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Atomic arrangement of spontaneously ordered $Al_{0.5}In_{0.5}P/GaAs$

Masahiko Kondow, Hiroshi Kakibayashi, and Shigekazu Minagawa
Central Research Laboratory, Hitachi, Ltd., Kokubunji, Tokyo 185, Japan

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The atomic arrangement of $Al_{0.5}In_{0.5}P$ grown by organometallic vapor-phase epitaxy has been investigated using transmission electron microscopy (TEM) and Raman scattering measurement. The TEM image reveals that the long-range periodic atomic arrangement is distributed throughout almost the entire epilayer. However, between ordered and disordered alloys, there is little difference in the Raman spectrum. This is probably due to the presence of deviations in atomic positions from the regular zinc-blende structure.

I. INTRODUCTION

The discovery of ordered structure in III-V alloy semiconductors has recently become an important topic in semiconductor physics.[1–9] This is because the atomic arrangement in alloy semiconductors on each sublattice was believed to be random, although deviation from the random distribution, such as short-range ordering, was thought to exist.[10]

If the ordering is perfect, for example, it can be expected that mobility in the atomic-layer superlattice increases, as has been predicted.[11,12] At the present time, however, the degree of orderliness in a spontaneously ordered structure is not clear. Most reports concerning spontaneous ordering employ transmission electron diffraction (TED) and/or transmission electron microscopy (TEM) as examining tools. These techniques can reveal the presence of long-range periodicity in the atomic arrangement. However, these techniques do not adequately reveal the variation of atomic position from the regular zinc-blende structure.

By contrast, Raman scattering can give information on the deviation in atomic position, since it probes the "bond." The Raman spectrum of a spontaneously ordered alloy was first reported in $Ga_xIn_{1-x}P/GaAs$ grown by organometallic vapor-phase epitaxy (OMVPE) by Gomyo *et al.*[13] Correlation between the valley depth between GaP-like and InP-like longitudinal-optical (LO) mode peaks and the anomalously small band gap was pointed out. The change in valley depth is explained by the presence of an additional peak caused by the zone-folded mode.[14] In $Ga_xIn_{1-x}P/GaAs$, $R\bar{3}m$ ordered structure, i.e., monolayer superlattice with doubling periodicity in the $\langle 111 \rangle$ direction, is generated.[6–9] If the ordering is perfect, the zone folding from the L point to the Γ point can be expected. The authors also confirmed the correlation between the valley depth and the band gap.[15] However, the valley-depth change was explained by the broadening of the peaks.[16] The broadening suggests that the degree of orderliness in the ordered structure is not high. Therefore these explanations are contradictory in evaluating orderliness in a spontaneously ordered structure. In $Ga_xIn_{1-x}P/GaAs$, the peaks of GaP-like and InP-like LO modes are close to each other in the Raman spectrum.[17–19] Moreover, unfortunately, a disorder-induced optical-phonon mode is located between these peaks.[19] Therefore it is difficult to determine the influence of ordering on the Raman spectrum of $Ga_xIn_{1-x}P/GaAs$.

Fortunately, in $Al_xIn_{1-x}P/GaAs$, the peaks of AlP- and InP-like LO mode are separated enough.[17,18] Moreover, it has been reported that the $R\bar{3}m$ ordering occurs in $Al_xIn_{1-x}P/GaAs$ as well as in $Ga_xIn_{1-x}P/GaAs$, and the degree of ordering is almost the same with $Ga_xIn_{1-x}P/GaAs$.[20,21] Therefore $Al_xIn_{1-x}P/GaAs$ is a suitable alloy for investigating the atomic arrangement in the spontaneously ordered structure.

The authors have reported the influence of growth temperature on the Raman spectrum of $Al_xIn_{1-x}P/GaAs$.[15] However, correlation with spontaneous ordering was not shown in the previous report. In this study, the atomic arrangement in spontaneously ordered $Al_xIn_{1-x}P$ is investigated by comparing the results of TEM and TED observation and Raman scattering measurement.

