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Effects of annealing on phase separated microstructures in InGaAsP epitaxial layers

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ABSTRACT : The influence of annealing on phase separated microstructures in lattice-matched InGaAsP epitaxial layers, grown on (001) InP substrates by liquid phase epitaxy, has been investigated. It is shown that the fine and coarse contrast modulations commonly observed in these layers are coupled. This observation is consistent with the suggestion that the fine scale structure causes the coarse modulations. Further, the carrier mobility and the carrier concentration increase on annealing.

1. INTRODUCTION

Following the theoretical work of de Cremoux et al. (1981), Onabe (1982) and Stringfellow (1982) on the occurrence of phase separation in ternary and quaternary III-V compound semiconductors, Henoc et al. (1982), Launois et al. (1982), Mahajan et al. (1984), Norman and Booker (1985), Chu et al. (1985), Treacy et al. (1985), Mahajan and Shahid (1989), Mahajan et al. (1989) and McDevitt (1990) have investigated the microstructural characteristics of InGaAsP epitaxial layers. Two types of contrast modulations are observed in lattice-matched layers grown on (001) InP substrates by liquid phase epitaxy (LPE) (Henoc et al. 1982, Mahajan et al. 1984, Norman and Booker 1985, Chu et al. 1985, Treacy et al. 1985, Mahajan and Shahid 1989, Mahajan et al. 1989 and McDevitt 1990). A fine-scale speckle structure is seen that is aligned along the <100> directions lying in the (001) growth plane (Mahajan et al. 1984 and Norman and Booker 1985). The wavelength of these modulations is ~12-15nm (Henoc et al. 1982, Mahajan et al. 1984, Norman and Booker 1985 and Chu et al. 1985), and depends on the growth temperature as well as on the orientation of the underlying substrate (McDevitt 1990). This structure is associated with two-dimensional strains along the directions of the modulations (McDevitt 1990). In addition, the layers show coarse contrast modulations whose period is ~125-150nm; these modulations are also oriented along the [100] and [010] directions (Henoc et al. 1982, Mahajan et al. 1984, Norman and Booker 1985, Chu et al. 1985, Treacy et al. 1985, Mahajan and Shahid 1989, Mahajan et al. 1989 and McDevitt 1990).

Several investigators have attempted to rationalize the formation of the two types of contrast modulations (Henoc et al. 1982, Launois et al. 1982, Mahajan et al. 1984, Norman and Booker 1985, Chu et al. 1985, Mahajan and Shahid 1989 and Mahajan et al. 1989). Two divergent viewpoints have emerged. Since the wavelength of the coarse modulations is very large, it is impossible to argue that these modulations could develop by phase separation in the bulk because bulk diffusion is extremely slow in these materials. To obviate this difficulty, Launois et al. (1982) have suggested that the modulations evolve by phase separation occurring at the surface while the layer is growing. An interesting question pertains to the formation of the fine scale speckle structure? Norman and Booker (1985) envisage that this is caused by phase separation in the bulk. Mahajan et al. (1984), Mahajan and Shahid (1989) and Mahajan et al. (1989) agree that the speckle structure is due to phase separation, but have argued that the

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*Present address: IBM Corporation, Essex Junction, VT 05452-4299 coarse contrast modulations may form to accommodate strains associated with the fine scale structure. Their argument is that the wavelength of the coarse modulations is very large and cannot evolve by surface diffusion during the time available between the deposition of two successive monolayers.

It is apparent from the above discussion that the fine and the coarse modulations are decoupled from each other according to Launois et al. (1982) and Norman and Booker (1985), whereas Mahajan et al. (1984), Mahajan and Shahid (1989) and Mahajan et al. (1989) envisage them to be coupled. Since the wavelength of the coarse modulations is about ten times longer than that of the speckle structure, the reversion of coarse modulations on annealing via bulk diffusion should take hundred times longer than that for the fine structure. On the other hand, the two features in the coupled case should revert simultaneously on annealing. We have carried out such experiments on InGaAsP epitaxial layers, and these results constitute the present paper.

2. EXPERIMENTAL DETAILS

For this study, InGaAsP epitaxial layers emitting at 1.3µm were grown at 600° C by LPE on (001) InP substrates. Some of the layers were annealed in the temperature range of 750-900° C. In order to prevent the thermal decomposition of the material during annealing, a dielectric capping layer was deposited on the surface of the epitaxial layers. The encapsulant consisted of 1-2nm of SiO followed by ~100nm of Si_3N_4. In addition, the encapsulated specimens were surrounded by pieces of InP to enhance thermal stability. Following the anneal, the dielectric layers were removed by etching in HF. The as-grown and annealed specimens were prepared for transmission electron microscopy by chemical etching as described by Chu and Sheng (1984). Thinned samples were examined in a Philips 420 electron microscopy operating at 120 keV.

