Atomic Ordering in $Ga_{0.47}In_{0.53}As$ and $Ga_xIn_{1-x}As_yP_{1-y}$ Alloy Semiconductors

M. A. Shahid, S. Mahajan, and D. E. Laughlin
Department of Metallurgical Engineering and Materials Science, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

and

H. M. Cox
Bell Communication Research, Red Bank, New Jersey 07701
(Received 30 January 1987)

GaInAs-InP and GaInAsP-InP multilayers have been investigated by transmission electron microscopy. Electron-diffraction studies on $(\bar{1}10)$ edge-on samples indicate that atomic ordering produces a phase with $R\bar{3}m$ symmetry. This is of different symmetry from the one observed previously in GaInAs, GaAsSb, and GaInAs. Only one or two variants of the ordered phase are observed in our layered structure.

PACS numbers: 68.65.+g, 61.16.Di, 61.55.Hg

Recent reports of long-range order in $Al_xGa_{1-x}As$ are interesting in that this material belongs to a completely miscible system for all values of x at temperatures commonly used to grow these materials.[1-4] Unlike $Al_xGa_{1-x}As$, $GaAs_{1-x}Sb_x$, $Ga_xIn_{1-x}As$, and $Ga_xIn_{1-x}As_yP_{1-y}$ III-V compounds are believed to have a miscibility gap in their phase diagrams. While ordered phases in $GaAs_{1-x}Sb_x$ [5] and $Ga_xIn_{1-x}As$ [6] have been observed, only spinodal decomposition and phase separation in $Ga_xIn_{1-x}As_yP_{1-y}$ have been reported.[7-13] In the present study we have used transmission-electron-microscopy and selected-area diffraction (SAD) techniques to study $Ga_{0.47}In_{0.53}As$ and $Ga_{0.37}In_{0.63}As_{0.82}P_{0.18}$ ($\lambda = 1.52$ μm) layers lattice matched to InP. Our results quite convincingly demonstrate that an ordered phase exists in these materials and that the structure of this ordered phase is different from those reported in $Al_xGa_{1-x}As$,[1,2] $GaAs_{1-x}Sb_x$,[5] and $Ga_xIn_{1-x}As$.[6]

Vapor levitation epitaxy[14,15] was used to grow two types of structures. The type-I samples consisted of a $\langle 001 \rangle$ InP substrate, a 1.5-μm-thick $Ga_{0.47}In_{0.53}As$ buffer layer, followed by ten pairs of alternating layers of InP and $Ga_{0.47}In_{0.53}As$, and a 0.68-μm-thick InP cladding layer. The type-II samples consisted of a Zn-doped p^+ $\langle 001 \rangle$ InP substrate, a 0.1-μm-thick buffer layer, a 0.2-μm-thick $Ga_{0.37}In_{0.63}As_{0.82}P_{0.18}$ active layer, and a 0.85-μm-thick layer of S-doped InP. The type-I and type-II samples were grown at 660 and 650 °C, respectively. Edge-on samples for transmission-electron-microscopy and SAD studies were prepared by the cleaving along the [110] direction of thin sections of these materials.

A typical edge-on electron micrograph of the type-I structure is reproduced as Fig. 1. This was produced with use of the 002 reflection which delineates $Ga_xIn_{1-x}As$ and InP layers such that the contrast from the former appears relatively darker than the latter. Figure 2 shows a $[\bar{1}10]$ SAD pattern obtained from a region similar to the one shown in Fig. 1. Two important features of this SAD pattern are the following. First, there are streaks along the [001] direction through the matrix spots. Second, weak superlattice spots are present halfway between the rows of basic matrix spots parallel to the [111] direction. As seen in Fig. 1 thicknesses of the nonuniformly spaced layers are not constant; therefore, the expected rows of discrete spots of modulated structure[16] have been replaced by a set of

