Interfacial Segregation and Electrodiffusion of Dopants in AlN/GaN Superlattices

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A first-principles theory of interfacial segregation of dopants and defects in heterostructures is developed and applied to GaN/AlN superlattices. The results indicate that the equilibrium concentrations of a dopant at two sides of an interface may differ by up to a few orders of magnitude, depending on its chemical identity and charge state, and that these cannot be obtained from calculations for bulk constituents alone. In addition, the presence of an internal electric field in polar heterostructures induces electromigration and accumulation of hydrogen at the appropriate interfaces.

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Properties of semiconductors and their devices rely entirely on accurate control of doping and stoichiometry. These, in turn, are determined by solubility of impurities and the presence of native defects. For this reason, the issue of equilibrium concentrations of dopants and defects in semiconductors has been extensively studied in the past decade. A general theory of doping efficiency has been formulated in the past decade [1–3]. This formalism, complemented by first-principles calculations to obtain detailed numbers in particular cases, allows one to relate the equilibrium concentrations of dopants and self-compensation by native defects with the conditions of crystal growth. However, semiconductor systems of current interest are often not bulk materials but rather epitaxial heterostructures, in which chemical compositions of various elements are different. A question therefore arises about the equilibrium distribution of dopants and defects in heterostructures. Experimentally, thermally activated redistribution of impurities through semiconductor heterointerfaces, i.e., interfacial segregation, has been investigated for Si/SiGe heterostructures, where the equilibrium concentrations of dopants in Si and in SiGe layers differ by a factor of 2–3 [4–7]. This effect is stronger in III-V heterostructures [8,9], where concentration differences may reach 2 orders of magnitude and affect the luminescence efficiency of light-emitting diodes [10]. At this point, however, fundamental understanding of segregation is still lacking, and only a phenomenological theory of segregation exists [11].

In this Letter, we formulate the theory of segregation in modern terms, which enable studies of segregation at and near interfaces by accurate *ab initio* methods. As the key example, we choose hydrogen in GaN/AlN superlattices (SLs); it is the dominant impurity that passivates dopants in structures grown by metal-organic chemical vapor deposition. In order to illustrate the general features that determine segregation, we also study typical dopants and defects in GaN/AlN structures. Our results show that the distribution of dopants in a heterojunction cannot, in general, be obtained from calculations performed for isolated bulk crystals. We find and explain large differences in segregation properties between cation- and anion-substituting dopants as well as between shallow and deep ones. We also analyze the impact of the Fermi level position on segregation. Finally, segregation is not the only effect that determines the equilibrium profile of H in AlN/GaN heterostructures. A characteristic property of III-nitrides or ZnO-based systems with the wurtzite structure is the presence of strong electric fields [12,13], which deeply affect the electronic properties of heterojunctions. We show that these fields give rise to a field-driven electrodiffusion of charged impurities, which can lead to, e.g., an accumulation of hydrogen close to the appropriate interfaces.

We first briefly recall the basic concepts describing the doping of a homogeneous solid. The equilibrium concentration of dopants is defined for given conditions of growth under the assumption of equilibrium with reservoirs of relevant atomic species characterized by their chemical potentials μ [1–3]. At these conditions, insertion of an impurity atom into a solid induces a change in the total energy of the system, which is the formation energy E_{form}. For example, E_{form} of a neutral interstitial H in GaN is

$$E_{\mathrm{form}} = E_{\mathrm{tot}}(\mathrm{GaN{:}H}) - E_{\mathrm{tot}}(\mathrm{GaN}) - \mu_{\mathrm{H}}, \qquad (1)$$

where E_{tot} is the total energy of the crystal with or without the impurity. Neglecting small changes in the vibrational entropy, one finds that the equilibrium concentration of dopants N_{imp} is equal to

$$N_{\mathrm{imp}} = N_0 \exp(-E_{\mathrm{form}}/k_B T), \qquad (2)$$

where N_0 is the density of the appropriate lattice sites.