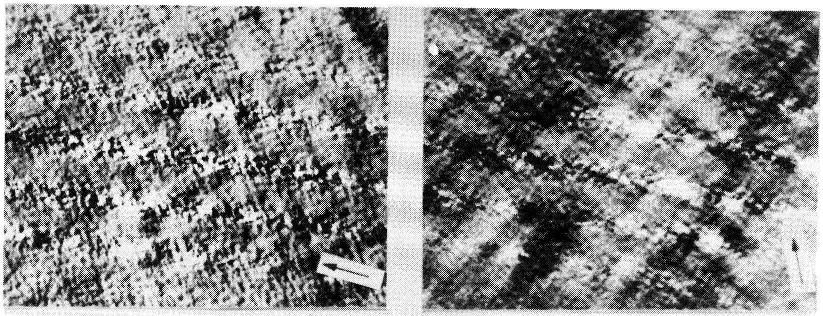
3. RESULTS

Shown in Fig. 1 are a series of dark-field electron micrographs obtained from the as-grown and the annealed layers; these images were taken with 220 reflections under dynamical conditions. Several important microstructural characteristics are evident in the micrographs. First, the as-grown layer, shows the two types of contrast modulations. The contrast experiments have shown that the strains associated with the modulations are along the [100] and [010] directions (McDevitt 1990). Second, when the layer is annealed at 750° C for 30 min., the contrast from both types of modulations is weak and becomes progressively weaker as the annealing temperature is raised. Third, the layer annealed at 900° C, Fig. 1(f), shows speckle structure that is much finer than that observed in the as-grown layer, Fig. 1(a).

Concomitantly, the changes in microstructures on annealing have been followed using selected area electron diffraction, and these results are reproduced as Fig. 2. The satellite spots which are seen clearly in the pattern obtained from the as-grown layer are barely discernible in the layer annealed at 800° C for 30 min., Fig. 2(c). Furthermore, the patterns from the specimens annealed at 850 and 900° C show very weak diffuse intensity.

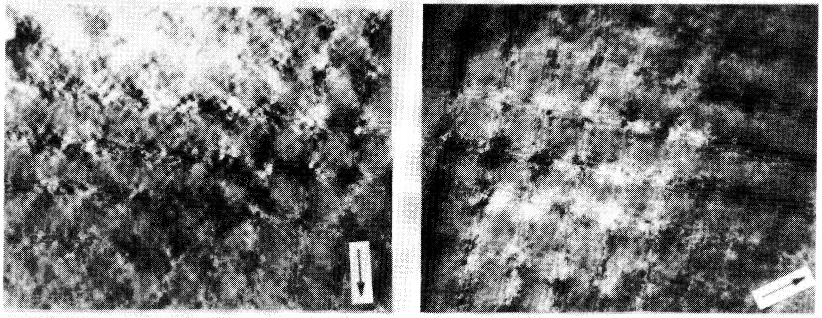
Figure 3 shows the contrast behavior of the fine scale structure observed in the sample annealed at 900° C. Comparing these results with those of the as-grown sample (McDevitt 1990) it is inferred that the contrast behavior of the speckle structure is identical to that of the fine scale structure observed in as-grown layers. The speckle structure is aligned along the [100] and [010] directions and has principal strains parallel to the directions of the modulations. The major difference between the annealed and as-grown microstructures is that the periodicity of the contrast in the annealed specimen is much smaller. The measurements of the period in Fig. 3 give a value of ~3-4nm, whereas the periodicity of the fine scale modulations in the as-grown samples is 8-10nm.

The effects of a 850° C anneal on carrier mobility and carrier concentration are depicted in Fig. 4. All layers show n-type conductivity. The mobility increases sharply after a 30 min. anneal. However, additional annealing does not produce a further increase in mobility. Surprisingly, the carrier concentration also shows a marked increase on annealing.



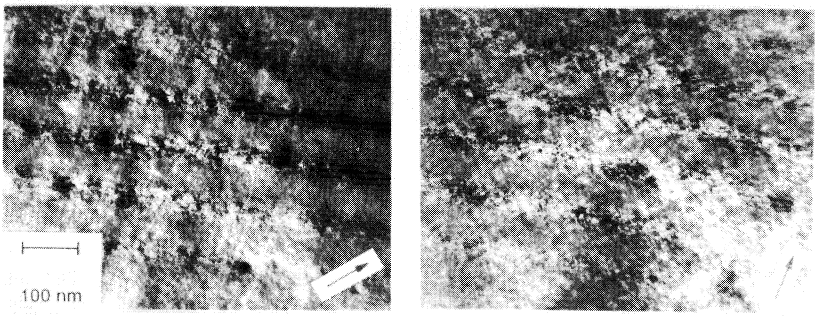
(a) As-Grown Microstructure.

(b) 30 Minute Anneal at 750° C.



