Dual-Surfactant Effect to Enhance *p*-Type Doping in III-V Semiconductor Thin Films

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Surfactant effects are usually achieved by the addition of a single surface element. We demonstrate by first-principles calculations a dual-surfactant effect of Sb and H on enhancing Zn doping in organometallic vapor phase epitaxially grown GaP thin films. The combined effects of Sb and H lower significantly the doping energy of Zn in GaP, while neither Sb nor H can function alone as an effective surfactant. Our finding suggests a general strategy for enhancing *p*-type doping of III–V semiconductors by using a metallic-element with H as dual surfactants.

Surfactants have been widely used in epitaxial growth, as an effective "additional" parameter, to control the thin film microstructure, composition and morphology and hence to improve the thin film properties and device performance. The surfactant effects may manifest in various forms, including modifying growth mode [1–3], reducing interface roughness [4], suppressing interface alloy intermixing [5], and enhancing the doping of semiconductors [6–9]. Different physical mechanisms may underlie different surfactant effects, as a surfactant can change growth thermodynamics, such as surface energy and reconstruction [1,5], as well as kinetics, such as surface diffusion [2] and step-edge barrier [3].

A surfactant is defined as an element that floats on top of the growing film surface. (In rare cases, it may also stay in the subsurface region [7].) The role of surfactant is usually considered to be achieved by one single foreign surface element that is different from the film. Here, we introduce a new "dual-surfactant" effect, for which the role of surfactant can only be achieved by the combined effects of two foreign surface elements while neither of the two can act alone as an effective surfactant. We will demonstrate the dual-surfactant effect for the case of enhancing *p*-type doping in III–V semiconductors. The doping of high band gap semiconductors has been a challenging problem for many years. Recently, it has been shown that the use of surfactants provides an effective method for doping of semiconductors [6–9]. Specifically, Sb has been used to enhance doping of Zn into GaInP [8,9]. However, the underlying doping mechanisms remain unclear. An interesting point is that H was observed to be coincorporated with Zn [8,9]. This has led to the postulate that H may also play a role along with Sb in the doping process.

We have carried out extensive first-principles calculations of Zn incorporation in the (001) GaP films under the influence of surface Sb and H. We found that Sb alone has little effect on the doping energy of Zn in GaP, and it is only when H is also present that the Zn-doping energy is substantially lowered by Sb. Also, surface H does not function as effectively alone without Sb. Thus, it is the combined effect of Sb and H that makes the Zn-doping process thermodynamically favorable, manifesting a unique dual-surfactant effect.

Our calculations were performed using the VASP code [10] within the local density approximation. We model the GaP (001) films by the common supercell slab technique [11] consisting of 4 layers of Ga and 5 layers of P atoms, plus a 12.8 Å vacuum layer. The bottom two atomic layers were fixed at their bulk positions with the last layer of Ga passivated by $\frac{3}{4}$ charged H. We used a plane wave cutoff energy of 340 eV and a $4 \times 4 \times 1$ *k*-point mesh for Brillouin zone sampling. Total energy minimization was performed until the atomic forces converged to less than 0.1 meV/Å. The Zn-doping energy was modeled by replacing one Ga atom in the second (Fig. 1) or fourth (Fig. 2) atomic layer with a Zn atom. The effect of surfactant Sb was modeled by replacing surface P dimers with Sb dimers. And the effect of H as the second surfactant was further studied by introducing different concentrations and configurations of H on the surface. The doping energy is defined as

$$\Delta E_{\text{doping}} = E_{\text{doped}} - E_{\text{undoped}} + \mu_{\text{Ga}} - \mu_{\text{Zn}}, \quad (1)$$
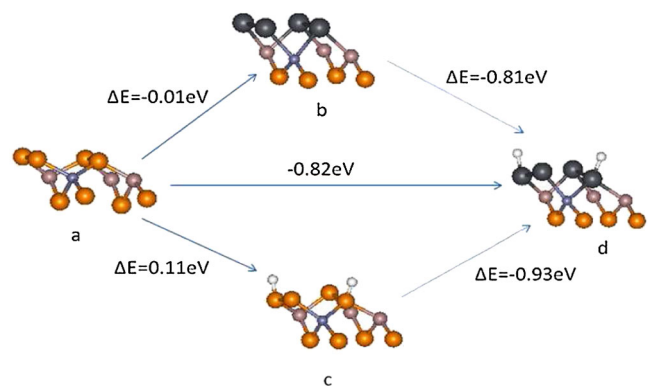