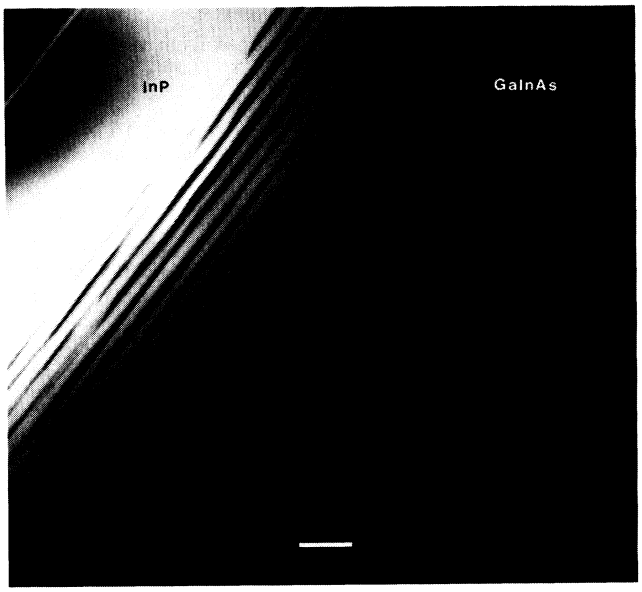

FIG. 1. A transmission electron micrograph showing an edge-on view of a multilayer structure of the type-I samples. The surface normal is close to $[\bar{1}10]$ and 002 reflection has been used to produce this image. The light and dark stripes represent InP and $Ga_{0.47}In_{0.53}As$, respectively. Marker represents 0.1 μm.

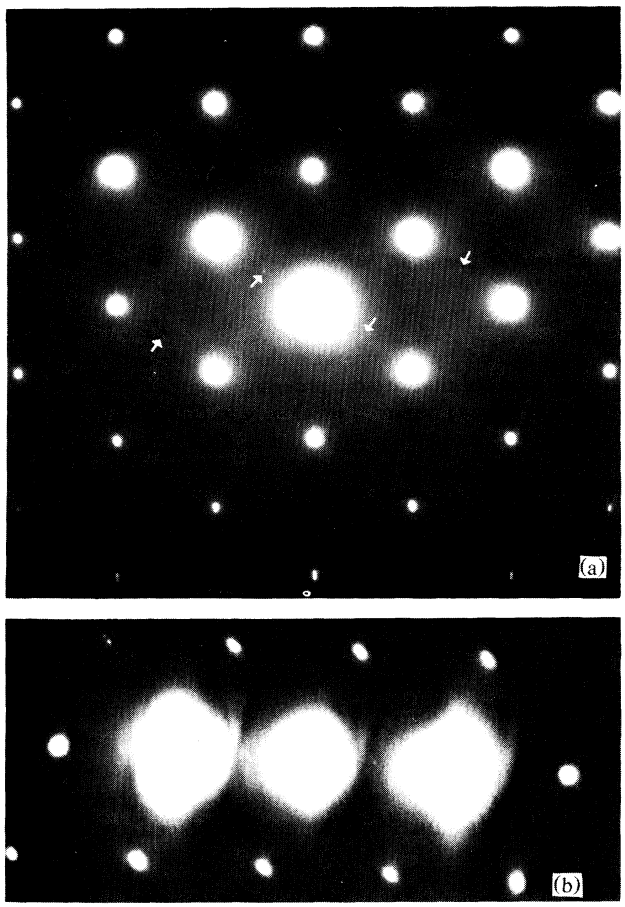

FIG. 2. (a) An SAD pattern obtained from the multilayer region of Fig. 1 for the [$\bar{1}$10] zone axis. Notice the weak superlattice reflections (indicated by arrows) between the fundamental reflections along the [111] direction. (b) An SAD pattern for an exact 111-reflection condition. Here the superlattice spots are clearly visible.

continuous streaks. In addition, these streaks in part may also be due to the interfacial strain between the layers.[17]

