

Effect of strain on atomic ordering and action of surfactants in ternary alloy thin films

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Effect of surfactant (Sb) on ordering in alloy thin films of (In,Ga)P and (In,Ga)As, lattice mismatched with the substrate, is studied using *ab initio* total energy calculations based on the density functional theory. Anion-terminated thin films of (In,Ga)As on the GaAs [001] substrate and (In,Ga)P on the GaP [001] substrate are assumed in the ordered CuPt-B geometry, with the $\beta 2(2 \times 4)$ -reconstructed surface. The results are compared with the previous calculations on the same alloy layers but lattice matched with the substrate. Consequences of strain (due to lattice mismatch) on the ordering in these films, bare and covered with surfactant, are discussed in relation with surface and interface geometries and in terms of the surface formation and interchange energies.

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Understanding the process of growth of semiconductor materials is important since the resulting atomic structures predestine their optoelectronic properties. Precise design of semiconductor devices requires understanding of the mechanisms that control material parameters, most importantly the band gap energy. The common approach in the “band structure engineering” consists in alloying two binary compounds with different band gaps and varying the composition of the alloy.^{1,2} In III–V semiconductor alloy films of the type $A_xB_{1-x}C$, the random arrangement of A and B atoms in one of the sublattices turns out to exhibit larger band gaps than the chemically (or atomically) ordered structures with same composition.³ Through the disorder one can achieve optical applications with shorter wavelength.^{1,2} But this approach requires *enforcing* structural disorder because, in alloy film, surface thermodynamics generally favors ordering.^{1,2} One way to modify the energetics is adding a small amount of surfactant during the growth.⁴ Recently we have carried out⁵ *ab initio* study of the effect of surfactants on atomic ordering, driven by *strain due to surface reconstruction* leading to site-selectivity in the subsurface layers, in (In,Ga)As and (In,Ga)P films, lattice matched with the substrates. The present paper aims at studying, in the same thin films with Sb as surfactant, an additional mechanism, viz. the effect of *underlying strain* consequent to *lattice-mismatch*.

In the literature, the role of strain on ordering of alloys has been addressed in different contexts:^{6–14} Some studies suggest that the resulting stress influences the ordering very little, while others report non-negligible effects; certain claim atomic ordering results from presence of stress. Earlier, ordering in alloys has been attributed to strain due to lattice mismatch but later it has been shown ordering occurs even in films which have no residual stress.⁶ It has been observed that ordering occurs independent of the strain distribution in the layers.⁷ The transmission electron microscopy (TEM) studies on superlattices of (Ga,As)Sb (Ihm *et al.*)⁸ and (Ga,As)P (Chen *et al.*)⁸ conclude about no significant role of lattice mismatch on chemical ordering in epilayers. On the contrary, a TEM study of highly strained heterostructures of (Cd,Zn)Te–GaAs⁹ observes formation of two ordered struc-

tures and suggests that their appearance might originate from minimization of the stress due to large lattice mismatch. Strain was proposed as the main mechanism controlling the atomic structure also in (In,Ga)As–(In,Al)As multiple quantum wells,¹⁰ in epitaxial (In,Ga)P¹¹ and in (In,Ga)N alloys.¹²

Zhang *et al.*¹⁵ showed, through theoretical calculations on (In,Ga)P, that different types of atomic ordering correlate with different surface reconstructions. It has also been well known that changes in atomic ordering of alloy thin films can be achieved by addition of *surfactants*, which leads to the question of *surface stress* and its relaxation. The main question we address here is whether the strain induced by the pseudomorphic growth of a thin film on a lattice mismatched substrate can affect the action of surfactant on the ordering. We limit ourselves to the thin films of (In,Ga)As on GaAs and (In,Ga)P on GaP substrates; covered with surfactant (Sb) or bare. We investigate the microscopic effects of lattice mismatch on the surface and interface geometries and the energetics. It is worth mentioning that crystal growth is influenced also by *kinetic factors* (migration, diffusion, segregation of atoms and alike). These aspects remain beyond the scope of the present study.

