Two-dimensional phase separation in $In_{1-x}Ga_xAs_yP_{1-y}$ epitaxial layers

T. L. McDevitt,* S. Mahajan, and D. E. Laughlin
Department of Materials Science, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

W. A. Bonner and V. G. Keramidas
Bellcore, Red Bank, New Jersey 07701
(Received 25 June 1991; revised manuscript received 27 September 1991)

Microstructures of lattice-matched $In_{1-x}Ga_xAs_yP_{1-y}$ epitaxial layers, grown on (001), (110), $(111)_A$, and (123) InP substrates by use of liquid-phase epitaxy, have been examined in detail by transmission electron microscopy. Results indicate that the fine-scale speckle microstructure is caused by two-dimensional phase separation occurring at the surface while the layer is growing; decomposition along the growth direction is not observed in either of the four cases examined. The decomposition is found to take place along those directions in the growth plane along which the elastic work associated with the transformation is a minimum. The temperature dependence of the wavelength of the fine-scale structure in (001) $In_{1-x}Ga_xAs$ epitaxial layers grown by use of molecular-beam epitaxy indicates that the wavelength evolution is controlled by the surface diffusion of As atoms.

I. INTRODUCTION

The $In_{1-x}Ga_xAs_yP_{1-y}$ and $In_{1-x}Ga_xAs$ materials are scientifically interesting and technologically relevant. They are used in the fabrication of solid-state lasers and detectors that form an integral part of the optical communication systems involving fused silica fibers as a transmission medium.

The above materials crystallize in the zinc-blende structure which consists of two interpenetrating face-centered cubic sublattices. One of the sublattices is displaced with respect to the other by $(a/4)\langle 111\rangle$, where a is the lattice parameter. Group-III elements reside on one sublattice, whereas group-V elements occupy the second sublattice. An interesting question is whether or not the atomic species in ternary and quaternary materials are distributed at random on their respective sublattices. The cumulative experimental evidence to date indicates that this is not so. Two types of deviations from randomness are observed: (i) phase separation,[1-10] and (ii) atomic ordering.[11-25] The emphasis of this paper is exclusively on phase separation.

Following the theoretical work of de Cremoux, Hirtz, and Ricciardi,[26] Stringfellow,[27] and Onabe[28] on the possibility of phase separation in ternary and quaternary materials, its occurrence has been confirmed experimentally by a number of investigators.[1-10,20] The study of Henoc *et al.*[1] on $In_{1-x}Ga_xAs_yP_{1-y}$ layers, grown on (001) InP substrates by use of liquid-phase epitaxy (LPE), indicates the presence of two types of contrast modulations in transmission electron micrographs: fine-scale speckle microstructure and coarse-contrast modulations; their wavelengths are 10 and 125 nm, respectively. Since the wavelength of the coarse modulations is very large, it is difficult to visualize that it could evolve by diffusion in the bulk, which is extremely slow. In order to obviate this difficulty, Launois *et al.*[29] have proposed that the coarse modulations develop at the surface while the layer is growing. Furthermore, Norman and Booker[4] envisage that the fine-scale speckle structure results from the occurrence of phase separation in the bulk. Mahajan *et al.*[2] concur with Norman and Booker[4] that the speckle structure is due to phase separation, but disagree with Launois *et al.*[29] that the coarse modulations result from the ocurrence of phase separation at the surface. This disagreement stems from the fact that the observed wavelength is too large for it to develop even by surface diffusion in the short-time interval between the deposition of successive monolayers.

The cross-sectional study of Chu *et al.*[3] on $In_{1-x}Ga_xAs_yP_{1-y}$ epitaxial layers, grown on (001) InP substrates by use of vapor-phase epitaxy, indicates the absence of decomposition along the [001] direction, i.e., the growth direction. To rationalize this observation, they have proposed that the fine-scale structure is due to phase separation occurring at the surface while the layer is growing. Combining this assessment with that of Mahajan *et al.*[2] that in the (001) $In_{1-x}Ga_xAs_yP_{1-y}$ layers decomposition occurs along the [100] and [010] directions, it can be concluded that the fine-scale structure results from two-dimensional phase separation occurring along the soft directions in the growth plane.

In order to assess the generic validity of the above result and to see also if the occurrence of phase separation can be suppressed because it has deleterious effects on carrier mobility,[29] we have examined $In_{1-x}Ga_xAs_yP_{1-y}$ layers, grown on (001), (110), $(111)_A$ and (123) InP substrates by LPE, both in plan view and in cross section by

transmission electron microscopy. The logic for the chosen orientations is as follows. Since in cubic crystals the elastic modulus increases in going from ⟨100⟩ to ⟨110⟩ to ⟨111⟩ directions, the two-dimensional decomposition could occur along the [010] and [100], [1$\bar{1}$0] and [001], [1$\bar{1}$0], [$\bar{1}$01] and [01$\bar{1}$], and [11$\bar{1}$] directions for the respective orientations. In case the elastic modulus along the [11$\bar{1}$] direction is considerably higher, phase separation may not occur in the (123) layers. In addition, we have investigated the influence of growth technique and growth temperature on phase separation. Results of these three studies constitute the present paper.

II. EXPERIMENTAL DETAILS

The (001), (110), and (123) InP substrates for epitaxial growth were prepared by chemical-mechanical polishing. The same procedure could not, however, be used for the $(111)_A$ surface because it is extremely resistent to chemical etchants. Therefore, the $(111)_A$ wafers were first polished with successively finer abrasives and then etched by anodizing and stripping the resulting oxides using hydrofluoric acid. We followed the anodizing-stripping procedure developed by Studna and Gualtieri[30] and Logan.[31]

Prior to growth, the LPE growth solution was baked for 18 h. at 600 °C to homogenize the melt and to volatilize impurities from the solution. Following the bakeout, the growth system was cooled to room temperature and the polished substrate was loaded. After a series of flushing cycles consisting of evacuation and refilling with purified hydrogen, the temperature was raised to the homogenization temperature and was held there for 60 min. To minimize thermal decomposition of the substrate, source-piece protection was provided during the equilibration period. Following the equilibration, the temperature was ramped to the growth temperature. Prior to the initiation of the growth, substrates were back melted using a pure In melt. The purpose of this step was to dissolve decomposed material from the surface of the wafer. Growth was then initiated by rotating the growth solution into contact with the substrate, and the temperature was ramped down. When the desired thickness had been deposited, the growth solution was removed from the substrate surface and the system was cooled to room temperature as rapidly as possible. Typical growth rates were in the range of about 0.25-0.4 μm/min.

