

# Surfactant-favored disorder in (001)-oriented CuPt-ordered $A^{\text{III}}(B^{\text{V}}, C^{\text{V}})$ alloy thin films: Action of Sb and Bi

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We perform *ab initio* calculations based on the density functional theory on thin films of III–V–V ternary alloys: Ga(As,Sb), Ga(As,P), In(As,Sb), and In(As,P), bare and covered with antimony and bismuth. We report optimized geometries of (001)-oriented, anion-terminated,  $\beta 2(2 \times 4)$ -reconstructed, CuPt-ordered thin films, and calculate the surface formation energies as well as "interchange energies" of the clean as well as Sb-covered and Bi-covered films. The work aims at probing the efficiency of Sb and Bi as surfactants which would lead to a disordered phase in the otherwise CuPt-ordered alloy thin films.

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## I. INTRODUCTION

The physics of semiconductor heterostructures has got important implications for development of optoelectronic semiconductor devices.<sup>1,2</sup> In the ternary and quaternary alloys forming the heterostructure a spontaneous atomic ordering occurs during the growth. Various types of ordering can be observed depending on the growth technique, structure, and orientation of the growth surface. While most of the III–V binary compound semiconductors crystallize in zinc blende structure, the semiconductor alloys of the type  $A_xB_{1-x}C$  (A, B being cations and C anion, or vice versa) may assume the following different structural arrangements: random, phase separation of A and B sublattices, and a definite atomic ordering of A and B atoms on the fcc sublattices. The phase separation into two bulk components is thermodynamically favored. However, there are many experimental observations of ordering, of copper-platinum (CuPt) type, in thin films of ternary alloys with 1:1 ratio of the two constituent binary compounds<sup>1,2</sup> for near(001) orientations of the substrates. For anion-terminated (001) oriented surfaces, triple-period ordering (TPO) in the subsurface layers with  $n \times 3$  type ( $n=2$  and 4) reconstructions on the top surface have also been observed.<sup>3,4</sup> One reason why ordering has gained so much attention is that the band gap ( $E_g$ ) is strongly dependent on the order parameter.<sup>5</sup> Controlling the degree of order would thus allow a fine tuning of the  $E_g$  and therefore, of different optical properties. From theoretical calculations, predictions exist for most III–V and II–VI atomically ordered alloys to have a decrease in band gap with respect to the disordered variant.<sup>6</sup> Extensive studies on atomic ordering propose that the surface thermodynamics is the cause of atomic ordering, while the growth kinetics is the propagator of the ordered arrangement.<sup>1,2,7,8</sup> The surface-dimer-induced subsurface stress mechanism for ordering has been proposed by Kelires and Tersoff,<sup>9</sup> further work was carried out by LeGoues *et al.*<sup>9</sup> The model proposed seems to be presently the best one to explain the wide range of ordering behavior observed in SiGe, III–V and II–VI alloy films grown on near (001) oriented substrates. Ordering energy calculations by the group of Zunger established a connection between the

surface thermodynamics and the experimental observation of the existence of a one-to-one correspondence between a particular surface reconstruction and a particular atomic ordering.<sup>1,10</sup> This leads to the idea of using impurity atoms to modify the structure of the surface and to influence the ordering in the semiconductor film. The surface impurity atoms, i.e., surfactants, if added during growth, segregate and accumulate at the surface modifying the bonding at the surface and changing the surface stress which, in turn, may affect the growth process near or at the surface. Studies of adsorbant-covered surfaces and surfactant mediated growth represent an interesting area of semiconductor physics.<sup>2,7,8,11</sup> For a detailed microscopic understanding of the role of surfactants modifying the ordering, as observed in the experimental studies on the epitaxial growth of III–III–V thin films,<sup>7,8</sup> it is important to study the energetics and the resulting atomic geometries of the surfactant-controlled growth. A considerable amount of theoretical studies on surfactant effects on III–III–V alloy films has accumulated in the literature.<sup>4,12</sup>