II. EXPERIMENT

$Al_{0.5}In_{0.5}P$ alloy was grown by atmospheric-pressure OMVPE using triethylaluminum, trimethylindium, and phosphine as source materials. Dimethylzinc was employed as a p-type dopant source. The substrate was exactly (001)-oriented GaAs. A 0.4-μm-thick GaAs layer was grown as a buffer layer prior to the growth of a 0.7-μm-thick $Al_xIn_{1-x}P$ layer. The growth temperature (T_g) was varied in the range of 610–740 °C. The $c^{\mathrm{V}}/c^{\mathrm{III}}$ ratio, i.e., the atomic ratio of phosphine to total group-III sources, was fixed at 180. In this growth condition, the epitaxial layer shows good crystallinity and excellent surface morphology. The growth rate of a phosphide layer was 1.4 μm an hour. Lattice mismatch between the epitaxial layer and the substrate was determined by a double-crystal x-ray diffractometer. The $Al_xIn_{1-x}P$ layer used in this work was virtually lattice matched. Lattice mismatch was within $\pm 0.1\%$.

The specimens for cross-sectional TEM observation were prepared by mechanical polishing followed by Ar-ion thinning down to about a 10 nm thickness. They

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were thinned parallel to the (110) crystal planes, because extra diffraction spots due to the long-range ordered structure appear in the (110) TED pattern but not in the $(1\bar{1}0)$ pattern.[22,23] TEM observation was performed using a Hitachi H-800 transmission electron microscope operated at an accelerating voltage of 200 kV with a double-tilt goniometer.

The Raman scattering spectrum was measured at room temperature using the 539.9-nm line of a krypton-ion laser operated at about 150 mW under the quasibackscattering geometry condition. The laser spot diameter on the sample was about 100 μm. The scattered light was analyzed using a Varian Associates Cary-82 system combined with a conventional photon counter. The resolution was 2–3 cm^{-1}. Since the measurement was performed in the atmosphere, no spectrum was obtained below 200 cm^{-1}.

III. RESULTS AND DISCUSSION

The lattice image of $Al_{0.5}In_{0.5}P$ observed from the [110] direction is shown in Fig. 1. This image was obtained using the beams including $1\bar{1}1$ and $\bar{1}1\bar{1}$. Doubling in periodicity of $(1\bar{1}1)$ and $(\bar{1}11)$ lattice fringes is observed. Periodic spacing is 0.66 nm. The *region* in which doubling in lattice fringes is clearly seen, for example, *A* and *B* in the figure, is laminal and is about 5 nm thick. It is tilted from the (001) plane by about 10°, as reported for $Ga_xIn_{1-x}P$.[24] The tilting angle is opposite in $(\frac{1}{2}\frac{\bar{1}}{2}\frac{1}{2})$ and $(\frac{\bar{1}}{2}\frac{1}{2}\frac{1}{2})$ ordering. The figure shows that the regions in which doubling in $(1\bar{1}1)$ and $(\bar{1}11)$ lattice fringes is clearly seen are entangled in a complicated manner, and that these regions are distributed throughout almost the entire epilayer. Out of these regions, overlap of doubling in $(1\bar{1}1)$ and $(\bar{1}11)$ lattice fringes can be observed in one place, for example, *C* in the figure, and an area of no abnormal contrast is observed in another place, for example, *D* in the figure. In spontaneously ordered alloy, it has been reported that there exist many antiphase boundaries of the monolayer superlattice.[1,8,9,23] If an antiphase boundary lies in the plane normal to the specimen, for example, the (001) plane, it will appear in a TEM image as such. However, if the boundary lies in the plane parallel to the specimen, i.e., the (110) plane, it cannot appear and the contrast of doubling in lattice fringes can strongly depend on the antiphase boundary position in the specimen. Therefore it is difficult to determine the ordering generation between the following two, one: the ordered structure exists as an isolated island in a disordered phase as seen in a TEM image; the other: although no abnormal contrast is observed in a TEM image, the actual ordered structure is continuous from the heterointerface to the epilayer surface almost without interruption, i.e., an ordered atomic arrangement is always formed on the growing interface.

