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(Citation)

Physical Review B, 53(23):15713-15718

(Issue Date)

1996-06-15

(Resource Type)

journal article

(Version)

Version of Record

(URL)

<https://hdl.handle.net/20.500.14094/90000115>



Direct optical transitions in indirect-gap $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ by atomic ordering

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(Received 25 September 1995)

$(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$ alloys naturally constitute monolayer superlattices on GaAs(001) substrates by atomic ordering when they are grown by organometallic vapor-phase epitaxy. The spontaneous long-range ordering causes the band-gap reduction and band splitting at the valence-band maximum. When the Al composition in a $(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}\text{P}$ -random alloy is larger than ~ 0.4 , the optical transition is indirect, and the conduction-band minimum is at X_{6c} . From electroreflectance and photoluminescence measurements, we have found for long-range ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ that the Γ_{6c} valley crosses the X_{6c} by the band-gap reduction. The emission from the strongly ordered alloy is optically direct. The temperature dependence of photoluminescence intensity shows that statistical potential fluctuations and localized states in the low-energy part of the exciton resonance play an important role in the direct luminescence of the long-range ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$. [S0163-1829(96)08024-1]

I. INTRODUCTION

In alloy semiconductors, it is well known that atomic ordering during epitaxial growth generates superlattice structures such as layered trigonal, layered tetragonal, luzonite, chalcopyrite, and famatinite.¹ A band folding is caused by such periodic stacking of atomic planes. The new electronic band lineup shows a change of the band gap and a crystal-field splitting.¹⁻⁹ These properties can be continuously varied by controlling the long-range order parameter, which opens a new field of band-structure engineering. On the other hand, there has been a strong interest in indirect-gap semiconductors for their application to light emitting devices. However, an extremely low efficiency of light emission prevents the indirect-gap semiconductors from application to their optoelectronic devices. Three methods have been proposed to improve the efficiency of light emission from indirect-gap materials: (a) An isoelectronic trap in a host semiconductor relaxes the momentum conservation in the electron-hole recombination process. The isoelectronic trap realizes a strong green emission from GaP:N. (b) A confinement of excited or injected carriers is a useful method to improve the emission intensity. Recently, it has been observed that the luminescence intensities of SiGe/Si (Ref. 10) and GaAs_xP_{1-x}/GaP (Ref. 11) quantum-well structures are enhanced by the carrier confinement. However, the oscillator strength is not changed in this method. (c) Band-folding phenomena in superlattices can modify the oscillator strength of indirect-gap semiconductors. Some experiments have been reported on short-period superlattices of Si/Ge (Ref. 12), GaP/AlP (Refs. 13 and 14), and GaAs/AlAs (Refs. 15 and 16) oriented to the [001] direction. The new artificial periodicity folds the X point to Γ . In this system, a direct transition between the new folded $\Gamma(X)$ and the valence-band maximum (VBM) is expected. However, it was reported that the momentum conservation by interface scattering plays an important role in the indirect recombination process.¹⁶ In this study, we focus our attention on the band-structure engineering using monolayer superlattices spontaneously constituted during epitaxial

growth. A new type of direct transition is expected in indirect materials by utilizing the zone-folding and interactions between the Γ band and the folded band. The band interaction repels the two bands to the opposite sides. If the reduced Γ -band energy crosses an indirect valley, the band structure of the spontaneous superlattice becomes optically direct.