In the present paper we report a detailed study of the role of isoelectronic atoms, Sb and Bi in the CuPt-ordering of III–V–V alloy thin films. There are various reports on the CuPt-ordered III–V–V ternary alloys.<sup>1,2,13</sup> In many of these works, the ordering has been evidenced by transmission electron microscopic images and transmission electron diffraction patterns.<sup>13</sup> However, to the best of our knowledge, there is no microscopic study of the surfactant effect on the CuPt-ordering in III–V–V thin films in the literature. Hence, in this work, we concentrate on thin films of the following III–V–V ternary alloys: Ga(As,Sb), Ga(As,P), In(As,Sb), and In(As,P). We study the microscopic details of the surface geometry and the energetics of the (001)-oriented anion-terminated surfaces of the above thin films, with As-P dimers on top in Ga(As,P), In(As,P), and As-Sb dimers in Ga(As,Sb), In(As,Sb). We also study the same materials with Sb and Bi dimers on top, replacing the original heteroanion As-P and As-Sb dimers, in respective cases. These isoelectronic atoms are probed as candidates for surfactants the action of which would produce disorder in the CuPt-ordered alloys. We focus on Sb and Bi since these atoms were iden-

tified as promising candidates for surfactants in previous works on different III–III–V materials.<sup>4,7,8,12</sup> We probe how these atoms modify the bonding at the surface, which may result in changes in the surface energy. This, in turn, affects the growth and can lead to a disordered film. It is nevertheless worth noting that the thin film growth is also controlled by various kinetic factors which are beyond the scope of the present study.

## II. METHOD

Calculations of the total energy are performed employing the pseudopotential (PP) method within the density functional theory (DFT).<sup>14</sup> The Vienna *ab initio* simulation package (VASP) for electronic structure calculations<sup>15</sup> based on the PP technique is used to calculate total energies and forces within local density approximation. The ultrasoft Vanderbilt pseudopotentials<sup>16</sup> were obtained from the VASP pseudopotential database supplied by Kresse and Hafner.<sup>16</sup> The convergence of total energies with respect to  $k$ -point sampling and plane-wave cutoff was checked. In most of the calculations, a kinetic energy cutoff of 12.50 Ry has been employed. The electron density was calculated using the “special  $k$ -points”, sets generated under the Monkhorst–Pack scheme.<sup>17</sup> At least 64  $k$  points within the  $(1 \times 1)$  surface Brillouin zone were used for all surface calculations. Supercells consisting of several atomic layers are used for simulation of the alloy films with an anion-terminated surface (typically 12 atomic layers with about 100 atoms). In Fig. 1, we show a smaller eight-layer supercell used in the preliminary calculations. Here some discussion about the atomic arrangements on the surface is worth noting. In the top layer, we take heterodimers, for example, As-P, in case of Ga(As,P) and In(As,P). We note that surface segregation of certain atoms or species is well established in many of the ternary III–V systems. However, in the present systems the surface segregation was not considered for the following reasons. It is known from regular solution model<sup>18</sup> for a binary alloy that if there is a tendency for atomic ordering, individual atoms prefer to be surrounded by unlike nearest neighbors.<sup>13</sup> Moreover, to the best of our knowledge, no explicit evidence of surface segregation in the III–V–V systems studied here has been there in the literature. Instead it has been noted that no surface segregation of Sb has been observed in In(As,Sb) on GaAs (111)A substrate grown by molecular beam epitaxy.<sup>19</sup> Hence, we assume that there is no surface segregation of any of the anions, specifically the larger ones and so heterodimers are placed on the top in conformity with the ordering of anions in the subsurface layers.<sup>2,13</sup>

The bottom four atomic layers represent the substrate for the alloy thin film. In order to simulate the surface effects a sufficiently large vacuum layer (typically 10 Å) is put on one side of the supercell in order to separate the slab from its periodic image. The other side of the slab, terminated by cations, is passivated by pseudo-H atoms (charge  $Z=1.25$ ). Along the lateral directions (i.e., along the  $x$  and  $y$  axis), the starting lattice constant is taken to be that of the substrate. Then, in order to obtain the equilibrium structure, all atoms of the over-layer and two (out of four) atomic layers of the

