MICROSTRUCTURAL CHARACTERISTICS OF PHASE SEPARATED AND ORDERED EPITAXIAL LAYERS OF III-V COMPOUND SEMICONDUCTORS

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Microstructural characteristics of phase separated and ordered epitaxial layers of III-V compound semiconductors have been investigated by transmission electron microscopy. Phase separation is a common feature of InGaAs and InGaAsP layers grown by LPE, MBE and OMVPE and occurs at the surface during epitaxial growth. The wavelength of the fine scale structure resulting from phase separation depends on the growth temperature, growth technique and orientation of the underlying substrate. The overall morphology of the microstructure is also affected by the substrate orientation. The speckle microstructure is stable at temperatures considerably higher than the growth temperature. Also, the size of ordered domains in (Ga,Al)InP layers depends on the growth conditions.

1. INTRODUCTION

Epitaxial layers of ternary and quaternary III-V compound semiconductors have attractive electronic properties. As a consequence, they find extensive applications in technology. $In_{1-x}Ga_xAs_yP_{1-y}$ compositions, lattice matched to InP substrates, constitute the back bone of state-of-the-art lightwave communication systems involving fused silica fibers and operating in the 1.3-1.67 μm regime.

The ternary and quaternary layers crystallize in the zinc-blende structure that consists of two interpenetrating FCC units. One of the units is occupied by group III atoms, whereas atoms of group V reside on the second unit. An obvious question is the following: are atoms on the two sublattices distributed at random? The answer is an emphatic 'no'. These materials show departure from randomness in two ways: (i) phase separation and (ii) long range atomic order. Following the work of Henoc et al.[1], a number of investigators[2-9] have shown that $In_{0.53}Ga_{0.47}As$, $In_{1-x}Ga_xAs_yP_{1-y}$ and InGaP layers phase separate. $In_{1-x}Ga_xAs_yP_{1-y}$ epitaxial layers, lattice-matched to (001) InP substrates, have been investigated extensively and exhibit two types of contrast modulations. A fine scale speckle contrast is observed that is aligned along the <100> directions lying in the (001) growth plane[1-9]. The wavelength of these modulations is ~ 15 nm. In addition, the layers show coarse contrast modulations whose period is ~ 125 nm; these modulations are also oriented along the <100> directions[1-4]. A consensus exists that the fine scale modulations result from phase separation[1-4,8,9], whereas the situation is not satisfactorily resolved for the coarse modulations. Henoc et al.[1], Glas et al.[2], Treacy et al.[4] and Norman and Booker[5] have argued that the both types of modulations result from phase separation. On the other hand, Mahajan et al.[3] have suggested that the fine scale structure could evolve by phase separation, while the coarse contrast modulations may be due to the accommodation of strains associated with the fine scale microstructure. In addition, the recent work of McDevitt et al. [10] indicates that the strains associated with the fine scale structure are two-dimensional in nature and exist only along the <100> directions lying in the (001) plane.

Within the last few years, several reports have been published on the occurrence of long range order in a number of ternary and quaternary layers[11-21]. An interesting aspect of these studies is that they include materials which are completely miscible at the growth temperature and those which show a miscibility gap. Several structures have been reported for the ordered phases. At present it is not clear what factors determine the formation of a particular structure.

In the present paper, the following issues pertaining to phase separation and ordering have been addressed: (i) the occurrence of phase separation in layers grown by different growth techniques, (ii) influence of substrate orientation on the characteristics of phase-separated microstructures, (iii) thermal stability of phase-separated microstructure, and (iv) effects of growth rate on the domain structure in ordered epitaxial layers. The results of this study, taken together with those of the previously

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published studies, advance our understanding of the microstructure of the scientifically interesting and technologically relevant ternary and quaternary compound semiconductors.

2. PHASE SEPARATION IN LAYERS GROWN BY DIFFERENT GROWTH TECHNIQUES

Reproduced in Figs. 1(a) → (c) are representative plan-view microstructures observed in InGaAsP (emission wavelength - 1.33 μm), InGaAs (emission wavelength - 1.67 μm) and InGaAsP (emission wavelength = 1.33 μm) layers, grown on (001) InP substrates, by liquid phase epitaxy (LPE), molecular beam epitaxy (MBE) and organo-metallic vapor phase epitaxy (OMVPE), respectively. The fine scale speckle contrast is fairly well developed in Figs. 1(a) and 1(c), whereas it is just discernible in Fig. 1(b). The coarse contrast modulations are weakly developed in Fig. 1(a) and are absent in Figs. 1(b) and 1(c). Furthermore, the wavelengths of the speckle microstructure in Figs. 1(a), (b) and (c) are, respectively, ~ 10, 5 and 10 nm. It has also been demonstrated that the strains associated with the fine scale structure exist only along the <100> directions lying in the (001) plane.