Present calculations are performed employing the pseudo-potential method within the density functional theory.¹⁶ The Vienna *ab initio* simulation package¹⁷ is used within local density approximation and with the ultrasoft Vanderbilt pseudopotentials¹⁸ supplied by Kresse and Hafner,¹⁸ in exactly the same conditions as in our previous study.⁵ In Fig. 1, we present the schematic diagram of a typical supercell of 8 atomic planes: 4 for substrate and 4 for overlayer with ≈ 10 Å, for vacuum layer on top. The bottom side, terminated by cations is passivated by pseudo-H atoms (charge $Z=1.25$). First, all atoms of the over-layer as well as those of the two upper atomic planes of the substrate are relaxed. Then the total energy U_{tot} , calculated in the resulting equilibrium structure, is the starting point for evaluation of other energy-related quantities, e.g., the surface energy γ ; which can be expressed (e.g., for GaAs) as:¹⁹ $\gamma A = U_{\text{tot}} - n_{\text{Ga}}\mu_{\text{Ga}} - n_{\text{As}}\mu_{\text{As}}$; here A is the surface area of the film, n_X and μ_X are

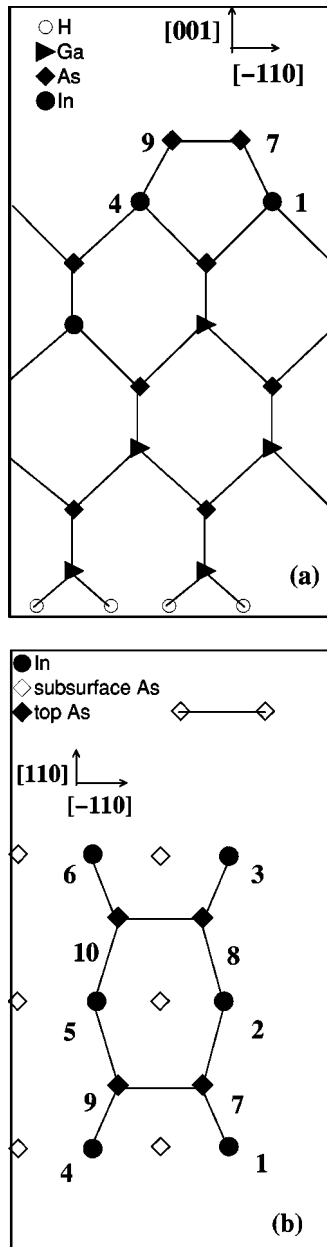


FIG. 1. Supercell with 8 atomic planes representing the anion terminated (In,Ga)As thin film on GaAs substrate: (a) side view and (b) top view. Atomic positions shown are before any relaxation and correspond to the geometry of the $\beta 2(2 \times 4)$ reconstruction. Subsurface cation plane consists of In only: Segregation of In to surface is established by both experiments and theory in both systems studied here Ref. (1). The empty space on top of the surface plane [Fig. (a)] signifies the vacuum layer (not in scale). In Fig. (b), the atoms 7, 9 and 8, 10 are forming the anion dimers characteristic of the $\beta 2(2 \times 4)$ reconstruction. Also there is a dimer formation in the second subsurface (anion) layer, as seen, e.g., in top right corner in (b).

the number and chemical potential of atom X, respectively. Discussion of more technical details can be found elsewhere.^{19,5}

