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MICROSTRUCTURAL STABILITY IN LPE $Ga_x In_{(1-x)}As_ySb_{(1-y)}/GaSb$ HETEROSTRUCTURES

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ABSTRACT

The morphological and structural characteristics associated with the growth of lattice matched $In_xGa_{(1-x)}As_ySb_{(1-y)}/GaSb$ (100) heterostructures is presented. The experiments focused on studying the effect of growth on vicinal surfaces tilted from the exact (100) orientation as well as variations in epilayer chemistry. It was found that variations in these process parameters had very strong effects on both the nucleation characteristics of the epilayer and the atomistic scale homogeneity of the alloy. The <100> and <110> variants in compositional modulation / phase separation were detected, as well as the evolution of weak (110) ordering. These results are discussed in the context of other studies on phase stability in III-V epitaxial structures, especially in terms of surface reconstruction and kinetic effects near conditions of spinodal decomposition.

INTRODUCTION

Ternary and quaternary III-V compound semiconducting materials having a low band gap (0.5 - 0.7 eV) have attracted attention for potential thermophotovoltaic applications. One of the challenges in growing high quality epitaxial layers of these multi-component systems is the fact that thermodynamically these alloys are known to exhibit compositional regimes, where phase instabilities such as spinodal decomposition and ordering can occur. Such structural changes can have a profound influence on fundamental properties such as the energy bandgap. Also, there is the challenge of understanding the influence of the chemical complexity of the epitaxial interface structure when such multicomponent systems are involved. While there are a number of studies on ternary systems, there is far less reported on quartenary epitaxial layers.

A thermodynamic analysis of $Ga_xIn_{1-x}As_ySb_{1-y}$ stability has been reported in the literature [1]. However the present study is the first on exploring in detail the microstructural characteristics on quaternary lattice matched $Ga_xIn_{1-x}As_ySb_{1-y}$ alloys grown by liquid phase epitaxy (LPE) on (100) GaSb. The influence of varying these growth parameters on both the nucleation and growth mechanisms of epitiaxial films as well as the type and length scale of microstructural inhomoegeneities were explored.

EXPERIMENTAL DETAILS

The growth parameter space used in this study involved independently examining the effects of epilayer chemistry and the role of substrate misorientation. A series of three different liquid compositions were grown by liquid phase epitaxy. The choice of composition was dictated by the requirement of achieving a 0.55 eV bandgap material, and yet at the same time staying in a single phase region (i.e., outside the spinodal boundary, Figure 1). An additional requirement was to maintain lattice matching to GaSb. Hence, the compositions that were considered all followed the iso-lattice parameter line as shown in Figure 1. Three samples were studied which followed the iso-lattice parameter line associated with lattice matched heterostructures, and yet laid outside the equilibrium 600°C spinodal boundary [2]. The samples were $Ga_{0.82}In_{0.18}As_{0.14}Sb_{0.86}$ (sample A), $Ga_{0.87}In_{0.13}As_{0.12}Sb_{0.88}$ (sample B), and $Ga_{0.92}In_{0.08}As_{0.07}Sb_{0.93}$ (sample C) grown on GaSb (001) substrates. The composition of sample A, $Ga_{0.82}In_{0.18}As_{0.14}Sb_{0.86}$,was used to study substrate misorientation effects (see Table I)

Table I : Substrate misorientations use for growth on vicinal surfaces

Substrate Orientation
(100)
2°→(111_A) on (100)
2°→(110) on (100)
6°→(110) on (100)
6°→(111_B) on (100)

A conventional horizontal graphite source-seed sliding boat in a Pd -diffused hydrogen atmosphere was used for the LPE process and the epilayers were grown on Te doped GaSb commercial wafers. After preparation of the constituent components and substrate cleaned by HF acid etch. The solution was remelted at 560 °C for 1 hour followed by a slow ramp to the liquidus temperature of 532 °C. The growth temperature conditions for all these films was 530 °C.

