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DOPING PROPERTIES OF AMPHOTERIC C, Si, AND Ge IMPURITIES IN GaN AND AlN

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Electronic structure of substitutional group-IV impurities C, Si, and Ge in hexagonal GaN and AlN were studied by quantum molecular dynamics. C_N is a very shallow acceptor, and thus a promising *p*-type dopant. Both Si and Ge are excellent donors in GaN. However, in AlGaIn alloys the DX configurations are stable for a sufficiently high Al content, which quenches the doping efficiency. Electronic structure of nearest-neighbor $X_{\text{cation}}-X_N$ pairs is also discussed.

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Current interest in wide band-gap nitrides is due to possible applications in blue/UV light-emitting diodes and lasers, and in high-temperature electronics [1, 2]. To exploit fully the potential of these materials, understanding and control of doping needs to be achieved. In the present paper we study substitutional group-IV $X = \text{C, Si, and Ge}$ impurities in the hexagonal (wurtzite) GaN and AlN. These species are potentially important dopants (e.g., Si is frequently used as a *n*-type dopant of epitaxial GaN). On the other hand, both C and Si may be unintentionally incorporated as contaminants during growth.

In general, a group-IV atom is likely to become a donor when incorporated on the cation site, and an acceptor on the anion site. This possibility of the amphoteric behavior critically depends on the conditions of growth. We have recently shown [3] that C is preferentially incorporated on the N site under Ga-rich conditions of growth, while both Si and Ge occupy cation sites under N-rich conditions. However, under other conditions self-compensation, i.e., a simultaneous incorporation of the dopant on both cation and anion sublattice, is expected. For this reason we discuss here the electronic structure of X_{cation} , X_N , and $X_{\text{cation}}-X_N$ nearest-neighbor pairs. We also consider a possible transition of X_{cation} from the substitutional to the DX-like configuration. Such a transition is commonly accompanied by a capture of electron on a stable (or metastable) state, which quenches the doping efficiency. Some of the results for C were published in [4]. The calculations were performed using quantum molecular dynamics [5]. Technical details were given in [6]. Soft pseudopotentials for N and C were used [7], while the pseudopotential of Ge was generated according to Ref. [8].

We first briefly discuss configurations of substitutional impurities and strain effects. A substitutional impurity in a wurtzite crystal has four nearest neighbors. One of them, located along the *c*-axis relative to the impurity (called here type-1 neighbor), is non-equivalent to the remaining three neighbors (called here type-2 neighbors). For the group-IV atoms considered here, this non-equivalence is small, since the bond lengths with type-1 and type-2 neighbors are equal to within 1 per cent. In all cases, we find breathing mode distortions preserving the local hexagonal symmetry. The calculated changes in bond lengths are given in Table, together with the energy gain E_{rel} due to the relaxation from the ideal substitutional configuration to the final one. As follows from Table, the inclusion of relaxation effects is necessary for a proper description of C_{cation} , Si_N , and Ge_N , due to the large differences between the atomic radii of the impurity and host atoms. The most drastic case is that of Ge_N in AlN: the lattice relaxation releases the elastic energy ΔE_{rel} of 7 eV, rises the acceptor level by 1.05 eV, and increases the Ge-N bonds by 17 per cent. Very similar results are obtained for AlN:Si. The calculated ΔE_{rel} are systematically greater for AlN than for GaN, reflecting the higher stiffness of AlN.

TABLE

Effects of atomic relaxations around impurities. Δb is the change of the bond length, ΔE_{rel} is the relaxation energy, E_{imp} is the position of the impurity level, with e.m. denoting the effective-mass state, and ΔE_{imp} is the relaxation-induced shift of the impurity level.

| | Δb [%] | ΔE_{rel} [eV] | E_{imp} [eV] | ΔE_{imp} [eV] |
|-------|----------------|------------------------------|-----------------------|------------------------------|
| GaN | | | | |
| C:Ga | -18.1 | 1.65 | e.m. | - |
| Si:Ga | -5.6 | 0.65 | e.m. | - |
| Ge:Ga | -1.4 | 0.25 | e.m. | - |
| C:N | -2.0 | 0.1 | $E_v+0.2$ | - |
| Si:N | 13.6 | 3.9 | $E_v+1.2$ | 0.8 |
| Ge:N | 13.5 | 4.1 | $E_v+1.35$ | 0.8 |
| AlN | | | | |
| C:Al | -17.2 | 2.6 | $E_c-0.4$ | 1.2 |
| Si:Al | -7.0 | 0.7 | e.m. | - |
| Ge:Al | -2.9 | 0.3 | e.m. | - |
| C:N | 2.0 | 0.4 | $E_v+0.4$ | 0.1 |
| Si:N | 16.5 | 6.75 | $E_v+1.7$ | 1.0 |
| Ge:N | 16.7 | 6.95 | $E_v+1.75$ | 1.05 |

As follows from Table, C, Si, and Ge occupying the cation site in both GaN and AlN are effective-mass donors. The only exception is C_{Al} in AlN, where the

C-induced level is at about 0.4 eV below the bottom of the conduction band. In GaN, because of its lower band gap, the C-derived level is a resonance situated at 0.9 eV above the bottom of the conduction band.