FIG. 1 (color online). Schematic illustration of various doping configurations, with one Zn atom replacing a Ga atom in the second atomic layer. ΔE indicates the change of doping energy from one configuration to another indicated by the arrows. Largest black sphere: Sb; Large orange sphere: P; medium wine sphere: Ga; small blue: Zn; smallest white sphere: H.
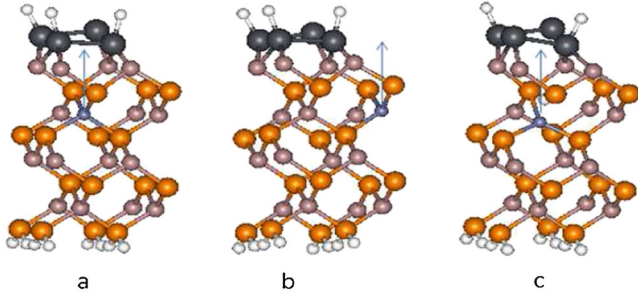
FIG. 2 (color online). Ball and stick schematic illustration of one Zn atom doped in the fourth atomic layer (the second cation layer). Atom labels are the same as in Fig. 1. (a) Zn atom doped at the site in between two surface dimers with 3 surface H. (b) Zn atom doped at the site below a surface dimer with 3 surface H. (c) Zn atom doped at the site below a surface dimer with 2 surface H and 1 bulk H next to Zn. (The arrows indicate the position of the zinc atom relative to the surface dimer).

where $E_{\text{doped}}(E_{\text{undopaed}})$ is the total energy of the doped (undoped) system; μ_{Ga} (μ_{Zn}) is the chemical potentials of Ga (Zn). In general, μ_{Ga} may vary from $\mu_{\text{Ga}}[\text{bulk}] + \Delta H_f[\text{GaP}]$ (the P-rich condition) to $\mu_{\text{Ga}}[\text{bulk}]$ (the Ga-rich condition) [12], where $\Delta H_f[\text{GaP}]$ is the GaP enthalpy of formation; μ_{Zn} equals $\mu_{\text{Zn}}[\text{bulk}]$. In calculating the change of doping energy due to surfactant Sb, μ_{Ga} and μ_{Zn} would not appear. In the case of H, the doping energy depends on the chemical potential of H (μ_{H}) if one additional H is added to the system upon doping. We have used the typical value of $\mu_{\text{H}} = -2.26$ eV, one-half of the energy of an H_2 molecule [12].

The typical reconstruction of clean (001) III/V semiconductor surfaces is (2×4) [13]. However, under organometallic vapor phase epitaxial (OMVPE) growth conditions, the presence of H on the surface, from decomposition of the P precursor via the pyrolysis process, converts the surface into a (2×2) reconstruction as observed by STM at room temperature [14], which was deduced to have 1 H attached to each surface dimer [14] to satisfy the electron counting rule (ECR) [15]. Therefore, we have used the (2×2)-reconstructed surfaces in our calculations. We expect that our results and physical interpretations are generally applicable, at least qualitatively, to other surface reconstructions of III/V films terminated with group-V dimers and H.

As a reference, we first calculated the Zn-doping energy in bulk GaP and obtained $\Delta E_{\text{bulk}} = 2.74$ eV $+ \mu_{\text{Ga}} - \mu_{\text{Zn}}$. Then, we calculated the Zn-doping energy in the surface positions of a clean GaP (001) film, by replacing the Ga in the second layer, as illustrated in Fig. 1(a). We obtained $\Delta E_{\text{2nd}}^P = 2.57$ eV $+ \mu_{\text{Ga}} - \mu_{\text{Zn}}$, where superscript "P" denotes P-terminated surface and subscript "2nd" denotes Zn dopant position in the second layer. We found the presence of the surface lowers the doping energy slightly by about 0.17 eV in reference to bulk.

