

Enhancing dopant solubility via epitaxial surfactant growth

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A general concept for enhancing dopant solubility via epitaxial surfactant growth is proposed. The key of the concept is to find the appropriate surfactants that generate high (low) levels that can transfer electrons (holes) to dopant acceptor (donor) levels in p -type (n -type) doping, thus significantly lowering the formation energy of dopants. Using first-principles density-functional calculations, our concept explains excellently the recently discovered dual-surfactant effect of Sb and H on enhancing Zn doping in epitaxially grown GaP(100) thin film and suggests that sole surfactant Te can also induce enhancement of N solubility in ZnSe(100) film. We also proposed the surfactants for enhancing p -type doping of ZnO with epitaxial growth with (000 $\bar{1}$) surface. General rules for selecting surfactants for enhancing both p -type and n -type dopings are provided.

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Most wide band-gap (WBG) semiconductors experience a serious doping asymmetry problem, i.e., they can be easily doped either p type or n type, but not both.^{1,2} This doping asymmetry problem has hindered the potential applications of many WBG materials. The limited dopant solubility, i.e., the high-formation energy of dopants in host systems, is one of the critical issues that causes the doping asymmetry problem. Therefore, significant efforts have been paid on how to enhance dopant solubility in WBG semiconductors. For example, it is proposed that dopant solubility may be enhanced by appropriate selection of chemical potentials of host elements and dopant sources,³ the passive donor-acceptor codoping,⁴ and the hydrogen-assisted doping.⁵ Recently an interesting dual-surfactant effect of Sb and H on enhancing Zn doping in organometallic vapor-phase epitaxially (OMVPE) grown GaP thin films has been reported.^{6,7} It was found that the solubility of Zn in GaP can be significantly enhanced when both surfactants Sb and H are available in the growth process. First-principles calculations have shown that H presented in the OMVPE processes plays a cooperative role with surfactant Sb in reducing the formation energy of Zn substitutionals (Zn_{Ga}) in the sublayer of the growth front.⁸ It was also suggested that such dual-surfactant effects may be a general strategy for enhancing p -type doping in III-V semiconductors. On the other hand, it has been reported that adding a small amount of Te in the growth can enhance hole-carrier densities of doped ZnSe for the (100) epitaxial growth.^{9,10} However, it is not clear if the dual-surfactant effect observed in III-V system is related to the effect of Te in II-VI systems and what are the principle guidelines for choosing the appropriate surfactants or surfactant pairs.

In this Brief Report, we propose a general concept for enhancing dopant solubility via epitaxial surfactant growth. In this concept, the surfactants generate high (low) levels that can transfer electrons (holes) to dopant levels in p -type (n -type) doping, thus significantly lowering the formation energy of dopant incorporation in the surface region near the growth front. Based on this concept and first-principles calculations, we are able to explain the physical origin of the dual surfactant of Sb and H in enhancing Zn solubility in GaP. Our understanding of the concept suggests that the need of hydrogen as a second surfactant is not an absolute require-

ment but rather depends highly on materials system and surface structure. In general, H as a second surfactant is needed only when extra electron (hole) is needed to occupy (empty) the original surfactant level. Our results, thus, explain why sole Te can be used as surfactant to enhance acceptor N_{Se} solubility in ZnSe for the (100) epitaxial growth. We further suggest surfactants for enhancing p -type doping of Ag_{Zn} in ZnO via epitaxial growth.

The calculations are based on the density-functional theory (DFT) as implemented in the VASP code.¹¹ We used the projector-augmented wave method with LDA potentials.¹² The GaP(100) surface is modeled by a supercell of 2×2 in x - y plane. Along z axis, the simulation slab includes five double layers of GaP and a vacuum of ~ 14 Å of which the bottom Ga layer is fixed and passivated by pseudohydrogen. Unlike the 2×4 reconstruction of a clean surface, the GaP(100) surface is favored by a 2×2 reconstruction during the OMVPE due to the existence of H that passivates the dangling bonds on P -terminated surface.^{13,14} The cut-off energy used for the plane-wave basis set is 280 eV and the integration in the Brillouin zone is done with a $4 \times 4 \times 1$ k -point mesh. The calculated equilibrium lattice constant for GaP is 5.425 Å (experiment: 5.48 Å). In order to get the relative positions of the surface and defect states, the $1s$ core levels of the bulk, such as Ga atoms in various structures are aligned up. The defect formation energies for the incorporation of Zn at surface are calculated using