We now turn to interfacial segregation. In an A/B heterostructure, the equilibrium concentrations of dopants at the A and B sides, N_{imp}^A and N_{imp}^B, respectively, are determined by the condition that the chemical potential of the dopant is the same in the whole system, i.e., at both sides of the interface. One finds that the segregation coefficient, which is the ratio of impurity concentrations at the two sides of the interface, is

$$k_{\mathrm{seg}} = N^A_{\mathrm{imp}}/N^B_{\mathrm{imp}} = (N^A_0/N^B_0)\exp(E_{\mathrm{seg}}/k_B T), \quad (3)$$

where $E_{\mathrm{seg}} = E^B_{\mathrm{form}} - E^A_{\mathrm{form}}$ is the segregation energy. Therefore, k_{seg} depends only on the difference between the formation energies and is independent of μ_{imp}.

In general, dopants and defects in semiconductors are ionized. Ionization of a defect affects its segregation in two ways. First, for a homogeneous crystal, E_{form} depends on the charge state of the defect. The transfer of q electrons from a defect level ϵ to the Fermi level E_F changes the formation energy by $q(E_F - \epsilon)$, which should be added to the left-hand side of Eq. (1) [1–3]. Consequently, since E_{seg} is the difference between E_{form} of the two materials, segregation depends on the charge state of the defect as well. The numerical results that we list below indicate that this dependence is, in general, weak for shallow defects but may be substantial for deep ones. Furthermore, the segregation of ionized defects is strongly affected by electric fields that may be present in a junction. This effect was seen experimentally for B in a Si homojunction [14].

Finally, interface segregation may occur during annealing, when the numbers of atoms of each species are conserved. Consequently, when considering the segregation of a *cation-substituting* defect X_{cation} in GaN/AlN, e.g., the migration of Si from the AlN to the GaN layer, we assume that $\mathrm{Si}_{\mathrm{Al}}$ moves to the GaN layer and becomes $\mathrm{Si}_{\mathrm{Ga}}$ by exchanging sites with a Ga atom from the GaN layer; this implies that a Ga atom moves into the AlN layer and becomes $\mathrm{Ga}_{\mathrm{Al}}$. In this case, the reaction $X_{\mathrm{Al}} + \mathrm{Ga}_{\mathrm{Ga}} \rightarrow X_{\mathrm{Ga}} + \mathrm{Ga}_{\mathrm{Al}}$ determines the segregation energy. E_{seg} is thus somewhat different from the difference between E_{form}, because of the presence of $\mathrm{Ga}_{\mathrm{Al}}$ after segregation. On the other hand, for N-substituting defects and interstitials, k_{seg} is determined by the difference between E_{form}.

To describe quantitatively the interfacial segregation, the above analysis needs to be supplemented by the first-principles calculations of the total energies. These are carried out within the density functional theory, using standard pseudopotentials [15] and a multigrid-based total-energy method that uses a real-space grid as the basis [16,17]. We begin by finding the equilibrium sites of H in GaN and AlN. They depend on the charge state: Similarly to the zinc-blende GaN, H^+ sits close to N anions, while H^- and H^0 prefer the interstitial region [18]. We consider 4 sites for H^+: the bond center *c*-BC and the antibonding *c*-AB, with the H-N bond parallel to the *c* axis, along with the bond center *a*-BC and the antibonding *a*-AB, where the H-N bond is almost perpendicular to the *c* axis. In AlN, the equilibrium site is *c*-BC, with the energy lower than those of *a*-AB and *c*-AB by 0.05 and 0.2 eV, respectively; see Table I. The energy of *a*-BC is higher than that of *c*-BC by 0.7 eV, which demonstrates a strong nonequivalence between the two types of Al-N bonds in AlN. In agreement with Ref. [19], a similar sequence of energies is found for GaN (Table I). Accordingly, in the superlattice calculations below, we assume that H^+ is at *c*-BC sites in both GaN and AlN layers. The most stable sites for both H^- and H^0 are interstitial at the center of the trigonal channel.