Next, we investigated the surfactant effect of Sb. In experiments, Sb was introduced continuously during OMVPE growth [8,9]. It stays on top of the surface replacing P surface dimers, due to its large atomic size and lower dangling bond energy, which has been demonstrated by surface photo reflection spectra [16] and first-principles calculations [17]. Thus, in our calculations we replaced surface P dimers with Sb dimers. Without H [Fig. 1(b)], we obtained $\Delta E_{\text{2nd}}^{\text{Sb}} = 2.56$ eV $+ \mu_{\text{Ga}} - \mu_{\text{Zn}}$. Importantly, we found that the Zn-doping energy with Sb surface dimers is almost the same as that with P dimers, Fig. 1(a) vs 1(b). This indicates that Sb alone does not significantly enhance Zn doping of GaP.

H is inevitably present on the GaP surface during OMVPE growth. Experiments have indicated significant concentrations of H incorporated into the GaP epitaxial film and formation of Zn-H and C-H complexes [8], suggesting that H may play an important role in the process of dopant incorporation. Fundamentally, from a thermodynamic point of view, one significant role H will play is to help the surface satisfy the ECR [15]. Note that the clean GaP(001)-(2×2) model surfaces we discussed above as a reference state does not satisfy the ECR.

The simplest way for the GaP(001)-(2×2) surface to satisfy the ECR is to add 1 H on each surface dimer on the alternating side, as shown by our calculations to have the lowest energy. The situation remains the same with surfactant Sb [see Fig. 1(d)], as Sb is isoelectronic with P. Thus, to investigate the role of H, we calculated the Zn-doping energy with surface H. First, we test the situation with surface H without Sb. Assuming the H coverage remained the same, with 2H/cell before and after Zn incorporation, we found $\Delta E_{\text{2nd}}^{\text{P}-2\text{H}\rightarrow 2\text{H}} = 2.68$ eV $+ \mu_{\text{Ga}} - \mu_{\text{Zn}}$. The doping energy with 2H/cell is 0.11 eV higher than the case without H, Fig. 1(a) vs Fig. 1(c). This gives us another important indication that without Sb, H alone does not enhance the doping. We believe that this is largely because the ECR is satisfied before doping but violated after doping.

Next, we investigated the combined effects of Sb and H. Assuming again a surface covered with 2H/cell before and after Zn incorporation, we found $\Delta E_{\text{2nd}}^{\text{Sb}-2\text{H}\rightarrow 2\text{H}} = 1.75$ eV $+ \mu_{\text{Ga}} - \mu_{\text{Zn}}$. Clearly, the Zn-doping energy is substantially reduced, by 0.81 eV, relative to the bare Sb-terminated surface without H from Figs. 1(b)–1(d) and by 0.93 eV relative to the H-covered P-terminated surface without Sb from Figs. 1(c) and 1(d). This observation illustrates the intriguing dual-surfactant effect of Sb and H: the two work together in a constructive manner in terms of lowering the Zn-doping energy, while they do not lower the Zn-doping energy individually.

The above results indicate that the surfactant effect of Sb is only realized when surface H is also introduced. The underlying physical reason giving rise to the effect of Sb is probably due to the lower electronegativity of Sb in comparison with P. In a similar spirit to the generalized ECR in the semiconductor surface with metal elements proposed recently [18], Sb is more metallic than P, so that Sb can

serve more effectively as an electron reservoir to accommodate the redistribution of electrons when a p-type dopant is present. Since the p-type dopant will violate the ECR by having one less electron, it is easier for Sb than for P to accommodate the missing electron in order to "partially" satisfy the ECR.

The ECR is violated after Zn is doped if the surface remains with 2 H. In order to resatisfy the ECR, one more H has to be added. This indicates that the Zn-doping process is possibly accompanied by H incorporation. To quantify the role of the extra H, we calculated the Zn-doping energy by assuming the surface covered with 2 H before but with 3 H after doping [see Figs. 3(b) and 3(c) below]. We found that $\Delta E_{2\text{nd}}^{\text{Sb}-2\text{H}\rightarrow3\text{H}} = -0.63$ eV $+ \mu_{\text{Ga}} - \mu_{\text{Zn}} - \mu_{\text{H}} = 1.63$ eV $+ \mu_{\text{Ga}} - \mu_{\text{Zn}}$. Clearly, by adding an extra H after doping to satisfy the ECR, the doping energy can be decreased further depending on the H chemical potential (μ_{H}).