$$\Delta E_f = E_{tot} - (E_s - \mu_{Ga} + \mu_{Zn}), \quad (1)$$

where E_{tot} is the total energy of the surface with Zn_{Ga} substitution; E_s is the total energy of the reference surface, i.e., the structure without Zn incorporation; and μ_{Ga} (μ_{Zn}) is the chemical potential of Ga (Zn). In this study, the formation energies rely on the chemical potentials but they contain the same term ($\mu_{Ga} - \mu_{Zn}$) so that the calculated formation energies for different surfaces can be compared directly. For the calculations of ZnO(000 $\bar{1}$) and ZnSe(100) surfaces, similar methods are employed.

The general concept for enhancing dopant solubility via epitaxial surfactant growth is schematically described in Fig. 1. It is known experimentally that the surfactants in epitaxial

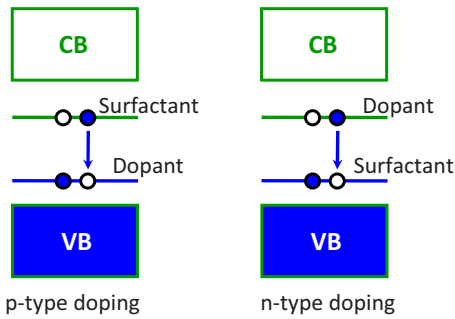


FIG. 1. (Color online) Band diagrams showing the concept of enhancement of dopant solubility via epitaxial growth with appropriate surfactants. Hollow and filled circles represent empty and filled electronic states, respectively. The arrows indicate the routes of charge transfer.

growth float on the top surface of the growth front.^{15,16} The enhancement of dopant solubility initiates in the sublayers below the surface. For *p*-type doping, dopants introduce acceptor levels with holes near the valence-band minimum (VBM) of the host system. On the other hand the surfactants on the growth surface will introduce surfactant levels. If the surfactant levels are higher in energy than the acceptor levels and have electrons available, the surfactants will donate the electrons to the acceptors and consequently leads to a Coulomb binding between the surfactant and the dopant. Such charge transfer reduces the energy of the system and consequently leads to effective reduction in the formation energy of dopant incorporation in the host. The formation energy reduction is large if the energy-level difference between the surfactant and acceptor levels is large. The same principle holds for *n*-type doping except that the charge transfer is from dopant level to empty surfactant level. In this case, the positions of dopant levels are close to the conduction-band minimum and the surfactant levels must be lower in energy than the dopant levels. Thus, the key for this concept is how to ensure that the surfactant levels are higher (lower) in energy than the dopant levels and there are indeed electrons (holes) in the surfactant levels in *p*-type (*n*-type) doping. We will see below that this depends highly on the selection of surfactants and the surface structure. In some cases, assistance from H is required to provide the needed electrons or holes.

We first show how this concept explains the recently reported dual-surfactant effect of Sb and H in enhancing Zn solubility in GaP, a case that requires the assistance of H. The growth front is GaP(100) surface, whose structure is well understood. In OMVPE the surface is terminated by P atoms and form P-P dimers.^{13,14} In a 2×2 surface supercell there are two dimers, as shown in upper panel of Fig. 2(a). This surface does not satisfy the electron-counting rule (ECR) and therefore produce one fully occupied surface state and one empty surface state. This is clearly seen from our calculated density of states (DOS), as shown in the middle panel of Fig. 2(a). The lower panel of Fig. 2(a) shows the schematic of the calculated surface levels. When surfactant Sb is presented in the growth, P atoms on (100) surface are replaced by Sb atoms, as shown in upper panel of Fig. 2(b). It is known that Sb 5*p* orbitals are significantly higher in