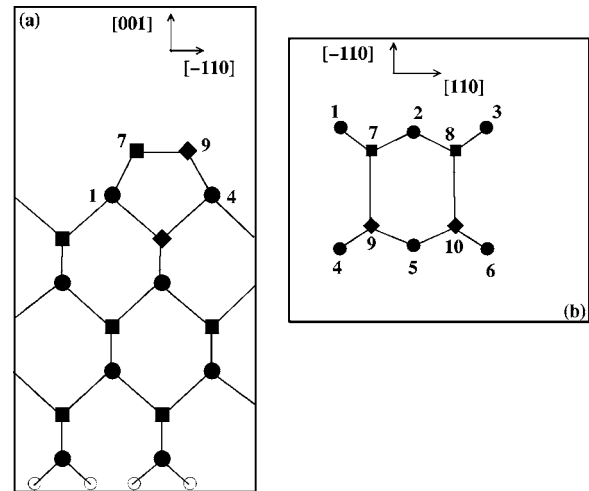


FIG. 1. (a) Side view of a slab having CuPt ordering in the anion sublattice representing an anion terminated thin film of Ga(As,P) on GaAs substrate. Diamonds represent phosphorus (P), squares are arsenic (As), and circles gallium (Ga) atoms. Top layer consists of As-P dimers (7-9), and in the surfactant covered cases, the Sb (and Bi) atom dimers replace the As-P dimers, similarly they replace the As-Sb dimers in the arsenide antimonide cases. The first subsurface layer consists of Ga atoms. Second subsurface layer consists of As and P atoms: the interchange energy involves the interchange of these As and P atoms. The smaller P atoms occupy the anion site directly below the top anion dimer 7-9 as part of the  $\beta 2(2 \times 4)$  reconstruction. Alternate anion and cation layers along the (001) direction are shown for a typical eight-layer slab. (b) Top view ( $XY$  plane projection) of anion terminated Ga(As,P) thin film on GaAs substrate; only two layers from the top are shown. As-P dimers form on the top surface along  $(\bar{1}10)$  (vertical direction) as a result of the  $\beta 2(2 \times 4)$  reconstruction.

substrate are relaxed until the forces are small. The bottom two atomic layers, as well as III–V–V the pseudohydrogen layers, are kept fixed in order to mimic the bulk substrate effect. The slab is electrically neutral but as a consequence of its nonsymmetric construction, it has a dipole moment, hence, we use a dipole correction.<sup>15</sup> The surface energy per unit area  $\gamma$ , for example of GaAs, may be expressed as a function of the chemical potentials,<sup>20</sup>  $\gamma A = U_{tot} - n_{Ga}\mu_{Ga} - n_{As}\mu_{As}$ , where  $U_{tot}$  is the total energy of a GaAs film and  $A$  is the surface area of the film.  $n_X$  and  $\mu_X$  are the number and chemical potential of atom  $X$ , respectively. Details on the calculations of  $\gamma$  can be found elsewhere.<sup>20</sup>

## III. RESULTS AND DISCUSSION

### A. Geometric structure

The calculated geometries of the top layers of (1) clean film surface, and (2) film surface covered with the surfactant atoms are summarized in Tables I–IV for Ga(As,P), Ga(As,Sb), In(As,P), and In(As,Sb), respectively. The thin films are studied with CuPt ordering in the anion sublattice and  $\beta 2(2 \times 4)$  reconstruction on the top, which is observed in most of the ternary alloys. Figures 1(a) and 1(b) give schematically the side and top views of a supercell of thin film

TABLE I. Geometry of top two layers of the 12 atomic layer thin film of Ga(As,P) and the cost of energy for As and P interchange in the second subsurface layer, the unit is electron-volt per supercell. "Regular" refers to a film with correct ordering of anions in the subsurface layers below and "interchanged" signifies that the anions in the second subsurface layer were interchanged (see text).

Bond length (Å)	Pure, As-P dimer		Sb-Sb dimer		Bi-Bi dimer	
	Regular	Interchanged	Regular	Interchanged	Regular	Interchanged
1-2(2-3)	3.93	3.93	3.95	3.95	3.95	3.95
4-5(5-6)	3.94	3.94	3.95	3.95	3.95	3.95
1-7(3-8)	2.38	2.39	2.63	2.62	2.70	2.70
2-7(2-8)	2.48	2.48	2.72	2.73	2.80	2.80
4-9(6-10)	2.49	2.50	2.62	2.62	2.70	2.70
5-9(5-10)	2.59	2.60	2.73	2.73	2.80	2.81
7-9(8-10)	2.34	2.35	5.06	5.07	4.88	4.90
Bond angle (deg)						
1-7-2(2-8-3)	108	108	95	95	92	92
4-9-5(5-10-6)	102	101	95	95	92	92
As/P interchange energy		1.01		-0.23		-0.17

