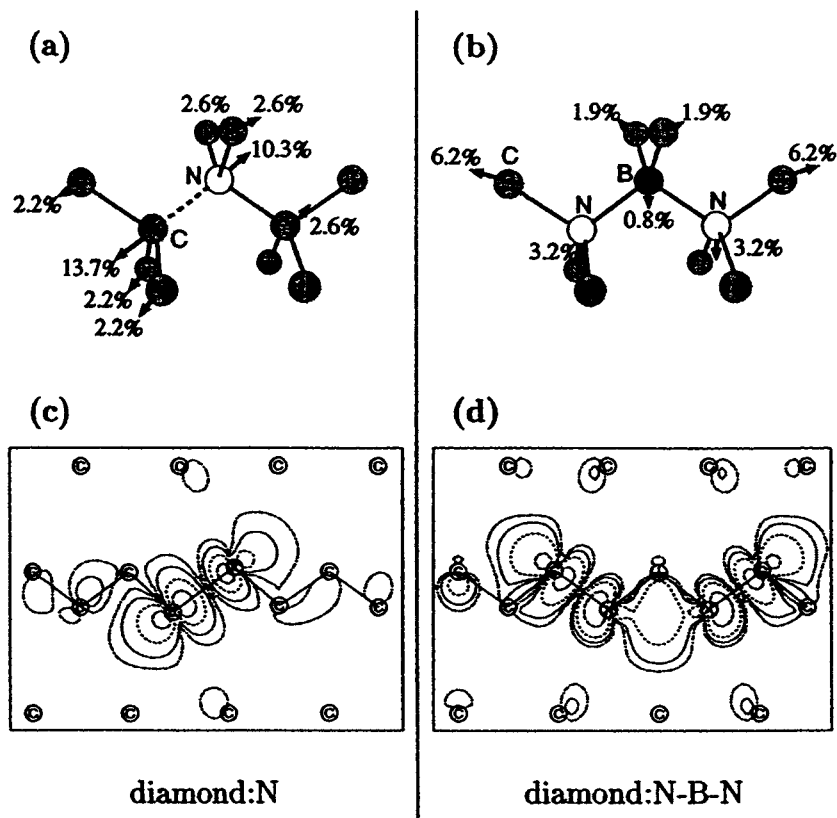
**Figure 7.** Carbon (C) site decomposed DOS of p-type AlN (a) doped with C alone and (b) co-doped with [2C + O].

n-type semiconductors at room temperature, i.e. it is difficult to realize the low-resistivity n-type conduction by the doping of a single dopant. This is consistent with, for instance, the experiment performed by Koizumi *et al* (1997), which achieved high-concentration doping of P up to  $2.5 \times 10^{19} \text{ cm}^{-3}$ , but did not achieve enough carrier concentration for the low-resistivity n-type conduction. Therefore one of our proposals for a doping method to realize the low-resistivity n-type conduction is to apply our idea of co-doping.

The N donor in diamond shows the bond breaking due to the pseudo-Jahn–Teller interaction. In order to avoid the bond breaking of N, we have designed the N–B–N complex formation in diamond by the co-doping method, which makes the delocalization of the donor electron wavefunction into the N–B–N complex. Our calculation for the N–B–N complex shows that the co-doping of N donors and B acceptors to form the N–B–N complex prevents bond breaking and restricts the atomic distortions from the normal substitutional site to less than 6.2% of the normal C–C bond length (figure 8). As can be seen in figure 8, the donor electron of the N–B–N complex spreads wider than that of single substitutional N. This wider spread of the donor electron foretells the low resistivity with the formation of the impurity band.

The depth of the donor level becomes shallow from the value of single N, 1.93 eV, to that for the complex, 1.17 eV. Nevertheless, this value is not small enough for the activation at room temperature. Fortunately the binding energy of this N–B–N complex is calculated to be a large negative value (−4.57 eV). Hence we propose the following doping method to achieve the low-resistivity n-type conduction: the co-doping of N donor and B acceptor forms a high concentration of the N–B–N complexes in diamond due to its large negative binding energy of −4.57 eV. Then the complexes produce the impurity band where thermally activated electrons run at room temperature due to the expected lower activation energy than that of 1.17 eV.