Next, the influence of growth temperature on the ordered structure was examined. Figure 2 shows TED patterns for the [110] electron beam incidence of $Al_xIn_{1-x}P$ layers grown at various temperatures. The extra spots are seen at $h\pm\frac{1}{2}\ k\mp\frac{1}{2}\ l+\frac{1}{2}$ positions for an $h\ k\ l$ matrix spot. These spots correspond to the presence of the $(\frac{1}{2}\frac{\bar{1}}{2}\frac{1}{2})$ and $(\frac{\bar{1}}{2}\frac{1}{2}\frac{1}{2})$ long-range ordering. In Figs. 2(b) and 2(c), there are also weak diffraction spots at the $h\ k\ l\pm1$ positions. These are due to the so-called dynamical electron diffraction effect but not to the (001) superstructure,

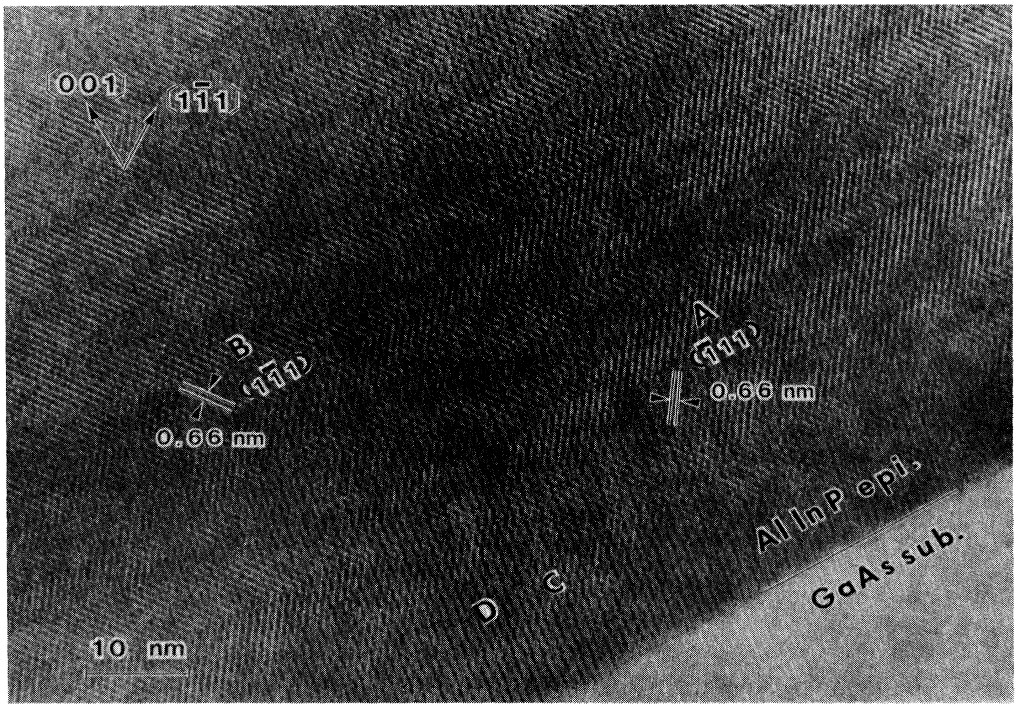

FIG. 1. Lattice image of $Al_{0.5}In_{0.5}P$ for [110] electron beam incidence. $T_g=700\,^{\circ}\text{C}$. $c^{\text{V}}/c^{\text{III}}=180$.

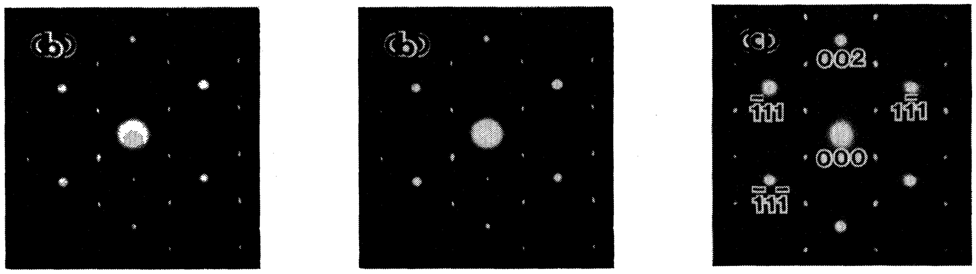

FIG. 2. TED patterns of $Al_{0.5}In_{0.5}P$ for [110] electron beam incidence. (a) $T_g = 610\,°C$, (b) $T_g = 700\,°C$, (c) $T_g = 740\,°C$.

because they are not seen in the $(1\bar{1}0)$ pattern, as can be seen in Fig. 1 of Ref. 25. The change in crystalline structure from a regular zinc-blende structure permits diffraction at $h\ k\ l \pm 1$ positions, which is forbidden in the original zinc-blende structure. Therefore the diffraction at the $h\ k\ l \pm 1$ position can indicate the degree of ordering.

