

Stabilization of Bulk p -Type and Surface n -Type Carriers in Mg-Doped InN {0001} Films

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The formation of p -type carriers in InN {0001} films by Mg doping is theoretically investigated by means of the highly precise thin film full-potential linearized augmented plane-wave method. The first-principles calculations simultaneously simulating both p -type and n -type carriers in the bulk and surface layers, respectively, demonstrate that the formation energies of a substitutional Mg atom in the surface region are lower than those in the bulk due to the compensation mechanism. The Mg is, however, stabilized in the bulk layers due to a large diffusion-barrier height, suggesting a possible mechanism for the stabilization of Mg in the bulk and the formation of p -type carriers.

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Both n -type and p -type conductivities are essential to realize many semiconductor devices, such as solar cells, light emitting diodes, thermoelectrics [1,2], etc. While n -type conductivities in many materials are common and easy to synthesize, obtaining p -type materials continues to be a severely challenging problem. This well-known situation is perhaps best illustrated in the case of semiconducting nitrides and oxides, where p -type doping is very difficult to achieve due to their propensity for forming n -type defects [3].

Very recently, the significant achievement of p -type conductivity was successfully demonstrated in the bulk layers of Mg-doped InN films by capacitance-voltage (C - V) measurements [3–5] with n -type conductivity dominating the surface region. The measured depth profile of the net charge concentration in the experiments clearly shows that it is of great importance to identify the surface contribution to n -type conductivity since the presence of the highly conducting donor-type layers near the surface region may hamper the experimental measurements for the acceptor-type conductivity due to the possible dominance of the surface layers in the measurements [5]. Also, these experiments immediately raise interesting questions regarding the donor-acceptor interactions between surface and bulk layers, formation energies of a target dopant species, and the stability of dopants in the bulk layers. These issues are addressed and resolved here so as to assist in the further design of materials for possible applications.

Using a first-principles all-electron approach, we have investigated p -type doping with Mg in the film geometry with n -type carriers at the surfaces, which reveals the relationship between the surface and the bulk layers for Mg doping. Mg near the surface has been found to have a lower formation energy compared to that in the bulk region. However, Mg diffusion to the surface is prohibited due to the large energy barrier, 5.7 eV—a large energy barrier that is essential for the stability of acceptors in the bulk layers and thus the formation of p -type carriers.

The theoretical calculations were performed within the local density approximation and the Hedin and Lundqvist form of exchange and correlation potential [6]. The thin film (single slab) full-potential linearized augmented plane-wave (FLAPW) method [7,8] used in this Letter has full 2-dimensional geometry and, thus, has no artificial 3-dimensional periodicity, as in the superslab methods with vacuum regions between the slabs. The cutoff of the LAPW basis is 13 Ryd and the k mesh in the Brillouin zone is 7×7 for the thin film geometry of a (2×2) unit cell, which is used for all calculations in this Letter.

To simulate n -type carriers at the surface and p -type carriers in the bulk layers at the same time, we used 8 bilayer InN {0001} films (c.f., Fig. 1) and passivated the opposite In surface layer with pseudohydrogens [9] in order to remove any interaction between the surfaces and thus to simulate the bulk layers as in a semi-infinite system. Based on recent calculations, which show that the In adlayer is one of the most stable surface reconstructions on N surface layers [10], we added an In adlayer onto the N

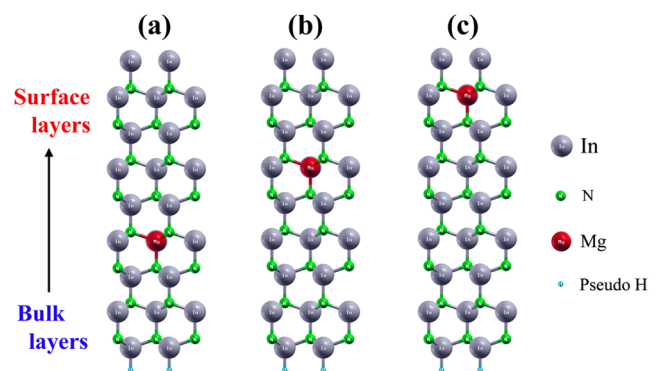


FIG. 1 (color online). Geometries of substitutional Mg located at (a) the fifth, (b) the third, and (c) the top bilayer from the surface of InN {0001} films. The total energies for Mg in (b) and (c) are -0.09 and -0.46 eV, respectively, relative to that for Mg in (a).