The donor energy level of an isolated P in diamond is too deep (430 meV, same as 4000 K) for thermal activation at room temperatures (300 K). In order to reduce the binding energy



**Figure 8.** Comparison of (a) the single substitutional N donor and (b) the co-doped N-B-N complex in diamond. Atomic displacements are indicated in the units of the C-C bond length of diamond. (c) and (d) are (110) cross sections of the charge densities of each donor state.

of the P donor, we propose a co-doping of H acceptors and P donors in diamond. Isolated H in diamond has two stable atomic positions at the tetrahedral interstitial site (Td site) and bond-centre (BC) site in our calculation (H at the BC site is 0.95 eV more stable than at the Td site, indicating a bistability (Patterson *et al* 1984)). Isolated H at the BC site (Td site) shows a deep acceptor level at 1.5 eV (2.2 eV) above the valence band maximum (VBM). We searched for the stable atomic configuration of the co-doped H and P in diamond using an *ab initio* molecular dynamics simulation. It was found that the anti-bonding (AB) site is the most stable site for the H around the substitutional P donor with the negative binding energy (-2.56 eV) (see figure 9). Although the absolute value of the binding energy of the BC site and the 001 site are smaller than that of the AB site, it was found that the two sites are meta-stable sites for H. Electron transfer from the substitutional P donor to the H is found when P and H make a bond:  $P + H \rightarrow P^+ + H^-$ . The large negative binding energy of the P-H complex helps the high-concentration doping of P. The appropriate ratio of concentration of doped P and H will produce an impurity band in which the donor electrons run, because single P donors supply donor electrons and the unoccupied state produced by the P-H complex or P-H pairs contributes to the conductive impurity band. It is easier for a donor electron to hop to an ionized donor than to an occupied donor atom, so that two electrons will not have to occupy the same site during charge transport. However, the defects that will be doped are P

atoms passivated by H atoms, i.e. P–H complexes. Therefore, an annealing to remove part of the H may become necessary in order to form the P–H–P complex (see figure 10).

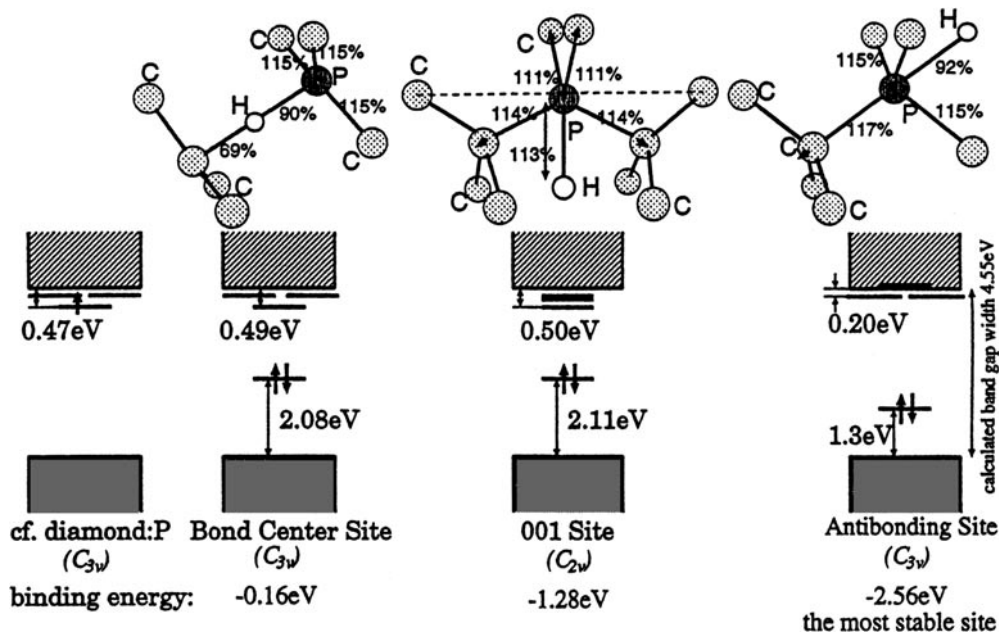


Figure 9. The P–H complexes in each configuration. Atomic displacement is indicated in the units of the C–C bond length. Each energy level in the band gap is shown with the binding energy of P and H.