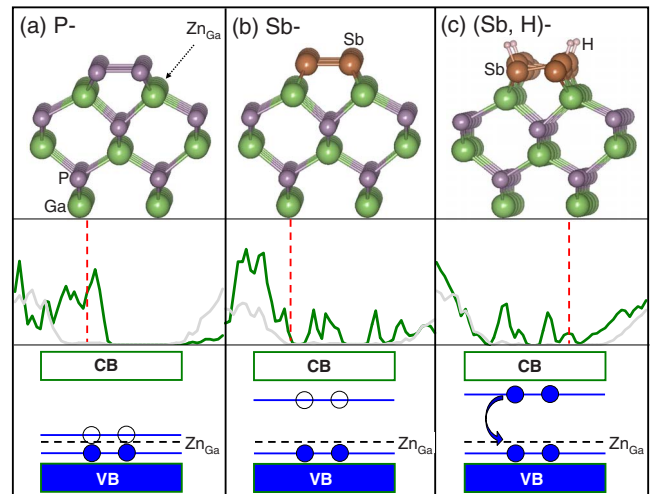


FIG. 2. (Color online) Structure, calculated DOS, and schematics of single-electron energy levels for P-, Sb-, and (Sb, H)-terminated GaP(001) surfaces. In the DOS the green curves (heavy) are for the surface atoms and the gray curves (light) are for the bulk atoms far away from the surface (the same is for Figs. 3 and 4). The red dashed lines indicate the highest occupied positions.

energy than the P 3*p* orbitals and the atomic size of Sb is larger than that of P. Thus, the replacement is expected to change the surface-energy levels in the band gap. The middle panel of Fig. 2(b) shows the calculated DOS of the (100) surface terminated with Sb dimers. The fully occupied surface state is still close to the VBM. However, the unoccupied surfactant state is much higher in energy due to the nature of Sb 5*p* orbital. The schematic of the calculated surface levels is given in the lower panel of Fig. 2(b). When both Sb and H are available in the growth, H atoms terminate the dangling bonds on Sb, as shown in the upper panel of Fig. 2(c). H atoms will transfer their electrons to the unoccupied surfactant levels. The middle panel of Fig. 2(c) shows the calculated DOS of the (100) surface with Sb dimers and H atoms. The schematic of the calculated surface levels are given in the lower panel of Fig. 2(c).

The above calculation explains very well conceptually why only the dual surfactant of Sb and H can enhance Zn solubility in the epitaxial growth. When Zn atoms are incorporated into GaP, they produce acceptor levels above the VBM of GaP (indicated by Zn_{Ga}). For both P- and Sb-terminated surfaces, the surface states with filled electrons are very close to the acceptor level. There is not much charge transfer between the surface states and acceptor levels and therefore no enhancement on Zn solubility would be observed with sole Sb-terminated surface. Apply H alone in the growth will also not help much the dopant solubility. This is because P dangling-bond states are low in energy. When H atoms passivate and fill the upper empty dangling-bond states, it can even lower the energy level of the surface states (not shown), thus, again not much charge transfer to Zn_{Ga} acceptor levels is realized. Therefore apply H alone would not enhance Zn solubility in GaP, as observed experimentally. However, when both Sb and H are simultaneously available, the high-energy surfactant levels are filled with electrons, which will transfer to Zn_{Ga} acceptor levels and

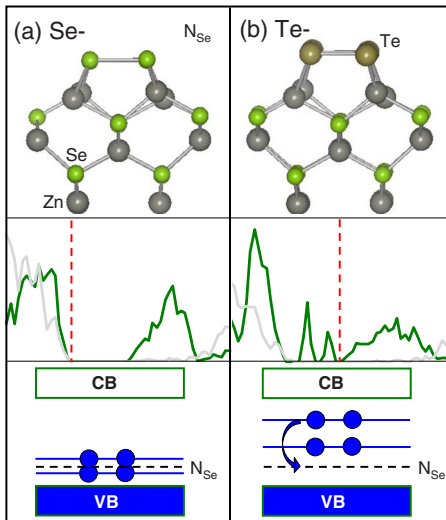


FIG. 3. (Color online) Structure, calculated DOS, and schematics of single electron energy levels for Se- and Te-terminated ZnSe(001) surfaces. The red dashed lines indicated the positions of highest occupied levels.

lower significantly the formation energy of Zn_{Ga} . Consequently, the dual surfactant of Sb and H enhances Zn solubility in GaP. Here, Sb and H play cooperative roles: the high-energy Sb $5p$ orbitals provide the high-energy levels and H atoms provide the needed electrons to occupy these levels.