EXPERIMENTAL RESULTS

1. Morphological Studies

Variations in epilayer chemistry for a given (100) GaSb orientation and in substrate misorientation for $Ga_{0.82}In_{0.18}As_{0.14}Sb_{0.86}$ (sample A) showed distinct changes in the morphology of the epitaxial layer. In some cases, the film growth resulted in continuous coverage and may be termed Frank-van der Merwe type. Of course, the length scales are much larger than monolayer dimensions. In other cases we found that a Stranski-Krastanov type of film growth mode, and only at a large thickness did island coalescence lead to a continuous film. In all of these misorientated substrate growth studies, only a single composition $Ga_{0.88}In_{0.12}As_{0.14}Sb_{0.86}$ was evaluated for the all orientations. A continuous film, Frank - van der Merwe growth mode was observed only at 2° toward (110) on (100) for the same nominal InGaAsSb quaternary composition. All the other orientations showed a typical Stranski-Krastinov growth mode as was observed in the composition studies previously described. The wetting characteristics of the quaternary alloy films are governed by the substrate orientation.

Another significant observation was that the island growth was quite anisotropic. The results are summarized in Tables II and III and Figures 2 and 3. Not only was there a sensitivity to the growth mode, but the morphology of the island growth also varied. There was also a high aspect ratio in the plane of the substrate. The strong facetting indicated a highly anisotropic growth mechanism. It was interesting to note that for all the islands the long axis was always perpendicular to the growth direction in these experiments. This anisotropic wetting behavior indicates that the nucleation behavior is strongly influenced by the substrate orientation and it led to the next set of studies, where the substrate orientations were varied as a function of a single composition to provide additional insight into these surface nucleation processes.

Table II: Effect of Composition on Island Morphology in Stranski-Krastanov Growth Mode

Sample			**Island Morphology**
	x	y	
A	0.82	0.14	Elongated oval - flat top
B	0.87	0.12	Elongated triangular
C	0.92	0.07	Elongated pyramidal - flat top

Table III: Effect of Substrate Misorientation on Island Morphology in Stranski-Krastanov Growth Mode - $Ga_{0.82}In_{0.18}As_{0.14}Sb_{0.86}$

GaSb Substrate Surface	**Island Morphology**
(100)	Elongated oval - flat top
2°→(111_A) on (100)	Elongated diamond – {111} facets
2°→(110) on (100)	Continuous film
6°→(110) on (100)	Continuous film
6°→(111_B) on (100)	Triangular island – {111} facets

2. Diffraction Studies

Table IV and Figures 4 and 5 summarize the structural changes as monitored by electron diffraction, associated with the varying growth parameters of the samples used. What is most significant in these observations is the presence of a {110} type ordering instead of the CuPt type ordering that is often reported [7]. As discussed in the next section of this paper, there have been however, some reports in the literature suggesting the possibility of such transformations. Clearly however, even these reports have not provided a clear explanation of the cause of such structural effects, as elaborated in this paper.

Table IV: Summary of electron diffraction results

Sample	**Variants of Diffuse Scattering**	**Ordering Type Reflections**
A	$[110]$&$[1\bar{1}0]$	Weak (110) type reflections
B	$[110]$&$[1\bar{1}0]$	None
C	$[110]$&$[1\bar{1}0]$ $[001]$&$[010]$	Weak (110) reflections
D (same composition as A; 2°→(110) on (100)	$[110]$&$[1\bar{1}0]$ $[001]$&$[010]$	Weak (110) reflections

DISCUSSION

The observations reported here are the first regarding the LPE growth of this quaternary system, although compositional modulations in LPE systems have been documented [3,4]

Kuwano et al. [6] have shown that LPE GaInAsP latticed matched on GaAs also exhibits compositional modulations with 100-200 nm wavelength. They attributed the long wavelength modulation to spinodal decomposition which is developed by the rapid diffusion of elements along the liquid – solid interface; a phenomena that they refer to as interfacial spinodal decomposition [3]. Kuwano et al. did find, as we have here in this study the development in the modulation of orthogonal variants in the [010] and [001] directions which they associated with a wavelength of approximately 10 nm.

The work of Suzuki et al. [7] has shown that there is a strong dependency on the nature of the sublattice ordering in the epilayer on the nature of the substrate orientation. Based on their studies on the quarternary AlGaInP system, they proposed the concept of "intra-plane ordering" which relates to ordering within each (100) plane. This mechanism aligns the Ga and In atoms into a series of alternate [110] direction Ga-atom lines and In-atom lines within each (100) plane. This type of mechanism may be operative here, since there is lateral modulation along the <100> directions and in some cases modulation in both the <100> and the <110> directions leading to weak ordering effects of a (110) type. Suzuki et al. suggested that an anisotropy in site occupancy affinity is a thermodynamic driving force for the ordering of alternate In and Ga atoms in the (100) plane [8]. Adapting the Suzuki model to our case, it may be suggested that a column V element (As or Sb) can stabilize the (100) plane with an In atom using the strain minimization prinicpal proposed by these workers.

