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Atomic ordering in In$_x$Ga$_{1-x}$As alloy thin films: Action of surfactants

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The effect of a surfactant (Sb and Bi) on ordering of alloy thin films of (In,Ga)As is studied using *ab initio* total energy calculations based on the density functional theory; ultrasoft pseudopotentials are applied in a plane-wave basis. Anion-terminated thin films of (In,Ga)As on the InP [001] substrate are assumed in the ordered CuPt-B geometry, with the $\beta2(2\times4)$-reconstructed surface. The energetics of disorder in the mixed cation plane (In,Ga) is examined quantitatively, comparing the films with clean surfaces and surfaces covered by surfactant. The analogous systems (In,Ga)P:(As, Sb, Bi) are studied at the same time, for comparison and in order to establish the differences in the action of the same surfactants. The mechanism of the action of different surfactant atoms is discussed in terms of the reduction of the strain in the subsurface layers. The variation of the surface formation energy with chemical potentials is compared at different coverages and for various positions of the surfactant atoms.

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Controlling the growth process is a major challenge in the production of materials for semiconductor devices.[1,2] Alloying two compounds with different band gaps offers the possibility of tailoring the gap energy by varying the composition. For the semiconductor alloys of the type $A_xB_{1-x}C$–A and B being cations of group III and C the anion of group V (or vice versa)—the random arrangement of A and B atoms in the cation sublattice turns out to exhibit larger band gaps than the ordered structures[3] which in the present case are of the CuPt-type with the $\beta2(2\times4)$ reconstruction on the top. This leads to optical applications with shorter wavelength.[1,2] In the alloy films, this approach nevertheless requires enforcing the structural disorder, because thermodynamics generally favors a ordering of CuPt type.[1,2] A promising way to modify the energetic relations consists of adding a small concentration of surfactants during the growth.[4] These surfactants are selected so as to stay on the surface of the material. They may modify the bonding at the surface, resulting in changes in surface stresses and the energetics. Understanding the mechanisms behind the action of surfactants and having control over different types of growth would enable, among other things, an appealing application: growing heterostructures consisting of a disordered phase grown on the ordered phase of the same material, without lattice mismatch but with different electronic properties of the two compounds. Obviously there are many possibilities of combining different surfactant atoms with various alloy films. In this work we concentrate on thin films of the ternary III-V compounds indium gallium arsenide [hereafter called (In,Ga)As] and also indium gallium phosphide [hereafter called (In,Ga)P] nearly lattice-matched with respective substrates, GaAs and InP. Surfactant atom used is antimony (Sb) and bismuth (Bi). The system (In,Ga)P:Sb (as well as:As and :Bi) has already been studied experimentally.[4] Some preliminary theoretical study on Sb-covered GaP surface has also been carried out[5] to understand the nature of the triple period ordering found in (In,Ga)P:Sb at a high surfactant concentration.[4] While the results on phosphide are well known, to the best of our knowledge no report on the effect of Sb and Bi on growth of (In,Ga)As thin films is available in the literature. Hence our results on the arsenide are theoretical predictions and our present study could lead to or rule out the need for certain important experimental studies on the isoelectronic surfactant effects on ordering in (In,Ga)As.

Calculations of the total energy are performed employing the pseudopotential method within the density functional theory.[6] The Vienna *ab initio* simulation package[7] is used for electronic structure calculations within local density approximation and the ultrasoft Vanderbilt pseudopotentials[8] were supplied by Kresse and Hafner.[8] The convergence of total energies with respect to the plane-wave cutoff (used 12.5 Ry) and k points[9] (we used the equivalent of 64 k points in the 1×1 cell) were carefully tested. Supercells consisting of several atomic planes (typically 12 atomic planes with about 100 atoms) are used for the simulation of the alloy films with an anion-terminated surface. In Fig. 1(a), we present the schematic diagram of the side view of a smaller supercell of eight atomic planes: four for the substrate and four for the overlayer, with approximately 10 Å for the vacuum layer on top. The bottom side, terminated by cations is passivated by pseudo-H atoms (charge $Z=1.25$). To obtain an equilibrium structure, the whole of the overlayer along with the two upper atomic planes of the substrate is relaxed until the forces are small. The slab is electrically neutral, but as a consequence of its non-symmetric construction, it has a dipole moment which is compensated for by using a dipole correction.[7]