$(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$ alloys, especially $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ and $\text{Al}_{0.5}\text{In}_{0.5}\text{P}$, are widely known to have atomically ordered phases when they are grown by organometallic vapor-phase epitaxy.^{1-9,17-25} The long-range ordered structure is equivalent to a monolayer superlattice alternating $(\text{Al}_x\text{Ga}_{1-x})$ - and In-rich atomic planes along the $[1\bar{1}1]$ or $[\bar{1}11]$ direction. The degree of long-range ordering in $(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$ can be controlled by the growth conditions, such as growth temperature, the gas-flow ratio of column-V and -III sources, and substrate orientation.^{1-9,17-25} The doubling periodicity along the $[1\bar{1}1]$ or $[\bar{1}11]$ direction causes a band folding of the L point to the Γ point. Here, the folded L band is labeled as $\Gamma(L)$. There are many reports about the electronic structures of long-range ordered $(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$, especially for $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ ^{1-8,17-22,24,25} and $\text{Al}_{0.5}\text{In}_{0.5}\text{P}$.^{9,21-23} In long-range ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$, the energy of the $\Gamma(L_{6c})$ band is higher than that of the Γ_{6c} band. The interaction between these two bands leads to a band-gap reduction (BGR). Furthermore, an anisotropy in optical transitions appears, because of the valence-band splitting (VBS).¹⁻⁹ The degree of ordering continuously changes the energies of the BGR and VBS. In long-range ordered $\text{Al}_{0.5}\text{In}_{0.5}\text{P}$, on the other hand, the energy of $\Gamma(L_{6c})$ is lower than that of the Γ_{6c} point. The $\Gamma(L_{6c})$ band shifts to the lower-energy side. A new transition related to $\Gamma(L_{6c})$ has been observed in electroreflectance (ER) measurement with a new photoluminescence line.⁹ However, the luminescence intensity is weak, because the conduction-band minimum (CBM) in this alloy is still at the X valley. Figure 1(a) shows theoretical transition energies of $(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}\text{P}$ random alloy obtained from the tight-binding method. Matrix elements used here are taken from the sp^3s^* parametrization including the spin-orbit interac-

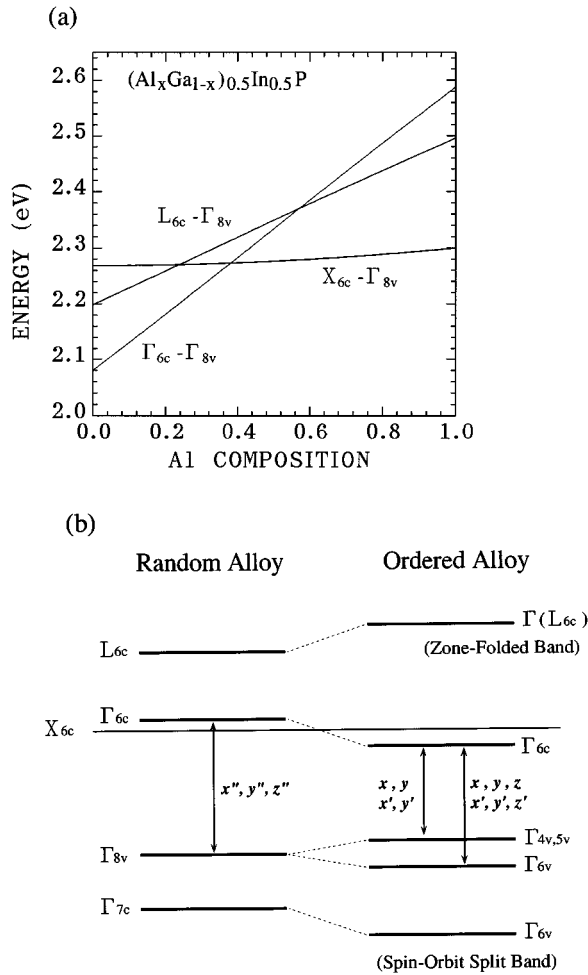


FIG. 1. (a) Theoretical transition energies of $(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}\text{P}$ random alloy calculated by the tight-binding method. (b) Schematic depiction of band structures for $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.5}\text{In}_{0.49}\text{P}$.