It is interesting to note that Ihm et al. [9] found 50 – 200 nm size domains in their study of ordering GaAsSb epitaxial layers grown by MBE. Similar in magnitude to the compositional modulations observed here. Kurtz et al. [10] in their observations of InAsSb ordering acknowledged the existence of extra diffraction spots in the <200> direction. While they did not provide an explanation of this observation, it is suggested here that the diffuse scattering in that direction observed in our present study is in fact an indication of the 'precursor' condition to the weak ordering observed that they observed. In our case, however, as shown in sample A, we observed weak spots halfway to the (022) spot rather than ¼ and ¾ of the distance to the (022) spot as seen in the InAsSb layers. The differences may in part be attributed to the different systems being studied, the fact similar results of the fine structure detail are observed in a wide variety of III-V systems involving different growth techniques suggests that some fundamental thermodynamic issues must be common in developing the different levels of compositional modulation / ordering observed in ternary and quaternary III-V systems. The sensitivity of ordering / superlattice variants with substrate misorientation has been reported for ternary GaInP [8,11], but the observations here on a quaternary do not follow the development of same CuPt type of ordering. On the other hand, the development of lateral phase separation along the <110> direction as observed in one of the samples has been reported for InGaAsP / (100) InP by Okada et al. [12]. It is suggested that this modulation is a surface mediated process controlled by surface reconstruction on the (100) surface.

The role of surface reconstruction has also been suggested as an explanation of the [110] modulation in GaAsSb grown by MBE (see, for example, Murgatroyd et al. [13]). While the physical mechanisms of deposition are different than LPE, these workers reported a modulation along the [110] direction with a periodicity of 4 times the (110) lattice spacing which is similar in magnitude to our observations. Our observations of modulations along the <100> type directions have been observed by other workers. For example, McDevitt et al. [14], in their study of GaInAsP emphasized the importance of surface diffusion for spinodal decomposition as the basis for developing a compositional modulation. While Ipatova et al.[15] developed a theoretical framework to rationalize these observations and suggested that <100> type modulations can indeed be stable and amplify depending upon the elastic anisotropy of the system. Compositional modulations were correlated to the crystallographic dependency of the fluctuations of the elastic energy.

Previous work by Rajan and co-workers [16,17] suggested that such compositional modulations can lead to weak long range order. Keeping in mind that the compositions studied here are nominally outside the spinodal, compostional instabilities can still occur in the single phase regions if the condition:

$$\frac{d^2G}{dc^2} < 0$$

is satisfied. Where G is the Gibbs free energy and c is the composition. With such a spinodal condition, an initially homogeneous solid solution is unstable to an initial infinitesimal fluctuation, so that some sinusoidal perturbation can grow; leading to compositional modulations. For such an inhomogeneous solid solution:

$$\frac{dG}{dc} = \frac{dG}{dc}_{\text{hom}\,o} - \frac{2K\nabla^2 c}{V_m}$$

where K is the gradient energy coefficient. Which is a function of the differences in the coordination number of the component species between the homogeneous (random) and inhomogeneous alloys (V_M is the molar volume). As this transformation is a continuous one (i.e. the initial and final structure share a common lattice) and is based solely on diffusion, the above thermodynamic parameters may be incorporated into a diffusion equation [18]. The diffusive flux is given as:

$$\tilde{J} = -M_D \frac{d^2G}{dc^2} \nabla c + 2M_D K \nabla^3 c$$

Fick's second law may then be expressed as:

$$\frac{dc}{dt} = M_D \frac{d^2G}{dc^2} \nabla^2 c - 2M_D K \nabla^4 c$$

where M_D is the diffusional mobility.

Unlike the spinodal decomposition case with $\frac{d^2G}{dc^2} < 0$ and $K > 0$, ordering can occur for the opposite case. With a strongly positive second order condition and a negative K, a system can go from a disordered phase to an ordered phase without a change in composition. Even though we are nominally outside the spinodal region, it is suggested here that the different variants and degree of compositional modulations and ordering are due to localized strain effects. The origins of these strain energy effects maybe akin to Suzuki's model for intra-plane ordering.