Lattice-matched layers of InAlAs[6] and InGaAs and InGaAsP[14], grown respectively by MBE and vapor levitation epitaxy on (001) InP substrates, are phase separated. Taken together, the preceding results show that, in immiscible ternary and quaternary III-V compound semiconductors, phase separation will occur regardless of the growth technique that is used.

The absence of contrast modulations along the growth direction implies that the phase separation responsible for the fine scale structure is two-dimensional in nature and occurs at the surface during growth. If this were not true, decomposition in (001) layers should occur along the three <100> directions, which are the softest directions. In fact, if the phase separation were to occur in the film following growth, it should be dominant along the [001] growth direction, because transformation-induced strains can be easily relaxed in this direction due to small thickness.

The results presented in Fig. 1 can be rationalized in terms of the above discussion. It can be argued that the wavelength of the fine scale structure would depend on the surface diffusion length of the constituent atoms. The diffusion lengths, in turn, will depend on the substrate orientation, method of growth and growth temperature. The difference in periodicity between LPE, MBE and OMVPE layers, that is shown in Figure 1, is thought to be the result of the last two factors. It is well known that both the critical wavelength and the wavelength of maximum stability decrease with temperature[23]. For the films which are grown at the higher temperatures, LPE and OMVPE, the

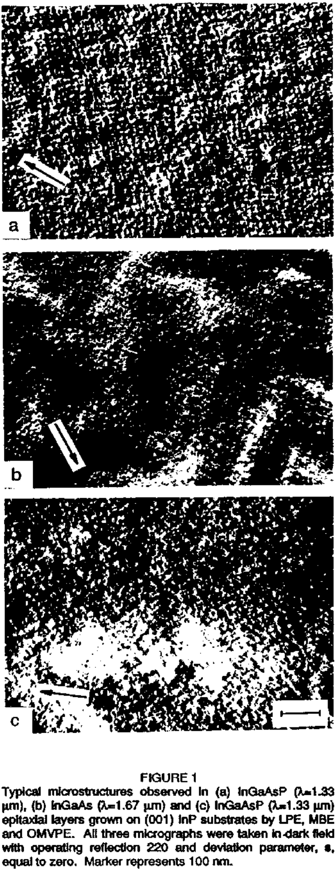

FIGURE 1
Typical microstructures observed in (a) InGaAsP (λ=1.33 μm), (b) InGaAs (λ=1.67 μm) and (c) InGaAsP (λ=1.33 μm) epitaxial layers grown on (001) InP substrates by LPE, MBE and OMVPE. All three micrographs were taken in dark field with operating reflection 220 and deviation parameter, s, equal to zero. Marker represents 100 nm.

period of this modulation is expected to be large. For the MBE films, grown at lower temperature, a smaller period is expected.

3. INFLUENCE OF SUBSTRATE ORIENTATION ON PHASE SEPARATION

In order to fully understand the two-dimensional decomposition behavior of InGaAsP materials, layers were grown by LPE on $(111)_A$, (110) and (123) InP substrates. The growth temperature in each case was 600° C. The emission wavelength of the layer deposited on the $(111)_A$ substrate was 1.54 μm, whereas it was 1.33 μm for the other two orientations. These layers were subsequently examined by transmission electron microscopy (TEM).

