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Surface-reconstruction-enhanced solubility of N, P, As, and Sb in III-V semiconductors

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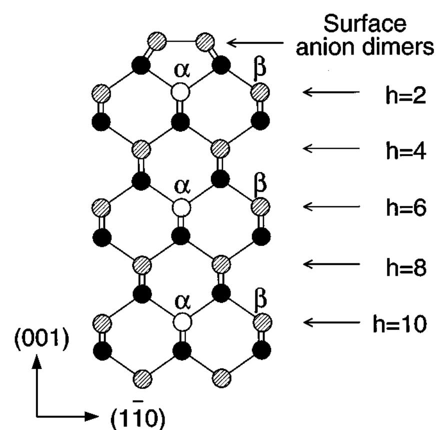
We show that surface reconstructions may play an essential role in determining the equilibrium solubilities of N, P, As, and Sb in various III-V compounds. In particular, anion–anion dimerization of the (001)-$b2(2 3 4)$ surface can enhance the solubility of N near the surface in GaAs, GaP, and InP by five, three, and two orders of magnitudes, respectively, at 1000 K. With certain assumptions on the growth kinetics, this high concentration of N may be frozen in as the crystal grows. © *1997 American Institute of Physics.* @S0003-6951~97!02731-9#

The solubility of nitrogen in III-V semiconductors is a subject of intensive study[1–3] as it holds the key to the success, as well as the limitations for making wide-band-gap GaNAs, GaNP, and InNP materials and devices. Recent vapor-phase growth experiments showed that 1% N can be incorporated into InP at $T5\,310–420\,°C$,[2] 16% N in GaP at $T5\,500–610\,°C$,[3] and 1.6% in GaAs at $T5\,500\,°C$.[1] However, a recent calculation,[4] based on the valence-force-field model[5] showed that the expected *bulk* solubility in these materials is far smaller, being 0.01%, 0.00001%, and 0.0000001% for InP, GaP, and GaAs, respectively, even at a much higher temperature of $T5\,727\,°C$. Thus, the physical origin for the observed high N solubility in these materials is not understood.

In this context, it is important to note that nitrogen, being a first row element, differs from the other Group V elements in that its tetrahedral radius is only 0.75 Å, that is, 29% smaller than the next smallest Group V element, P. The low solubility $n(T)$ of small atoms substituted in *bulk* III-V compounds, stems from the large substitution energy DE_s, reflecting strain.[6] However, it has recently been shown that the solubility of the small first row element, carbon, can be enhanced dramatically near the *surface* of Si.[7] According to a recent calculation,[8] the enhancement can reach five orders of magnitude relative to the bulk solubility. The dramatic increase of the solubility has two reasons: ''surface strain relief'' and ''surface reconstruction'' contributions. *First*, strain is more easily relieved near a surface than in the bulk, since near-surface atoms have more freedom to move. *Second*, surface reconstruction can relieve subsurface mismatch strain. This is illustrated in Fig. 1 that shows schematically an anion-stabilized ~001! surface of a III-V compound, whose main feature is the occurrence of a *surface dimer bond*. In the bulk, two phosphorus atoms are *next* nearest neighbors, but at the surface, when dimerized they become *first* nearest neighbors. Consequently, the anion site directly *under* this strained dimer ~labeled *a*! is under *compression*, while the anion site, above which there are no dimers ~labeled *b*!, feels *tension*. Of course, this subsurface selectivity exerted by surface dimers diminishes as one moves deeper into the film. However, this selectivity implies that if one places, sufficiently close to the surface, small solute atoms ~e.g., N! at the *a* site, and larger ~solvent! atoms at the *b* site, the overall strain energy DE_s will be reduced, so the solubility $n(T)$ will rise. The mechanism of reconstruction-enhanced solubility is similar to that producing CuPt-like ordering in $GaInP_2$,[9,10] where Ga ~In! atoms occupy *a*-like ~*b*-like! sites under the P–P dimer, except that unlike GaAs:N, here the concentration of the ''solute atom'' can reach 50%.

In this letter we will calculate the substitution energy $DE_s^{(h)}(AC{:}B)$ of an A atom by a B atom in the h-th subsurface layer of a binary $AC(001)$ film. Our discussion follows the same spirit of Ref. 8. We will assume simplistically the same, geometric, $2 3 1$ reconstruction for all III-V compounds, so as to illustrate generic surface effects versus bulk effects. Since, however, the real surface reconstruction modes of InP[11] differ from GaAs,[12] we expect that the calculated trends between different solvent semiconductors will be only qualitative. We will consider nine cases—GaAs:N, GaAs:P, GaAs:Sb, InP:N, InP:As, InP:Sb, GaP:N, GaP:As, and GaP:Sb, where the host material ~solvent! is shown on the left, while the dopant ~solute! is indicated on the right. We find that while in the *bulk*, the solvent-to-solute size mismatch tends to *increase* the substitution energy and *reduce* solubility, at the dimerized *surface*, size mismatch may actually *lower* the substitution energy near the surface and *enhance* solubility.

