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Effects of substrate orientation on phase separation in InGaAs and InGaAsP epitaxial layers

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ABSTRACT: LPE InGaAsP layers and MBE InGaAs layers grown on (001) and (111) InP substrates have been examined by cross-sectional and plan-view TEM in order to assess the effect of substrate orientation on modulated microstructures in these layers. The fine-scale contrast modulations have been observed to be two dimensional regardless of substrate orientation. This observation has been shown to be consistent with spinodal decomposition at the surface of the film.

1. INTRODUCTION.

The InP:$In_{1-x}Ga_xAs_yP_{1-y}$ compound semiconductor system is of scientific and technological interest for several reasons. By suitable adjustment of x and y, the emission wavelength may be varied from 1.0 to 1.65 μm while maintaining lattice matching to InP. This wavelength range is of interest because fused silica fibers exhibit minimum dispersion and loss in this regime. InGaAsP:InP device wafers are therefore used to fabricate emitters and detectors for lightwave communications systems.

One of the most interesting features of the system is the existence of a miscibility gap in the quaternary and ternary alloys. The miscibility gap was first predicted from thermodynamic calculations (de Cremoux et al. 1981, Stringfellow 1982 and Onabe 1982) and modulated microstructures attributed to phase separation were later reported (Henoc et al. 1982, Mahajan et al. 1984 and Norman and Booker 1985).

Most electron microscopy studies on LPE films grown on (001) InP substrates report periodic contrast modulations, characteristic of spinodal decomposition, on two length scales (Henoc et al. 1982, Mahajan et al. 1984 and Norman and Booker 1985). One is a fine scale structure with period approximately 10 nm and the other a coarse scale modulation whose wavelength is approximately 0.1 μm. Both the fine scale modulation and the coarse scale modulation have principal strain components along the elastically soft <100> directions lying in the growth plane. Similar studies on vapor phase grown layers report only a fine scale structure with a period shorter than the LPE layers (Norman and Booker 1985, Chu et al. 1985).

Mahajan et al. (1984) have proposed that the fine scale modulations evolve by spinodal decomposition, whereas the coarse contrast modulations may be due to relaxation of stresses associated with the fine scale decomposition. In addition, Norman and Booker (1985) have suggested that the fine scale modulations may develop during cooling from the growth temperature. On the other hand, Henoc et al. (1982), Treacy et al. (1985) and Norman and Booker (1985) suggest that the coarse modulations are due to composition modulations that develop at the surface during growth. Treacy et al. (1985) have shown that the observed contrast may be rationalized in terms of surface relaxation of shear stresses set up from periodic composition modulations.

If the clustering that produces the fine scale modulations occurs during cooling from the growth temperature, decomposition along the growth direction should dominate because it is easy to relax decomposition induced stresses normal to the substrate. However, if the clustering should occur at the surface during growth, the modulations should lie in the growth plane and the direction along which decomposition occurs should be determined by the orientation of the surface of the crystal. To distinguish between the two alternatives, the effects of substrate orientation of the microstructure of InGaAsP layers grown by LPE on (001), $(111)_{In}$ and $(\bar{1}\bar{1}\bar{1})_P$ InP substrates and InGaAs layers grown by MBE on (001) and $(\bar{1}\bar{1}\bar{1})_P$ substrates have been examined. The as-grown layers were examined by TEM in plan-view and edge-on orientations. The results of this study constitute the present paper and provide further insight into the occurrence of phase separation in these materials, particularly the origin of the fine scale contrast modulations.

2. EXPERIMENTAL DETAILS.

2.1 LPE Growth. The (001) and $(\bar{1}\bar{1}\bar{1})_P$ wafers were polished using 1% bromine-methahol solution, cleaned, etched and rinsed in the standard fashion prior to growth. The wafer preparation for the $(111)_{In}$ samples was more difficult due the resistance of this surface to chemical etching. These wafers were mechanically polished using progressively finer grades of commercially available alumina and then cleaned in solvents and deionized water. The substrates were then anodized at 115 V, and the resulting oxide stripped from the wafer surface using hydrofluoric acid (Logan et al. 1983). The anodizing-stripping process was repeated three times and the substrates were then cleaned in solvents and deionized water and immediately loaded into the boat for growth.

The LPE films were grown in a cylindrical slider-boat using a vertical reactor. The growth solutions were prepared by weighing the appropriate amounts of In, InAs, GaAs and InP to produce a single phase solution with liquidus temperature 600° C. An additional quantity of InP, 3% in excess of that required for saturation, was added to allow for phosphorus loss during a 16 h pre-bake at 600° C. Following the bake out, the reactor was cooled to room temperature, the substrate loaded and, after a series of evacuation-flushing cycles, the system was heated to 600° C for 1 hr. After equilibration the furnace was ramped to 595°; at this point the wafers were etched for 6 sec in a pure In-melt to remove the thermally decomposed material and then brought into contact with the growth solution. The (001) specimens were grown for 1 min, whereas $(111)_{In}$ layers were grown for 15 min. During the growth, the temperature was ramped at a rate of 0.3° C/min. Following the growth cycle, the furnace was removed from the growth zone of the reactor and the specimen was cooled rapidly to room temperature with a small fan which was directed onto the portion of the quartz tube which contained the boat.