Geometric study. The calculated geometries of top layers of (1) clean film surface, and (2) film surface covered with

the surfactant atoms are summarized in Table I. The thin films are studied with CuPt ordering in the cation sublattice and $\beta 2(2 \times 4)$ reconstruction on top, which is observed at higher growth temperatures as well as at lower anion flow. Some of the other common reconstructions for these systems, are $c(4 \times 4)$, 2×3 , 4×3 . Figures 1(a) and 1(b) give schematically the side and top views of a supercell of thin film with anion-termination. At this point we can compare the geometry of the strained system with the lattice matched films studied in our earlier work.⁵ In the $\beta 2(2 \times 4)$ reconstruction, the distances 1-2 and 2-3 [Fig. 1(b)] are equivalent; distances 4-5 and 5-6, nonequivalent to 1-2 and 2-3, turn out to have equal lengths as well. We observe from Table I that, in the (In,Ga)P systems, the length 1-2 (and 4-5) between the subsurface In atoms is 3.40 (and 3.41) Å, for the clean surface (P-P dimers on top). With fully surfactant, Sb-dimer, covered surfaces it becomes 3.51 (and 3.51) Å. Compared to the results on films lattice matched with the substrate,⁵ the distances change by only less than $\approx 3\%$. Similar observations hold for the top anion dimers: Their lengths are 2.23 Å, for clean surface and 2.85 Å, for Sb-covered surfaces—which are very close, again, to the topmost P-P and Sb-Sb lengths in the lattice matched (In,Ga)P thin film, 2.21 and 2.84 Å, respectively. We note from our previous calculations that, in presence of the larger atoms, Sb and Bi, the longer distances between the cations in the subsurface layer and between the anions in the top layer indicate a release of strain on the subsurface layers, as already pointed out in the literature.^{1,2,4,5} Hence the larger Sb-Sb distance in the present case may indeed be leading to weakening of the CuPt ordering, causing the disorder of the cation sublattice of the alloy film, for a certain concentration of the surfactant and beyond, as was experimentally observed.⁴ The typical In-anion-In angle, (1-7-2 or 4-9-5 in Fig. 1) for (In,Ga)P is $\approx 85^\circ$ for clean surface but for fully Sb covered surface it becomes smaller, $\approx 78^\circ$. The comparison with the lattice-matched thin film shows a maximum deviation of $\approx 3\% - 6\%$ for the two sets of lengths 1-2 (2-3) and 4-5 (5-6) as well as for the In-anion-In angle. From the data on (In,Ga)As films we observe from the Table I that the underlying strain consequent to the lattice mismatch does not affect the listed lengths and angles much, when compared to our previous lattice matched results.⁵ It is apparent that even the interlayer distances between the top and the next lower layer containing Sb and In, respectively, are similar (2.17 vs 2.13 Å), independent of the material (In,Ga)P and (In,Ga)As (Table II), confirming thus that the overall geometry of the top layers is determined essentially by the particular type of anion dimer on the top and very little influenced by the layers below.^{4,5,20} Hence in the present case the negligible difference in the geometry of the surface, between the lattice matched and the lattice mismatched cases, both with and without surfactant, clearly indicates that, *the effect of a lattice mismatch on the ordering of thin films and on the effect of surfactant on ordering, is only small.*

In contrast, and as expected, the geometry of the interface in the lattice matched and the mismatched cases are largely different. In fact, there are contradictory conclusions in the literature concerning the effect of the strained film growth on

TABLE I. Geometry of top two planes for two different terminations strained films of (In,Ga)P on substrate of GaP[001] and (In,Ga)As on GaAs[001]. The atom numbering refers to Fig. 1.

Length (Å)	P on top of film (In,Ga)P	Sb on top of film (In,Ga)P	As on top of film (In,Ga)As	Sb on top of film (In,Ga)As
1-2(2-3)	3.40	3.51	3.43	3.61
4-5(5-6)	3.41	3.51	3.55	3.59
7-9(8-10)	2.23	2.85	2.45	2.83
angle (deg.)				
1-7-2(2-8-3)	84.4	77.8	82.8	80.7
4-9-5(5-10-6)	84.9	77.8	85.1	80.2