The results described above indicate a complex interaction between interface structure at the epitaxial interface and epilayer chemistry on both the nucleation characteristics of epitaxial growth as well as the chemical homogeneity at the atomic level. It is suggested that the role of substrate surface structure and energy which governs the compositional modulations also governs the wetting behavior of the epilayer. The variations in wetting behavior are manifested in the variations in the morphology of the Stranski-Krastanov island growth.

CONCLUSIONS

The present study has outlined for the first time a set of microstructural characteristics for LPE grown $In_xGa_{(1-x)}As_ySb_{(1-y)}$ epitaxial layers grown on GaSb (100) substrates:

1. It was shown that the nucleation mode of quaternary epitaxial layers is strongly dependent on both the alloy chemistry and the structure of the vicinal surface of the substrate.
2. The anisotropy in wetting behavior and its dependency on substrate tilt and epilayer chemistry is strongly suggestive of the importance of surface structure on the nucleation mechanisms of epitaxial growth in LPE.
3. Concurrent to the changes in morphology, there is also the development of compositional modulations at the atomistic scale as detected by electron diffraction.
4. Different crystallographic variants in compositional modulation have been observed along with the development of weak (110) ordering.
5. A generalized coupled thermodynamic/ kinetic formulation based on the concepts of continuous ordering has been outlined as a framework for characterizing phase stability in these systems.

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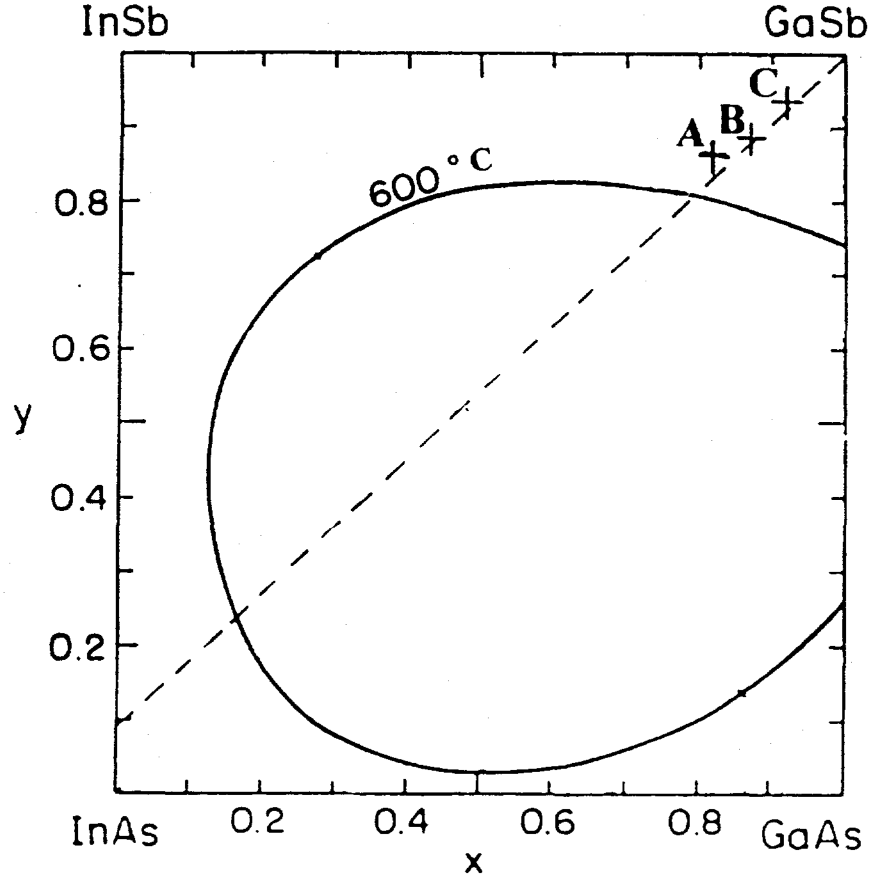

FIG. 1. Phase diagram shows the relative positions of samples **A**, **B** and **C**. The solid curve is Spinodal isotherm for $In_{1-x}Ga_xAs_{1-y}Sb_y$ at temperature 600 °C. Dashed line represents compositions for lattice-matching to GaSb. From reference 2.