The pattern of $Al_xIn_{1-x}P$ shown in Fig. 2(c) is very similar to that shown in Fig. 2(b). The degree of ordering in $T_g = 740\,°C$ is almost the same as that for 700 °C. However, in the pattern for 610 °C, Fig. 2(a), the extra spot intensity is weak, and the extra spot shape changes wavy and streaky along both [001] and $[00\bar{1}]$ directions. This change in the shape is explained by "domain effect"[26] and/or "local lattice distortion."[9] In either case, it indicates imperfection of the ordered structure. The pattern of $Al_xIn_{1-x}P$ grown at 610 °C is similar to that of $Ga_xIn_{1-x}P$ grown at 660 °C, at which the Raman spectrum is most broad.[16]

It is concluded that the long-range ordered structure in $Al_xIn_{1-x}P$/GaAs alloy forms at higher temperatures, gradually changing into a short-range ordered structure with a low degree of ordering as growth temperature decreases. This tendency is the same as for $Ga_xIn_{1-x}P$/GaAs.[16,27]

Figure 3 shows Raman scattering spectra of $Al_xIn_{1-x}P$. The samples used in this measurement are the same as those used for the TED observations shown in Fig. 2. The peaks at 460, 340, and 320 cm^{-1} are identified as AlP-like and InP-like LO modes, and transverse-optical (TO) modes, respectively.[17,18] The presence of a TO mode suggests that atomic arrangement is displaced from the regular atomic sites in the zinc-blende structure. The peak located at 292 cm^{-1} originates from the GaAs substrate since $Al_xIn_{1-x}P$, which is an indirect transition material, has a low absorption coefficient for the incident light.

The spectrum for higher growth temperatures ($T_g = 740$ and 700 °C), at which the TED pattern shows firm extra spots, is sharp. On the other hand, the spectrum for $T_g = 610\,°C$ appears to become broad. The peaks of the TO mode and InP-like LO mode are not readily distinguished in this sample. Since a highly ordered structure is generated at higher growth temperatures, this is due to the broadening of peaks but not to the presence of an additional peak caused by zone folding.

Broadening in the Raman spectrum is caused mainly by fluctuations in the "bond," i.e., in the bond length and/or the bonding angle. [Extended x-ray-absorption fine structure (EXAFS) spectra of the ordered $Ga_xIn_{1-x}P$/GaAs showed that the bond length of nearest neighbors changes according to the anomalous band-gap change. At the present time, it is certain that there exists some variation in atomic arrangement of neighboring atoms, although further study is necessary to be consistent with the present results.[28]] Therefore the present result indicates that there exist deviations in atomic position from the regular zinc-blende structure in the spontaneously ordered alloy, and that the develop-

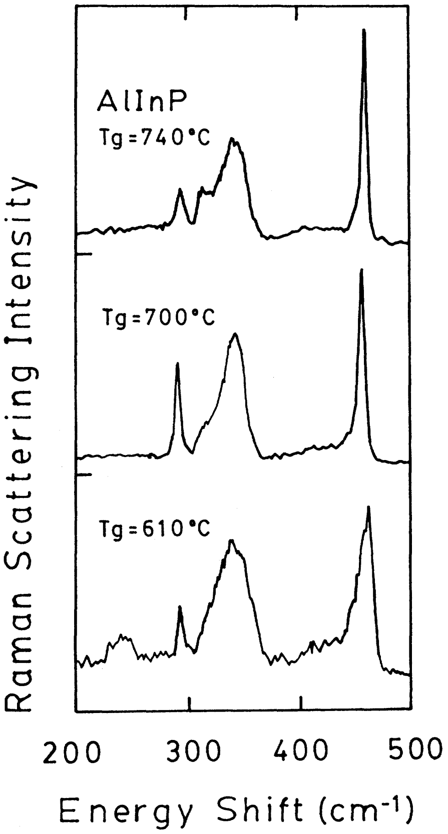

FIG. 3. Raman scattering spectra of $Al_xIn_{1-x}P$ grown at 740, 700, and 610 °C.