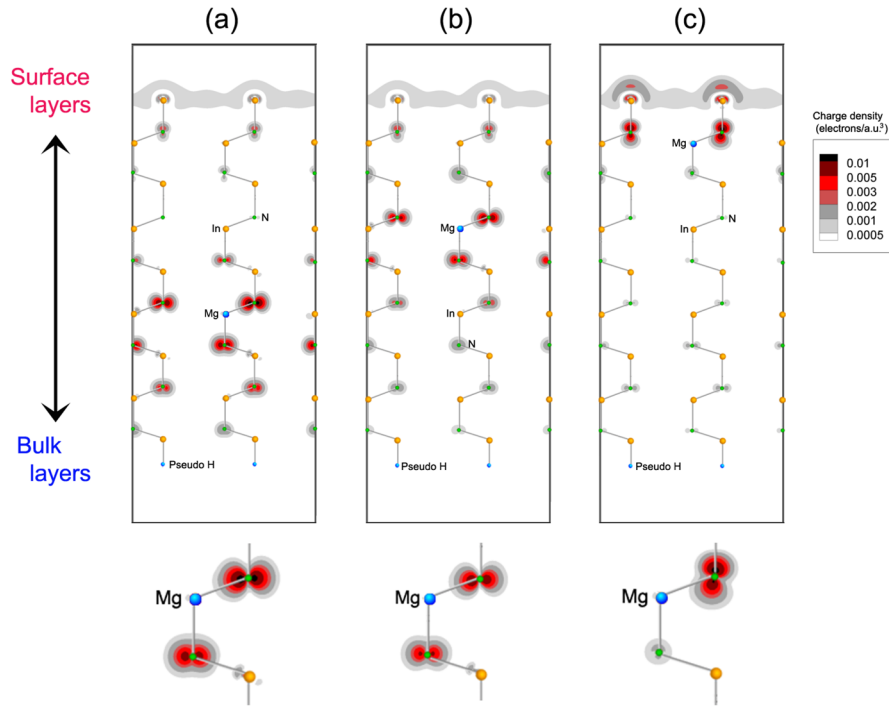


FIG. 2 (color online). Cross sectional $[11\bar{2}0]$ charge densities for states in an energy slice between E_F and $E_F + 0.25$ eV in Mg-doped InN $\{0001\}$ films; here, (a), (b), and (c) correspond to the film structures of (a), (b), and (c) in Fig. 1, respectively. The enlarged contour plots in the bottom detail the charge densities near Mg.

surface, which creates n -type carriers in the surface region. For p -type carriers in the bulk layers, we substituted a Mg for one of the In atoms. One important feature in this model is that the internal electric field of the dipolar structure is greatly reduced due to the pseudohydrogen passivation and the additional In adlayer [11,12].

To determine how the different type carriers behave, the Mg was substituted at three different In sites from *bulk* to surface layers (cf. Fig. 1). In Fig. 2, charge densities for states in a slice of energy between E_F and $E_F + 0.25$ eV [13] clearly show that hole carrier densities become smaller as Mg moves from the bulk to the surface, which implies that unoccupied (p -type) states of N's around Mg are compensated by extra electrons (n -type) of an In

adlayer as Mg approaches the surface. This illustrates the simple picture for the depth profile of the net charge concentration, in which the p -type carriers dominate in the central bulk layers [Figs. 2(a) and 2(b)] and the n -type carriers dominate in the surface region [Fig. 2(c)]. This is also confirmed by the projected density of states shown in Fig. 3: when Mg is closer to the surface, the surface states of the In adlayer move towards E_F as indicated by the arrows in Fig. 3. The unoccupied N states near Mg are then compensated by the occupied surface states of the In adlayer. As a result, the density of states of the N p -orbitals near E_F decrease as shown in Figs. 3(a)–3(c). Eventually, when Mg is closest to the In adlayer, the N states around Mg are hybridized with the In surface states,