Chemical potential and surface formation energy: The surface energy γ, for example of GaAs, may be expressed as a function of the chemical potentials,[10]

$$\gamma A = U_{tot} - n_{Ga}\mu_{Ga} - n_{As}\mu_{As}, \tag{1}$$

where U$_{tot}$ is the total energy of a GaAs film and A is the surface area of the film. n_X and μ_X are the number and chemical potential of atom X, respectively. Details on the calculations of γ can be found elsewhere.[10,11]

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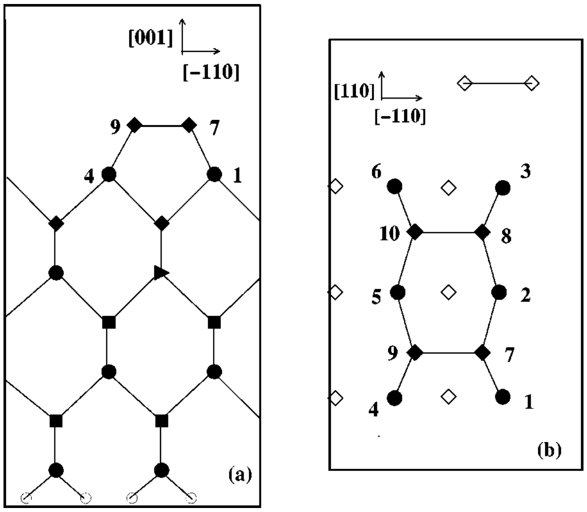

FIG. 1. Schematic (a) side view and (b) top view of a supercell with 8 atomic planes representing the anion terminated (In,Ga)As thin film on InP substrate. Atomic positions shown are without any relaxation. Meaning of symbols: diamonds, As; circles, In; right-handed triangles, Ga; squares, P; empty circles, H. On the top view (b), filled diamonds: topmost As plane; empty diamonds: second subsurface plane of As. Subsurface cation plane consists of In only: segregation of In to surface is established by both experiments and theory in both systems studied here (Ref. 1). In (a) empty space on top of the surface plane signifies the vacuum layer (not in scale). In (b) the atoms 7, and 9 and 8, and 10 are forming the anion dimers resulting in the $\beta 2(2\times 4)$ reconstruction. Also there is a dimer formation in the second subsurface (anion) layer, as seen in top right corner in (b).

Relaxed atomic positions for both (In,Ga)As and (In,Ga)P alloy thin films are translated into bond lengths and bond angles [Figs. 1(a) and 1(b)] and summarized in Table I. The CuPt-B type ordering is expected to be weaker in (In,Ga)As than in (In,Ga)P. This is due to the fact that the P dimer length on the top is much smaller than the As dimer length (Table I). Hence the strain in the subsurface layers is expected to be more in case of the phosphide. As a result, the effectiveness of Sb and Bi, as surfactant, in reducing ordering is expected to be less in the arsenide than in the phosphide and it is the quantitative effect of Sb and Bi as surfactant on (In,Ga)As thin film that will be addressed below. In order to situate our results on (In,Ga)As in a broader context, we also studied in the same geometry, the (In,Ga)P alloy thin films with different surfactants (As, Sb, Bi). In this case the results can be confronted with the experiments.[4,12] This provides additional support of the analysis carried out on (In,Ga)As results.