(c) 30 Minute Anneal at 800° C.

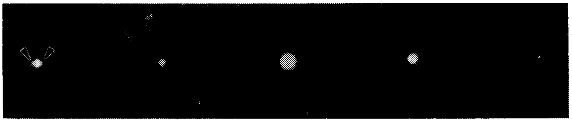
(d) 30 Minute Anneal at 850° C.



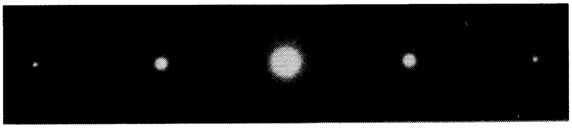
(e) 60 Minute Anneal at 850° C.

(f) 30 Minute Anneal at 900° C.

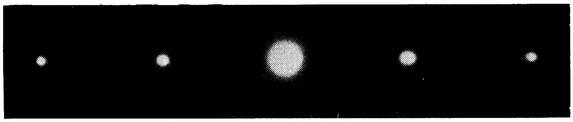
Figure 1. Dark-field electron micrographs showing the behavior of the fine and coarse contrast modulations during the annealing of (001) InGaAsP epitaxial layers at different temperatures. All micrographs were taken under dynamical diffraction conduction with the 220 reflection satisfied.



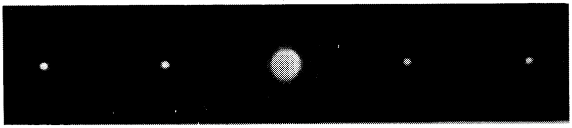
(a) As-Grown



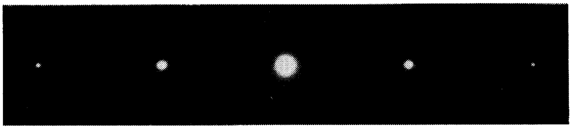
(b) 30 Minute Anneal at 750° C.



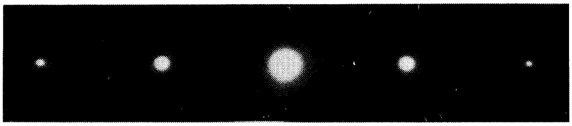
(c) 30 Minute Anneal at 800° C.



(d) 30 Minute Anneal at 850° C.



(e) 60 Minute Anneal at 850° C.



(f) 30 Minute Anneal at 900° C.

Figure 2. Sections of the selected area diffraction patterns, showing the $\bar{4}00$ to 400 reflections, obtained from the specimens shown in Fig. 1. The pattern from the as-grown film shows satellites indicated by arrows in (a), whereas the patterns from the specimens annealed at 850 and 900° C show very weak diffuse intensity.

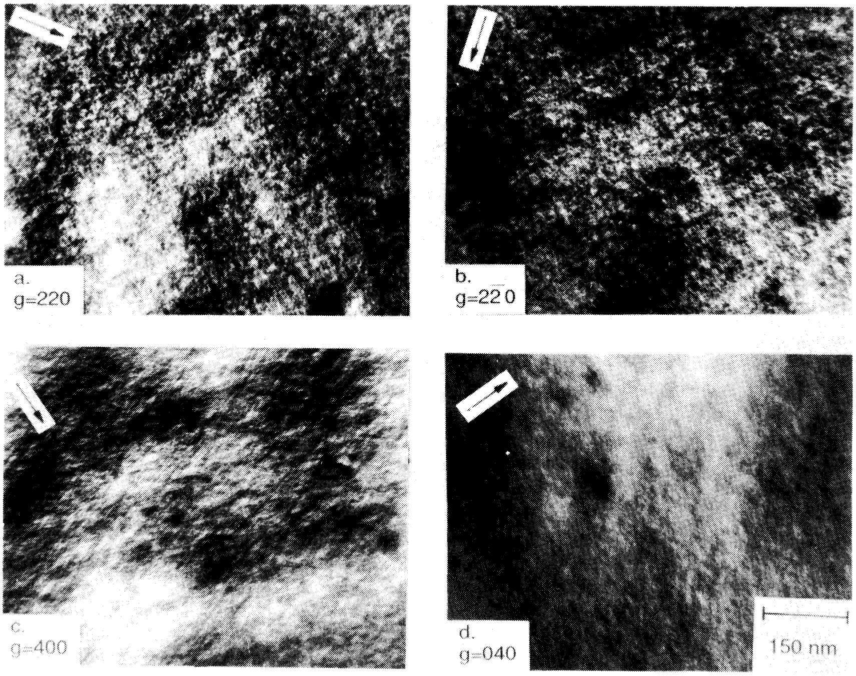
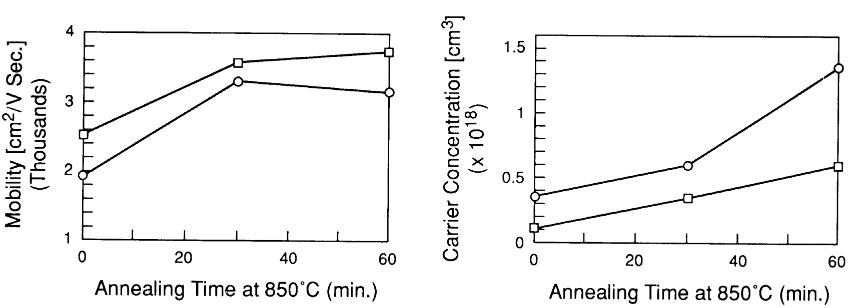