The results presented above clearly demonstrate that the ordered structure observed in the present experiments is different from all the ordered phases reported in III-V compound semiconductors. The structures of the reported ordered phases in III-V compounds are the following: famatinite ($I\bar{4}2m$, Cu_3SbS_4 type) in $Ga_xIn_{1-x}As$,[6] tetragonal ($P\bar{4}m2$, where one sublattice is ordered as CuAu-I)[18] in $Al_xGa_{1-x}As$[1,2] and $GaAs_{1-x}Sb_x$,[5] and chalcopyrite ($I\bar{4}2d$, $CuFeS_2$ type)[18] in $GaAs_{1-x}Sb_x$.[5] The ordered phase we have observed is similar to the one reported in the strained SiGe-Si superlattice ($R\bar{3}m$, CuPt type).[18,19]

Since $Ga_xIn_{1-x}As$ has the zinc-blende structure ($F\bar{4}3m$), for a given value of the parameter x, the group-III sublattice of this alloy is believed to consist of a random distribution of Ga and In atoms such that a {111} plane of this sublattice has an average Ga/In ratio defined by the parameter x. Under these conditions no superlattice spots should be present in the [$\bar{1}$10] SAD pattern. The presence of superlattice spots halfway between the rows of fundamental spots in the [111] direction shows that the real-space translation periodicity in this direction is twice that of the zinc-blende structure. One way of achieving this is for the new structure to have the alternate (111) planes of the group-III sublattice rich in Ga and In atoms, respectively, so that for a Ga rich (111) plane, the Ga/In atomic ratio is greater than that defined by x and vice versa. For the sake of discussion, consider a cubic unit cell twice the edge length of the basic structure. The new unit cell will in fact consist of eight unit cells of the basic structure and for $x=0.5$ will contain 64 atoms (In=Ga=16, As=32). Now arrange these atoms in the new unit cell as they would be in the zinc-blende structure except that the (111) set of planes of the group-III sublattice are alternated by unmixed Ga and In atoms. This structure has the space group $R\bar{3}m$, and Pearson symbol $hR64$. A projection on the ($\bar{1}$10) plane of the ordered $Ga_{0.5}In_{0.5}As$ unit cell is shown in Fig. 3(a). It is readily apparent that the periodicity in the [111] direction has doubled. On the other hand because of the atomic "mixing" on the (11$\bar{1}$) planes the periodicity of the basic structure is retained in the [11$\bar{1}$] direction. A computer-generated diffraction pattern of the ($\bar{1}$10)* plane of the reciprocal structure of this ordered unit cell is shown in Fig. 3(b). A comparison of this pattern with the experimental SAD pattern in Fig. 2 shows that the match between the positions of the diffraction spots in the two patterns is excellent. The apparent differences in the relative intensities in the experimental and simulated patterns are due to the fact that the former represents a contribution from all the phases present in the sample, namely InP, $Ga_xIn_{1-x}As$, and ordered $Ga_xIn_{1-x}As$, while the latter represents the ordered $Ga_{0.5}In_{0.5}As$ only.

The question that remains unanswered concerns the origin and observed bias of the ordered phase, i.e., the occurrence of only one ordered variant. It is important to point out that similar experiments on thick (1–3 μm) $Ga_xIn_{1-x}As$ layers did not show extra diffraction spots due to ordering. Furthermore, in another experiment a 1.5-μm-thick $Ga_xIn_{1-x}As$ layer grown on InP by liquid-phase epitaxy was annealed at 650 °C for 90 min. Edge-on samples from this annealed material did not reveal any superstructure. The superlattice reflections have been observed only in the multilayered regions of samples in which a set of many InP-$Ga_xIn_{1-x}As$ interfaces was present. It seems that the presence of interfacial strain facilitates the formation of a superstructure. Furthermore, the $Ga_xIn_{1-x}As$ layers appear to undergo phase separation because a miscibility gap exists in the