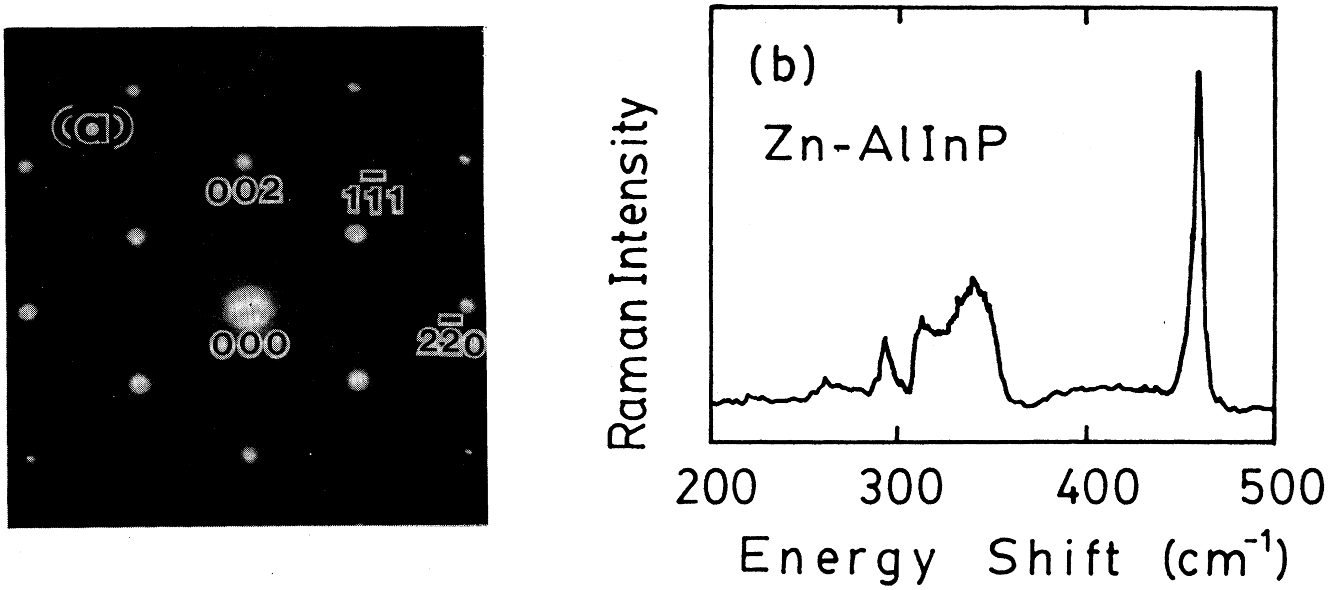

FIG. 4. (a) TED pattern and (b) Raman spectrum of $Al_xIn_{1-x}P$ doped with zinc. $p=1\times10^{18}$ cm^{-3}. $T_g=640\,°C$. $c^{V}/c^{III}=180$.

ment of this deviation is associated with imperfection of the long-range ordered structure.

In the Raman spectrum for lower growth temperatures, a broad signal around 200–250 cm^{-1} was sometimes observed. Since the highly ordered structure generates at higher temperature, this signal is probably due to the phonon mode associated with disordering but not to the zone-folded acoustic-phonon mode.

In Fig. 4, the TED pattern and Raman spectrum of $Al_xIn_{1-x}P$ doped with zinc ($p=1\times10^{18}$ cm^{-3}) are shown. It is found by Fig. 4(a) that the crystalline state of this specimen is disordered, i.e., no ordered structure exists, and that high zinc doping in $Al_xIn_{1-x}P$ hinders the generation of an ordered structure in the same way as $Ga_xIn_{1-x}P$ and $(Al_xGa_{1-x})_{1-y}In_yP$ do.[22,29] Meanwhile, the Raman spectrum shown in Fig. 4(b) is as sharp as that for ordered $Al_xIn_{1-x}P$ grown at higher temperatures. This result indicates that regularity of bond in a disordered alloy is higher than that in an imperfectly ordered alloy grown at lower temperatures. Indeed, in $Ga_xIn_{1-x}P$/GaAs, the Raman spectrum of the almost disordered alloy is sharper than that of the moderately ordered alloy.[16]

The reason there is little difference between the spectra of a highly ordered alloy grown at higher temperatures and a disordered alloy is probably that the orderliness in the spontaneously ordered alloy is not so high that Raman scattering cannot be affected by the orderliness of a spontaneously ordered structure because of the presence of the deviation of atomic position. (Raman scattering probes basically the "bond," but not the long-range periodicity of the atomic arrangement in this alloy.) In other words, it is because, although Al and In atoms are alternately arranged on the group-III sublattice, the sublattice itself is irregularly distorted.