tion. Lattice distortions are incorporated locally in each nearest-neighbor matrix element through the d^{-2} scaling law,²⁶ where d is the bond length. We used bond lengths predicted by using a valence-force field.²⁷ The Γ_{6c} - Γ_{8v} transition energies of $(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}\text{P}$ random alloys are in the range of 2.08–2.59 eV at the Al-mole fraction of $x=0$ –1. When the Al-mole fraction is larger than ~ 0.4 , $(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}\text{P}$ is optically indirect, and the CBM is at the X point. The Al-mole fraction used in this experiment is 0.5. In this case, as shown in Fig. 1(b), one can expect that a band-gap tuning by long-range ordering produces an optically direct semiconductor. In this paper, we show results of ER and photoluminescence (PL) measurements on ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$. From these results, it is found that the emission from the strongly ordered alloy is optically direct. The temperature dependence of photoluminescence intensity shows that statistical potential fluctuations and localized states in the low-energy part of the exciton resonance play an important role in the direct luminescence of the long-range ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$.

II. EXPERIMENT

Epitaxial films of $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ alloys were grown on n^+ -GaAs(001) and -GaAs(115)A substrates by or-

ganometallic vapor-phase epitaxy. Source gases are trimethylaluminum, triethylgallium, trimethylindium, and phosphine. The growth temperature and the gas pressure were 670°C and 30 Torr, respectively. The input gas-flow ratio of $f(\text{V})/f(\text{III})$ was 122. The relative composition of Al/Ga was precisely controlled by tuning the gas flows of trimethylaluminum and triethylgallium. The ratio of Al/Ga was confirmed by measuring an optical band gap of a Zn-doped random alloy on GaAs(001). The film thickness was 1.8 μm . From double-crystal x-ray diffraction, the films are horizontally lattice matched to the GaAs substrates within $\Delta a/a=0.1\%$, where $\Delta a = |a(\text{GaAs}) - a[(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}]|$ and $a = a(\text{GaAs})$. a is the horizontal lattice constant. The orientation of the substrate changes the degree of ordering. In $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$, the band-gap energy depends on misorientation angles of the GaAs substrate.²⁰ The misorientation toward $[111]\text{A}$ shows a monotonous increase of the band-gap energy, i.e., a suppression of atomic ordering. From the transmission-electron diffraction (TED) observation, the $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}/\text{GaAs}(001)$ shows super-reflection spots of the CuPt-type appearing at $(1/2, 1/2, 1/2)$ and $(1/2, 1/2, 1/2)$. On the other hand, the epitaxial film on GaAs(115)A does not clearly show such superlattice diffraction. Since long-range ordering is manifested by the appearance of removal of the valence-band degeneracy and altered polarization in optical spectroscopy with the appearance of superlattice diffraction spots in the TED pattern, we did a sensitive check of the presence of ordered phases by observing the optical anisotropy.

A semitransparent $\text{Au}/(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ Schottky-barrier diode was used for a modulation of the surface-electric field in the ER measurements. The modulating voltage and frequency were ± 1.0 V and 1 kHz, respectively. A monochromatic light passed through a single monochromator irradiates the (001) surface within an incident angle of 10° . The reflectance signal was detected by a silicon photodiode. The extinction coefficient of the linear polarization is 10^{-5} . The 488-nm line of an Ar^+ laser was used for excitation in the PL measurements. The detector was a photomultiplier for all PL measurements. For time-resolved PL measurements, excitation pulses were obtained from the same line of the Ar^+ laser by using an acoustic-optic modulator. The pulse width and repetition frequency were 30 ns and 2.5 kHz, respectively. The exciting power was ~ 350 nJ/cm^2 ($\sim 8.6 \times 10^{11}$ photons/ cm^2). This extremely low pulse power is enough to suppress an increase of effective temperature.¹⁶

In the ER and PL measurements, $[1\bar{1}0]$ - and $[110]$ -polarization spectra were observed to confirm the selection rule for electronic-dipole transitions relating to the VBS.^{1–9} In Fig. 1(b), x , y , and z allowed in the Γ_{6c} - Γ_{8v} transition correspond to the directions of the unit vectors of $F\bar{4}3m$ of the zinc-blende structure. The transition of a random alloy is then isotropic. On the other hand, x' (x''), y' (y''), and z' (z'') correspond to the directions of the unit vectors of the rhombohedral symmetry $R3m$ of ordered $(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$ alloys for the $[1\bar{1}1]$ ($[111]$) ordering. x', y' (x'', y'') and x', y' , and z' (x'', y'' , and z'') are allowed for the Γ_{6c} - Γ_{4v} , Γ_{5v} and Γ_{6c} - Γ_{6v} transitions, respectively.

