Proc. XIX International School of Semiconducting Compounds, Jaszowiec 1990

SURFACE STABILITY OF ORDERED $Ga_{0.5}In_{0.5}P$ AND $GaAs_{0.5}Sb_{0.5}$ ALLOYS

P. BOGUSŁAWSKI

Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warszawa, Poland

(Received August 8, 1990)

Formation enthalpies of (001) surfaces terminating ordered $Ga_{0.5}In_{0.5}P$ and $GaAs_{0.5}Sb_{0.5}$ alloys were calculated using the VFF model. For several ordered phases, chemically ordered surfaces were found to be stable against surface segregation. In particular, even phases unstable against bulk segregation may be terminated by a stable surface.

PACS numbers: 68.65.+g, 68.60.Dv, 61.55.Hg

Thermodynamic stability has recently been investigated theoretically for several ordered lattice-mismatched alloys [1-4]. It was found that both (001) and (111) lattice-mismatched monolayer superlattices (MSL's) are intrinsically unstable at T = 0, and should segregate into pure end compounds. The instability of these systems persists even when the epitaxial stabilization is taken into account. As it was shown in [1], the instability is due to the excess elastic energy of bonds distorted by the lattice misfit.

In the above context, the unintentional growth of both (001) and (111) lattice-mismatched MSL's is unexplained. Epitaxial growth of these phases has been recently reported for several III-V alloys [5]. The most frequent form of ordering, reported for all systems investigated so far, is a (111)-oriented MSL. On the other hand, the theory indicates that this phase is more unstable than both the (100) MSL and the random phase. Its metastability was confirmed experimentally [7]. One should observe, however, that the previous theoretical approaches neglected active role of the surface processes in epitaxy.

In particular, it was suggested [8] that the growth of an ordered epitaxial alloy originates in a 2D ordering of atoms at the surface during growth. This, in turn, may be driven by the stability of chemically ordered surfaces. To verify this possibility, we have investigated surface stability against 2D segregation at T = 0, which is given by the surface formation enthalpy

$$\Delta E_{sur}(\alpha) = E(\alpha) - \frac{1}{2}[E(\alpha; A) + E(\alpha; B)].$$

(125)

Here, $E(\alpha)$ and $E(\alpha; X)$ are the total energy of the substrate covered by *n* overlayers of the phase α , and the total energy of the substrate covered by (n-1)overlayers of that phase and by segregated X atoms (X = A or B in the case of $A_{1-x}B_xC$ alloy) at the surface, respectively. Total energies were obtained within the valence-force-field (VFF) model [9], applied with success to study both bulk [2] and surface [10] problems. Thus, only the excess elastic energy is considered. Details of calculations are given in [6].

TABLE 1.

| of infinite epitaxial systems ΔE_{epi} (in meV/atom). | | | | | |
|---|------------------|------------------|------------------|------------------|--|
| · | GaP/InP | | GaAs/GaSb | | |
| 2-5 | ΔE_{sur} | ΔE_{epi} | ΔE_{sur} | ΔE_{epi} | |
| (111) MSL | +1 | +8.5 | +1 | +7.7 | |
| (11Ī) MSL | -12 | + 8.5 | -13 | + 7.7 | |
| (100) MSL | -13 | -1.6 | -14 | -1.6 | |
| $(\overline{1}10)$ BSL | -1 | -4.4 | -1 | -4.5 | |
| (110) BSL | -24 | -4.4 | -25 | -4.5 | |

| Calculated surface formation enthalpies |
|---|
| ΔE_{sur} (in meV/surface atom) and formation enthalpies |
| of infinite epitaxial systems ΔE_{epi} (in meV/atom). |

Calculations are done for epitaxial ordered GaAs_{0.5}Sb_{0.5} and Ga_{0.5}In_{0.5}P alloys grown on nearly lattice-matched GaAs and InP (001) substrates, respectively. We have considered the phases of (100) and (111) MSL's and (110) bilayer superlattices (BSL's). The calculated surface formation enthalpies are summarized in Table I. We begin by observing that the presence of a free surface lowers the symmetry in comparison with the case of infinite systems. In particular, four < 111 > directions equivalent in the zinc-blende structure are split into two pairs of equivalent axes, namely ([111], [111]) and ([111], [111]). Similarly, [110] and [110]directions are not equivalent. Surface formation enthalpies of nonequivalent variants are different from each other, see Table I. Comparing first $(\overline{111})$ and $(11\overline{1})$ GaP/InP MSL's we see that the former one is stable against segregation into Ga- and In-covered surface, which follows from the negative $\Delta E_{sur}(\bar{1}11) = -12$ meV/surface atom. In contrast, ΔE_{sur} of the (111) MSL equal to 1 meV/surface atom is negligibly small. This qualitative difference stems from different relaxations of subsurface atoms in the two cases. In the case of $(\overline{1}11)$ MSL, $[1\overline{1}0]$ -oriented chains of anion dangling bonds at the surface are saturated by one type of cations. Thus, by symmetry, anions relax along the [001] direction only. The same situation occurs for the surface covered by segregated Ga or In. On the other hand, in the (111) MSL case, the chains of dangling bonds are saturated by alternating Ga and In. Here anions relax not only along [001], but also along the $[1\overline{1}0]$ direction. This allows for a more efficient minimization of the elastic energy [8], which stabilizes the ordered surface of $(\overline{1}11)$ MSL with respect to the segregation. Also in the case of the (100) MSL, the chains of dangling bonds are saturated by alternating Ga and In. This allows again for the stabilizing lateral relaxation of substrate As atoms, and the (001) surface of (100) (or of the equivalent (010)) GaP/InP MSL is stable with $\Delta E_{sur} = -13$ meV/surface atom.