For molecular-beam epitaxy (MBE), the (001) substrates were first etched in solution consisting of $[H_2SO_4]$:$[H_2O_2]$:$[H_2]$(2:1:1) and were then indium mounted on the specimen holder. Deoxidation was carried out *in situ* by heating to 580 °C under arsenic over pressure and verified by monitoring the reflection high-energy electron diffraction patterns. The temperature was then reduced to the growth temperature. $In_{1-x}Ga_xAs$ layers were grown using the V/III ratio of ~60 at a growth rate of 1 μm/h. The substrate was rotated during growth to ensure homogeneity.

The emission wavelengths of the layers, and thus their compositions, were ascertained using low-temperature photoluminescence and Fourier transform infrared spectroscopy. The emission wavelength of the quaternary layers grown on substrates of different orientations was determined to be 1.3 μm, whereas the ternary layer emitted at 1.67 μm.

The planview samples for transmission electron microscopy were prepared by chemical thinning in a solution consisting of 1.5% Br-methanol. For the cross-sectional specimens we followed the grid-masking technique of Chu and Sheng[32] involving thinning in a Br-methanol solution. Thinned samples were examined in a Phillips EM 420 operating at 120 keV.

III. RESULTS

Results of the present study are subdivided into the following three sections: (i) influence of substrate orientation on phase separation, (ii) effects of growth technique on phase separation, and (iii) influence of growth temperature on phase separation. The respective details are presented below.

A. Influence of substrate orientation on phase separation

Figure 1 shows a series of dark-field electron micrographs obtained from a (001) $In_{1-x}Ga_xAs_yP_{1-y}$ epitaxial layer. Both the coarse and fine-scale modulations are visible. When the sample is imaged using the ⟨220⟩ reflections, the fine-scale modulations exhibit speckle contrast, and the coarse modulations are seen to lie along the [100] and [010] directions. It is also apparent from Fig. 1 that the microstructure consists of two sets of fine-scale modulations that go out of contrast alternately for

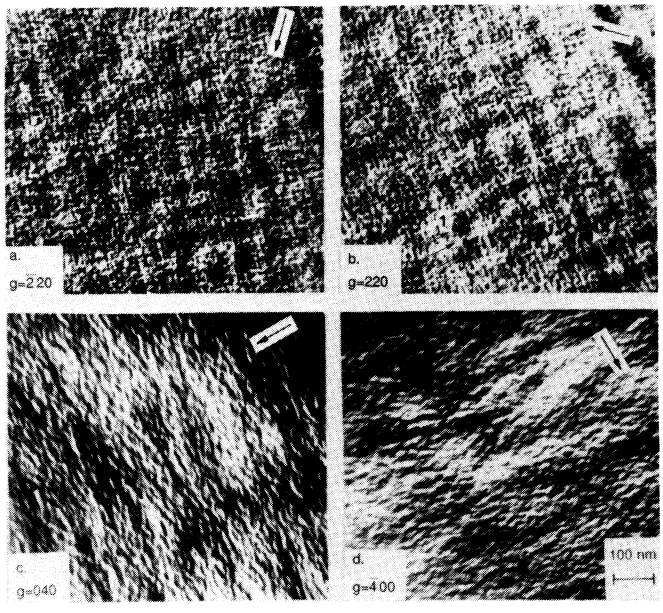

FIG. 1. Series of dark-field electron micrographs obtained from a (001) $In_{1-x}Ga_xAs_yP_{1-y}$ epitaxial layer grown by LPE; the emission wavelength of the layer is 1.3 μm. The operating reflections in (a), (b), (c), and (d) are, respectively, $\bar{2}22$, 220, 040, and $\bar{4}00$.

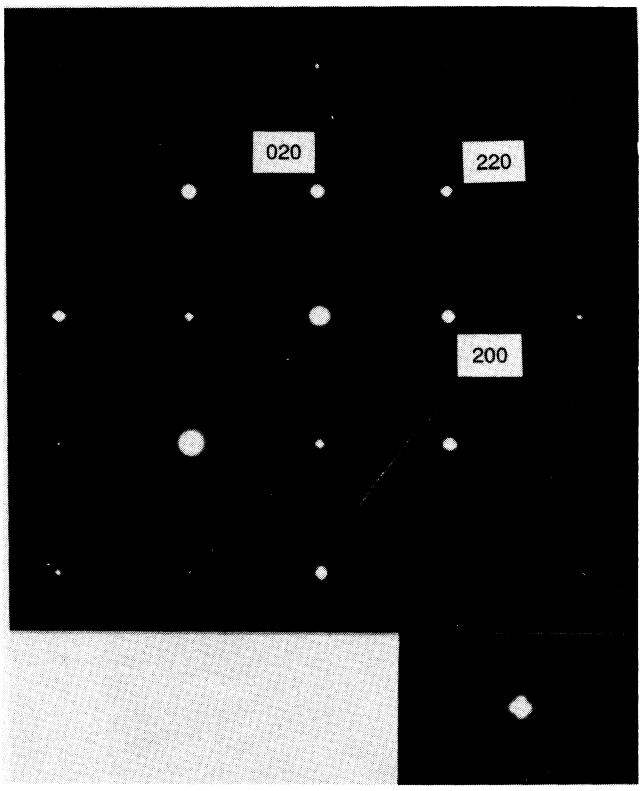

FIG. 2. (001) diffraction pattern obtained from the layer shown in Fig. 1. The pattern shows satellites in the vicinity of (220), (020), and higher-order spots that result from the alignment of periodic fine-scale contrast modulations. One of the higher ordered spots is enlarged at the lower right-hand corner to show detail.

the (040) and ($\bar{4}$00) reflections [see Figs. 1(c) and 1(d)]. Specifically, for $\mathbf{g}=(\bar{4}00)$ the coarse and fine modulations lying along the [010] direction are out of contrast, and the second set of modulations is invisible for $\mathbf{g}=(040)$. These results demonstrate that the principal strains associated with the modulations are parallel to the directions along which they are aligned. This assessment is consistent with the earlier work of Mahajan *et al.*[2] and Norman and Booker.[4] Further, the periodicity of the fine-scale modulations as measured from the (040) and ($\bar{4}$00) images is $\sim 8\pm 1$ nm, whereas the periodicity of the coarse modulation is ~ 90 nm [see Figs. 1(b) and 1(c)].