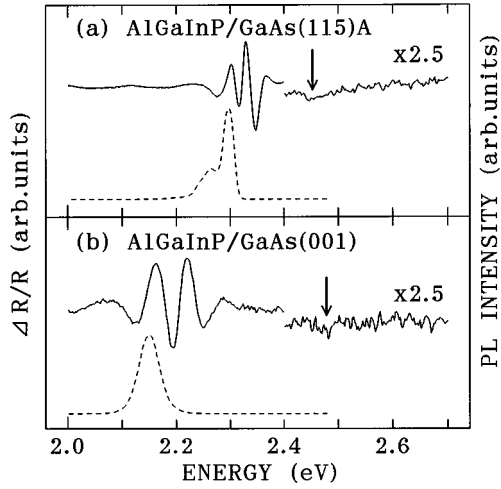


FIG. 2. ER and PL spectra of $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on (a) GaAs(115)A and (b) GaAs(001) at 15 K. Solid and dashed lines indicate the ER and PL spectra, respectively.

III. RESULTS AND DISCUSSION

A. Electronic structure by atomic ordering

Figure 2 shows ER and PL spectra of $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(115)A and GaAs(001) substrates at 15 K. Solid and dashed lines show the ER and PL spectra, respectively. In the ER spectrum of the alloy on GaAs(115)A shown in Fig. 2(a), the signal ~ 2.30 eV is the Γ transition. Here, we define that the band-gap energy is between the Γ_{6c} and the Γ_{4v}, Γ_{5v} , and that the VBS is between the Γ_{4v}, Γ_{5v} and the Γ_{6v} . Since the $\Gamma_{6c}-\Gamma_{8v}$ energy in Fig. 1(a) for a random alloy is 2.33 eV, the BGR is about 30 meV. On the other hand, the ER signal appears around 2.16 eV for the ordered alloy on GaAs(001). The BGR is about 170 meV. The ER spectra in Figs. 2(a) and 2(b) are split by VBS as shown in Fig. 1(b). The split signals are due to the $\Gamma_{6c}-\Gamma_{4v}, \Gamma_{5v}$ and $\Gamma_{6c}-\Gamma_{6v}$ transitions. The VBS energies are about 30 meV and 50 meV for the two ordered samples, respectively. The relation between the measured BGR and VBS of the two samples shows the similar trends as to a case of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$.^{1,2} From the above results, both alloys on GaAs(115)A and GaAs(001) are ordered. The degree of ordering of the alloy on GaAs(001) is stronger than that on GaAs(115)A. In this paper, we call strongly (weakly) ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$ [wo- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$].

The PL spectrum of wo- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$ on GaAs(115)A shows two peaks at 2.26 eV and 2.30 eV. The peak at 2.30 eV corresponds to the ER signal due to the $\Gamma_{6c}-\Gamma_{4v}, \Gamma_{5v}$ transition. The peak at 2.26 eV corresponds to an indirect transition from the X valley to the VBM. The energy position of this luminescence is almost the same as the energy difference between the X_{6c} and the Γ_{8v} of a random alloy [Fig. 1(a)]. Detailed PL properties about the indirect luminescence are discussed in the next subsection. The PL spectrum of so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$ on GaAs(001), on the other hand, shows a single peak at 2.16 eV. The single PL signal appears at the $\Gamma_{6c}-\Gamma_{4v}, \Gamma_{5v}$ transition energy obtained from an analysis of the ER spectrum in Fig. 2(b). Because of the large BGR, the observed PL energy of the