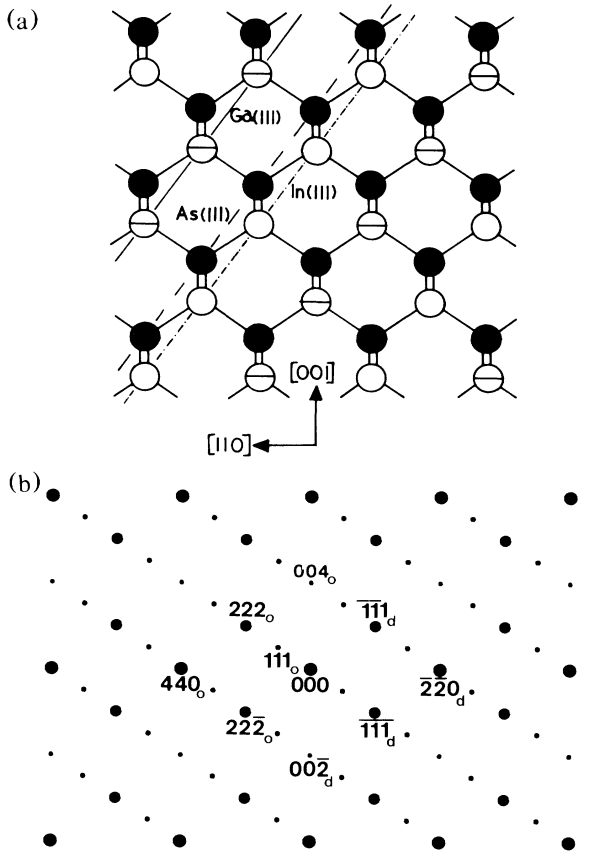

FIG. 3. (a) A schematic diagram showing a $(\bar{1}10)$ projection of an ordered $Ga_{0.5}In_{0.5}As$. Notice that the periodicity along the [111] direction has doubled because of alternating (111)In and (111)Ga planes. (b) A computer generated diffraction pattern for the ordered $Ga_{0.5}In_{0.5}As$ for the $[\bar{1}10]$ zone axis. The indices with subscript d represent reflections due to disordered $Ga_{0.5}In_{0.5}As$ parent phase, while indices with subscript o represent reflections from the ordered phase. The presence of superlattice reflections in Fig. 2 is consistent with this pattern and hence the atomic ordering shown in Fig. 3(a).

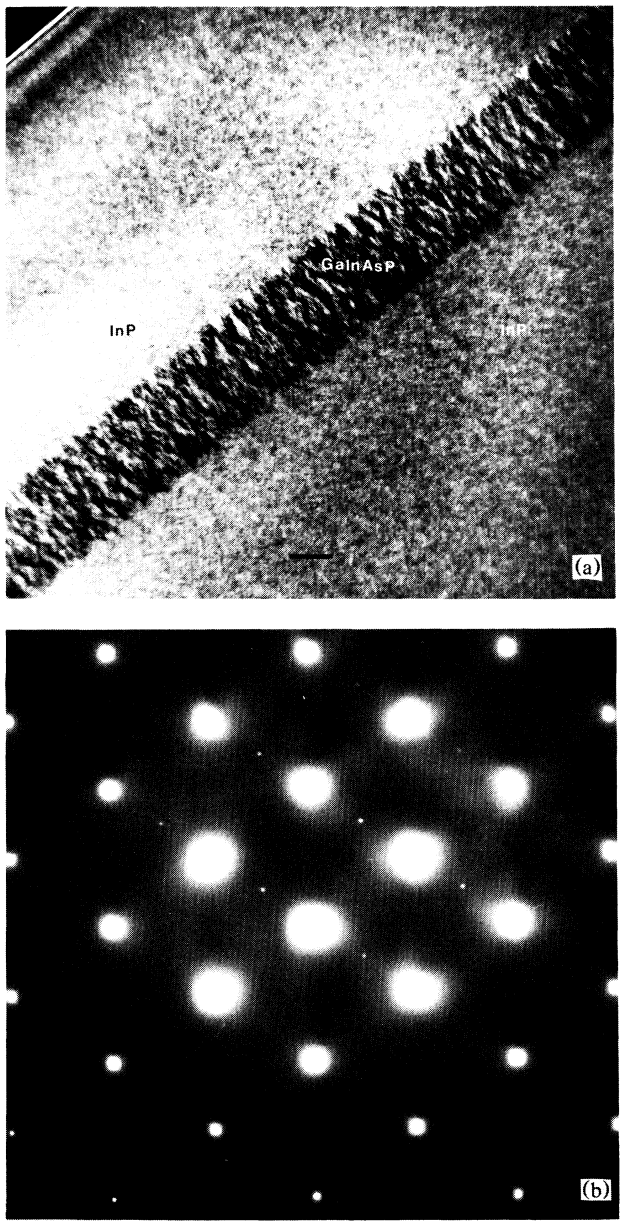

FIG. 4. (a) A transmission electron micrograph showing an edge-on view of the type-II samples. Marker represents 0.1 μm. (b) A $(\bar{1}10)$ SAD pattern reproduced from a region enclosing the quaternary layer. Compare this pattern with the SAD patterns of Figs. 2(a) and 3(b).