A selected area electron diffraction pattern obtained from the sample shown in Fig. 1 is reproduced as Fig. 2. The pattern shows satellite spots along the [100] and [010] directions. Since the spacing of the satellites is characteristic of the periodicity of the modulations,[33] the modulation period has been calculated using the following expression:

$$\lambda=\frac{a}{\sqrt{h^2+k^2+l^2}}\frac{|\mathbf{g}|}{|\Delta\mathbf{g}|}\ , \tag{1}$$

where λ is the period of the modulation, a is the lattice parameter, h,k,l are indices of a diffraction spot described by a vector $\mathbf{g}$, and $|\Delta\mathbf{g}|$ is the spacing of the satellite reflection from the main Bragg spot. The application of Eq. (1) to the results shown in Fig. 2 gives a value of 7 nm for λ that correlates well with the measurements from Fig. 1.

Figure 3 shows dark-field micrographs obtained from a (110) cross section of an LPE-grown (001) layer. The fine-scale modulations are clearly seen in Fig. 3(a), but they are out of contrast for $\mathbf{g}$ parallel to the growth direction [Fig. 3(b)]. Further, careful examination of Fig. 3(b) reveals faint between contrast along the [1$\bar{1}$1] and [$\bar{1}$11] directions. This type of contrast has been observed by Norman[34] in this system and by a number of researchers in a wide variety of metallic systems.[35–37].

Figure 4 shows a series of dark-field electron micrographs obtained from an LPE film grown on a (110) InP substrate. The fine-scale speckle microstructure is evident for $\mathbf{g}=(2\bar{2}2)$. When the sample is imaged with the ($\bar{2}$20) and (00$\bar{4}$) reflections, it becomes apparent that the microstructure is composed of two orthogonal modulations along the [001] and [1$\bar{1}$0] directions. The [001] modulation appears to be out of contrast for $\mathbf{g}=(\bar{2}20)$, whereas the [110] modulation is invisible for $\mathbf{g}=(004)$. This shows that, as in the case of the (001) specimen, the principal strain components of the contrast modulations are parallel to the directions of the modulations. The periods of the modulations along the [001] and [1$\bar{1}$0]

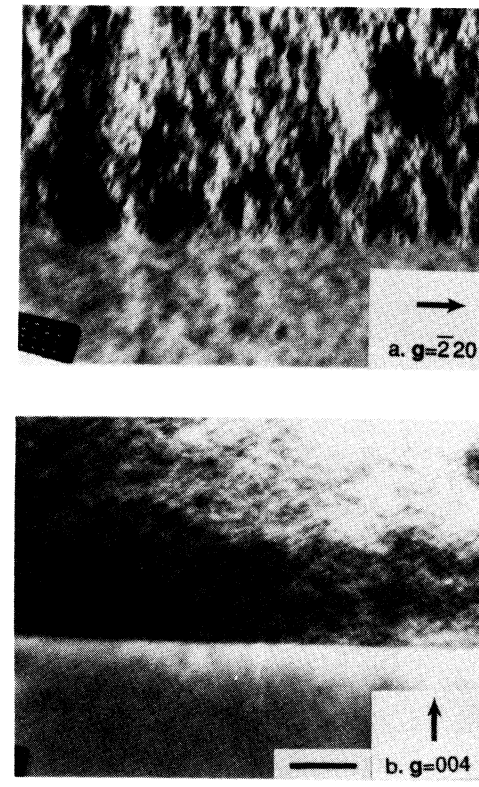

FIG. 3. Dark-field micrographs obtained from cross section of a (001) LPE grown $In_{1-x}Ga_xAs_yP_{1-y}$ layer. The operating reflections in (a) and (b) are ($\bar{2}$20) and (004), respectively. These images demonstrate the absence of decomposition along the growth direction. Marker represents 50 nm.

directions are, respectively, 6 and 5 nm.

A series of dark-field images obtained from an epitaxial layer grown on a $(111)_A$ InP substrate are shown in Fig. 5. A fine speckle contrast, similar to that seen in the (001) and (110) layers, is observed in all of these micrographs. In Figs. 5(a) and 5(b), coarse modulations can also be seen and they are indicated by the arrows in Fig. 5(b). In addition, the alignment of the fine-scale modulations is not well defined.

To assess the alignment of the fine-scale modulations, laser diffraction patterns were obtained from the negatives used to print the micrographs in Fig. 5. These results are shown in the upper left-hand corner of each of