So far, we have shown the dual-surfactant effect of Sb and H in enhancing the Zn doping in the second atomic layer, i.e., the surface position. Next we examine the possibility of Zn doping into the fourth atomic layer, i.e., the subsurface or "bulk" positions. Based on the above results, we will focus only on the Sb-terminated surface with 2 H before and 3 H after Zn doping. We consider two possible configurations: one with Zn doped in the fourth atomic layer in between two surface Sb dimers [Fig. 2(a)] and the other below the surface Sb dimer [Fig. 2(b)]. The respective doping energies are $\Delta E_{4\text{th,between}}^{\text{Sb}-2\text{H}\rightarrow3\text{H}} = 1.72$ eV $+ \mu_{\text{Ga}} - \mu_{\text{Zn}}$ and $\Delta E_{4\text{th,below}}^{\text{Sb}-2\text{H}\rightarrow3\text{H}} = 1.80$ eV $+ \mu_{\text{Ga}} - \mu_{\text{Zn}}$. The 0.08 eV difference between the two reflects the dependence of Zn-doping energy on the "atomic-level" stress at these sites [19] and Zn is slightly favored at the tensile sites between surface dimers relative to the compressive sites directly below surface dimers.

Lastly, we have investigated the codoping of Zn and H into GaP. Experiments observed that complexes of Zn, P, and H form during doping of Zn in GaP [20]. This suggests some H atoms do not always remain on the surface, but go into the bulk. To examine this possibility, we have calculated the energies associated with 1 H incorporation into

the bulk with Zn, and determined the Zn-P-H complex structures. Figure 2(c) shows the doping of a Zn atom in the subsurface (or bulk) position along with an H atom next to it. There will be two H atoms remaining on the surface [in comparison to 3 H in Fig. 2(b)], so that the ECR is still satisfied.

When a surface H goes into the bulk, it changes the Zn bonding configuration in forming a Zn-P-H complex. Without H, the Zn bonds with 4 neighboring P atoms in an $sp3$ hybridization [a tetrahedral structure, Fig. 2(b)]. With the extra H, one Zn-P bond is broken to form a P-H bond, and the Zn bonds with 3 neighboring P atoms in an $sp2$ hybridization [a planar structure, Fig. 2(c)]. This can also be explained by the ECR. The Zn provides two valance electrons and the H provides one. For both P-H and P-Zn bonds, it takes $\frac{3}{4}$ electrons, so their sum gives 3 electrons total to satisfy the ECR. Thus, when H is codoped with Zn, it changes the Zn bonding configuration from $sp3$ to $sp2$ hybridization, forming three Zn-P bonds plus an empty orbital.

The codoping of H with Zn into bulk is also found energetically favorable. The doping energies at the bulk positions forming the Zn-P-H complex are calculated to be $\Delta E_{4\text{th,between}}^{\text{Sb}-2\text{H}\rightarrow1\text{bulkH}} = 1.40$ eV $+ \mu_{\text{Ga}} - \mu_{\text{Zn}}$ for the sites in between surface dimers, and $\Delta E_{4\text{th,below}}^{\text{Sb}-2\text{H}\rightarrow1\text{bulkH}} = 1.64$ eV $+ \mu_{\text{Ga}} - \mu_{\text{Zn}}$ below surface dimers. Both are lower by 0.2–0.3 eV than the corresponding cases with all three H atoms remaining on the surface. This suggests that there exists a thermodynamic driving force for one H atom to go into the bulk with Zn, i.e., codoping of Zn with H. On the other hand, it is known that H would compensate Zn in bulk GaP, mitigating the doping effect [21,22]. To activate the acceptor, annealing can be done after the doping process to remove the H [21,22]. In other words, the codoped H must be removed after it serves its purpose to assist the Zn incorporation.