Typical plan-view microstructures observed for the $[111]_A$, [110] and [123] orientations are shown, respectively, in Figs. 2(a) → (c). Comparing Figs. 1(a) and Figs. [2(a) → (c), it is apparent that the microstructures depend sensitively on the orientation of the underlying substrate and these differences are highlighted as follows. As indicated earlier, phase separation within the (001) layers, Fig. 1(a), occurs along the [100] and [010] directions and the fine scale speckle contrast is fairly well developed. In the $(111)_A$ layers, Fig. 2(a), the speckle contrast is discernible, but does not appear to be aligned along specific crystallographic directions. On the other hand, the (110) layers, Fig. 2(b), show contrast modulations along the [001] and $[1\bar{1}0]$ directions. The orientation effect is particularly dramatic in the case of the (123) layers, Fig. 2(c). These layers show very strong contrast modulations along the $[0\bar{3}2]$ direction, whereas modulations along the $[30\bar{1}]$ direction are not that well developed. For all specimens shown in Figure 2, cross sectional TEM has shown the decomposition to be two dimensional. Therefore, the phase separation must occur by surface processes during the growth of the film.

The wavelengths of the speckle contrast observed in the above three cases are the following: (i) 4 nm for the $(111)_A$ growth, (ii) 6 and 5 nm along the [001] and $[1\bar{1}0]$ directions for the (110) growth, and (iii) 27 and 9 nm along the $[0\bar{3}2]$ and $[30\bar{1}]$ for the (123) growth.

The above observations may be rationalized by considerations of the elastic anisotropy of the substrate crystal in the plane of growth. Since cubic crystals are elastically isotropic in the (111) plane, well-defined, aligned modulations should not occur. Figure 2(a) shows a speckled microstructure and the absence of crystallographic alignment. The (110) surface is highly anisotropic. It contains the elastically soft [001] direction, the $[1\bar{1}1]$ and $[1\bar{1}\bar{1}]$ directions, which are hard, and the $[1\bar{1}0]$ which is relatively soft but not as soft as [001]. Indeed, the sample shown in Fig. 2(b) shows modulations along the [001] and $[1\bar{1}0]$ directions. The findings on the (123) specimen shown in Fig. 2(c) are

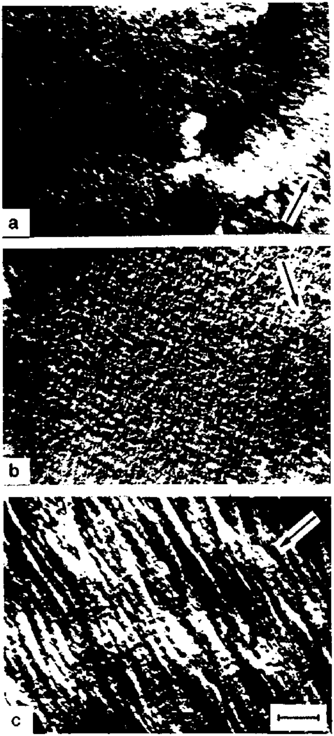

FIGURE 2

Dark-field micrographs obtained from InGaAsP epitaxial layers grown on (a) $(111)_A$, (b) (110), and (c) (123) InP substrates by LPE. The growth temperature in each case is 600° C and emission wavelengths of the respective layers are 1.55, 1.33 and 1.33 μm. The operating reflections in (a), (b), and (c) are, respectively, $\bar{2}02$, $2\bar{2}2$ and $2\bar{4}2$, $s=0$. Marker represents 100 nm.

consistent with the other orientations; modulations are found to lie along the [0$\bar{3}$2] and [30$\bar{1}$] directions which are the two softest directions lying in the growth plane.

The observed variations in the wavelengths of the speckle contrast in the three cases are significant. These variations must reflect the differences in surface mobilities of the constituent atoms as well as the elastic properties of the plane of growth.

4. THERMAL STABILITY OF PHASE-SEPARATED MICROSTRUCTURE

To assess the thermal stability of phase-separated microstructures, InGaAsP epitaxial layers, emitting at 1.33 μm, were grown on (001) InP substrates by LPE. These layers were then encapsulated with SiO_2/Si_3N_4. The encapsulated layers were annealed in the temperature range of 750° - 900° C. After annealing, the encapsulant was removed and the layers were examined in plan-view by TEM.

Shown in Fig. 3 are typical micrographs obtained from the as-grown layer, Fig. 3(a), and the layer annealed at 850° C for 30 min., Fig. 3(b). Comparing these figures it is apparent that the fine scale structure is still present after annealing and coexists with weakly-defined coarse contrast modulations. Two interesting conclusions can be drawn from these observations. First, the fine scale speckle microstructure is stable at temperatures considerably higher than the growth temperature. In view of the fact that homogenization involves bulk diffusion and the microstructure evolves by surface spinodal decomposition, this result is not surprising. Second, the fine and the coarse contrast modulations appear to be interrelated. This again can be understood if the coarse contrast modulations form to accommodate the two-dimensional strains associated with the fine scale structure[6].