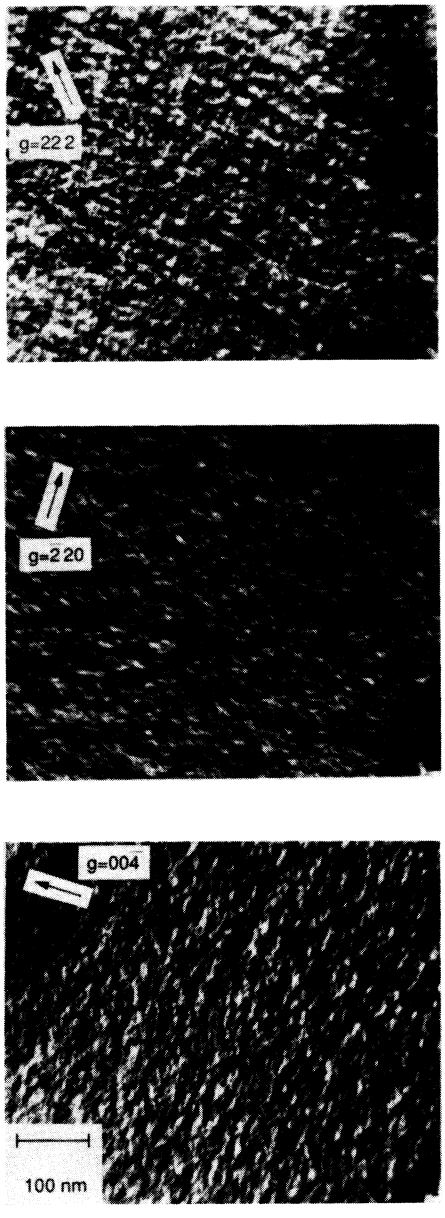

FIG. 4. Dark-field electron micrographs obtained from a (110) $In_{1-x}Ga_xAs_yP_{1-y}$ layer grown by LPE; its emission wavelength is 1.3 μm. The speckle contrast observed for $\mathbf{g}=(2\bar{2}2)$ appears to consist of two orthogonal modulations along the [001] and [1$\bar{1}$0] directions.

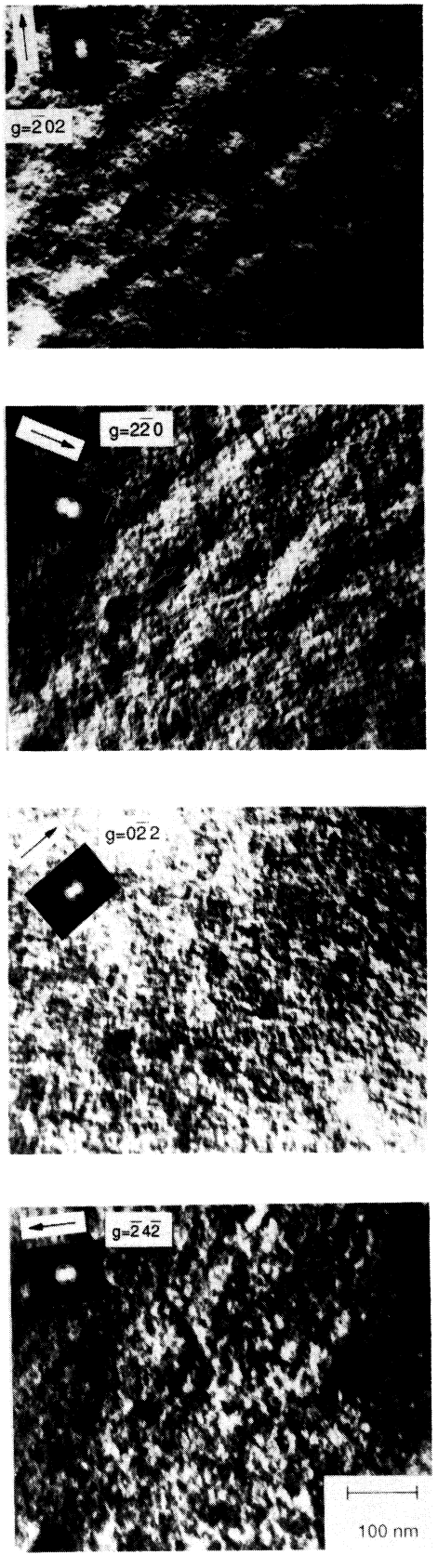

FIG. 5. Dark-field micrographs obtained from a $(111)_A$ $In_{1-x}Ga_xAs_yP_{1-y}$ layer grown by LPE; its emission wavelength is 1.3 μm. Laser diffraction patterns in the upper right-hand corner of each micrograph show diffuse intensity parallel to the operating reflection in each case. These observations imply that modulations are periodic, but are randomly oriented.

the micrographs. Each pattern shows diffuse intensity which is characteristic of diffraction from periodic modulated microstructures. However, in every case the observed elongation is parallel to the operating reflection. These results are consistent with an assessment that the modulations are periodic, but are not aligned crystallographically.

Figure 6 shows a series of dark-field micrographs obtained from a (123) layer. The $(22\bar{2})$ image, Fig. 6(a), shows sets of two nearly orthogonal modulations along the $[0\bar{3}2]$ and $[\bar{3}01]$ directions. Since the (123) orientation does not contain low-index reflections suitable for diffraction contrast analysis, the specimen was tilted to the [011] zone axis to analyze the plan-view microstructures. Using **g**'s near this zone, the $[\bar{3}01]$ and $[03\bar{2}]$ modulations can be rendered invisible for $\mathbf{g}=(02\bar{2})$ and $(\bar{4}00)$, respectively. Further, it can be shown that the $[01\bar{1}]$ and $[\bar{1}00]$ vectors project onto the (123) plane along the $[1\,16\,1\bar{1}]$ and $[\bar{1}3\,2\,3]$ directions. As these directions are nearly normal and perpendicular to the $[\bar{3}01]$ and $[0\bar{3}2]$ vectors, it is inferred that the principal strains associated with the modulations are again parallel to the directions of the modulations. It was ascertained from cross-sectional samples that phase separation does not occur along the growth direction for the (110), (111), and (123) overgrowths, a result consistent with that obtained from the (001) overgrowth.

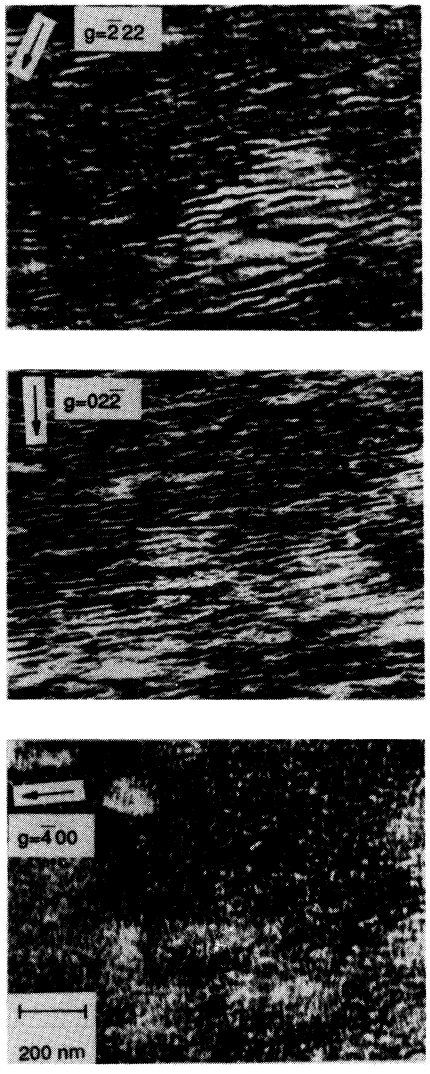

FIG. 6. Series of dark-field electron micrographs obtained from a (123) $In_{1-x}Ga_xAs_yP_{1-y}$ layer emitting at 1.3 μm.