2.2 MBE Growth. The $(\bar{1}\bar{1}\bar{1})_P$ and (001) substrates were polished, etched and indium-mounted on the substrate holder. The samples were deoxidized in situ by heating under arsenic pressure. The deoxidation determined by the transition of reconstructions (2x4) to (4x2) of the RHEED pattern achieved between 550 and 580° C was monitored on InP (001). The temperature was then dropped to 500° C for growth. InGaAs layers were grown with a V/III ratio of 60 and a growth rate of 1 µm/h. The sample holder was rotated during growth to ensure homogeneous deposition on both wafers.

2.3 Characterization. The band gap of the layers was determined by measuring the optical transmission of the samples, while the degree of lattice matching was assessed using standard diffractometry techniques. The cross section specimens for TEM were prepared by chemical etching in bromine methanol (Chu and Sheng 1984). The (001) and $(111)_{In}$ plan-view specimens were prepared by etching from the substrate side, whereas for the $(\bar{1}\bar{1}\bar{1})_P$ specimens low temperature ion milling was used. The thinned specimens were examined in a Philips EM420 operating at 120 keV.

3. EXPERIMENTAL RESULTS.

3.1 LPE Films. Figure 1 (a-d) is a series of four dark field TEM micrographs obtained from a (001) InGaAsP layer. The band gap of this specimen was

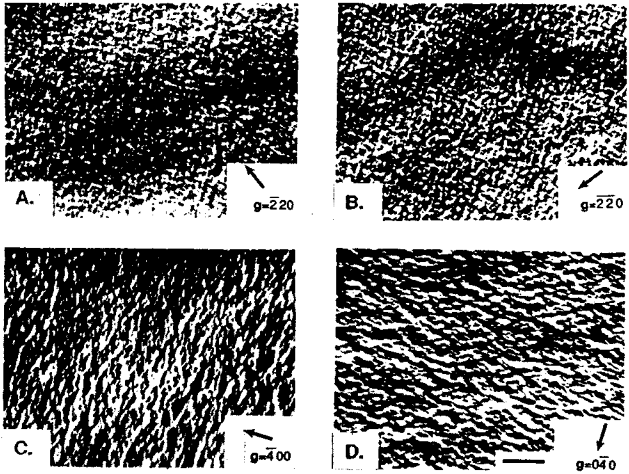

Figure 1. A series of four dark field TEM micrographs obtained from a (001) InGaAsP layer with band gap 1.03 eV (1.20 µm), (a) g=$\bar{2}20$, (b) g=$\bar{2}\bar{2}0$ (c) g=$\bar{4}00$ and (d) g=$0\bar{4}0$. Marker represents 0.1 µm.

determined to be 1.03 eV (1.20 µm). Figures 1 (a) and (b) were obtained using $g=\bar{2}20$ and $\bar{2}\bar{2}0$, whereas operating reflections in (c) and (d) are $\bar{4}00$ and $0\bar{4}0$, respectively. The following observations can be made from these micrographs. First, when the sample is imaged with the two <220> reflections which lie in the growth plane, the contrast modulations along both the [100] and [010] directions are visible and the resultant contrast appears as a fine speckled or modulated structure. Second, when the <400> reflections are used, one of the modulations goes out of contrast, i.e., the structure becomes invisible when the direction of contrast modulation is perpendicular to g. The periodicity of the modulations in this specimen were determined to be approximately 6 nm.

Figures 2 (a) and (b) show edge-on views of a (001) layer with the same composition as that shown in Figure 1. It can be seen that the fine scale contrast modulations are visible when imaged with $g=\bar{2}20$ and are out of contrast when g=004, parallel to the growth axis. These observations are consistent with those of Norman and Booker (1985) and Chu et al. (1985) on InGaAsP layers grown by LPE and VPE. Further, these results indicate that the decomposition is two-dimensional and the associated strains lie in the growth plane.

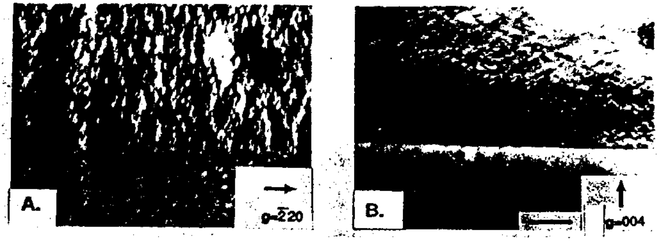

Figure 2. Edge-on view of the (001) layer shown in Figure 1, (a) $g=\bar{2}20$ and (b) g=004. Marker represents 0.1 µm.