Now, based on all the above calculations, we postulate a plausible complete Zn-doping process in GaP driven by the dual-surfactant effect of Sb and H, as illustrated in Fig. 3. The doping of Zn in the original P-terminated surface covered with 2 H is shown in Fig. 3(a). In the first step,
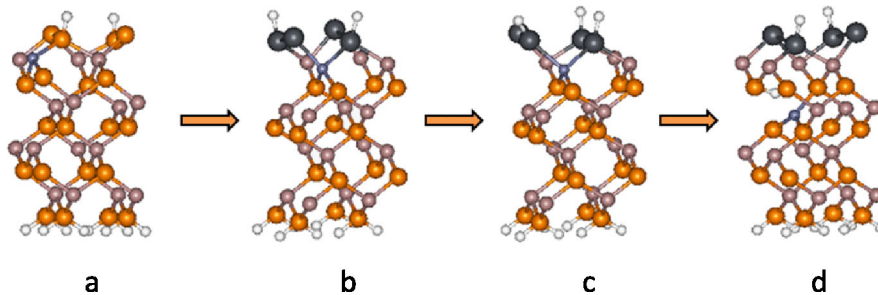

a   b   c   d

FIG. 3 (color online).   Schematic illustration of a plausible doping process, with one Zn atom replacing a Ga atom in GaP film. Atom labels are the same as in Fig. 1. (a) Zn doped into the second atomic layer with surface P dimers. (b) Zn doped into the second atomic layer replacing Ga with surface Sb dimers. (c) One additional H is added onto the surface to resatisfy ECR. (d) H codoped with Zn into bulk to form a Zn-P-H complex.
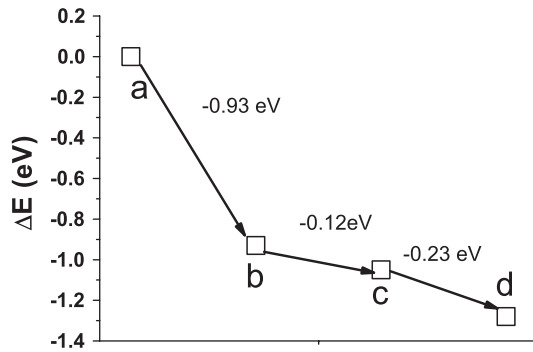
FIG. 4.   Change of doping energy at each corresponding step as shown in Fig. 3.

with the Sb replacing the P dimers, a Zn atom is doped at the second atomic layer [Fig. 3(b)], where in assisting the doping process, 2 surface H plays the role to satisfy ECR before doping and the Sb plays the role by providing an electron reservoir to accommodate the redistribution of electrons when the ECR is violated after doping. In the second step, one additional H is added to the surface [Fig. 3(c)] to further assist the doping process by adding one more electron to resatisfy the ECR. In the third step, the Zn atom goes into the bulk and replaces a Ga atom in the fourth or lower atomic layers, and at the same time, a surface H goes together with Zn into the bulk as a codopant to form a Zn-P-H complex, as shown in Fig. 3(d), where the ECR is satisfied both at the surface and in the bulk at the complex site.

Figure 4 shows the energy landscape corresponding to the proposed doping steps in Fig. 3. Our theoretical picture of dual-surfactant effect and its underlying physical mechanism based on the ECR is qualitatively consistent with the experimental observation of both the enhanced Zn doping with Sb introduction during OMVPE growth and the coincorporation of H with Zn [8,9]. However, because the computation is limited to small cell size, we can only calculate a few representative cases of surface structures, surface coverage, and dopant concentrations. Therefore, the actual energy values may vary with these conditions and should be treated with caution, but the overall trend of the calculated energy changes is expected to be generally correct. Also, other effects, such as temperature and kinetic rates of atom exchange and incorporation, need to be taken into account in the future study in order to obtain a more complete picture of the dual-surfactant effect. For example, from the energy scales shown in Fig. 4, temperature is expected to have a lesser effect on the Zn-doping energy (1.0 eV in step 1) than on the H codoping energy (0.2 eV in step 3). However, temperature changes surface H coverage which will in turn affect doping energy. The kinetic barriers associated with each step of the process are also expected to be important.

In conclusion, we have discovered an interesting dual-surfactant effect of Sb and H for Zn-doping enhancement. The dual surfactant with two surface elements will greatly broaden the scope and application of the conventional surfactant effect with one surface element. Specifically, in order to accommodate the p-type (Zn) dopant incorporation, the role of first surfactant Sb (a "metallic" element) is to provide an electron reservoir to redistribute electrons, while the role of second surfactant H (a "single electron") is to add one electron by each H to help satisfy the ECR. We believe the dual-surfactant effect we disclose here can be used as a general strategy for enhancing p-type doping of III–V semiconductors.

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