In addition to the substitutional configuration of X_{cation} donors, we have investigated the stability of the DX-like configuration [9]. In this configuration one bond between the impurity and its first neighbor is broken, and one of these atoms (or both) are shifted to an interstitial site. We have analyzed only one possible DX state, namely that with the broken bond between the impurity and the type-1 neighbor; the configuration with the broken bond to the type-2 N atom should have very similar properties.

We first consider GaN. We find that C_{Ga}^* is metastable not only in the negative but also in the neutral charge state. The energy of C_{Ga}^* is higher than that of the substitutional C_{Ga} by 0.54 and 0.35 eV for the neutral and the negative charge state, respectively. In the DX state both the host N atom and the impurity are significantly displaced along the c -axis (see Ref. [4] for details). In contrast, Si is unstable in the DX state, since there is no energy barrier for the transition from the initial DX configuration to the substitutional one. This holds for both the neutral and the negatively charged Si. Finally, a DX state is metastable for the negatively charged Ge, and its energy is higher by 0.3 eV than that of Ge_{Ga}^- . Unlike for C_{Ga}^* , Ge atom is located at the lattice site, and the nearest-neighbor N atom is displaced along the c -axis. The Ge-N distance is 2.61 Å, to be compared with 1.93 Å for the substitutional configuration. $\text{Ge}_{\text{Ga}}^*(-)$ introduces a singlet at about 0.4 eV below the bottom of the conduction band. For the neutral charge state, the DX configuration is unstable.

Turning to AlN, we find that in the negative charge state C_{Al}^* is more stable than C_{Al}^- by 0.2 eV. In the neutral charge state C_{Al}^* is metastable, as its energy is higher by 0.48 eV than that of the ground state. Unlike in GaN, the DX configurations are *stable* for both Si and Ge in the negative charge state. Their energies are lower by 0.15 and 1.2 eV than those of the respective substitutional cases. In both cases the impurity remains on the substitutional site, and the N atom is strongly displaced. For Si_{Al}^* the distance to the N atom is 2.95 Å compared to 1.78 Å for Si_{Al} , and for Ge the respective values are 2.83 and 1.86 Å. $\text{Si}_{\text{Al}}^*(-)$ introduces a level at -1.5 eV below the bottom of the conduction band. For Ge, the gap state is even deeper, at -2.0 eV below the bottom of the conduction band. Finally, the DX configurations are unstable for both Si and Ge in the neutral charge state.

The different DX configurations found for C, as opposed to Si and Ge, are in part due to atomic size effects. For example, when C substitutes the much bigger Ga atom, the C-N bonds are highly stretched, because they are shorter than the equilibrium Ga-N bonds by about 15%. In the DX state one C-N bond is broken, and C is free to relax and to shorten the three remaining C-N bonds. Consequently, the C_{Ga}^* -N bonds are shorter by about 7% than C_{Ga} -N bonds in the substitutional case. At equilibrium, C^* forms a nearly planar configuration with the type-2 neighbors. Such a geometry is additionally stabilized by the tendency of C to form planar sp^2 bonds. Both factors may contribute to the stabilization of C_{Ga}^* in the neutral charge state. In contrast, these factors are not operative for Si and Ge impurities, which remain on the substitutional site.

We shall now consider the acceptors X_N . In zinc-blende crystals, acceptor levels of group-IV atoms are threefold degenerate. Due to the wurtzite symmetry of GaN and AlN, the triplets are split into doublets and singlets by the energy E_{split} . In all cases considered here, the energies of doublets (given in Table), E_D , are higher than those of singlets, E_S . Both the acceptor energies and the splittings strongly depend on the impurity. We find that C is a shallow acceptor with $E_D = 0.2$ eV in GaN, which is in excellent agreement with the recent experimental data [10]. Thus, C is a promising p -type dopant, since it is a shallower acceptor than the commonly used Mg [2]. In AlN, C is deeper ($E_D = 0.4$ eV) and more localized. The doublet-singlet splitting E_{split} is about 0.2 eV in both materials. In contrast, both Si and Ge are deep acceptors. For GaN:Si $E_D = 1.2$ eV and $E_{\text{split}} = 0.6$ eV, and for GaN:Ge $E_D = 1.35$ eV and $E_{\text{split}} = 0.6$ eV. In AlN the binding energies and the splittings are even higher, and we find $E_D = 1.7$ (1.75) eV and $E_{\text{split}} = 0.7$ (0.7) eV for Si_N and Ge_N, respectively.

Finally, we turn to the electronic structure of the nearest-neighbor $X_{\text{cation}}^+ - X_N^-$ pairs. Compared to the case of distant X_{cation} and X_N impurities, the main modification is a substantial increase in the doublet-singlet splittings. In the case of GaN, E_{split} rises from 0.6 to 1.0 eV for Si-Si pairs, and from 0.6 to 1.05 eV for Ge-Ge pairs. For AlN, the increase is from 0.7 to 1.4 eV for Si-Si pairs, and from 0.7 to 1.35 eV for Ge-Ge pairs. This effect is due to the close proximity of the X_{cation} donor, located along the c -axis relative to the acceptor X_N . The presence of the donor enhances the non-equivalence between the z -symmetry singlet and the (x, y) -symmetry doublet states.

As it follows from our results, properties of Si and Ge are similar, but they are qualitatively different from those of C. These differences are due to both different atomic energies of their atomic p orbitals and differences in atomic radii, which affect both atomic relaxations and hybridization of the orbitals.

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