B. Influence of growth technique on microstructures

Figure 7 shows a series of dark-field images of a (001) lattice-matched $In_{1-x}Ga_xAs$ epitaxial layer grown by MBE; the growth temperature was 500 °C. The observed modulated microstructure is finer than that seen in the LPE films. It is difficult to discern the alignment of modulations in Figs. 7(a) and 7(b). However, it is apparent from Figs. 7(c) and 7(d) that the speckle microstructure is composed of two orthogonal modulations which lie along the two in-plane $\langle 100 \rangle$ directions. Also, the principal strains associated with the modulations are along their propagation directions, a result identical to those obtained for the LPE layers. The period of the modulations is ~5–6 nm as measured from the $\langle 400 \rangle$ images.

The selected area diffraction pattern from the layer showed diffuse intensity around the $\langle 200 \rangle$ and higher-order spots. The presence of the diffuse intensity indicates the absence of a single dominant wavelength in the microstructure. Further, decomposition along the growth direction was not observed.

C. Influence of growth temperature on microstructures

Figure 8 shows dark-field, planview micrographs obtained from (001) $In_{1-x}Ga_xAs$ epitaxial layers grown by MBE at different temperatures. The modulations are observed even in the layer grown at 400 °C. The dominant effect of the reduced-growth temperature is to decrease the period of the modulations. The respective periods in (a), (b), and (c) are 3, 3.5, and 7 nm.

IV. DISCUSSION

Several interesting observations emerge from the present study. First, for the (001), (110), $(111)_A$, and (123) $In_{1-x}Ga_xAs_yP_{1-y}$ epitaxial layers, grown by use of LPE at the same temperature and emitting at 1.3 μm, the fine-scale speckle structure evolves by phase separation along the directions which lie in the growth plane; decomposition along the growth direction is not observed in either of the four cases examined. Second, for a fixed-growth temperature, the wavelengths of the speckle microstructure depend on the orientation of the underlying substrate and vary with the direction of the modulation. Third, the characteristics of microstructure observed in (001) $In_{1-x}Ga_xAs$ layers grown by use of MBE are identical to those of the LPE layers except that the wavelength of the modulations is smaller. Fourth, the growth temperature has a very strong effect on the wavelength of modulations observed in MBE grown $In_{1-x}Ga_xAs$ epitaxial layers.

If the fine-scale modulations were to evolve in the bulk as suggested by Norman and Booker,[4] decomposition

along the growth direction should dominate. This is inferred because the layer is thin along this direction so it should be easier to accommodate phase-transformation-induced strains. This is, however, not borne out by the experimental results. Further, based on the suggestion of Norman and Booker,[4] the directions along which the modulations form for different orientations of the substrate cannot be rationalized. Since decomposition in the (001), (110), and (123) layers is observed along the directions lying in the growth plane, the fine-scale structure must evolve by two-dimensional phase separation occurring at the surface while the layer is growing. The same assessment applies to the $(111)_A$ layer even though the modulations do not form along any particular direction

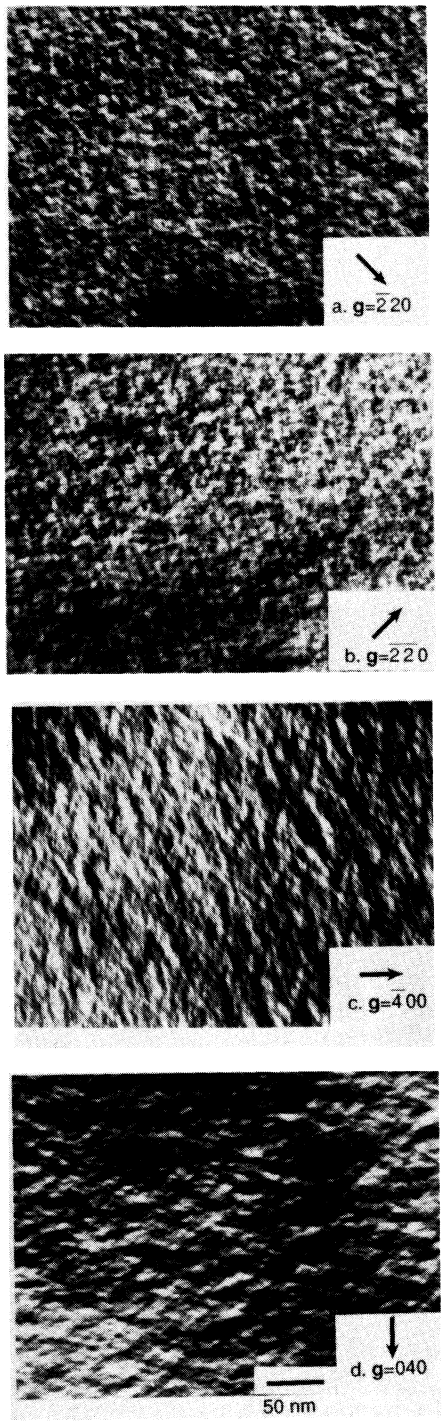

FIG. 7. Series of dark-field images obtained from a (001) $In_{1-x}Ga_xAs$ film grown by MBE; its emission wavelength is 1.67 μm. Comparing Figs. 1 and 7, it is apparent that the strain fields associated with the speckle structure in the MBE film are identical to those of the LPE layer.