Our calculated formation energies confirm quantitatively the above conceptual explanation. The calculated formation energies for Zn_{Ga} in the sublayer [the intended substitutions are shown in the upper panels of Fig. 2] are 2.24, 2.59, 2.63, and 1.78 for P-terminated surface, Sb-terminated surface, (P,H)-terminated surface, and (Sb,H)-terminated surface, respectively. Here, bulk Zn and Ga metals are used as reference chemical potentials and the trend of the defect formation energy is not affected by the LDA band-gap errors. It is seen clearly that the presence of dual surfactants, Sb and H significantly lowers the formation energy. These results are also consistent with the recently reported theoretical calculations in Ref. 8.

We now discuss the cases of surfaces that no H as a second surfactant is needed to enhance acceptor solubility. ZnSe(100) is such a surface. ZnSe has the same structure as GaP (zinc blende) but is an II–VI semiconductor. Thus, the dimerized ZnSe(100) surface satisfies the ECR. It has been reported that adding a small amount of Te in the growth can enhance hole carrier density of N-doped ZnSe for the (100) epitaxial growth.^{9,10} The mechanism for this puzzling observation has not been fully understood. Here we show that Te induces enhancement of N solubility in ZnSe through surfactant effect as described in Fig. 1. The upper panel of Fig. 3(a) shows the structure of Se-terminated ZnSe(100) surface with Se-Se dimers. The calculated DOS [middle panel of Fig. 3(a)] of this surface reveals that there are two fully occupied surface states slightly above the VBM of bulk ZnSe. The schematic of the calculated surface levels are given in the lower panel of Fig. 3(a). It is seen clearly from the calculation that when N atoms are incorporated into ZnSe, they

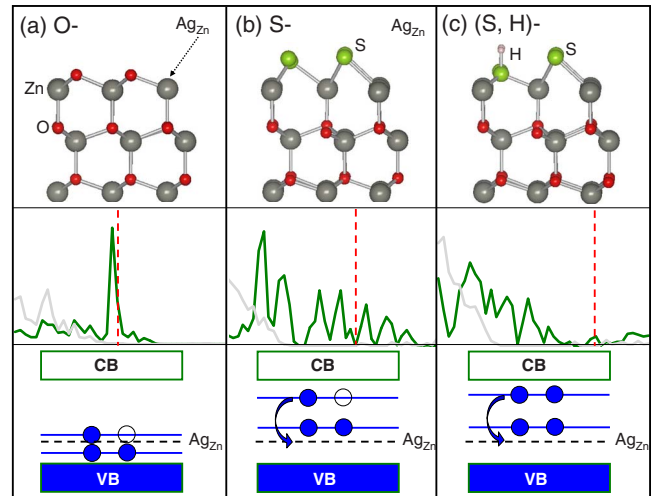


FIG. 4. (Color online) Structure, calculated DOS, and schematics of single-electron energy levels for O-, S-, and (S, H)-terminated (000 $\bar{1}$) ZnO surfaces. The red dashed lines indicate the positions of the highest occupied levels.

introduce shallow acceptor levels, which are close to the surface states. Thus, charge transfer between the surface states and acceptor levels would not lower significantly the energy of the system and no large formation energy reduction would be expected as compared to bulk growth. However, when Te is added as surfactant, the situation becomes different. The surface will be terminated by Te as shown in the upper panel of Fig. 3(b). The calculated DOS [middle panel of Fig. 3(b)] shows that the surfactant levels are not only high in energy but also completely filled. The high-energy position of the surfactant level is due to the fact that Te $5p$ orbital is higher than Se $4p$ orbital. The full occupation of the surfactant states is due to the satisfaction of ECR for the surface. These electrons at high energy will transfer to N acceptor levels and lower significantly the energy of the system. Subsequently, the formation energies of N_{Se} [as shown in the upper panels of Fig. 3] will be reduced dramatically for the (100) epitaxial growth with Te than the case without Te. In this case, the assistance from H is not required because the surfactant level is already occupied. Our calculated formation energy of N_{Se} is 0.8 eV lower for Te-terminated surface than for Se-terminated surface. Thus, our concept explains well why adding a small amount of Te in the growth can enhance acceptor N_{Se} solubility in ZnSe for the (100) epitaxial growth.