TABLE I. The total energy of H^+ in GaN and AlN relative to the *c*-BC bond-center site. See text for the explanation of the four sites.

	c-BC	*a*-BC	*c*-AB	*a*-BC
AlN	0.0	0.05	0.20	0.70
GaN	0.0	0.05	0.25	0.30

Figure 1(a) shows the total energy E_{tot} of hydrogen in the three charge states H^+, H^0, and H^- as a function of the position in GaN/AlN. As follows from the figure, there are three features characterizing the energetics and the spatial distribution of H in a SL: namely, (i) the total energy of the neutral H is constant within both GaN and AlN layers, while E_{tot} of charged H varies linearly with its location due to the electric field; (ii) at interfaces, i.e., between the layers 6 and 7 or 1 and 12, there is a discontinuity in the total energy, which is the segregation energy E_{seg}; and (iii) E_{seg} depends on the charge state of H. The same effects occur for the nitrogen vacancy V_{N}; see Fig. 1(b). In fact, these are universal features of interface segregation, and we discuss them in detail below.

Electric fields.—Electric fields in a AlN/GaN SL act on charged defects by Coulomb forces and give rise to a linear variation of the total energy on the defect's position within AlN or GaN; see Fig. 1. (Neutral defects are not sensitive to the field.) Periodic boundary conditions require that the electrostatic potential is periodic, which in turn implies that the electric fields $\mathcal{E}_A$ and $\mathcal{E}_B$ in the layers A and B of

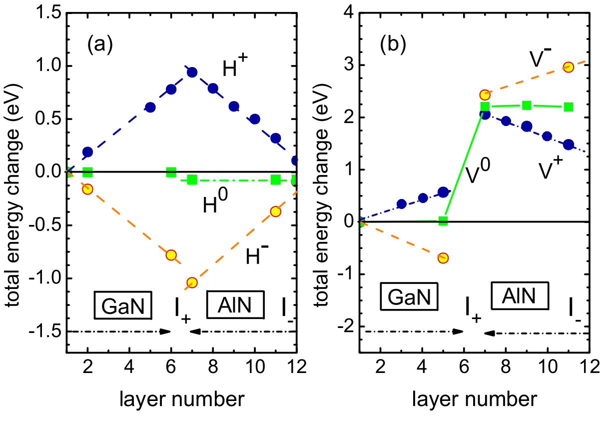

FIG. 1 (color online). Calculated total energy of (a) H^+, H^0, and H^- and (b) V_{N}^+, V_{N}^0, and V_{N}^- as a function of their locations in the $(\mathrm{GaN})_6(\mathrm{AlN})_6$ superlattice. Bilayers 1–6 are GaN and 7–12 are AlN. I_+ is the positively charged interface. The lines are only guides for the eye.

thicknesses L_A and L_B obey the relation $\mathcal{E}_A L_A + \mathcal{E}_B L_B = 0$ [20]. Therefore, the direction of the field changes sign between AlN and GaN. The difference in electric polarization at both sides of an interface and the valence charge accumulated at this interface are linked by Poisson's equation. The sign of the excess charge density alternates at consecutive interfaces, which we label I_+ and I_-, respectively. The electric field leads to an accumulation of H^+ in the vicinity of I_- interfaces and of H^- in the vicinity of I_+. The most interesting case is that of p-doped wurtzite structures; in this case, H^+ accumulates in GaN close to I_- interfaces with $E_{\rm seg}(+) = 0.13$ eV; see Fig. 1(a). The value of the field $\mathcal{E}$ [$\mathcal{E} = \Delta E/(e\Delta L)$, where ΔE is the energy change over the distance ΔL, and e is the elementary charge] deduced from Fig. 1, about 7×10^6 V/cm, agrees with that obtained from material constants given in Ref. [13]. We stress that the predicted accumulation of H close to the appropriate interfaces leads to screening of the field, analogous to free carrier screening. This effect may have an important impact on the electronic states and on both optical and transport properties of GaN/AlN-based heterostructures, which are to a large extent determined by the fields [21].