According to the present calculations, the growth of GaP/InP (110) BSL is energetically the most favorable. This structure may be regarded as a periodic sequence of monolayers of [111]- and [111]-oriented MSL's, grown in [001] direction. Its high stability is driven by the configuration at the P-terminated surface, discussed in [6].

The results obtained for ordered $GaAs_{0.5}Sb_{0.5}$ are similar to these for $Ga_{0.5}In_{0.5}P$ due to a similarity of lattice misfits and elastic constants.

Within the model of epitaxial growth assumed tacitly here (active processes at the surface, and the lack of 3D diffusion), stability of a given surface coverage depends on the atomic configuration at the surface, but is independent of the global stability of the system. For example, as it follows from Table I, an infinite epitaxial (I11) GaP/InP MSL is unstable with the formation enthalpy $\Delta E_{epi} =$ +8.5 meV/atom, but its cation-terminated (001) surface is stable. In contrast, a (110) GaP/InP BSL is globally stable with $\Delta E_{epi} = -4.4$ meV/atom, but its $\Delta E_{sur} \simeq 0$.

In spite of the model character of the calculations, the present results reasonably agree with the morphology of ordered $Ga_{0.5}In_{0.5}P$ and $GaAs_{0.5}Sb_{0.5}$ grown at low temperatures. In particular, we account for the growth of only two orientations of (111) MSL's (reported for all systems investigated so far), and of only one (110) BSL variant (reported for GaP/InP [11]). Further, ΔE_{sur} for (100) and ($\overline{111$) MSL's are close to each other, which may explain the growth of both phases reported for GaAs_{0.5}Sb_{0.5} [12,13]. On the other hand, high ordering of Ga_{0.5}In_{0.5}P in the phase of ($\overline{111}$) MSL occurring for high growth temperatures is not explained by the present approach, and is possibly due [8] to the presence of monolayer steps at the surface.

In summary, surface formation enthalpies of ordered $Ga_{0.5}In_{0.5}P$ and $GaAs_{0.5}Sb_{0.5}$ alloys have been estimated within the VFF model. (001) surfaces of (100) and (111) MSL's and of (110) BSL's have been considered. Chemically ordered surfaces terminating the observed variants of these systems are found to be stable against segregation at the surface at T = 0. The unobserved variants are terminated by surfaces with negligible formation enthalpies. Surface stability is independent of the global stability of the alloy.

References

- P. Bogusławski, A. Baldereschi, Solid State Commun. 66, 679 (1988); Phys. Rev. B 39, 8055 (1989).
- [2] J.E. Bernard, L.G. Ferriera, S.-H. Wei, A. Zunger, Phys. Rev. B 38, 6338 (1988).
- [3] J.S. Nelson, I.P. Batra, Phys. Rev. B 39, 3250 (1989).
- [4] R. Magri, C. Calandra, Phys. Rev. B 40, 3896 (1989).
- [5] For a review of experimental data, see G.B. Stringfellow, J. Cryst. Growth 98, 108 (1989);

P. Bogusławski, Acta Phys. Pol., in print, and Ref. [6].

[6] P. Bogusławski, Phys. Rev. B 42, 3737 (1990).

- [7] P. Gavrilovic et al., J. Cryst. Growth 93, 426 (1988).
- [8] T. Suzuki, A. Gomyo, S. Iijima, J. Cryst. Growth 93, 396 (1988).
- P.N. Keating, *Phys. Rev.* 145, 637 (1966). Elastic constants given by A.B. Chen, A. Sher, *Phys. Rev. B* 32, 3695 (1985) are used.
- [10] G.-X. Qian, D.J. Chadi, J. Vac. Sci. & Technol. B 4, 1079 (1986).
- [11] S. Yasuami et al., Appl. Phys. Lett. 52, 2031 (1988).
- [12] Y.-E. Ihm, N. Otsuka, J. Klem, H. Morkoc, Appl Phys. Lett. 51, 2013 (1987).
- [13] H. R. Jen, M. J. Cherng, G.B. Stringfellow, Appl. Phys Lett. 48, 1603 (1986).