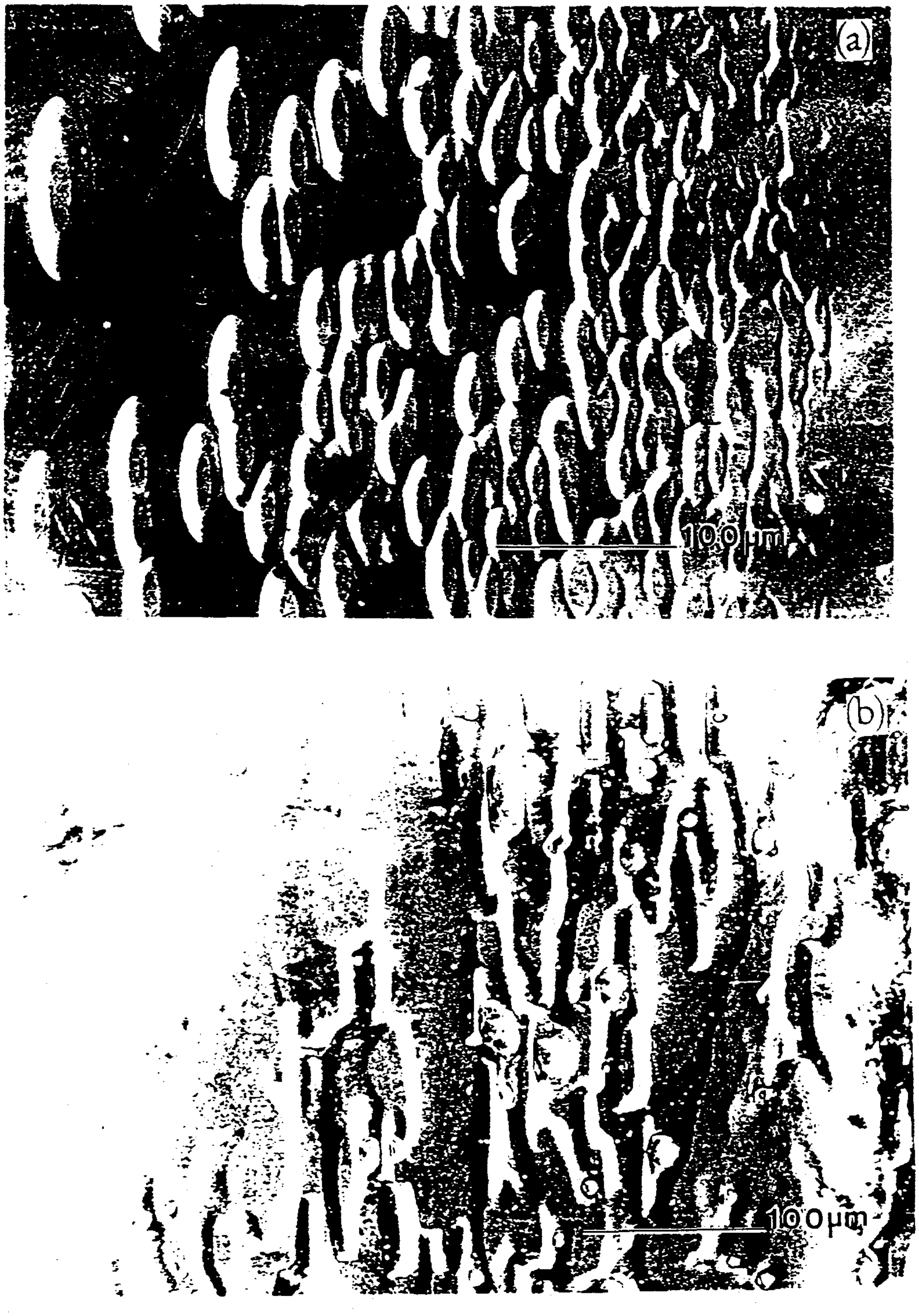

FIG. 2. Scanning electron microscopy (SEM) images of quaternary (a) $Ga_{0.82}In_{0.18}As_{0.14}Sb_{0.86}$, sample **A**, and (b) $Ga_{0.92}In_{0.08}As_{0.07}Sb_{0.93}$, sample **C**, compositions of epitaxial films grown on (100) GaSb substrate showing the effect of different compositions on changes in film morphology.