Diffusion of H in GaN/AlN has an activated character and proceeds by jumps between local minima separated by energy barriers. The presence of a macroscopic electric field leads to left-right asymmetry of barrier heights and, thus, to electromigration. In our case, the migration is driven by *internal*, rather than external, electric fields. This effect is evidenced in Fig. 2, which shows the total energy of H^- as a function of its location along the c axis in one unit cell of AlN. We find that the average barrier is 1.67 eV [22] and that the left barrier is lower than the right one by 0.16 eV.

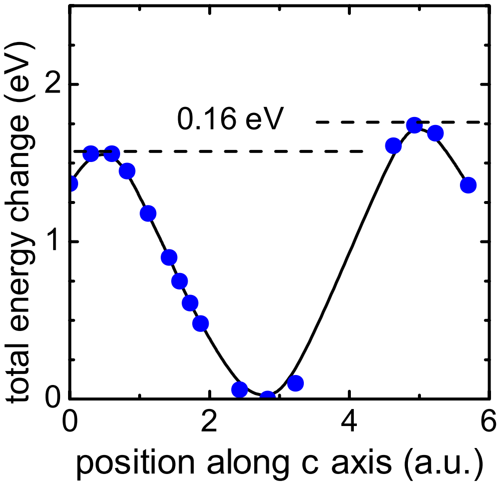

FIG. 2 (color online). Calculated total-energy changes of H^- as a function of its location in the AlN unit cell in the $(\mathrm{GaN})_6 \times (\mathrm{AlN})_6$ superlattice. The lines are only guides for the eye.

Segregation energies.—We begin by analyzing neutral defects. The calculated values of $E_{\rm seg}$ are summarized in Table II. For H^0, we find $E_{\rm seg}(0) = -0.07$ eV in the wurtzite and -0.2 eV in the cubic structure, respectively. The negative sign found for both structures indicates that H^0 has a tendency to accumulate in AlN layers. In contrast, the remaining defects have a tendency to accumulate in GaN layers. From Table II, it follows that this tendency is weak (since $E_{\rm seg}$ is small) for cation-substituting defects (Mg, $\mathrm{Si_{cation}}$, and $V_{\rm cation}$), but it is very pronounced for N-substituting defects ($\mathrm{Si_N}$ and $V_{\rm N}$). This difference is due to the fact that the nearest neighbors of a cation-substituting defect are N atoms at both sides of the interface. Therefore, the number of bonds of all types before and after the segregation does not change, while the segregation of a N-substituting defect, e.g., $\mathrm{Si_N}$, from GaN to AlN changes the number of Si-Ga and Si-Al bonds. This effect is further enhanced by the high bond energies of the nitrides. A similar effect occurs for vacancies in AlGaN and SiGe alloys, which are preferentially terminated by Ga and Ge atoms, respectively [23]. Finally, we note that even a modest $E_{\rm seg}$ value of 0.1 eV leads to defect equilibrium concentration that is 3 times higher in GaN than in AlN at 800 °C.

Dependence of $E_{\rm seg}$ on the defect charge state.—In Table II, we also list the values of $\Delta E_{\rm seg} = E_{\rm seg}(+) - E_{\rm seg}(-)$, the difference between $E_{\rm seg}$ for the positive and negative charge states. For comparison, we have also considered a AlN/GaN (001)-oriented superlattice with GaN and AlN in the zinc-blende structure, where no field is present. We find that $E_{\rm seg}$ of the substitutional dopants and of the vacancies in the two structures are equal to within 0.05 eV. This is due to the same defect coordination in both structures. In contrast, the number and coordination of neighbors of interstitial H differ between the two structures. In this case, the difference in $E_{\rm seg}$ is 0.15 eV.