Results on indium gallium arsenide—geometric analysis: To assess the strength of CuPt-B type ordering in (In,Ga)As from a structural point of view, in Table I we summarize the calculated geometries for two cases: (1) a clean (In,Ga)As film surface where only As-As dimers are present, and (2) a film surface covered with the surfactant atoms when the top surface anion dimers become Sb-Sb and Bi-Bi. Figures 1(a) and 1(b) give schematic side and top views of a supercell with eight atomic planes representing the anion-terminated (In,Ga)As thin film grown on InP(001) substrate. The bonds 1-2 and 2-3 are equivalent [Fig. 1(b)] and though different from bonds 1-2 and 2-3, bonds 4-5 and 5-6 are equivalent as well. This is possibly because in the second subsurface anion layer there is a dimer adjacent to bonds 1-2 and 2-3 but not to bonds 4-5 and 5-6, in the first subsurface layer: making them two different sets of bonds. We observe that the bond length 1-2 (and 4-5) of the subsurface In atoms for the clean surface is 3.65 Å (and 3.69 Å), and 3.72 Å (and 3.71 Å) with fully surfactant-dimer covered surfaces (with Sb and Bi used as surfactants). It is noted that as the cation-cation distance in the bulklike substrate (zinc-blende phase) is about 4.13 Å, the In-In distance is strained in the clean film, but the strain is reduced with the larger surfactant atoms. The same argument holds when the bond lengths 7-9 and 8-10 are compared (2.45 vs 2.84 Å, for clean and Sb covered surfaces, respectively; for the Bi-covered surface, this dimer bond length is 3.00 Å). The typical In-anion-In bond angle, (1-7-2 or 4-9-5) is about 90° for a clean surface but for fully Sb and Bi covered surfaces becomes smaller, about 83° and 81°, respectively. Together with the observed shift of the top anions towards higher z i.e., in the [001] direction, the above analysis indicates less strain in the subsurface layers for the surfactant-covered cases.

TABLE I. Geometry of top two planes and In/Ga interchange energy (ΔE) calculated on 12 atomic plane thin films of (In,Ga)As and (In,Ga)P. The atom numbering refers to Fig. 1.

Bond length (Å)	As-As dimer on (In,Ga)As	Sb-Sb dimer on (In,Ga)As	Bi-Bi dimer on (In,Ga)As	P-P dimer on (In,Ga)P	As-As dimer on (In,Ga)P	Sb-Sb dimer on (In,Ga)P	Bi-Bi dimer on (In,Ga)P
1-2(2-3)	3.65	3.72	3.72	3.40	3.42	3.59	3.58
4-5(5-6)	3.69	3.71	3.71	3.50	3.55	3.59	3.58
7-9(8-10)	2.45	2.84	3.00	2.21	2.45	2.84	3.00
bond angle (deg.)							
1-7-2(2-8-3)	88.3	83.8	80.9	84.8	82.3	80.6	77.6
4-9-5(5-10-6)	89.0	83.3	80.7	87.3	85.5	80.2	77.6
ΔE (eV/supercell)							
	0.49	0.42	0.32	0.61	0.59	0.02	0.05