Figure 3. Dark-field electron micrographs showing the contrast behavior of very fine speckle microstructure observed in an InGaAsP layer after annealing at 900° C for 30 mins. The operating reflection in each micrograph is delineated by an arrow.



(a) (b)

Figure 4. Plots showing the dependence of (a) carrier mobility and (b) carrier concentration in an InGaAsP layer on annealing time at 850° C. Both the mobility and the carrier concentration increase on annealing.

4. DISCUSSION

Several interesting observations emerge from the preceding investigation. First, the fine and the coarse contrast modulations in InGaAsP epitaxial layers are coupled. Second, an extremely fine speckle structure is observed even after annealing at 900° C for 30 min., but the coarse modulations are not visible.

The above results clearly demonstrate that the two types of modulations are coupled. Therefore, as argued in the Introduction Section, they are inconsistent with the explanations of Launois et al. (1982) and Norman and Booker (1985); i.e., the two features could not have formed independently.

The origin of the coarse modulations can be rationalized as follows. By studying the dependence of the speckle structure in InGaAsP layers on the orientation of the underlying substrate, McDevitt et al. (1991) have demonstrated unequivocally that the fine scale structure results from two-dimensional phase separation occurring at the layer surface during growth. In addition, phase separation is not observed along the growth direction for each of the four orientations examined. If the speckle structure were to evolve in the bulk as suggested by Norman and Booker (1985), decomposition would have dominated along the growth direction because of the thinness of the layer the transformation-induced strains could be accommodated more easily. Coupling the above result with the presence of strains along the [100] and [010] directions due to phase separation, it is inferred that the layer is under a biaxial stress state.

Now imagine a situation where the underlying substrate has been removed and the layer is thinned so that it is transparent to 120 keV electrons. As suggested by Alerhand et al. (1988) the ground state for such a system is surface domains. The break up of surface into domains would cause periodic, localized bending of planes in the surface regions. We envisage that this effect is responsible for the coarse contrast modulations.

Treacy et al. (1985) have observed that the contrast from the coarse modulations depends on the thickness of the region under examination. They do not see the modulations in the thicker and thinner regions. This observation can be rationalized as follows. Since the two-dimensional surface stresses are responsible for the periodic buckling discussed above, an optimal balance between the thickness of the region and the magnitude of the biaxial stresses is required. In the thinner regions, the stresses are not high enough for buckling to occur, whereas the thicker regions require much higher buckling stresses.

A plausible explanation for the observed speckle structure in the layer annealed at 900° C, Figs. 1(f) and 3, is that the fine scale structure contains a range of wavelengths. Thus, the structure observed on annealing represents remanence of the coarser component of the microstructure.

The observed increase in carrier mobility may be rationalized in terms of the Blood-Grassie model (1984). Their approach assumes that phase separated microstructures can be modeled as a series of heterojunctions between materials differing slightly in compositions. They have proposed that the mobility of carriers in such a system would be lower than in a random alloy because the carriers may be confined to troughs in the conduction band. The carriers would then migrate by a percolation process occurring along these minima in the band structure. Further, we at present do not understand the concomitant increase in carrier concentration on annealing. It could be that there are carrier traps in the phase separated material that are eliminated on annealing.

The microstructure of InGaAsP epitaxial layers appears to be simpler than that envisaged earlier (Henoc et al. 1982, Launois et al. 1982, Norman and Booker 1985 and Treacy 1985). In the (001) layers, the two-dimensional composition modulations occur along the [100] and [010] directions. Their wavelength and amplitude can be tailored by changing the growth temperature, the growth technique and the orientation of the underlying substrate McDevitt et al. (1991). Since these microstructural features appear to affect the electronic properties (Launois et al. 1982 and McDevitt 1990), it should be possible to manipulate microstructures to produce epitaxial layers having unique electronic behavior.

In summary, it has been demonstrated by annealing experiments that the fine and coarse contrast modulations observed in InGaAsP layers, grown by LPE, are coupled. The fine scale speckle evolves by two-dimensional phase separation occurring at the surface while the layer is growing, whereas the coarse contrast modulations are an artifact of thin foils. Furthermore, the carrier mobility is increased on annealing.

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