5. INFLUENCE OF GROWTH CONDITIONS ON ORDERED DOMAINS

To study the influence of growth conditions on the size of ordered domains, (Ga,Al)InP layers were grown on (001) GaAs substrates by OMVPE. The layers were deposited at 650° and 680° C and the respective growth rates were 1.08 and 0.67 μm/hr. These layers were examined in plan-view by TEM.

Typical micrographs obtained from the above layers are reproduced as Fig. 4. Domains are extremely small in the sample grown at the higher rate, Fig. 4(a), whereas the average size is fairly large, ~ 0.5 μm, in layers grown at the slow rate, Fig. 4(b). In addition, it was occurred on the ($\bar{1}$11) and (1$\bar{1}$1) planes.

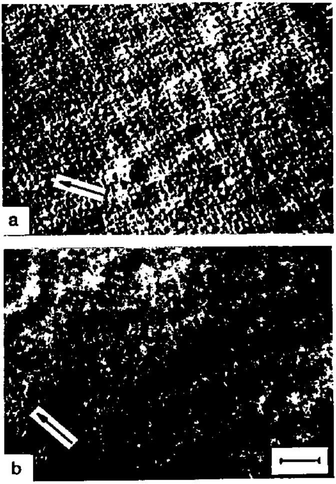

FIGURE 3
Dark-field micrographs illustrating the influence of annealing at 850° C for 30 mins. on the stability of fine scale microstructure: (a) as-grown layer, and (b) after annealing for 30 mins. at 850° C. The operating reflection in each case is 220, s=0. Marker represents 100 nm.

Suzuki et al.[22] have proposed a model to rationalize the formation of CuPt-type ordered structures in ternary III-V compound semiconductors. They have argued that due to strain considerations, the growth of $In_{0.5}Ga_{0.5}P$ layers on the (001) GaAs substrates could involve alternate rows of In and Ga atoms along the [1$\bar{1}$0] direction. Furthermore, they assume that the growth is initiated at steps present on the substrate surface. Invoking the above model, two distinct situations could arise during growth: (i) the ordered regions on either side of the step are commensurate with each other, and (ii) the ordered regions are separated from each other by the tubes of disordered material. The position of these tubes shift laterally during growth. It is proposed that these tubes are responsible for the domain contrast observed in Fig. 4.

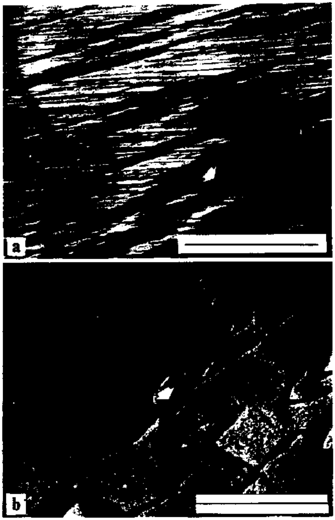

FIGURE 4
Domain boundaries observed in (Ga,Al)InP layers grown at different rates on (001) GaAs substrates by low pressure OMVPE: (a) high, and (b) low growth rate. Reflections used for forming images in (a) and (b) are, respectively, $\bar{1}11$ and $3\bar{1}1$ superlattice spots. Markers in (a) and (b) represent 0.2 and 0.5 µm respectively.

6. CONCLUSIONS

(i) InGaAs and InGaAsP epitaxial layers grown on (001) InP substrates by MBE, LPE and OMVPE are phase separated, and this occurs at the surface during growth. The wavelength of the resulting fine scale structure is determined by the growth technique and the growth temperature.

(ii) Microstructures produced by phase separation reflect the elastic anisotropy of the underlying substrate.

(iii) Results of annealing studies show the reversion kinetics to be very slow even at temperatures considerably higher than the growth temperatures. This observation is consistent with conclusion that phase separation occurs at the surface during growth, whereas homogenization involves bulk diffusion.

(iv) The size of ordered domains in (Ga,Al)InP epitaxial layers depends on the growth temperature and the growth rate. Larger domains are observed in samples grown at higher temperatures and low growth rates.

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