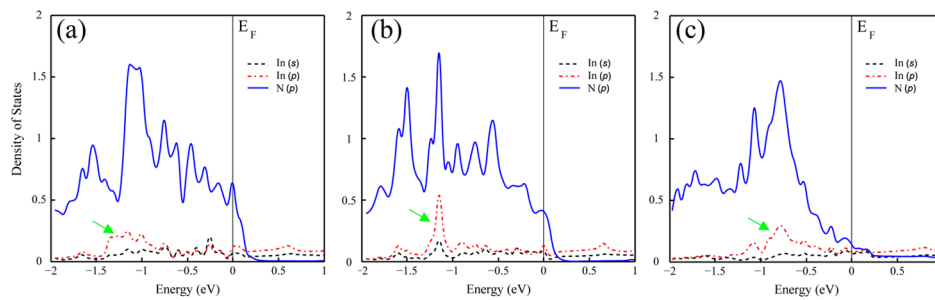


FIG. 3 (color online). Angular momentum-decomposed (s - and p -) density of states in Mg-doped InN $\{0001\}$ films: (a), (b), and (c) correspond to the atomic configurations of (a), (b), and (c) in Fig. 1, respectively. As Mg moves towards the surface, the density of states for N p -orbitals near E_F decrease due to the compensation by extra electrons of the In adlayer. The arrows in (a), (b), and (c) below E_F indicate the prominent surface states peak of the In adlayer p -orbitals.

which results in a resonance of the states [Fig. 3(c)]. Note that, although the main contribution of the In surfaces comes from about 0.8 eV below E_F in Fig. 3(c), the In surface states are very delocalized (the large band width of In surface states), which makes the compensation possible. For instance, the surface states may penetrate several bilayers of InN below the surface [11]. The optimized geometry for the In adlayer shows the compensation nature as well. The In adlayer for Mg in the 3rd and 1st bilayer shown in Figs. 1(b) and 1(c) shrinks towards the bulk region by 0.01 and 0.07 Å, respectively, compared to that for Mg in the 5th bilayer shown in Fig. 1(a). Since the compensation lowers the total energy, the tendency of the In adlayer relaxation towards the Mg indicates the larger compensation and thus the lower total energy, which is consistent with the total energy behavior as explained below.

We found that the total energy gets lower as Mg is located closer to the surface: total energies for Mg in the 3rd bilayer [Fig. 1(b)] and the 1st bilayer [Fig. 1(c)] from the surface are -0.09 eV and -0.46 eV, respectively, which are relative to that for Mg in the *bulklike* 5th bilayer [Fig. 1(a)]. Using these total energies, we calculated the formation energies for the neutral Mg impurity in the InN {0001} films of Figs. 1(a)–1(c), to be 1.63, 1.55, and 1.17 eV, respectively [14,16,18], while the formation energies for Mg near the surface are significantly lower. Mg may exist in the bulk layers without being compensated (no significant source of donors there), but if the Mg in bulk layers diffuses to the surface, they will be mostly compensated by donors from an In adlayer [Fig. 2(c)]. In thermodynamic equilibrium, if Mg is readily able to diffuse towards the surface, the concentration of Mg in the bulk layers would be significantly lower compared to the surface region due to its higher formation energy and diffusion [19]. The low and nonuniform concentration of dopants due to the possible diffusion then may deteriorate the application performance [20].

Since the key to Mg behavior lies in the energy barrier for its diffusion from the bulk to the surface region, we have calculated this energy when Mg exchanges its position with one In atom at the surface [21]. We do this by a constraint minimization technique [22], in which steepest descent paths can be found by minimizing the potential in all directions except the direction of the path. As before, we have modeled this situation with an additional In layer on top of the N surface layer and the bottom surface layer passivated with pseudohydrogens, but with 3 bilayers of InN in our film. We next considered the concerted exchange mechanism which was proposed to explain one of the self-diffusion mechanisms in Si [23], but also appears to be the most relevant diffusion mechanism for Mg.

Indeed, we find the response of the surface layers is very large when Mg diffuses to the surface as in Fig. 4. For instance, when one of the In atoms near the surface leaves its position to exchange with Mg, an In in the surface layer

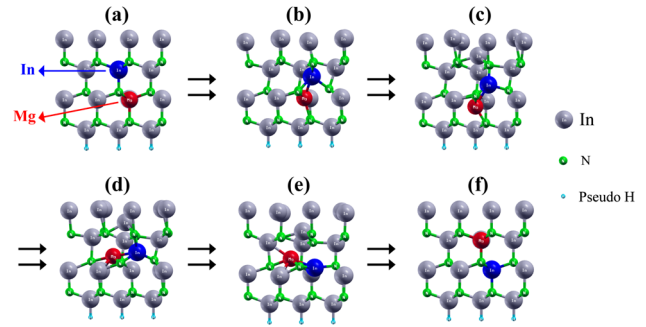


FIG. 4 (color online). Migration of Mg from the bulk to surface layers in InN {0001} films. Mg which is initially located in the 2nd bilayer from the surface as shown in (a), exchanges its position with one In atom in the 1st bilayer from the surface. At the beginning, In near the surface moves first towards the Mg position as in (b) since one In atom at the adlayer may fill in the In vacancy below as in (c), which leads to a lower total energy. As Mg leaves, In occupies its position as in (d) and (e). Finally Mg completes the exchange process with In as in (f).