Energetic study: To understand the decrease of strength of ordering with the replacement of As by larger atoms on the surface, we calculated the energetic cost of interchanging *all* the Ga and the In atoms in the third subsurface layer for the clean alloy films and the surfactant covered films. It is expected that this interchange energy, ΔE, is indicative of the strength of ordering since the surface stress and reconstruction (and the associated ordering) drives the smaller atoms (Ga) to occupy the positions just below the top anion dimer [Fig. 1(a)].[1,2,13,14] However, we note here that we try to arrive at a relative estimate of the difference of the degree of ordering which in reality depends on many other factors during growth, most importantly the growth rate and other growth related parameters, such as surface mobility, steps and incorporation at step edges, to mention a few which cannot be dealt with from the energetics alone. ΔE in the clean-surface case (0.49 eV per supercell) is somewhat smaller than in (In,Ga)P (0.61 eV per supercell). In presence of the Sb surfactant, ΔE decreases only slightly (from 0.49 to 0.42 eV per supercell), hence the strength of ordering for surfactant covered film is expected to be only mildly reduced. This is in stark contrast with the (In,Ga)P films where the same ΔE is reduced to a much smaller value (0.61 vs 0.02 eV per supercell: see further on). We must note here that the top anion dimer lengths are 16% different for As and Sb dimers, whereas for P and Sb dimers they are 28% different—the stress reduction is likely to be more pronounced in (In,Ga)P than in (In,Ga)As. Geometry and energy analysis results indicate that although Sb may induce disorder to some extent in (In,Ga)As, its effect is *expected to be smaller* than in (In,Ga)P. In other words, Sb is expected to be less effective as a candidate for surfactant *in producing disorder* in (In,Ga)As than in (In,Ga)P films. Further calculations suggest that the effect of Bi as surfactant on (In,Ga)As films can be expected to be similar to that of Sb. We observe that ΔE for (In,Ga)As : Bi case is 0.32 eV per supercell, of similar order of magnitude as in (In,Ga)As : Sb case. Figure 2 for surface formation energies also supports this similarity of Sb and Bi since the formation energies are close to each other. The difference in formation energy value is about 1.7 meV per area for (In,Ga)As (Fig. 2) and 1.5 meV per area for (In,Ga)P.

Site selectivity of Sb on the (In,Ga)As surface: In this subsection we discuss the specific aspect of site selectivity of Sb on (In,Ga)As surface, if there is any. Also we would probe to find any indication if the Sb atoms prefer to replace the top anion atoms or form an additional layer on the top. From the optimization of the atomic positions we observe that the geometry undergoes a systematic change when Sb atoms replace top four As atoms, one by one, as in the case of incomplete surfactant coverage. Figure 3 gives the surface formation energies for the (In,Ga)As, four different cases have been plotted. Case 1 is for clean film with top As dimers, and case 2 for one mixed dimer, Sb-As. Case 3 is for two As dimers on the top surface with an additional layer of only one Sb atom sitting at top of the center of the square made by the two As dimers a layer below. Case 4 is for two Sb dimers on the surface. The *x* axis gives the relative As chemical pressure, with respect to the As bulk, i.e., zero corresponds to a very high As partial pressure. For low pressure of the surfactant the surface formation energy is always lowest (bottom panel of figure 3) for clean film (case 1). However, at a moderate pressure of the surfactant, the films fully covered with surfactants (case 4) have a lower surface formation energy below a certain value of As chemical pressure (top panel of Fig. 3). This indicates the stabilization of the surfactant covered film beyond a critical concentration of surfactants and below a critical chemical pressure of As.

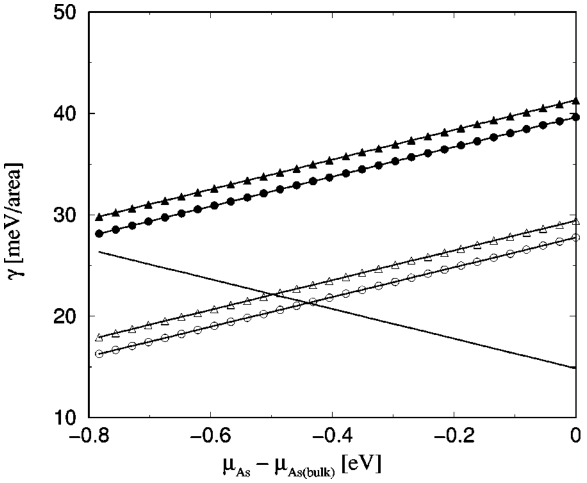

FIG. 2. Plot of surface formation energy (γ) vs As chemical potential in (In,Ga)As. Meaning of symbols: line without symbols, clean surface with As dimers on top; triangles, Sb dimers on top replacing As dimers; circles, Bi dimers on top replacing As dimers. Filled symbols are for low surfactant pressure and empty symbols for medium pressure of surfactants. For Sb, medium pressure corresponds to a chemical potential of μ_{Sb}-$\mu_{Sb(bulk)} = -0.4$ eV and low pressure corresponds to -0.8 eV in our calculations. All is similar for Bi. All plots assume μ_{Ga} and μ_{In} equivalent, i.e., partial pressures for both are similar.