phase diagram of this material.[4,7,13] It is envisaged that after a $Ga_xIn_{1-x}As$ layer is grown at an elevated temperature the In- and Ga-rich regions form as the temperature falls below the critical temperature. Concomitant to this, or following this, the atomic ordering occurs. If it occurs after the phase separation, it happens after the composition variations reach a critical point.[20,21]

A similar set of superlattice spots was also observed in the type-II samples. An SAD pattern and the area from which the pattern was obtained are reproduced in Fig. 4. The intensities of the superlattice reflections relative to those of fundamental reflections are clearly greater for the quaternary samples. This could be due to ordering on both sublattices, a greater volume fraction of the ordered phase, and/or a higher value of long-range order parameter within the ordered regions. Furthermore, relatively weak superlattice reflections due to ordering on $(\bar{1}11)$ planes are also observed in the case of the quaternary alloy. This indicates that at least one other variant is also present but is only weakly developed. The same may be true for the ternary alloy.

In summary, using the SAD technique we have demonstrated that ordered phases are present in $Ga_{0.47}In_{0.53}As$ and $Ga_xIn_{1-x}As_yP_{1-y}$ ($\lambda = 1.52$ μm) al-

loy semiconductors lattice matched to InP. Ordering is observed along one of the four ⟨111⟩ directions and may arise due to the presence of alternate In- and Ga-rich (111) planes in the group-III sublattice of the ternary alloy. In the case of the quaternary semiconductor more than one ordered variant is observed.

One of the authors (S.M.) acknowledges fruitful discussions with J. H. Wernick and V. G. Keramidas of Bell Communications Research, Inc. Also the financial support of the National Science Foundation through Grants No. DMR-8405624 and No. DMR-8413115 is acknowledged by M.A.S., S.M., and D.E.L.

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

[2]T. S. Kuan, in *Proceedings of the Forty-Fourth Annual Meeting of the Electron Microscopy Society of America, Albuquerque, NM, 1986,* edited by G. W. Baily (San Francisco Press, San Francisco, 1986), p. 398.

[3]A. C. Gossard, P. M. Petroff, W. Wiegmann, R. Dingle, and A. Savage, Appl. Phys. Lett. **29**, 323 (1976).

[4]G. B. Stringfellow, J. Phys. Chem. Solids **33**, 665 (1972).

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

[6]H. Nakayama and H. Fujita, in *Gallium Arsenide and Related Compounds—1985,* edited by M. Fujimoto, IOP Conference Proceedings No. 79 (Institute of Physics, Bristol and London, 1986), p. 289.

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

[8]F. Glas, P. Henoc, and H. Launois, in *Microscopy of Semiconducting Materials—1984,* edited by A. G. Cullis and D. B. Holt, IOP Conference Proceedings No. 76 (Institute of Physics, Bristol and London, 1985), p. 251.

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

[10]S. Mahajan, B. V. Dutt, H. Temkin, R. J. Cava, and W. A. Bonner, J. Cryst. Growth **68**, 586 (1984).

[11]K. Onabe, Jpn. J. Appl. Phys. **21**, L323 (1982).

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

[13]B. deCremoux, P. Hirtz, and J. Ricciardi, in *Gallium Arsenide and Related Compounds—1980,* edited by H. W. Thim, IOP Conference Proceedings No. 56 (Institute of Physics, Bristol and London, 1981), p. 115.

[14]H. M. Cox, J. Cryst. Growth **69**, 641 (1984).