As follows from Table II, $\Delta E_{\rm seg}$ is about 0.2 eV for the two shallow dopants Mg and $\mathrm{Si_{cation}}$, and it is larger for the defects that induce deep states in the gap (H, $\mathrm{Si_N}$, and both vacancies). The stronger dependence of $E_{\rm seg}$ on the charge state of deep defects is due to two factors: (i) In general, the

TABLE II. Segregation energies $E_{\rm seg} = E_{\rm form}^{\rm AlN} - E_{\rm form}^{\rm GaN}$ and their differences $\Delta E_{\rm seg}$ between positive and negative charge states of the defect [eV].

	$E_{\rm seg}(0)$	$\Delta E_{\rm seg}$
H in wurtzite	−0.07	0.40
H in cubic	−0.2	0.48
Mg	0.05	0.18
$\mathrm{Si_{cation}}$	0.15	−0.15
$V_{\rm cation}$	0.0	0.40
$\mathrm{Si_N}$	2.6	−0.35
$V_{\rm N}$	2.2	−1.55

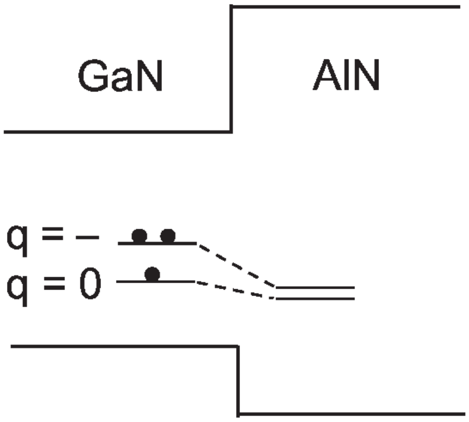

FIG. 3. Schematic of the energy levels of H at a GaN/AlN heterojunction.

energy levels of deep states are different at the two sides of the interface, and (ii) the energy levels depend on the occupation because of the electron-electron interaction. Both features are schematically illustrated in Fig. 3 for H. Hydrogen in the negative and the neutral charge states induces a singlet about 1 eV above the top of the valence band. Consequently, when H migrates from GaN to AlN, the energy of q electrons that occupy this level changes by $\delta = q(\epsilon^{\mathrm{H}}_{\mathrm{AlN}} - \epsilon^{\mathrm{H}}_{\mathrm{GaN}})$. We find that $\delta = E_{\mathrm{seg}}$ to within 0.05 eV for both H^0 and H^-, due to the smallness of the electron-electron interaction. Analogous results hold for the remaining deep defects. Thus, the electronic contribution to the total energy is the dominant factor that determines the charge state dependence of E_{seg}. On the other hand, in the case of a shallow dopant, the electron (or hole) is in the well independently of the defect location in the junction. For this reason, the electronic contribution to the segregation energy is smaller than in the case of deep defects.

In summary, we generalized the theory of semiconductor doping in order to describe segregation and distribution of dopants and defects at heterojunctions. We showed that the profile of dopants depends strongly on the interface, and it cannot be obtained from calculations for bulk components alone. The general features of interface segregation were illustrated by considering H and typical dopants and defects in GaN/AlN. The relative concentration of dopants at both sides of an interface are determined by (i) the dopant charge state and the band offset at the interface and (ii) the atomic site of a dopant or a defect. For example, a cation-substituting dopant has 4 N neighbors in either component of the nitride junction. Therefore, its segregation energy is an order of magnitude lower than that of a N-substituting dopant. Finally, the macroscopic electric fields present in polar structures based on, e.g., (0001)-oriented wurtzite or (111)-oriented zinc-blende crystals lead to field-driven diffusion of H and its accumulation close to the appropriate interfaces. This electromigration screens the electric fields similarly to free carrier screening and, thus, affects the electronic structure of the junction.