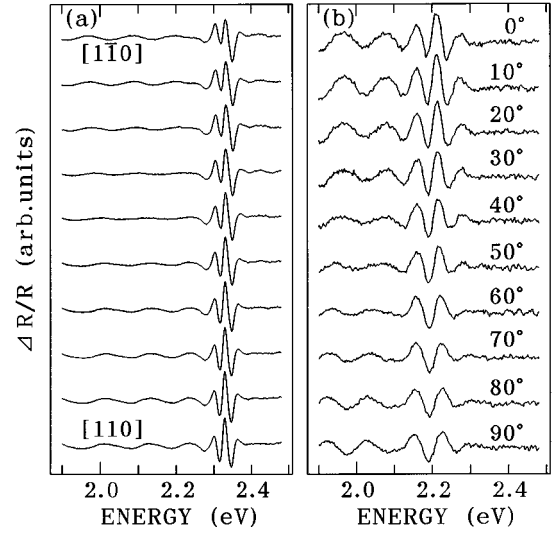


FIG. 3. ER polarization spectra of $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on (a) GaAs(115)A and (b) GaAs(001) at 15 K. The spectra labeled 0° and 90° correspond to the $[1\bar{1}0]$ and $[110]$ polarizations, respectively.

so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$ is low rather than that of the indirect $X_{6c}-\Gamma_{4v}, \Gamma_{5v}$ luminescence. This result shows that the indirect $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ alloy becomes a direct material by atomic ordering.

Both ER spectra show weak ER signals above 2.4 eV. These signals correspond to a transition from the $\Gamma(L_{6c})$ band folded from the L point to the Γ point. The observed energies related to the $\Gamma(L_{6c})$ bands of the wo- and so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.49}\text{In}_{0.49}\text{P}_y$ are 2.44 and 2.48 eV, respectively. Then, the increase of the degree of ordering enhances the level repulsion between Γ_{6c} and $\Gamma(L_{6c})$.

Figures 3(a) and 3(b) show ER-polarization spectra of wo- and so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$, respectively. The measurement temperature was 15 K. The spectra at 0° (90°) correspond to the $[1\bar{1}0]$ ($[110]$) polarization. Interference oscillations observed at the lower-energy sides of the E_0 signal are caused by the presence of below-gap states, which show a cancellation of the phase at 45°, i.e., the $[100]$ polarization. The polarization spectra of both samples are anisotropic. This anisotropy is especially strong for the so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$ as shown in Fig. 3(b). Since the $\Gamma_{6c}-\Gamma_{4v}, \Gamma_{5v}$ transition allows the x' and y' (x'' and y''), this transition leads to a change of the ER intensity and does not relate to the ER shape. The $\Gamma_{6c}-\Gamma_{6v}$ transition, on the other hand, has allowed polarizations along the x' , y' , and z' (x'' , y'' , and z''). A dielectric anisotropy causes a strong change of the ER-line shape. Similar phenomena have been observed in long-ranged ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$.⁷

B. Photoluminescence of ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$

Figure 4 is a PL spectrum of wo- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$ on GaAs(115)A. The vertical axis is a logarithm of the PL intensity. A peak at 2.30 eV is due to the $\Gamma_{6c}-\Gamma_{6v}$ transition. Two satellite peaks are observed with a non-phonon (NP) line of the $X_{6c}-\Gamma_{4v}, \Gamma_{5v}$ luminescence at 2.26 eV. The energies at the Γ point of the longitudinal-optical (LO) [the transverse-optical (TO)] phonons are 43 (38), 50

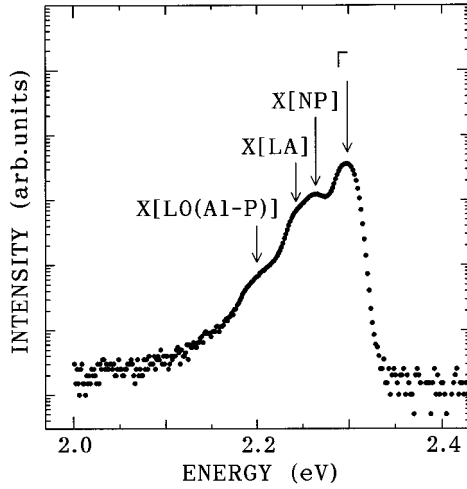


FIG. 4. PL spectrum of $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(115)A. The vertical axis is a logarithm of the PL intensity.