Besides, in both disordered and ordered alloys, asymmetry in Raman signals, i.e., tailing toward the low-energy side, is observed. This asymmetry is explained by a relaxation of $\mathbf{q}=0$ selection rule caused by distribution of the interatomic interaction force.[30–33] Therefore it is indicated that fluctuations in interatomic interaction, i.e., fluctuation in atomic positions, exist in a spontaneously ordered alloy as well as in a disordered alloy.

IV. CONCLUSION

The TEM image has revealed that the long-range periodic ordered atomic arrangement is distributed throughout almost the entire epilayer. However, between ordered and disordered alloys, there is little difference in the Raman spectrum measured in the quasibackscattering geometry condition. The result of Raman scattering measurement suggests that deviations in atomic position from the regular zinc-blende structure exist in a spontaneously ordered alloy as well as in a disordered alloy. In addition, the degree of this deviation develops according to the imperfection of the spontaneously ordered structure.

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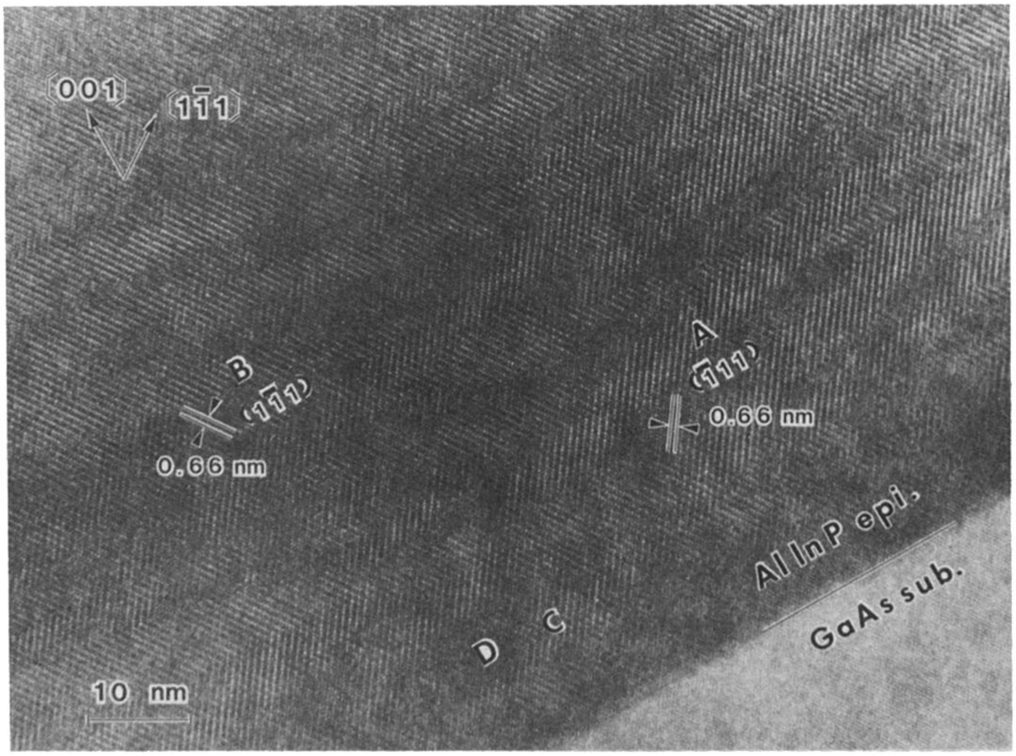

FIG. 1. Lattice image of $Al_{0.5}In_{0.5}P$ for [110] electron beam incidence. $T_g = 700\,^\circ C$. $c^{V}/c^{III} = 180$.