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[1] D. B. Laks *et al.*, Phys. Rev. Lett. **66**, 648 (1991).
[2] C. G. Van de Walle *et al.*, Phys. Rev. B **47**, 9425 (1993).
[3] S. B. Zhang and John E. Northrup, Phys. Rev. Lett. **67**, 2339 (1991).
[4] S. M. Hu *et al.*, Phys. Rev. Lett. **67**, 1450 (1991).
[5] N. Moriya *et al.*, Phys. Rev. Lett. **75**, 1981 (1995).
[6] T. T. Fang *et al.*, Appl. Phys. Lett. **68**, 791 (1996).
[7] S. Kobayashi *et al.*, J. Appl. Phys. **86**, 5480 (1999).
[8] Be at InP/InGaAs: W. Haussler, J. W. Walter, and J. Muller, Mater. Res. Soc. Symp. Proc. **147**, 333 (1989); Be and Zn at AlGaAs/GaAs: T. Humer-Hager *et al.*, J. Appl. Phys. **66**, 181 (1989); Zn at InGaAsP/InP: R. Weber *et al.*, J. Electrochem. Soc. **138**, 2812 (1991).
[9] A. Gaymann, M. Maier, and K. Kohler, J. Appl. Phys. **86**, 4312 (1999).
[10] K. Kohler *et al.*, J. Appl. Phys. **97**, 104914 (2005).
[11] S. M. Hu, Phys. Rev. Lett. **63**, 2492 (1989); Phys. Rev. B **45**, 4498 (1992).
[12] M. Buongiorno Nardelli, K. Rapcewicz, and J. Bernholc, Phys. Rev. B **55**, R7323 (1997); F. Bernardini, V. Fiorentini, and D. Vanderbilt, *ibid.* **56**, R10 024 (1997).
[13] O. Ambacher *et al.*, J. Appl. Phys. **87**, 334 (2000).
[14] R. D. Chang, P. S. Choi, and D. L. Kwong, Appl. Phys. Lett. **72**, 1709 (1998).
[15] D. R. Hamann, Phys. Rev. B **40**, 2980 (1989).
[16] E. L. Briggs, D. J. Sullivan, and J. Bernholc, Phys. Rev. B **52**, R5471 (1995); **54**, 14 362 (1996).
[17] The grid spacing is 0.25 a.u. We use a $(\mathrm{GaN})_6(\mathrm{AlN})_6$ superlattice pseudomorphic to a GaN substrate, with the 2 × 2 periodicity in the interface plane. Test calculations for the 3 × 3 in-plane periodicity confirm the convergence with respect to the size of the supercell. Brillouin zone summations are approximated with 2 k points. Equilibrium sites of H in pure GaN and AlN are found using 72-atom supercells and 3 k points. The cubic phase is studied with a $(\mathrm{GaN})_4(\mathrm{AlN})_4$ superlattice with 128 atoms in the ideal unit cell.
[18] J. Neugebauer and C. G. Van de Walle, Phys. Rev. Lett. **75**, 4452 (1995).
[19] A. F. Wright *et al.*, J. Appl. Phys. **94**, 2311 (2003); S. Limpijumnong and C. G. Van de Walle, Phys. Rev. B **68**, 235203 (2003).
[20] J. L. Sanchez-Rojas, J. A. Garrido, and E. Munoz, Phys. Rev. B **61**, 2773 (2000).
[21] B. S. Kang *et al.*, Appl. Phys. Lett. **84**, 4635 (2004).
[22] This value is very close to 1.7 eV obtained for H^- in GaN by S. M. Myers *et al.*, J. Appl. Phys. **88**, 4676 (2000).
[23] P. Bogusławski and J. Bernholc, Phys. Rev. B **59**, 1567 (1999).