(45), and 63 (55) meV for InP, GaP, and AlP, respectively. The energies of the LO (TO) phonons at the X point are 38 (34) and 45 (44) meV for InP and GaP, respectively.²⁸ Though the LO and TO phonon energies at the X point of AlP have not been reported, it is expected that the phonon energies at the X point are smaller than those at the Γ point. The longitudinal-acoustic (LA) [transverse-acoustic (TA)] phonons are 16 (8) and 31 (13) meV for InP and GaP, respectively.²⁸ The phonon energies of GaP- and AlP-like LO modes in the alloy become small rather than those of each binary alloy.^{22,23} From the phonon energies, the PL side band at 2.24 eV can be assigned as due to the replicas of the LA phonons at the X point. The structure at 2.20 eV is the AlP-like LO phonon replica at the Γ point. A relaxation of momentum conservation, i.e., the coupling between the excitons at 15 K and the AlP-like LO phonons at the Γ point is caused by a localization of the excitons.

PL decay profiles at 15 K of wo- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ are shown in Fig. 5. The inset shows the PL spectrum plotted by linear scale. The arrows indicate detection energies of 2.25, 2.26, and 2.30 eV. The PL decay can be explained by a double exponential given by $I(t) = A_f \exp(-t/\tau_f) + A_s \exp(-t/\tau_s)$, where τ_f (τ_s) is a decay-time constant of the fast (slow) component in the PL decay. The estimated τ_f and τ_s are about 0.40 and 1.56 μs , respectively. The fast component becomes weak at the lower detection energy. We consider that the fast component originates from relaxation processes of exciton localization. Then, the slow component, which almost dominates all the decay shapes, corresponds to the intrinsic PL decay. A faster component, which is apparently observed at 2.30 eV, is <30 ns. This component shows the luminescence due to the Γ_{6c} - Γ_{4v} , Γ_{5v} transition. The time constant of this component is faster than our time resolution in this experiment. Though the direct transition dominates the time-integrated PL intensity at 2.30 eV (see Fig. 4), it is observed that the slow component dominates the decay profile. This result shows thermal coupling between the Γ_{6c} and X_{6c} bands. Since the energy difference between the Γ and $X[\text{NP}]$ is about 40 meV, the thermal coupling at 15 K shows the appearance of the localized states that

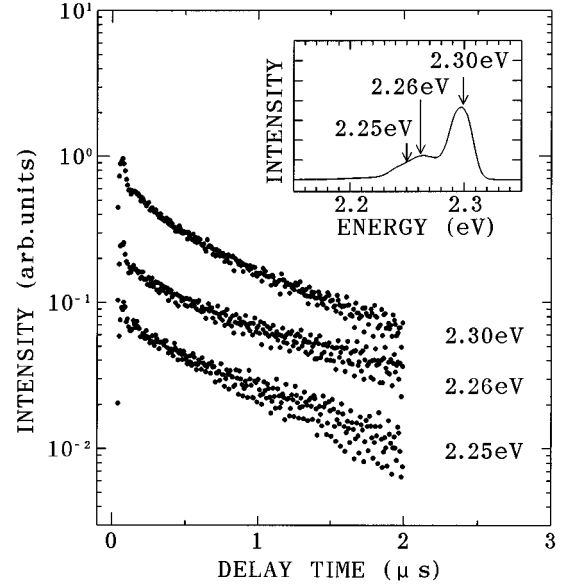


FIG. 5. PL-decay profiles of $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(115)A at 15 K. The inset shows the spectrum of $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(115)A. Arrows indicate detection energies.

may be created by the potential fluctuations in the wo- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$.²⁹ In so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$, the time constant of the PL decay was faster than the resolution. Ultrashort pulse measurements are necessary for the detailed investigations of the PL decay.