[15]H. M. Cox, S. G. Hummel, V. G. Keramidas, and H. Temkin, in Ref. 6, p. 735.

[16]M. R. Taylor, M. Hockly, D. A. Andrew, and G. J. Davies, in Ref. 8, p. 297.

[17]J. W. Edington, *Electron Diffraction in the Electron Microscope, Monograph 2* (Macmillan, New York, 1975), p. 70.

[18]J. L. Martins and A. Zunger, J. Mater. Res. **1**, 523 (1986).

[19]A. Ourmazd and J. C. Bean, Phys. Rev. Lett. **55**, 765 (1985).

[20]D. E. Laughlin, K. B. Alexander, and L. L. Lee, in *Decomposition of Alloys: The Early Stages,* edited by P. Hassen, V. Gerold, R. Wagner, and M. F. Ashby (Pergamon, New York, 1984), p. 221.

[21]W. A. Soffa and D. E. Laughlin, in *Solid-Solid Phase Transformations,* edited by H. I. Aaronson, D. E. Laughlin, R. F. Sekerka, and C. M. Wayman (The Metallurgical Society of the AIME, Warrendale, PA, 1982), p. 159.

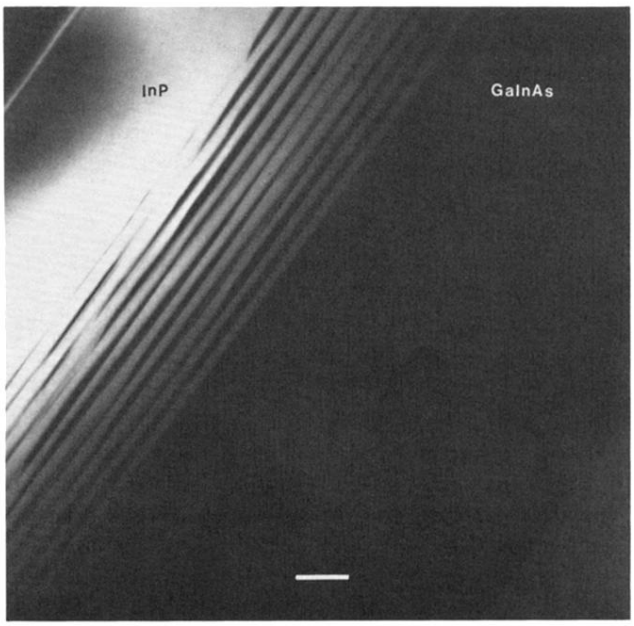

FIG. 1. A transmission electron micrograph showing an edge-on view of a multilayer structure of the type-I samples. The surface normal is close to [$\bar{1}$10] and 002 reflection has been used to produce this image. The light and dark stripes represent InP and $Ga_{0.47}In_{0.53}As$, respectively. Marker represents 0.1 μm.