Figures 3 a-c are dark field micrographs from a plan-view specimen of an LPE layer grown on a $(111)_{In}$ substrate. The band gap of the film was determined to be 0.9 eV (1.37 µm). In Fig. 3(a), $g=2\bar{2}0$ is satisfied and in Figs. 3(b) and 3(c) the $0\bar{2}2$ and $\bar{2}02$ reflections are used. Although weakly developed linear features may be observed in some regions of these micrographs, well-defined periodic structures, as observed in the (001) specimens are not apparent. The speckled microstructure of these films is nearly isotropic.

Figure 4 (a-d) shows a cross section of a $(\overline{111})_P$ oriented LPE film. The bandgap of this film is 0.85 eV (1.45 µm). A fine columnar structure, parallel to the growth direction, is observed when the specimen is imaged with g=004 and weak speckle contrast is observed when 220 and $22\bar{2}$ are satisfied. The structure is invisible when imaged with g=222 parallel to the growth direction. The period of this columnar structure is approximately 4 nm. These results show that, for the {111} layers, well defined modulation directions do not develop. A nearly isotropic structure is observed in plan-view and a fine columnar structure, is observed in cross section. The plan-view and cross-section results in Figs. 3 and 4 show that

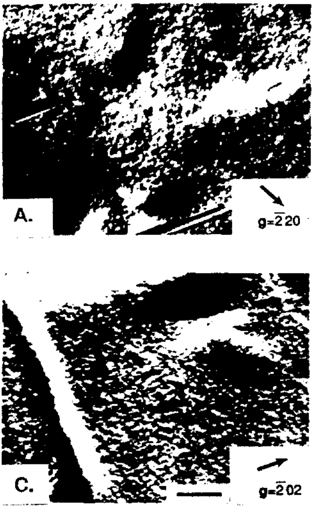

Figure 3. Dark field micrographs from a plan-view specimen of an LPE layer grown on $(111)_{In}$ substrate, the band gap of the film was determined to be 0.9 eV (1.37 µm), (a) g=2$\bar{2}$0 (b) g=0$\bar{2}$2 and (c) g=$\bar{2}$02. Marker represents 0.1 µm.

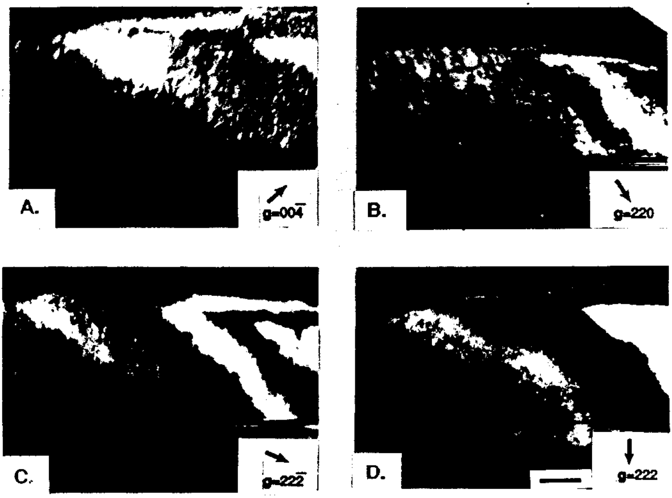

Figure 4 Cross section of a $(\overline{1\,1\,1})_P$ oriented LPE film, with bandgap 0.85 eV (1.45 µm), (a) g=004, (b) g=220, (c) g=22$\bar{2}$ and (d) g=222. Marker represents 50 nm.

when layers are grown on {111} substrates, the contrast modulations are two dimensional and lie in the growth plane.

3.2 MBE Films. TEM Examination of plan-view sections from InGaAs layers grown by MBE on (001) substrates give results similar to those observed in the LPE films and in previous studies (Norman and Booker 1985). The periodicity of the fine scale contrast modulations, in (001) layers, is smaller, approximately 3 nm, and they are aligned aligned along the two <100> directions which lie in the growth plane. Invisibility of one variant at a time may be obtained using g=400 and 040. Cross-section TEM of edge-on (001) samples shows results similar to those shown in Fig. 2, i.e., no contrast modulations are shown parallel to the growth direction. Figure 5 (a-d) shows a cross section of a InGaAs layer grown on a $(\overline{1\,1\,1})_P$ oriented substrate. The band gaps of the MBE layers were determined to be 0.78 eV (1.68 μm). The contrast modulations observed in this specimen are very similar to those observed in the $(\overline{1\,1\,1})_P$ oriented LPE film. A weakly developed columnar structure, parallel to the growth direction, is observed when g=004 and $\bar{2}20$ are satisfied and invisibility is obtained for g=$\overline{2\,2\,2}$ parallel to the growth direction.