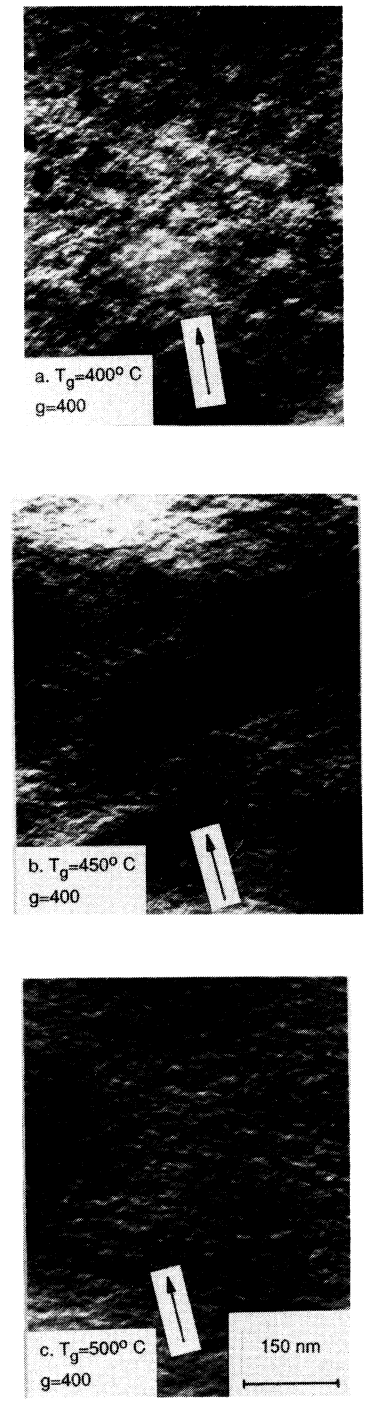

FIG. 8. Dark-field electron micrographs obtained from $In_{1-x}Ga_xAs$ films grown at different temperatures by MBE. All images were taken with $\mathbf{g}=(400)$.

in the growth plane. In addition, the preceding conclusion is independent of the growth technique. It is therefore concluded that the fine-scale microstructures shown in Figs. 1 and 4–7 evolve by two-dimensional phase separation occurring at the layer surface.

To rationalize the observed directions along which phase separation occurs in differently oriented layers, McDevitt[10] has computed the elastic work associated with the occurrence of composition modulations along various directions in the (001), (110), (111), and (123) planes. These calculations were made by computing the amount of work that is required to elastically deform a film which contains a modulation in lattice constant so that the overall lattice constant of the film matches that of the underlying substrate. Since the amplitude of these modulations is not well known, the calculations have been normalized for a [100] modulation on a (001) substrate. The polar plots of the relative values of elastic work that are associated with the creation of composition modulations in the substrate plane are shown in Fig. 9. Comparing the results of Figs. 1, 4, and 6 with those of Fig. 9, it is apparent that modulations in the (001), (110), and (123) layers occur along those directions in the substrate surface along which the elastic strain energy of the transformation is at a minimum, i.e., along the soft directions in the growth plane. Also, since the (111) surface is elastically isotropic, the lack of alignment of the modulated structure in the $(111)_A$ layer, Fig. 5, can be comprehended.

Since the phase separation is two dimensional in nature and occurs by the movement of atoms at the layer surface, the wavelength of the resulting microstructure will depend on the growth technique, the growth temperature, and orientation of the underlying substrate. This assessment is compatible with the results of this study and those of McDevitt.[10] Furthermore, consideration of the transformation mechanism that is proposed here suggests that bulk thermodynamics may be useful only in predicting trends and tendencies. Accurate information concerning wavelength, amplitude, critical temperature, etc., can only be provided by surface thermodynamics and two-dimensional phase diagrams.

An attempt will be made to analyze quantitatively the temperature dependence of the wavelength observed in (001) $In_{1-x}Ga_xAs$ layers grown by MBE. Since the composition modulations must develop by surface diffusion, the wavelength of the modulation (λ) may be related to the surface diffusion coefficient (D_s) by the following relation:

$$\lambda^2 = AD_s t \ , \tag{2}$$

where A is a constant of proportionality and t is time required for the deposition of a monolayer. It is implicitly assumed in Eq. (2) that the atomic arrangement at the surface is frozen in the bulk because bulk diffusion is extremely slow in these materials. It can be shown that for a constant growth rate, i.e., constant t, λ is related to temperature (T) via the following equation:

$$\lambda^2 = B \exp(-E_s/kT) \ , \tag{3}$$

where B is a constant and E_s is the activation energy for surface diffusion of the atomic constituent that is rate controlling. It is apparent from Eq. (3) that $\ln\lambda$ vs $1/T$ should exhibit a linear relation. For the MBE layers this is shown in Fig. 10. It is clear that within the limits of experimental scatter, the observed relationship is linear. Furthermore, E_s is estimated to be ~ 0.35 eV. This value is slightly larger than the activation energy of ~ 0.25 eV associated with the diffusion of As atoms on the (001) GaAs surface.[38] This difference could occur from the fact that the (001) $In_{1-x}Ga_xAs$ surfaces contain two types of group-III atoms. Thus, the observed value could represent the activation energy for the diffusion of As atoms on the (001) $In_{1-x}Ga_xAs$ surface. This correlation implies that the evolution of phase-separated regions in

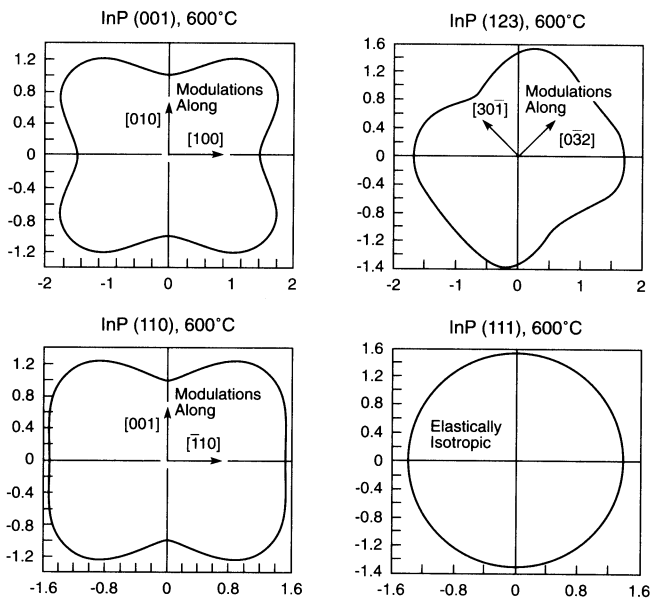

FIG. 9. Polar plots of the relative values of elastic work that is associated with the creation of composition modulations in the plane of the substrate for the (001), (110), (111), and (123) orientations.