with anion termination. In the  $\beta 2(2 \times 4)$  reconstruction, the distances between the subsurface cations 1-2 and 2-3 [Fig. 1(b)] are equivalent; distances 4-5 and 5-6, which are non-equivalent to 1-2 and 2-3, turn out to have equal lengths as well. The interplanar anion-cation distances 1-7(3-8), 2-7(2-8), 4-9(6-10), and 5-9(5-10) are tabulated in Tables I-IV for all four materials. In the clean films, when there are mixed anion dimers on the top (e.g., As-P, As-Sb), the distribution of these anion-cation distances is different compared to the distribution in the surfactant covered films with the pure dimers on top (e.g., Sb-Sb or Bi-Bi). As expected, the interplanar anion-cation length distribution is more symmetric for the pure dimers, compared to the mixed dimers on the top.

From Tables I-IV, for all the III-V-V alloy thin films studied here, when the top layer anion-anion distances 7-9 (and 8-10) are compared on clean and surfactant (Sb and Bi) covered surfaces, it is observed that the anion-anion lengths are larger in the cases with surfactants, as expected for larger

surfactant atoms. This implies that the surface strain will be reduced when the top anion dimers consist of the larger surfactant atoms. From Tables I-IV, it is also clear that the typical cation-anion-cation bond angles, (1-7-2, 2-8-3 or 4-9-5, 5-10-6) are smaller in cases which involves larger Sb and Bi atoms. Together with the observed shift of the top anions towards higher  $z$ , i.e., in the (001) direction, found in presence of Sb and Bi on top, the above analysis suggests *less strain in the subsurface layers for the surfactant-covered cases compared to the clean film* of some of the III-V-V materials studied here. It is also interesting to note the following relation. The top anion dimer lengths are  $2.34 \pm 0.01$  Å for As-P dimer in Ga(As,P) and In(As,P), and it is  $2.66 \pm 0.03$  Å for As-Sb dimer in both Ga(As,Sb) and In(As,Sb). In cases of In(As,Sb) and Ga(As,Sb), for Sb and Bi-covered surfaces, the top anion-anion lengths ( $2.86 \pm 0.03$  and  $3.01 \pm 0.04$  Å, respectively) are comparable with the Sb-Sb and Bi-Bi bond lengths in their elemental solid phase

TABLE II. Geometry of top two layers of the 12 atomic layer thin film of Ga(As,Sb) and the cost of energy of interchange of As and Sb in the second subsurface layer, unit is electron-volt per supercell. Regular refers to a film with correct ordering of anions in the subsurface layers below and interchanged signifies that the anions in the second subsurface layer were interchanged (see text).

Bond length (Å)	Pure, As-Sb dimer		Sb-Sb dimer		Bi-Bi dimer	
	Regular	Interchanged	Regular	Interchanged	Regular	Interchanged
1-2(2-3)	4.11	4.11	4.11	4.11	4.11	4.11
4-5(5-6)	4.11	4.11	4.11	4.11	4.11	4.11
1-7(3-8)	2.50	2.51	2.67	2.68	2.74	2.76
2-7(2-8)	2.61	2.61	2.77	2.77	2.84	2.85
4-9(6-10)	2.68	2.70	2.66	2.67	2.74	2.76
5-9(5-10)	2.78	2.79	2.77	2.77	2.84	2.85
7-9(8-10)	2.67	2.69	2.87	2.89	3.01	3.05
Bond angle (deg)						
1-7-2(2-8-3)	107	107	98	98	95	94
4-9-5(5-10-6)	98	97	98	98	95	94
As/Sb interchange energy		1.08		1.02		0.19

TABLE III. Geometry of top two layers of the 12 atomic layer thin film of In(As,P) and the cost of energy for the interchange of As and P atoms in the second subsurface layer, unit is electron-volt per supercell. Regular refers to a film with correct ordering of anions in the subsurface layers below and interchanged signifies that the anions in the second subsurface layer were interchanged (see text).