In presence of higher concentration of Sb during the growth two possibilities may occur. Sb may start replacing As atoms or it may start sitting on top of the existing As top layer. From our calculations it is observed that energetically it is favorable if the Sb atom starts replacing As atoms on the surface (see middle and bottom panels of Fig. 3): case 3 always is much higher up in energy. We observe that for low and moderate Sb pressures (bottom and mid panel of Fig. 3, respectively), case 2 with mixed dimer is favored over an additional layer of Sb on top of As layer. While replacing the top As atoms by Sb, there exists a site selectivity for the Sb atom in occupying different surface sites. Examined more closely, it is energetically more favorable (by 0.018 eV per supercell) if the Sb atom occupies sites 9 and 10 than sites 7 and 8 [Fig. 1(b)]. In the second subsurface layer, there is a dimer formation of the anions close to the sites 7 and 8 in the first subsurface layer. Hence there may be a steric reason for this energetic favoring of sites 9 and 10 over 7 and 8. Also it turns out that the replacement of the pair 9 and 10 is somewhat easier than replacement of pairs 7 and 9 or 8 and 10 (energetically lower by 0.01 and 0.02 eV per supercell, respectively). It is hence indicative that during growth with surfactant atoms present, if two Sb atoms are to replace two

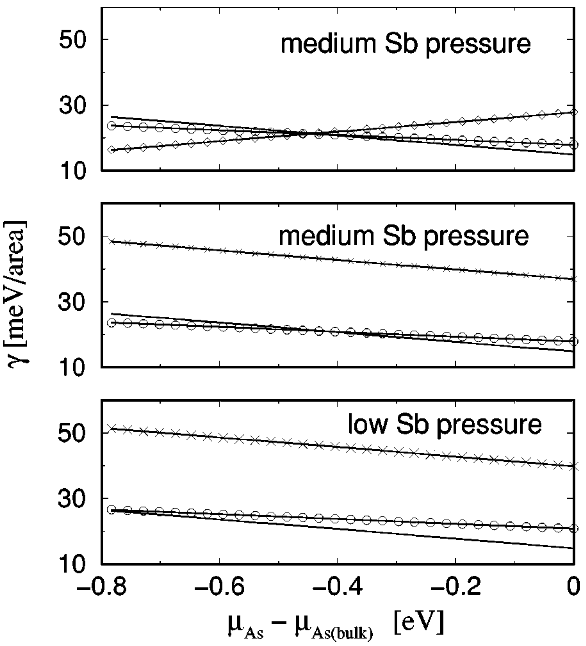

FIG. 3. Surface formation energy (γ) vs As chemical potential in (In,Ga)As. Meaning of symbols: lines without symbols, clean surface, with As dimers on top; circles, one Sb replacing one out of four As on top; crosses, one Sb (additional layer) sitting on top of the already $\beta2(2\times4)$ reconstructed surface with two As dimers; diamonds, two Sb dimers, replacing both As dimers. In the top and middle panels the Sb chemical potential is the same. In the top panel the comparison is between the film which has one As replaced by Sb with the film which has a full Sb coverage on top for medium Sb pressure. In the middle panel the comparison is between the film which has one As replaced by Sb with the film which has one additional Sb on top of already reconstructed surface with two As dimers, for medium Sb pressure. In the lowest panel the comparison is between the film which has one As replaced by Sb with the film which has one additional Sb on top of an already reconstructed surface with two As dimers, for low Sb pressure. The γ for clean film is shown for reference in all the panels. For Sb, the medium pressure corresponds to a chemical potential of μ_{Sb}-$\mu_{Sb(bulk)}$ $=-0.4$ eV, and the low pressure corresponds to -0.8 eV, in our calculations. All plots assume μ_{Ga} and μ_{In} are equivalent, i.e., partial pressures for both are similar.