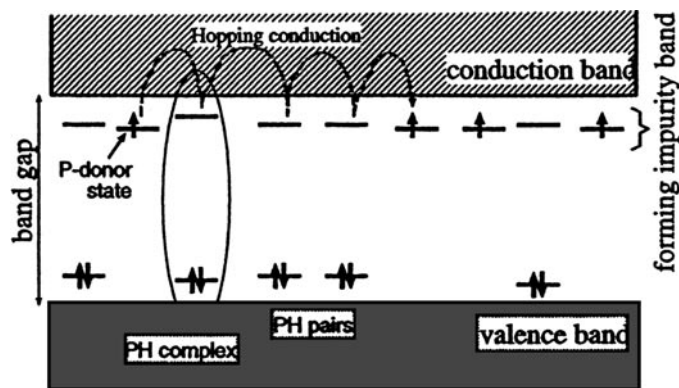


Figure 10. Mechanism of the n-type conduction by forming the impurity band of P and H doped diamond.

We consider that a similar situation may arise in P-doped diamond in a high enough concentration with the presence of H at around room temperature because its activation energy is too large to be activated at room temperature. In this case, the impurity band is formed by P donors and ionized (unoccupied) P donors such as the P–H complex producing empty levels nearer than the conduction band. Not only S–H complexes but also other kinds of P and H pairs that have sufficient distance between them may also contribute to the formation of the impurity

band. It seems that such impurity band conduction occurred in the experiment by Nishimori *et al* (1997) whose diamond thin film was a H-rich one. Nishimori *et al* (1997) observed the activation energy of 120 meV for P under H-rich conditions. If there are not enough H and ionized (unoccupied) P-donors to form the impurity band, the normal conduction in the conduction band with the activation energy 430 meV becomes dominant at room temperature. Measured smaller values of electron mobility ( $20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at  $400^\circ\text{C}$  by Nishimori *et al* (1997) than that of conduction in the conduction band ( $2000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) are also support for this consideration because it is consistent with the short mean free path of the impurity conduction.

We compare our theoretical prediction with the recent successful experiments by Nishimori *et al* (2001) for the fabrication of low-resistivity n-type diamond film prepared by gas source MBE with methane and tri-n-butylphosphine. The electrical conductivity of this n-type diamond was measured to be  $0.33 \Omega^{-1} \text{ cm}^{-1}$  with an activation energy of 120 meV (very shallow donor level relative to the 430 meV of isolated P in diamond (Koizumi *et al* 1997)). The Hall measurement showed n-type conduction and a measured carrier concentration of  $1.6 \times 10^{18} \text{ cm}^{-3}$  (the same order of P concentration is measured by the SIMS) at  $400^\circ\text{C}$ . These results indicate the formation of shallower P donor levels with high electrical activation efficiency. Based upon the SIMS measurement, they find the same or much higher orders of H concentration in the film compared with the P concentration, and the P concentration is increased with increasing H concentration. This experimental evidence is compatible with our prediction of co-doping in which H acceptors and P donors are doped at the same time to form the P–H–P complexes with a reduction in their donor level and formation energy.