Finally, we discuss how this concept can be used to enhance p -type doping in ZnO.^{17–19} ZnO is different from the cases of GaP and ZnSe. Although ZnO is also an II–VI semiconductor, unlike ZnSe, it usually possesses the wurtzite structure, and epitaxial growth of wurtzite ZnO is commonly along its (000 $\bar{1}$) O-terminated polar surface, as shown in the upper panel of Fig. 4(a). The middle panel of Fig. 4(a) shows the calculated DOS of O-terminated ZnO(000 $\bar{1}$) surface and the lower panel shows the schematic of the calculated surface levels, revealing one fully occupied and one half filled surface states, near the VBM of ZnO. Therefore, our model predicts no significant enhancement of acceptor dopants such

as Ag_{Zn} (Refs. 20 and 21) with $\text{ZnO}(000\bar{1})$ epitaxial growth as compared to nonepitaxial growth. However, if surfactants such as S, Se, or Te which are in the same group as O are presented in the growth, the surface will be terminated by these surfactants. Because S $3p$, Se $4p$, and Te $5p$ orbitals are much higher in energy than O $2p$ orbital, the surfactant states will be much higher in energy than the surface states of O-terminated surface. The upper panel of Fig. 4(b) shows the structure of S-terminated $\text{ZnO}(000\bar{1})$ surface. The calculated DOS of this structure is shown in the middle panel of Fig. 4(b) and the lower panel shows the schematic of the calculated surface levels, showing that the surfactant states are much higher than VBM of ZnO . Therefore charge transfer from these levels to acceptor levels and consequent reduction in the dopant formation energy is expected. We have calculated the formation energy for substitutional Ag_{Zn} in the sublayer [as shown in the upper panel of Fig. 4(a)] and found that the formation energy is lowered by 2.3 eV with S as surfactant as compared to that without surfactant. Because there is no dimer formed on the $(000\bar{1})$ surface, the surfactant state is half filled, which allows one H to passivate it. With H passivation [upper panel of Fig. 4(c)] the fully filled state shifts to higher energy [middle panel of Fig. 4(c)] due to the enhanced Coulombic repulsion. The schematic energy levels are plotted in the lower panel of Fig. 4(c). This will further reduce the formation energy of the dopants and enhance the solubility. Indeed, our calculated formation energy for Ag_{Zn} is 0.4 eV lower for S-terminated surface with additional H as compared to that without H.

Our proposed concept works in principle for both p -type and n -type doping. However, the choice of surfactants that enhance n -type doping is much less than the case of p -type doping. This is because, as surfactants for enhancing n -type doping, they must have larger atomic sizes and simultaneously be more electronegative than the host elements. Most anion surfactants do not satisfy these requirements. Thus, cation surfactants should be used. For example, for n -type doping of ZnTe , Hg may be used as the surfactant. Hg is larger than Zn and due to large relativistic effects Hg $6s$ orbital is much deeper in energy than Zn $4s$ orbital. Thus the surfactant level can be as low as the VBM.

In conclusion, we have proposed a concept to enhance dopant solubility via epitaxial surfactant growth. Using this concept, we were able to explain the physical origin of the dual-surfactant effect of Sb and H in enhancing Zn solubility in GaP. We found that the need of hydrogen as a second surfactant is not an absolute requirement but rather depends highly on the materials system and the surface structure. Our DFT results also explain the mechanism of why adding a small amount of Te in the growth can enhance acceptor N_{Se} solubility in ZnSe for the (100) epitaxial growth. We have also provided solutions on how to enhance p -type doping of ZnO through surfactant epitaxial growth on $(000\bar{1})$ surface.

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