finds the empty space below and tries to fill it in order to have maximum bondings available and, thus, to have lower total energy during the process, as in Figs. 4(c)–4(e). In addition, when Mg exchanges its position with one of the In atoms near the surface, they do not move in a symmetric way: the In moves first since the In at the adlayer may possibly fill in the In vacancy to have lower total energy [Figs. 4(b) and 4(c)]. As soon as Mg leaves its position, In occupies that position to maintain the maximum possible bondings [Fig. 4(e)]. When Mg approaches the final position, the In which tried to fill in the In vacancy moves back to the adlayer [Fig. 4(f)]. To repeat, the concerted exchange mechanism occurs in such a way that the system tries to maintain the maximum possible bondings and thus to obtain the lowest total energy for each diffusion step.

This asymmetric diffusion path is also well represented in Fig. 5. When In leaves its surface position as in the diffusion steps (b) and (c) in Fig. 4, the energy barrier height reaches only approximately 3 eV as in Fig. 5(b) due to the In adlayer response, but the highest energy barrier is approximately 5.7 eV as in Fig. 4(d) and the point (d) in Fig. 5; this large value prevents Mg from diffusing to the surface and from being compensated by n -type carriers there. Now Mg can be incorporated into the bulk region during the nonequilibrium growth process, which results in a very high concentration of Mg ($\sim 10^{21}/\text{cm}^3$) as that in the experiments [3,5] due to immobile Mg's. With the high energy barrier, Mg should be stable in the bulk layers, which is essential for the formation of p -type carriers in the bulk region and the uniformness of dopant concentration.

We have shown that the formation energy of the Mg near surface layers becomes lower than that in the bulk. It is thus envisioned that the compensation mechanism stabilizes donors and acceptors when they coexist and can interact. To stabilize the dopants in the bulk layers, the large energy

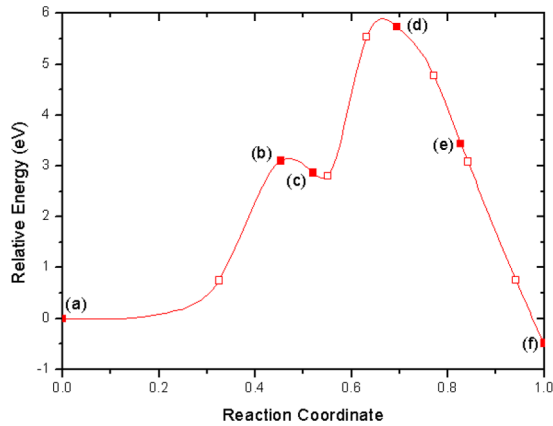


FIG. 5 (color online). Energy for migration of Mg from the bulk to surface layers in InN {0001} films. The energies are relative to (a), which corresponds to the atomic configuration (a) in Fig. 4. The solid squares correspond to the atomic configurations in Fig. 4 while the open squares indicate the intermediate atomic configurations between (a) and (f), which are not shown in Fig. 4.

barrier preventing the dopant diffusion toward the surface is desirable when the surface has the opposite type-carriers. Our first-principles calculations for Mg diffusion in InN {0001} films yield the very high energy barrier, which realizes *p*-type doping in the bulk.

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[12] Note that this is a desirable situation for *p*-type doping with Mg as indicated in our formation energy calculations; the formation energy for Mg is lowered by the reduction of the internal electric field.
 [13] $E_F + 0.25$ eV is chosen so as to include the Mg-induced levels near the valence maximum.
 [14] For the In, N, and Mg chemical potentials, we have used In rich and thermal equilibrium conditions with InN bulk and Mg_3N_2 bulk [15]. Note that the formation energies for Mg in Figs. 1(a) and 1(b) are comparable to those calculated for Mg in bulk InN in the literature [15].
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