The substitution energy is modeled here by the valence force field approach. The impurity-host bond energy of



chemical origin is ignored. This is reasonable because (i) the chemical energy is not sensitive to height h and (ii) only the (small) second difference of the chemical energy enters the calculation of the equilibrium impurity concentration $n(T,h)$. For $X = n(T,h)/A \ll 1$, we have

$$n(T,h) = A e^{-\Delta E_s^{(h)}/kT}, \qquad (1)$$

where A is the number of substitution sites, $\Delta E_s^{(h)} = E_{\mathrm{strain}}^{(h)} + \Delta E_{\mathrm{chem}} - (\mu_i - \mu_h)$ with $E_{\mathrm{strain}}^{(h)}$ being the strain energy, ΔE_{chem} is the difference between the chemical energy of the impurity (i) and that of the host atom (h) being removed, and the μ's are the chemical potentials. For simplicity, we consider here only the case of substituting impurity *molecules* into the host, e.g., substituting GaN molecules from a bulk GaN reservoir into GaAs, so the chemical potentials here are those of bulk GaN and bulk GaAs, respectively. Thus, $(\mu_i - \mu_h)$ is also a chemical energy difference between the impurity and the host molecules in their respective bulk, and $\delta\Delta E = \Delta E_{\mathrm{chem}} - (\mu_i - \mu_h)$ is the second difference in chemical energy. First-principles linearized augmented plane wave calculation[13] showed that $\Delta E_s^{\mathrm{bulk}} = 1.9$ eV versus our strain-only energy of 1.8 eV for GaAs:N, thus $\delta\Delta E \approx 0.1$ eV. Since we neglect all other choices of the chemical potentials, only the *lower bound to the solubility limit* is obtained.

We minimize the $E_{\mathrm{strain}}^{(h)}$ (consisting of bond bending and bond stretching) with respect to all atomic displacements, subject to the constraint that surface dimers are fixed. Contributions from fixed dimer atoms are omitted from the energy $E_{\mathrm{strain}}^{(h)}$. Comparisons with first-principles results for GaInP alloy showed[9,10] that this omission is a valid approximation. The dimer geometry for GaAs is obtained from self-consistent first-principles pseudopotential calculations[14] and for GaP and InP, the dimer geometries are obtained by scaling the pseudopotential results for GaP and InP films coherently strained on a GaAs substrate.[15] We use as input to the calculations the bulk bond lengths and bond bending/bond stretching force constants determined from first-principles pseudopotential calculations for GaAs, GaP, and InP.[9] Because of the lack of pseudopotential force constants for GaN and InN, we used instead $\alpha_{\mathrm{GaN}} = 81.01$ N/m and $\beta_{\mathrm{GaN}} = 18.01$ N/m and $\alpha_{\mathrm{InN}} = 70$ N/m and $\beta_{\mathrm{InN}} = 8.06$ N/m, derived from measured elastic constants using the formula of Martin.[16] This yields $\Delta E_s[\mathrm{GaAs:N}] = 1.78$ eV/N, compared with $\Delta E_s = 1.70$ eV/N obtained with the recent local-density approximation derived force constants.[17] Our calculated nitrogen *bulk* solubilities at $T = 727\ ^\circ\mathrm{C}$ (Table I) are in reasonable agreement with the results of Ref. 4.

Figure 2 shows the calculated impurity substitution energies $\Delta E_s^{(h)}(X)$ as a function of its height h below the surface layer for N, P, As, and Sb impurities in GaAs, InP, and GaP, respectively. We have used in these calculations a 4×4 surface cell $(X = 6.25\%)$, so the nearest impurity–impurity distance is $2\sqrt{}a_0$ where a_0 is the bulk lattice constant. We observed the following:

Trends with vertical and lateral impurity positions: The substitution energy is a strong function of the height h of the impurity below the surface: Taking GaAs:N as an example, at $h = 2$, the N-to-As substitution energy (with nitrogen in the α site) is only 0.7 eV, while deeper in the film ($h = 10$, which is bulklike) it is ≈ 1.8 eV. There is thus a reduction of 1.1 eV if an N atom is brought from the bulk to the surface. There are two underlying physical reasons for this:[8] strain relief near the surface and surface reconstruction. The former occurs since the surface is always free to relax along its normal. This lowers the substitution energy by a moderate 0.4 eV [see the dotted line in Fig. 2 giving $\Delta E_s^{(h)}$ for *unreconstructed* surfaces]. Surface reconstruction lowers the substitution energy by another 0.7 eV. Near the surface, the N atoms are also very site selective: for $h = 2$, it takes 1.7 eV to move a nitrogen atom from the α site to the β site, hindering N diffusion across the dimer rows. There is a significant repulsion between the strain fields produced by different N atoms in a given subsurface layer h. This is shown in Fig. 3 illustrating the substitution energy $\Delta E_s^{(h=2)}(X)$ as a function of the lateral nitrogen concentration X in this layer. We see that the substitution energy per atom versus X fits well into a

is. Thus, the substitution energy is largest for N