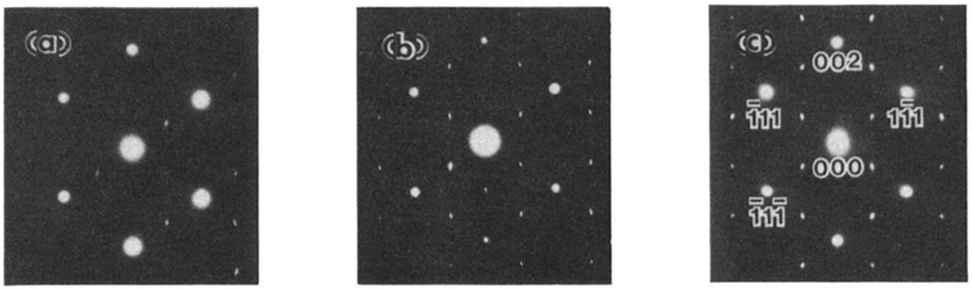

FIG. 2. TED patterns of $Al_{0.5}In_{0.5}P$ for [110] electron beam incidence. (a) $T_g = 610\,°C$, (b) $T_g = 700\,°C$, (c) $T_g = 740\,°C$.

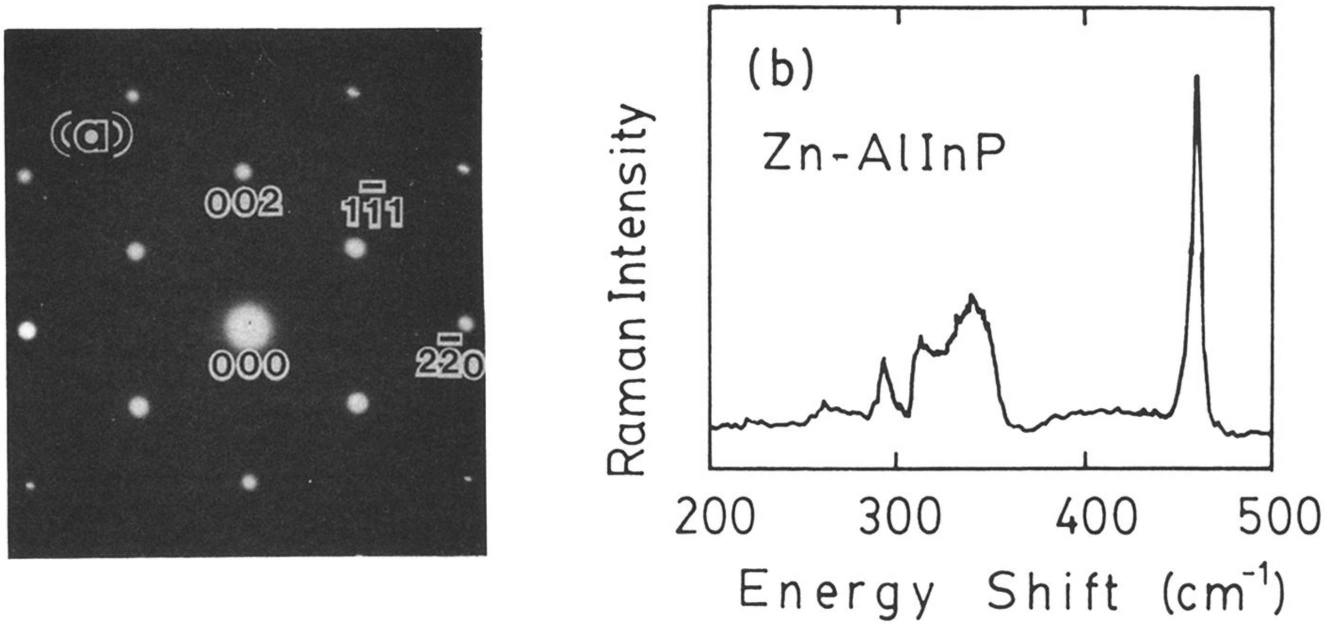

FIG. 4. (a) TED pattern and (b) Raman spectrum of $Al_xIn_{1-x}P$ doped with zinc. $p = 1 \times 10^{18}$ cm^{-3}. $T_g = 640$ °C. $c^{V}/c^{III} = 180$.