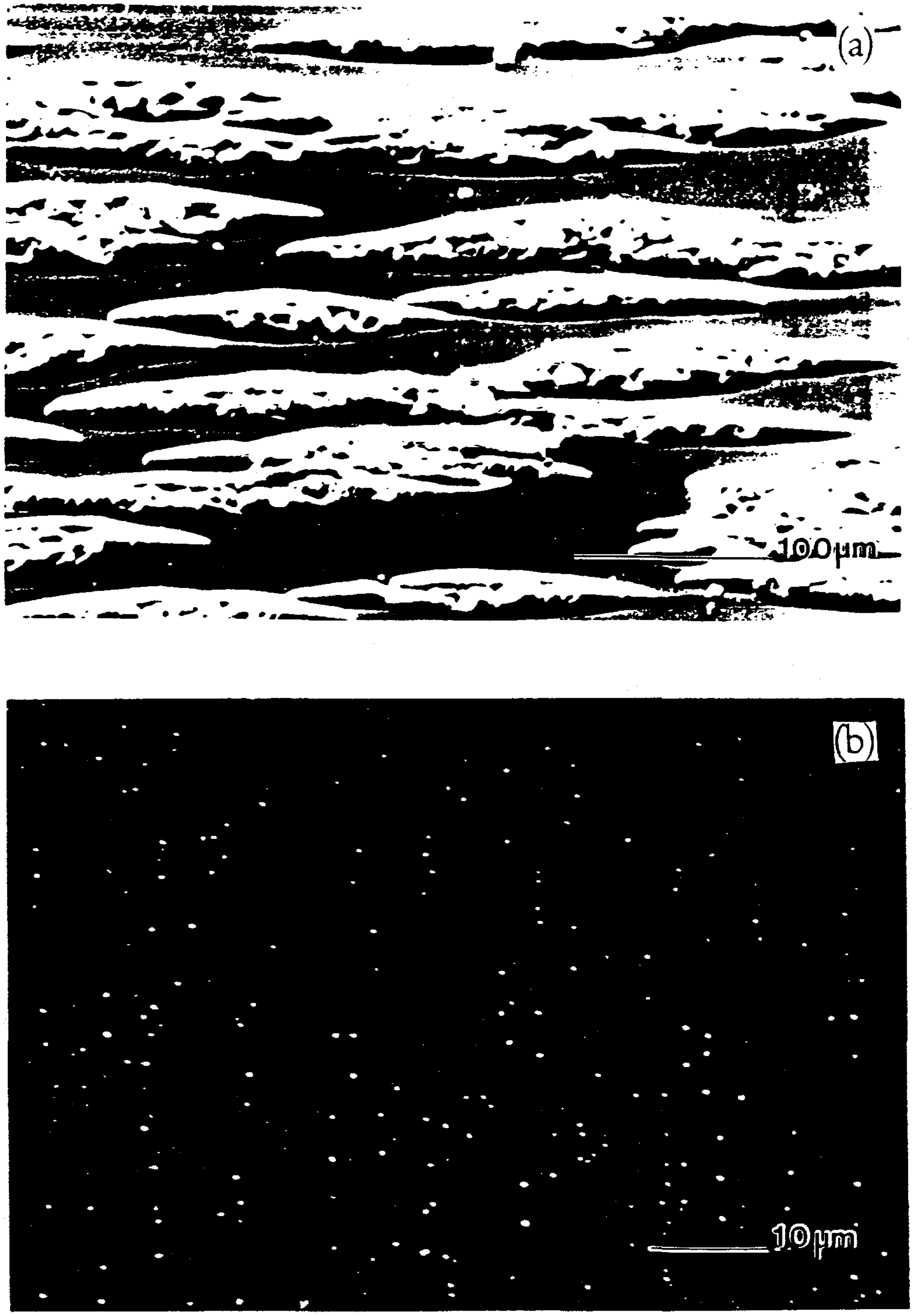

FIG. 3. SEM images of selected growth morphologies for various GaSb substrate orientations with quaternary $Ga_{0.88}In_{0.12}As_{0.14}Sb_{0.86}$ composition, (a) 2°→(111A) on (100) and (b) 2°→(110) on (100).