Bond length (Å)	Pure, As-P dimer		Sb-Sb dimer		Bi-Bi dimer	
	Regular	Interchanged	Regular	Interchanged	Regular	Interchanged
1-2(2-3)	3.68	3.67	3.71	3.71	3.71	3.71
4-5(5-6)	3.65	3.52	3.74	3.74	3.72	3.72
1-7(3-8)	2.48	2.49	2.72	2.72	2.80	2.79
2-7(2-8)	2.61	2.61	2.89	2.89	2.97	2.97
4-9(6-10)	2.56	2.57	2.73	2.73	2.81	2.80
5-9(5-10)	2.71	2.71	2.85	2.86	2.94	2.93
7-9(8-10)	2.33	2.34	2.84	2.85	5.24	5.26
Bond angle (deg)						
1-7-2(2-8-3)	93	92	83	83	80	80
4-9-5(5-10-6)	88	84	84	83	81	81
As/P interchange energy		0.49		0.23		-0.31

2.90 and 3.09Å, respectively. A similar relation was noticed by Li *et al.* who compared the bonding properties of adsorbed P, As, and Sb on the GaAs (001) surface.<sup>21</sup> The P atoms exhibit the shortest dimer bond length and the strongest backbonds to Ga: the dimer bond-lengths are 2.23, 2.50, and 2.86Å, for adsorbed P, As, and Sb atoms on the GaAs surface,<sup>21</sup> respectively. We observe that *the top anion dimer bond lengths are quite similar in any environment*—from both theoretical and experimental studies on III–III–V and III–V–V films with anion termination at the top surface.<sup>7,8,12,21,22</sup> This observation is very general irrespective of the host material surface on which the dimers are formed.

### B. Interchange energies

In order to quantitatively understand the decrease in the strength of ordering with the total replacement of P, As, Sb

by surfactant atoms on the top, we report in Tables I–IV the energetic cost of interchanging all pairs of anions in the subsurface anion layer (second layer from the top: refer to Fig. 1). This means interchanging in the second subsurface layer the smaller anion below the top anion dimers, (which is driven by the reconstruction) by the larger anions, both in the clean alloy film and the surfactant covered film. This cost in total energy is indicative of the strength of ordering.<sup>1</sup> Since the presence of the anion dimer on the top surface induces strain in the subsurface layers, which leads to the occupation of the anion site below the top dimer by the smaller anion and, hence, favors ordering, the above-mentioned interchange of bigger and smaller atom pairs in the subsurface layer acts against the propensity to ordering. Table I shows that the energy-difference between Ga(As,P) clean film and the same film with As and P atoms interchanged in the second subsurface layer is of 1.01 eV per supercell. When the

TABLE IV. Geometry of top two layers of the 12 atomic layer thin film of In(As,Sb) and the cost of energy for interchanging of As and Sb atoms in the second subsurface layer, unit is electron-volt per supercell. Regular refers to a film with correct ordering of anions in the subsurface layers below and interchanged signifies that the anions in the second subsurface layer were interchanged (see text).

Bond length (Å)	Pure, As-Sb dimer		Sb-Sb dimer		Bi-Bi dimer	
	Regular	Interchanged	Regular	Interchanged	Regular	Interchanged
1-2(2-3)	3.59	3.60	3.74	3.72	3.73	3.73
4-5(5-6)	3.73	3.60	3.75	3.73	3.74	3.74
1-7(3-8)	2.53	2.55	2.71	2.73	2.79	2.80
2-7(2-8)	2.68	2.69	2.88	2.89	2.96	2.95
4-9(6-10)	2.73	2.72	2.73	2.73	2.80	2.80
5-9(5-10)	2.83	2.86	2.83	2.84	2.91	2.92
7-9(8-10)	2.63	2.65	2.83	2.85	2.99	3.01
Bond angle (deg)						
1-7-2(2-8-3)	87	87	84	83	81	81
4-9-5(5-10-6)	84	80	85	84	82	82
As/Sb interchange energy		0.51		0.39		0.32