the local film geometry, and we recollect here only two. Earlier calculations¹⁴ predict that pseudomorphic growth of (In,Ga)As on GaAs[001] may result in a bond length strain that is accommodated primarily by the distortion of the longer In-As rather than the shorter Ga-As bonds. On the contrary, the experimental study of Woicik *et al.*¹³ of (In,Ga)As on GaAs has demonstrated that the In-As and Ga-As bond lengths are *uniformly distorted*. The interface geometries of strained thin films obtained in our calculations are given in Table II. The interface between (In,Ga)P and GaP consists of indium (In), gallium (Ga), and phosphorous (P) atoms. For the unstrained film, there are additionally arsenic (As) atoms. It was observed in the unstrained case that there are two sets of bonds, one long and one short. Among the In-anion bonds, the longer bond corresponds to In-As type (bond length of 2.57 Å), and the shorter one (2.48 Å) corresponds to the In-P bonds. Ga-anion bonds are 2.37(±0.01) and 2.46 Å, the shorter ones being of Ga-P type and the longer ones of Ga-As type. Comparing with the strained case we note that, for (In,Ga)P on GaP substrate, only the In-P

and Ga-P bonds are present. We observe reasonable compression of both the types of bonds. The bond angles seem to be much less affected by the strain on the interface as a result of the lattice mismatch. By considering also the (In,Ga)As case (Table II) we can conclude that in both types of thin films, (In,Ga)P and (In,Ga)As, the surfactant has nearly no effect on the interface geometry. Also the bond lengths, bond angles and the vertical distance between the cation-anion layers, $d\bar{z}$, at the interface are very similar for the lattice matched and mismatched films, irrespective of whether these are covered by surfactants or not (see Table II).

Energetic study. To understand the effect of surfactant on ordering, i.e., the increased likelihood of disorder with the replacement of the anions of the films by larger anions on the surface, we calculated the energetic cost of interchanging *all* the Ga and the In atoms in the 3rd subsurface layer for the clean alloy films and the surfactant covered films. As explained in our previous work,⁵ we expect this interchange energy, ΔE , to be indicative of the strength of ordering—since the surface stress and reconstruction (and the associ-

TABLE II. Interface geometry, calculated for 12 atomic plane thin films of (In,Ga)As and (In,Ga)P on lattice-matched and lattice-mismatched substrates. The numbering of the layer is from bottom upwards: L1 represents layer 1, closest to the substrate and L12 contains the top anion dimers. $d\bar{z}$ is the average distance between layers. In/Ga interchange energy (ΔE) calculated on 12 atomic plane thin films of (In,Ga)As and (In,Ga)P.

Length (Å)	P-covered unstrained (In,Ga)P on GaAs	P-covered strained (In,Ga)P on GaP	Sb-covered strained (In,Ga)P on GaP	As-covered unstrained (In,Ga)As on InP	As-covered strained (In,Ga)As on GaAs	Sb-covered strained (In,Ga)As on GaAs
In-anion	2.48,2.57	2.44,2.47	2.44–2.47	2.54,2.61–2.62	2.54–2.59	2.54–2.58
Ga-anion	2.37,2.46	2.29,2.33	2.29,2.31–2.33	2.42,2.50–2.52	2.38,2.47–2.49	2.37,2.46–2.48
angle (deg.)						
Anion-In-anion	106–109,112	101,109–113	100,109–113	103–108,119	100–103,115	101,114–117
Anion-Ga-anion	109–114	109–110	107–111	109,111	106–108	107
$d\bar{z}$						
L2-L1	1.40	1.35	1.35	1.46	1.40	1.40
L5-L4	1.53	1.40	1.40	1.35	1.48	1.48
L6-L5	1.39	1.45	1.43	1.51	1.53	1.53
L12-L11	1.73	1.81	2.17	1.78	1.90	2.13
ΔE (eV/supercell)						
	0.61	1.15	0.15	0.49	0.29	0.28