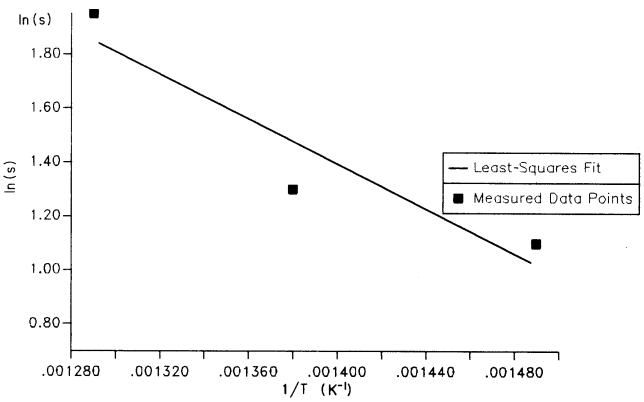

FIG. 10. Plot showing the observed logarithmic variation of the wavelength of the modulations (λ) with inverse temperature (T) for (001) $In_{1-x}Ga_xAs$ layers grown by MBE.

$In_{1-x}Ga_xAs$ epitaxial layers, grown by MBE, is controlled by the surface diffusion of As atoms.

If the strain energy associated with phase separation is taken into consideration, the critical temperatures for bulk phase separation are quite low.[27] However, when the bulk constraint is relaxed, phase separation occurs quite readily as shown in this and earlier studies.[1-10,20] It is argued that the atomic arrangement produced by surface-phase separation is retained in the subsurface layers because bulk diffusion is extremely slow. The preceding discussion implies that the microstructures produced by two-dimensional phase separation are metastable in the bulk.

The results on the variation of wavelengths with orientation of the underlaying substrate demonstrate that we have considerable latitude in tailoring the wavelength of the fine-scale modulations. For example, the wavelength can be varied from 5 to 27 nm by replacing the (110) InP substrates with the (123) substrates. If these changes in wavelength are accompanied by changes in amplitude, then we have a way to tailor microstructures having optimal optical and transport properties for a specific device application. If sufficiently large composition amplitude differences between the phase-separated regions can be developed, two-dimensional arrangement of "quantum dots" can be produced. The composition difference between the two neighboring dots which, in turn, determines the band offsets, can then be tailored by changing the growth temperature, the growth technique, the substrate orientation, and by post-growth annealing.

Chu *et al.*,[3] Norman and Booker,[4] Mahajan and coworker,[6,7] Ueda, Takechi, and Komeno,[8] and McDevitt[10] have examined ternary and quaternary layers grown by VPE, MBE, and organometallic vapor-phase epitaxy (OMVPE). Without exception, phase separation is observed in every case. These studies demonstrate that phase separation cannot be suppressed using nonequilibrium growth techniques, such as OMVPE and MBE, as suggested by Stringfellow and co-workers.[39,40]

The coarse-contrast modulations are an artifact of thin foils.[6,7] Two-dimensional strains associated with the fine-scale structure could lead to periodic buckling of a thin film. This suggestion is consistent with the recent calculations of Alerhand *et al.*[41] It is envisaged that the layer undergoes buckling after thinning. The occurrence of buckling, in turn, depends on the thickness of the layer: thinner regions may not buckle because strains are not large enough, while strains may not be sufficient to buckle thicker regions of the layer. This assessment is borne out by the results of Treacy, Gibson, and Howie[5] on the thickness dependence of the occurrence of coarse-contrast modulations in $In_{1-x}Ga_xAs_yP_{1-y}$ epitaxial layers.

V. CONCLUSIONS

We conclude as follows.

(1) It has been demonstrated that phase separation in $In_{1-x}Ga_xAs_yP_{1-y}$ layers, grown on (001), (110), (123), and $(111)_{In}$ InP substrates by LPE, is two-dimensional in nature and occurs along the directions lying in the growth plane; decomposition along the growth direction is not observed in either of the four cases. Phase separation takes place along those directions along which the strain energy of the transformation is a minimum, and occurs at the surface while the layer is being grown. Two-dimensional phase diagrams are necessary to compute amplitudes of the phase-separated regions. Further, the amplitudes may be tailored by changing the growth temperature, the growth technique, and the substrate orientation.

(2) The evolution of the wavelength of phase-separated microstructures in $In_{1-x}Ga_xAs$ epitaxial layers grown by MBE appears to be controlled by the surface diffusion of As atoms.

(3) The occurrence of phase separation in ternary and quaternary epitaxial layers cannot be suppressed using nonequilibrium growth techniques, such as OMVPE and MBE.

(4) The coarse contrast modulations are an artifact of thin foils that is caused by two-dimensional strains associated with the fine-scale structure.

ACKNOWLEDGMENTS

The work at Carnegie Mellon University was supported by the Department of Energy through Grant No. DE-FG02-87ER45329 and T.L.M., S.M., and D.E.L. gratefully acknowledge the support. In addition, S.M. acknowledges fruitful discussion with Professor W.W. Mullins and Professor M. Skowronski of Carnegie Mellon University.

*Present address: IBM Corporation, Essex Junction, Vermont 05452-4299.

[1]P. Henoc, A. Izrael, M. Quillec, and H. Launois, Appl. Phys. Lett. **40**, 963 (1982).

[2]S. Mahajan, B. V. Dutt, H. Temkin, R. J. Cava, and W. A. Bonner, J. Cryst. Growth **68**, 589 (1984).

[3]S. N. G. Chu, S. Nakahara, K. E. Strege, and W. D. Johnston, Jr., J. Appl. Phys. **57**, 4610 (1985).

[4]A. G. Norman and G. R. Booker, J. Appl. Phys. **57**, 4715 (1985).