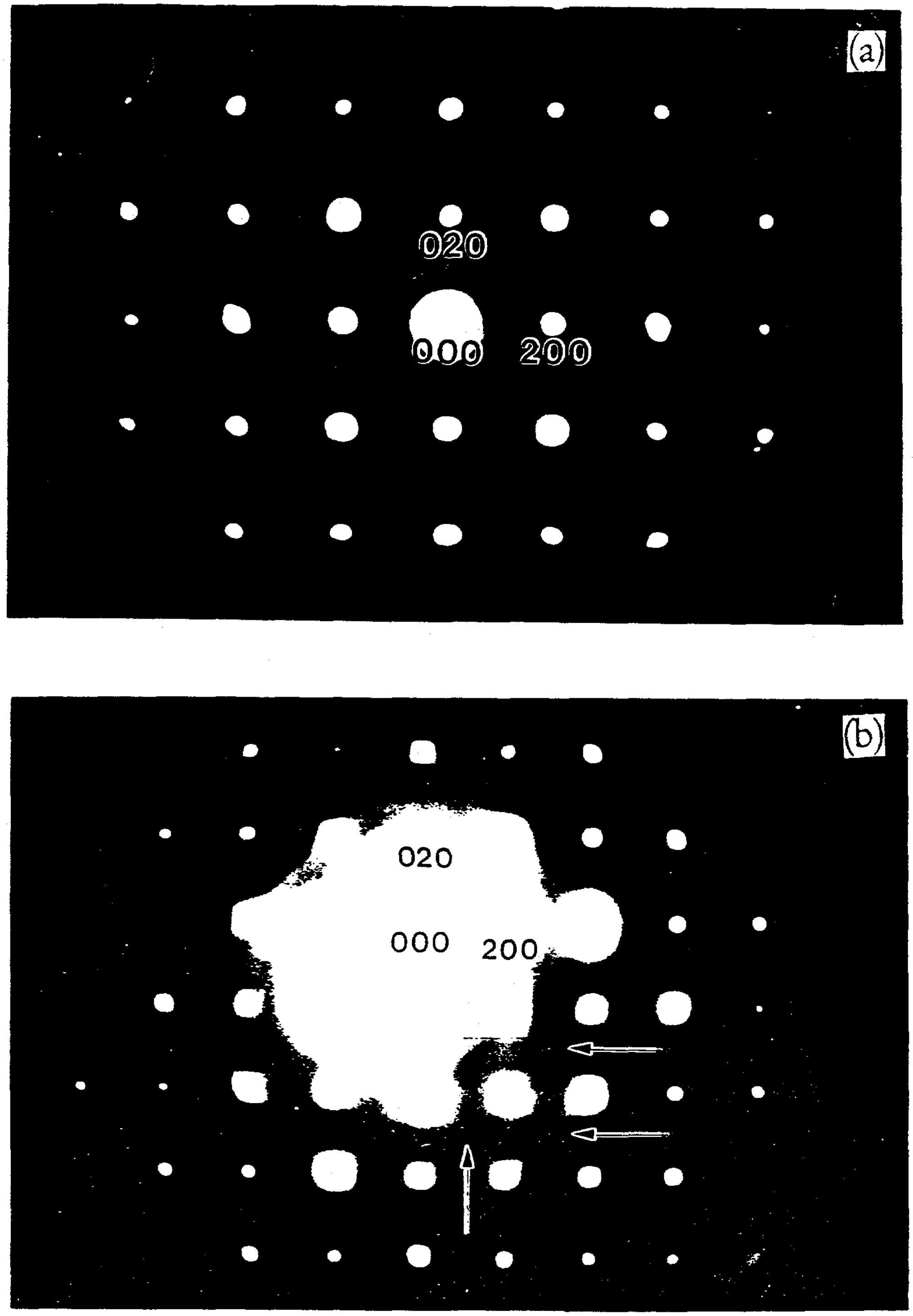

FIG. 4. (a) Transmission electron microscopy (TEM) diffraction pattern of $Ga_{0.87}In_{0.13}As_{0.12}Sb_{0.88}$, sample **B**, showing weak diffuse scattering in [110] and [1$\bar{1}$0] directions. (b) TEM diffraction pattern of $Ga_{0.92}In_{0.08}As_{0.07}Sb_{0.93}$, sample **C**, showing strong diffuse scattering in [110] and [1$\bar{1}$0] directions and in [100] and [010] directions with weak reflection at (110) type positions.