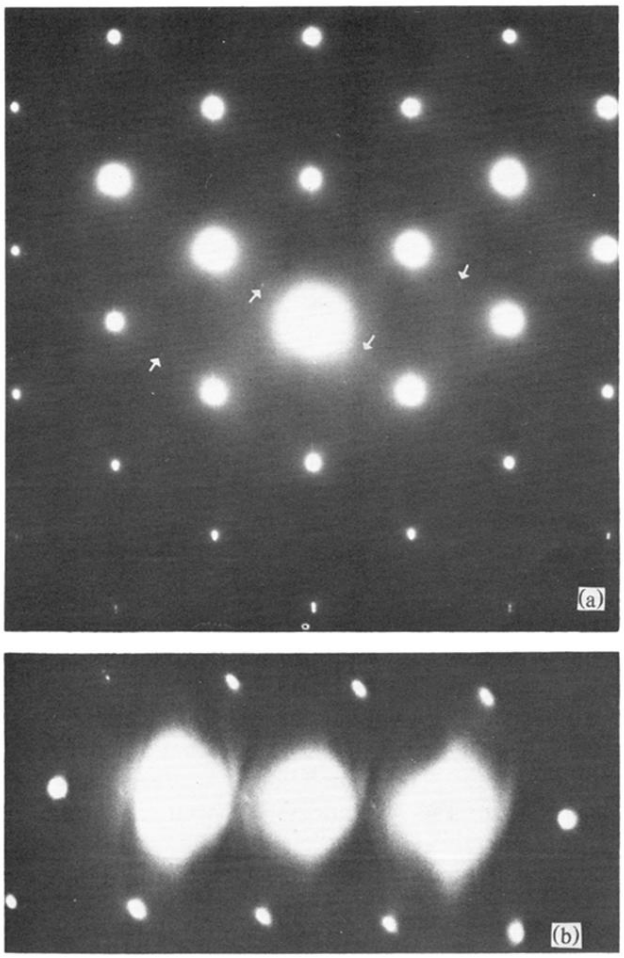

FIG. 2. (a) An SAD pattern obtained from the multilayer region of Fig. 1 for the [$\bar{1}$10] zone axis. Notice the weak superlattice reflections (indicated by arrows) between the fundamental reflections along the [111] direction. (b) An SAD pattern for an exact 111-reflection condition. Here the superlattice spots are clearly visible.

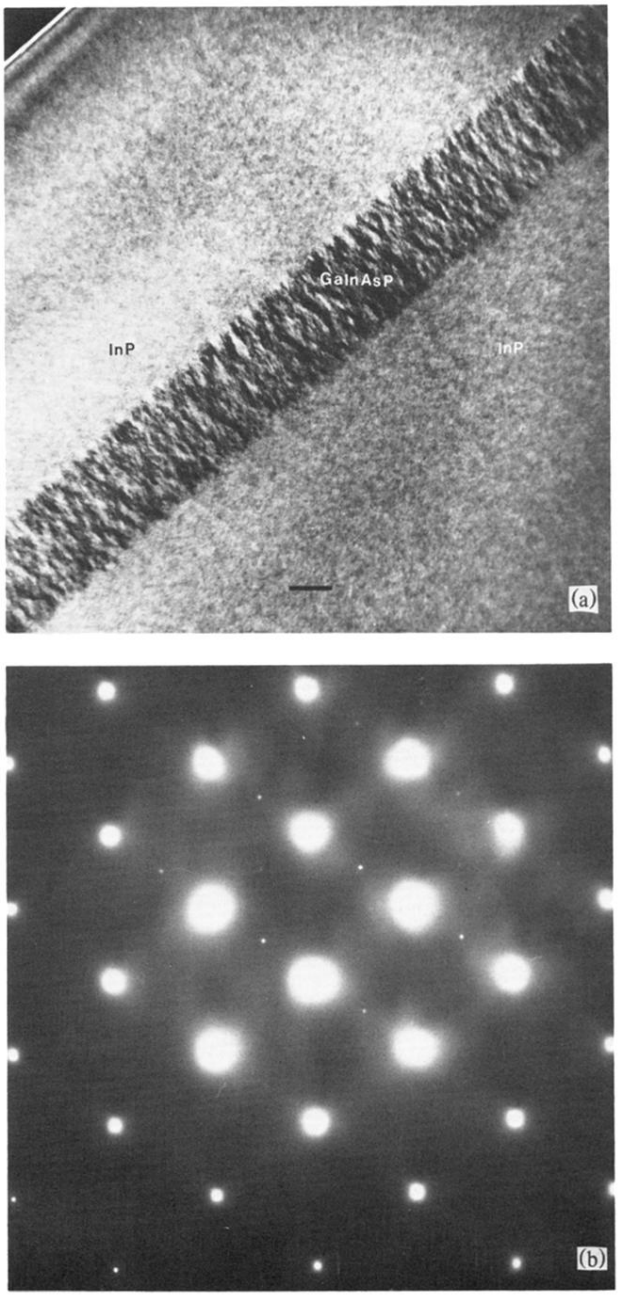

FIG. 4. (a) A transmission electron micrograph showing an edge-on view of the type-II samples. Marker represents 0.1 μm. (b) A ($\bar{1}10$) SAD pattern reproduced from a region enclosing the quaternary layer. Compare this pattern with the SAD patterns of Figs. 2(a) and 3(b).