It is found that, similarly to the P donor, case, the AB site is the most stable site for a H atom around a substitutional S donor with the negative binding energy ( $-2.18 \text{ eV}$ ) (see figure 11). Although the absolute values of the binding energies of the BC site and the 001 site are smaller than that of the AB site, it is found that the two sites are metastable sites for H. A complicated binding scheme is found for the S–H complex when the H is at the AB site. Because the S–H bond is so strong that the anti-bonding  $A_1$  state arises just below the conduction band, a donor electron occupies another  $A_1$  state that has the amplitude of its wavefunction on the S atom. The occupied  $A_1$  level is 1.07 eV below the conduction band.

For the co-doping of S double donors and the H case, the donor electron will be supplied by S–H complexes as a single donor; and S–H complexes from the impurity band with S–H<sub>2</sub> complexes and other kinds of ionized (compensated) S with two H in other atomic configurations. This is the doping method with which we propose to fabricate the low-resistivity n-type diamond using S–H complexes. A similar co-doping may occur in the experiment with S-doped thin film, which was a H-rich one fabricated by Sakaguchi *et al* (1999).

## 6. Conclusions

We have reviewed our new valence control method of co-doping compared with the recent successful co-doping experiment. We have studied systematically the electronic structure of p-type GaN, p-type AlN and n-type diamond by the simultaneous co-doping of acceptors and reactive donors using *ab initio* band structure theory. We have proposed materials designed for various co-doping candidates for the fabrication of the low-resistivity wide band-gap semiconductors (Katayama-Yoshida *et al* 1998a, Nishimatsu *et al* 2001): (1) p-type GaN:[Si + 2Mg(or Be)], [H + 2Mg (or Be)], and [O + 2Mg(or Be)], (2) p-type AlN:[O + 2C], (3) n-type diamond:[B + 2N], [H + 2P] and [H + S] (Nishimatsu *et al* 2001, Katayama-Yoshida JP patent 2000, Katayama-Yoshida JP patent 2001).

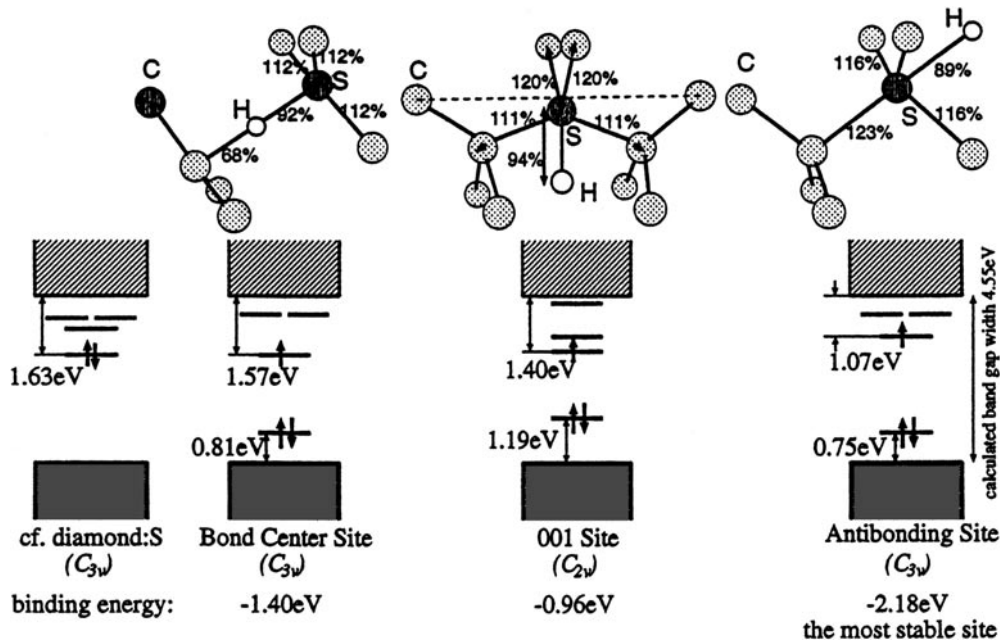


Figure 11. The S–H complexes in each configuration. Atomic displacement is indicated in the units of the C–C bond length. Each energy level in the band gap is shown with the binding energy of S and H.

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