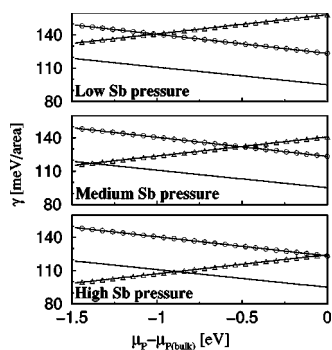


FIG. 2. Surface formation energy (γ) versus chemical potential of P in (In,Ga)P. Meaning of symbols—Lines without symbols: Clean surface, with P-dimers on top, the film unstrained on GaAs substrate; circles: Clean surface with strained film on GaP substrate; triangles: two Sb-dimers, replacing both P-dimers and strained. The “low” and “medium” Sb pressures are chosen to be $\mu(\text{sb}) = -0.8$ and -0.4 eV, respectively. The “high” pressure in the bottom panel corresponds to the bulk Sb pressure. All plots assume μ_{Ga} and μ_{In} equivalent, i.e., partial pressure for both are similar. Lateral area for the strained InGaP is about 116.36 \AA^2 , for GaP substrate.

ated ordering) drive the smaller atoms (here Ga) to occupy the positions just below the top anion dimer [Fig. 1(a)].^{1,2,5,15} An interchange of the smaller atom, Ga, and larger atom, In, alters the degree of ordering. We keep in mind that the degree of ordering depends on many factors pertaining to the growth, such as growth rate and other growth related parameters (surface mobility, steps and incorporation at step edges etc) and we expect ΔE to be merely one such parameter. For strained (In,Ga)As films, ΔE takes a value of 0.29 eV per supercell (Table II). For the strained film which is covered by the surfactant it becomes 0.28 eV per supercell. Thus the strength of ordering for surfactant covered film is expected to be similar to that of the clean film. This suggests a weak efficiency of Sb as surfactant for (In,Ga)As films—the same conclusion as arrived at in the unstrained case.⁵ The result for (In,Ga)P films is in stark contrast with that of (In,Ga)As films since the interchange energies behave quite differently in both cases. For (In,Ga)P films, ΔE for strained case, is 1.15 and 0.15 eV per supercell, respectively, for films with-

out and with Sb surfactant atoms, indicating better efficiency of surfactant Sb in case of (In,Ga)P. The surface formation energy as a function of chemical potential of P for (In,Ga)P is shown in Fig. 2. When two clean films, lattice matched and mismatched with the substrate are compared, it is observed that the lattice mismatched one is always higher in surface energy, by ≈ 30 meV per area. For the mismatched heteroepitaxial growth, the layers first grow pseudomorphically and accumulate elastic strain energy. This accumulation makes the layers increasingly metastable and, beyond a critical thickness, they begin to relax. Also the surfactant covered films, with two Sb-Sb dimers on top, are always placed higher in surface energy plot than the unstrained clean film, except at a very low pressure of P and at very high Sb pressure, which is comparable with the bulk Sb pressure.

To conclude, the present work deals with the optimized structures of strained films of (In,Ga)As and (In,Ga)P, bare and covered with surfactants. We have demonstrated, from purely static point of view, that (a) top layer geometry remains practically unchanged irrespective of the presence or absence of strain on the layers below, (b) at the interface, short and long cation-anion bonds are approximately uniformly distorted under strain, (c) the interface geometry has little effect on the properties at the surface of thin film of In and Ga based ternary alloys, and most importantly, (d) the effect of surfactant, Sb, on ordering in (In,Ga)P (and the absence of it in (In,Ga)As) remains *unaltered by the underlying strain consequent to lattice mismatch*. In brief, the present work suggests that the influence of strain on the effect of surfactants on ordering in ternary alloy thin films is negligible. This result is expected to be of technological relevance in ternary alloy thin film growth.

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¹MRS Bulletin 22(7), (1997).

²*Common Themes and Mechanisms of Epitaxial Growth*, edited by P. Fuoss, J. Tsao, D. W. Kisker, A. Zangwill, and T. Kuech (Materials Research Society, Pittsburgh, 1993); *Spontaneous Ordering in Semiconductor Alloys*, edited by A. Mascarenhas (Kluwer Academic/Plenum Publishers, 2002); and references therein.