[5]M. M. J. Treacy, J. M. Gibson, and A. Howie, Philos. Mag. A **51**, 389 (1985).

[6]S. Mahajan and M. A. Shahid, in *Advances in Materials, Processing and Devices in III-V Compound Semiconductors,* edited by D. K. Sadana, L. E. Eastman, and R. Dupuis, MRS Symposia Proceedings No. 144 (Materials Research Society, Pittsburgh, 1989), p. 169.

[7]S. Mahajan, M. A. Shahid, and D. E. Laughlin, in *Microscopy of Semiconducting Materials,* Proceedings of the Institute of Physics Conference, edited by A. G. Cullis and J. L. Hutchison, IOP Conf. Proc. No. 100 (Institute of Physics and Physical Society, London, 1989), p. 143.

[8]O. Ueda, M. Takechi, and J. Komeno, Appl. Phys. Lett. **54**, 2312 (1989).

[9]T. L. McDevitt, S. Mahajan, D. E. Laughlin, W. A. Bonner, and V. G. Keramidas, in *Epitaxial Heterostructures,* edited by

D. W. Shaw, J. C. Bean, V. G. Keramidas, and P. S. Peercy, MRS Symposia Proceedings No. 198 (Materials Research Society, Pittsburgh, 1990), p. 609.

[10]T. L. McDevitt, Ph.D. dissertation, Carnegie Mellon University, Pittsburgh (1990).

[11]T. S. Kuan, T. F. Kuech, W. I. Wang, and E. L. Wilkie, Phys. Rev. Lett. **54**, 201 (1985).

[12]H. R. Jen, M. J. Cherng, and G. B. Stringfellow, Appl. Phys. Lett. **48**, 1603 (1986).

[13]T. S. Kuan, W. I. Wang, and E. L. Wilkie, Appl. Phys. Lett. **51**, 51 (1987).

[14]H. Nakayama and H. Fujita, in *Gallium Arsenide and Related Compounds,* Proceedings of the Institute of Physics Conference, edited by M. Fujimoto, IOP Conf. Proc. No. 79 (Institute of Physics and Physical Society, London, 1985), p. 289.

[15]M. A. Shahid, S. Mahajan, D. E. Laughlin, and H. M. Cox, Phys. Rev. Lett. **58**, 2567 (1987).

[16]A. G. Norman, R. E. Mallard, I. J. Murgatroyd, G. R. Booker, A. H. Moore, and M. D. Scott, in, *Microscopy of Semiconducting Materials,* Proceedings of the Institute of Physics Conference, edited by A. G. Cullis and P. A. Augustus, IOP Conf. Proc. No. 87 (Institute of Physics and Physical Society, London, 1987), p. 77.

[17]Y. E. Ihm, N. Otsuka, J. Klen, and H. Morkoç, Appl. Phys. Letts. **51**, 2013 (1987).

[18]A. Gomyo, T. Suzuki, K. Kobayashi, S. Kawata, and I. Hino, Appl. Phys. Lett. **50**, 673 (1987).

[19]A. Gomyo, T. Suzuki, and S. Iijima, Phys. Rev. Lett. **60**, 2645 (1988).

[20]M. A. Shahid and S. Mahajan, Phys. Rev. B **38**, 1344 (1988).

[21]M. Kondow, H. Kakibayashi, and S. Minagawa, J. Cryst. Growth **88**, 291 (1988).

[22]T. Suzuki, A. Gomyo, and S. Iijima, J. Cryst. Growth **93**, 396 (1988).

[23]M. Kondow, H. Kakibayashi, T. Tanaka, and S. Minagawa, Phys. Rev. Lett. **63**, 884 (1989).

[24]I. J. Murgatroyd, A. G. Norman, and G. R. Booker, J. Appl. Phys. **67**, 2310 (1990).

[25]G. S. Chen, D. H. Jaw, and G. B. Stringfellow, Appl. Phys. Lett. **57**, 2475 (1990).

[26]B. de Cremoux, P. Hirtz, and J. Ricciardi, in *Gallium Arsenide and Related Compounds,* Proceedings of the Institute of Physics Conference, edited by H. W. Thim, IOP Conf. Proc. No. 56 (Institute of Physics and Physical Society, London, 1981), p. 115.

[27]G. B. Stringfellow, J. Cryst. Growth **58**, 194 (1982).

[28]K. Onabe, Jpn. J. Appl. Phys. **21**, 1323 (1982).

[29]H. Launois, M. Quillec, F. Glas, and M. M. J. Treacy, in *Gallium Arsenide and Related Compounds,* Proceedings of the Institute of Physics Conference, edited by G. E. Stillman, IOP Conf. Proc. No. 64 (Institute of Physics and Physical Society, London, 1982), p. 537.

[30]A. A. Studna and G. J. Gualtieri, Appl. Phys. Lett. **39**, 965 (1981).

[31]R. A. Logan, Prog. Cryst. Growth Charact. **12**, 215 (1986).

[32]S. N. G. Chu and T. T. Sheng, J. Electrochem. Soc. **131**, 2663 (1984).

[33]V. Daniel and H. Lipson, Proc. R. Soc. London Ser. A **181**, 368 (1943).

[34]A. G. Norman, D. Philosophy dissertation, University of Oxford, 1987.

[35]L. E. Tanner, Philos. Mag. **14**, 111 (1966).

[36]D. E. Laughlin, R. E. Sinclair, and L. E. Tanner, Scr. Metall. **14**, 373 (1980).

[37]I. M. Robertson and C. M. Wayman, Philos. Mag. A **48**, 421 (1983).

[38]J. H. Neave, P. J. Dobson, B. A. Joyce, and J. Zhang, Appl. Phys. Lett. **47**, 100 (1985).

[39]G. B. Stringfellow and M. J. Cherng, J. Cryst. Growth **64**, 413 (1988).

[40]M. Cherng, G. B. Stringfellow, and R. M. Cohen, Appl. Phys. Lett. **44**, 550 (1986).

[41]O. L. Alerhand, D. Vanderbilt, R. D. Meade, and J. D. Joannopoulos, Phys. Rev. Lett. **61**, 1973 (1988).