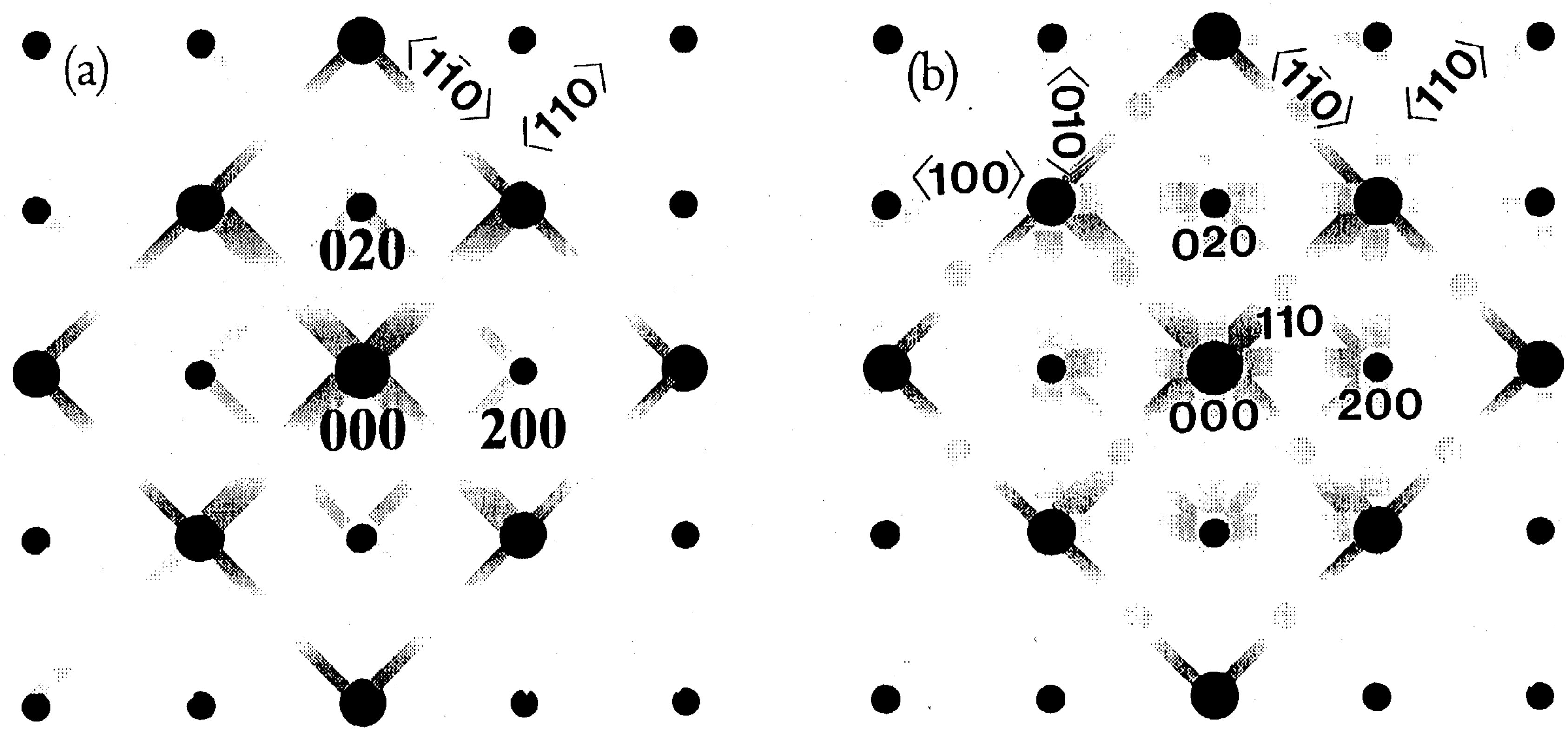

FIG. 5. Schematic diagrams of the TEM diffraction patterns of (a) $Ga_{0.82}In_{0.18}As_{0.14}Sb_{0.86}$, sample **A**, and $Ga_{0.87}In_{0.13}As_{0.12}Sb_{0.88}$, sample **B**, showing weak diffuse scattering in [110] and [1$\bar{1}$0] directions. (b) $Ga_{0.92}In_{0.08}As_{0.07}Sb_{0.93}$, sample **C**, and $Ga_{0.82}In_{0.18}As_{0.14}Sb_{0.86}$, sample **D**, showing strong diffuse scattering in [110] and [1$\bar{1}$0] directions and in [100] and [010] directions and the evolution of weak (110) type reflection.