top surface As-P dimers are replaced with Sb-Sb dimers, the cost of interchanging the As and P in the second subsurface layers becomes  $-0.23$  eV per supercell and, similarly, with the Bi surfactant the interchange energy is  $-0.17$  eV per supercell. Hence, we observe that, when the Sb and Bi dimers replace the As-P dimers on the surface, the energetic cost of interchanging As and P in the second subsurface layer is reduced by a large amount, actually favoring the interchange, and the strength of ordering is thus expected to be significantly reduced. Both the surface geometry and the interchange energy analysis thus indicate that the larger atoms Sb and Bi may be good candidates as surfactant materials aiming at reducing the order and leading to a disordered phase in Ga(As,P). In addition, our study (Table I) indicates that the action of Sb and Bi is similar in producing subsurface disorder in the Ga(As,P) material. For the other systems, Ga(As,Sb), In(As,P), and In(As,Sb), the geometries of the top layers and the interchange energies are shown in Tables II–IV, respectively. One can see that for Ga(As,Sb) the atom of Bi may have a small effect as a disorder-producing agent, whereas for In(As,Sb) neither Sb nor Bi would be expected to have any effect in producing disorder. On the other hand, in case of In(As,P), Bi may have a significant effect as a subsurface-disorder-producing material, while Sb is expected to have no effect. Another correlation which can be observed from Tables I–IV: in all situations where a surfactant (Sb or Bi) is expected to have a significant effect on the subsurface disorder, the corresponding top surface surfactant dimer length has increased by a substantially large amount.

### C. Surface energetics

We expect that the effects of Sb and Bi are very similar since for both clean and surfactant-covered films of Ga(As,P), surface energies are very close to each other and also the stability range of the Bi-covered surfaces is very close to that of the Sb-covered ones. More interestingly, there is a large range of cation, “chemical pressure”  $\mu_{Ga}$  where the surface energies of the films with Sb or Bi on top are lower than those of the clean film (Fig. 2), which indicates that Sb and Bi have significant, favorable effect on the surface structure of Ga(As,P)—as the low surface formation energy is a measure of the ease of surface formation. In the case of In(As,P), on the contrary, the surface energies of the clean and the Bi-covered film (Fig. 2) suggest a less pronounced effect of Bi as surfactant, compared to Ga(As,P); this can also be observed on the As and P interchange energies (Tables I and III, respectively). Figure 2 shows that the range of cation chemical pressure  $\mu_{In}$  is much less in In(As,P) where the surface energy of the film with Bi on top is lower compared to the clean film. Hence, the surface energetics corroborates with the results of the geometric and interchange energy studies.

### IV. CONCLUSION

Our first-principles calculations on (001)-oriented, anion-terminated,  $\beta 2(2 \times 4)$ -reconstructed CuPt-ordered III–V–V

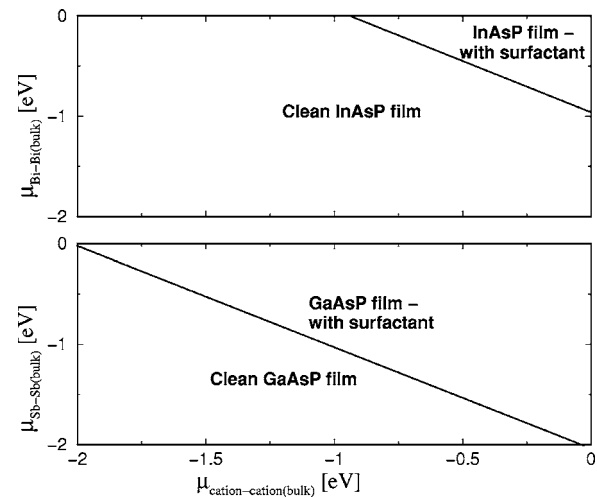


FIG. 2. Phase diagram of the relative surface energies for Ga(As,P) and In(As,P) films. The figure gives the ranges of chemical potentials (of cations and surfactants) in which one or another type of the film (clean or surfactant-covered) is energetically preferred (with lower surface energy). We note that the range of stability of the Bi-covered surface of In(As,P) is much smaller than in the case of the Ga(As,P) films (see text).

thin films show the following. (i) The effects of surfactants Sb and Bi in favoring disorder in the subsurface anion layers are similar, and are expected to be strong in the Ga(As,P) thin films. (ii) In case of In(As,P) thin films, it is only Bi which may have any significant effect. (iii) The calculations for the arsenide-antimonides, viz. Ga(As,Sb) and In(As,Sb), show that Sb and Bi are not expected to have any significant effect in blocking the subsurface ordering during the growth of these films. (iv) Our study of geometry and energetics of the III–V–V thin films with anion-terminated surfaces support the on-going discussion<sup>1,2</sup> which suggests that the ordering mechanism is the same in both III–III–V and III–V–V types of ternary alloy films,—namely, the subsurface strain induced by dimerisation of the anions at the surface. The results of the present study can be of relevance in the growth of ternary alloy thin films of III–V–V type.

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