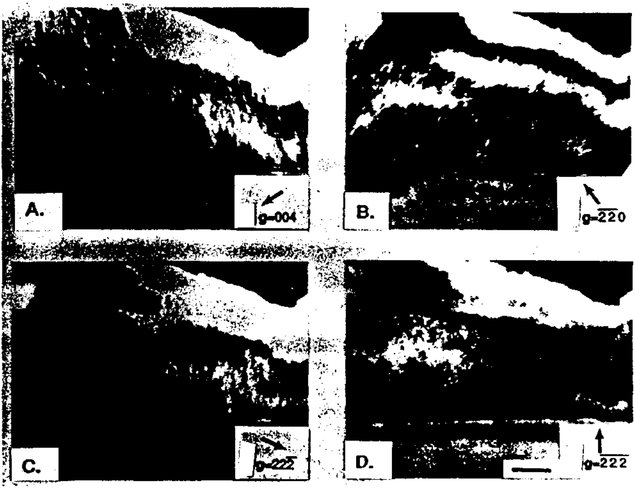

Figure 5. Edge-on view of a $(\overline{1\,1\,1})_P$ oriented InGaAs film with band gap 0.78 eV (1.68 μm), (a) g=004, (b) g=$\bar{2}20$, (c) g=$22\bar{2}$ and (d) g=$\bar{2}22$. Marker represents 50 nm.

4. DISCUSSION.

The principal observations which emerge from the present study are the following: (i) the fine-scale contrast modulations in (001) samples grown by both LPE and MBE are two-dimensional and are not observed parallel to the growth direction, and

(ii) {111} specimens also show two dimensional contrast modulations; these samples show a nearly random, speckle-like contrast when viewed in plan-view and in cross section, a columnar structure, finer than that seen in LPE specimens, is observed.

The above observations are consistent with the hypothesis that the fine scale contrast modulations are due to spinodal decomposition occurring during growth. The case of (001) layers is considered first. The fact that no contrast modulation is observed along the growth direction is inconsistent with decomposition occurring within the film after growth. If the decomposition were to occur in the film after growth, decomposition would be observed along the growth axis as well as in the cube directions which lie in the growth plane. Since the layers are thin, elastic relaxation of stresses associated with composition modulations should be easier parallel to the growth direction and contrast modulations should be more developed along the growth direction if this were true.

The observations on the {111} specimens may be explained from considerations of elastic isotropy. When films are grown on (001) substrates, composition modulations will occur in the growth plane, along the soft <100> and <010> directions in order to minimize the elastic energy. However, cubic materials are elastically isotropic in the {111} plane and the modulations are not constrained to lie along crystallographic directions. Under these circumstances, decomposition should occur in the form of random clustering, such as that observed in Fig. 3. The columnar structure which is observed in the {111} cross sections, is thought to develop as incoming atoms seek atomic positions, in the surface, that minimize bonds with dissimilar atoms in a direction normal to the surface. Therefore, the first few atomic layers which are deposited provide a pattern that is carried through the thickness of the film.

Observations on the period of the modulations, or in the case of the {111} specimens, the size of the columnar structure in the cross sectional images, are consistent with the surface decomposition hypothesis and provide additional support. For both growth techniques, the (001) oriented layers have larger periodicity than the (111) layers. Also, the period of the LPE films is larger than that of the MBE films. The orientation effect could be explained two ways. First, it is likely that there is additional elastic energy associated with phase separation in the absence of soft cube directions. Alternatively, surface mobilities are lower on close packed planes. It is likely that these two effects are combined. The fact that the MBE films have shorter period than the LPE films is probably related to the difference in growth temperature between the two techniques and the resultant decrease in atomic interfacial mobility.

The origin of coarse contrast modulations have not been addressed in this paper. It is possible that the coarse modulations arise to accommodate stresses associated with the two-dimensional fine scale composition modulations (Mahajan et al. 1984). This might explain why the coarse modulations are not observed in MBE and VPE films where the fine structure is less well developed due to the lower processing temperatures.

5. CONCLUSIONS.

The LPE and MBE epitaxial layers grown on (001) and (111) oriented substrates have been characterized by plan-view and cross sectional TEM to study the resulting phase-separated structures. Well-defined, two-dimensional, contrast modulations are observed in (001) oriented specimens. In the {111} specimens, randomly oriented clusters lying in the growth plane have been observed; these clusters have also been shown to be two dimensional. These observations have been rationalized by considerations of the elastic isotropy of the surface of the film and have been shown to be consistent with spinodal decomposition at the growth interface.

6. ACKNOWLEDGMENTS.

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