³W. S. Han, B. Lee, J. H. Baek, J. -H. Lee, B. S. Jung, E. -H. Lee, and Byungsung O, Appl. Phys. Lett. **72**, 1905 (1998); T. Suzuki, A. Gomyo, S. Iijima, K. Kobayashi, S. Kawata, I. Hino, and T. Yuasa, Jpn. J. Appl. Phys., Part 1 **27**, 2098 (1998).

⁴J. K. Shurtleff, R. T. Lee, C. M. Fetzer, and G. B. Stringfellow, Appl. Phys. Lett. **75**, 1914 (1999); G. B. Stringfellow, J. K. Shurtleff, R. T. Lee, C. M. Fetzer, and S. W. Jun, J. Cryst.

Growth **221**, 1 (2000); J. K. Shurtleff, R. T. Lee, C. M. Fetzer, G. B. Stringfellow, S. Lee, and T. Y. Seong, *ibid.* **234**, 327 (2002); and references therein.

⁵Aparna Chakrabarti and Karel Kunc, Phys. Rev. B **68**, 045304 (2003).

⁶F. K. LeGoues, V. P. Kesan, S. S. Iyer, J. Tersoff, and R. Tromp, Phys. Rev. Lett. **64**, 2038 (1990), and references therein.

⁷E. Muller, H. -U. Nissen, M. Ospelt, and H. von Kanel, Phys. Rev. Lett. **63**, 1819 (1989).

⁸Y.-E. Ihm, N. Otsuka, J. Klem, and H. Morkoc, Appl. Phys. Lett. **51**, 1013 (1987); G. S. Chen, D. H. Jaw, and G. B. Stringfellow, J. Appl. Phys. **69**, 4263 (1991).

⁹H. S. Lee, J. Y. Lee, T. W. Kim, D. U. Lee, D. C. Choo, and H. L.

- Park, Appl. Phys. Lett. **79**, 1637 (2001).
- ¹⁰T. W. Kim, D. U. Lee, H. S. Lee, J. Y. Lee, and M. D. Kim, J. Appl. Phys. **89**, 2503 (2001).
- ¹¹J. Jiang, A. K. Schaper, Z. Spika, and W. Stolz, Phys. Rev. B **62**, 15 826 (2000).
- ¹²L. K. Teles, L. G. Ferreira, J. R. Leite, L. M. R. Scolfaro, A. Kharchenko, O. Husberg, D. J. As, D. Schikora, and K. Lischka, Appl. Phys. Lett. **82**, 4274 (2003).
- ¹³J. C. Woicik, J. G. Pellegrino, B. Steiner, K. E. Miyano, S. G. Bompadre, L. B. Sorensen, T. -L. Lee, and S. Khalid, Phys. Rev. Lett. **79**, 5026 (1997), and references therein.
- ¹⁴A. AmoreBonapasta and G. Scavia, Phys. Rev. B **50**, 2671 (1994).
- ¹⁵S. B. Zhang, S. Froyen, and A. Zunger, Appl. Phys. Lett. **67**, 3141 (1995).
- ¹⁶P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. Sham, Phys. Rev. **140**, A1133 (1965).
- ¹⁷G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); **49**, 14 251 (1994); G. Kresse and J. Furthmuller, *ibid.* **54**, 11 169 (1996); Comput. Mater. Sci. **6**, 15 (1996).
- ¹⁸D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990); G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).
- ¹⁹N. Moll, A. Kley, E. Pehlke, and M. Scheffler, Phys. Rev. B **54**, 8844 (1996); J. E. Northrup and S. Froyen, Phys. Rev. Lett. **71**, 2276 (1996); and references therein.
- ²⁰C. H. Li, L. Li, Q. Fu, M. J. Begarney, and R. F. Hicks, Appl. Phys. Lett. **77**, 2139 (2000).