As atoms, the replacement may not take place dimer by dimer.

Results on indium gallium phosphide—geometric analysis: We see from Table I that the length 1-2 (and 4-5) between the subsurface In atoms is 3.40 (and 3.50) Å, for the clean surface (P-P dimers). With fully surfactant-dimer covered surfaces it becomes 3.42 (and 3.55), 3.59 (and 3.59), 3.58 (and 3.58) Å, for As, Sb and Bi, respectively. The cation-cation distance in the bulk-like substrate is about 3.97 Å; hence the In-In distance is strained in all the films but the strain reduces with the larger surfactant atoms. The anion dimer lengths are 2.21 Å, and 2.45, 2.84, and 3.00 Å for P (clean surface), As, Sb, and Bi-covered surfaces, respectively—comparable with the P-P, As-As, Sb-Sb and Bi-Bi bond lengths in the elemental solid phase 2.21, 2.49, 2.90, and 3.09 Å, respectively. We take a note of a related study in the literature : Li *et al.* compared the bonding properties of adsorbed P, As and Sb on GaAs (001) surface.[15] The P atoms are shown to exhibit the shortest dimer bond length and the strongest backbonds to Ga. Consequently, P displaces the subsurface Ga atoms the most from their equilibrium positions. The dimer bond lengths are 2.23, 2.50, and 2.86 Å, for P, As, and Sb, respectively. We note that from our first principles calculations, the Sb-Sb dimer spacing on (In,Ga)P surface comes to be similar to that on the GaAs surface. We observe from the combined theoretical and experimental studies[4,12] that these anion dimer bond lengths are very similar irrespective of the surface on which the dimers are formed.

We note that in presence of the larger atoms, Sb and Bi, the longer distances between the cations in the subsurface layers and between the anions in the top layers indicate a release of strain on the subsurface layers. These larger lengths may indeed lead to a weakening of the CuPt ordering causing the disorder of the cation sublattice of the alloy film for a certain concentration of the surfactant.

Energetics study: As in the (In,Ga)As case, we calculate the cost in total energy of interchanging In and Ga in the third subsurface cation layer (ΔE). We see from Table 1 that with clean surface (P dimers) $\Delta E = 0.61$ eV per supercell. Upon replacement of P by As on the top, ΔE becomes 0.59 eV, of the same order as the value for the clean film. On the other hand, when the larger atoms Sb and Bi dimers replace top P dimers, the cost in energy of interchanging is reduced by order of magnitude: ΔE becomes 0.02 and 0.05 eV per supercell, respectively. This shows that though As may induce disordering to some extent, the effect of As is significantly smaller than Sb and Bi. This observation corroborates the experimental studies.[12] Our results (Table I) also indicate that the effects of Sb and Bi on the geometry and energetics are similar for (In,Ga)P [and also (In,Ga)As] thin films. Similar is the finding from the experiment[12] for (In,Ga)P.

To conclude, our first principles calculations corroborate to the experimental finding that (1) As is much less effective in producing subsurface cation sublattice disorder than Sb and Bi; (2) the effects of Sb and Bi as surfactant are similar in (In,Ga)P. On the contrary, from the results of our calculations on the (In,Ga)As thin films, from purely static or thermodynamic point of view, we expect that Sb and Bi will not be so much efficient in blocking the ordering in (In,Ga)As compared to (In,Ga)P. Finally it is to be recalled that the growth is controlled not only by energetics but also influenced by various kinetic factors which are beyond the scope of the present study.

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