Figures 6(a) and 6(b) show temperature dependences of PL spectra of wo- and so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$, respectively. The solid and dashed lines indicate the [110]- and $[\bar{1}\bar{1}0]$ -polarization spectra, respectively. The PL spectra of both samples show an anisotropic character reflecting the degree of ordering such as the ER spectra in

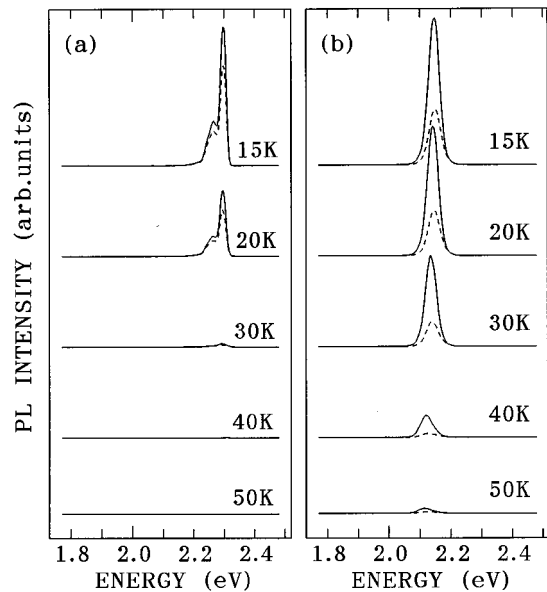


FIG. 6. Temperature dependence of PL spectra for $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on (a) GaAs(115)A and (b) GaAs(001). Solid and dashed lines indicate [110] and $[\bar{1}\bar{1}0]$ polarization spectra, respectively.

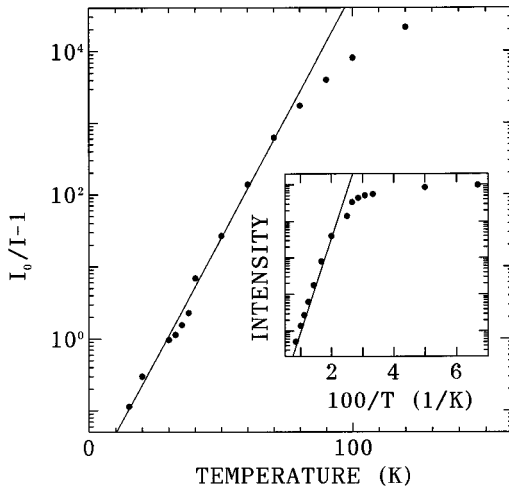


FIG. 7. Temperature dependence of $I_0/I(T) - 1$, where I is the integrated PL intensity of $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(001) and I_0 the extrapolated intensity at 0 K. The inset shows the plot of $\ln I$ as a function of $100/T$.

Fig. 3. PL intensity at the $[110]$ polarization of the so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$ is three times larger than that at the $[1\bar{1}0]$ polarization. This anisotropy is consistent with the result from the selection rule as shown in Fig. 1(b). With increased sample temperature, the PL intensity of the wo- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$ rapidly decreases in contrast to that of the so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$. Though the PL intensity at 15 K of the so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$ is almost the same as that of the wo- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$, the relative PL intensity of the so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$ to the wo- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$ rapidly increases and reaches about 100 at 50 K. Figure 7 shows the measured temperature dependence of $I_0/I(T) - 1$ for so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$, where I_0 is the PL intensity at 0 K extrapolated by the measured data. When the temperature dependence of the PL intensity is dominated by localized states, $I_0/I - 1$ is proportional to the relative probabilities for nonradiative and radiative recombinations given by $\exp(T/T_0)$.³⁰ The observed linear relation at <70 K shows the presence of localized states that may be caused by the potential fluctuations in ordered epitaxial film.²⁹ According to the above analysis, T_0 is 6.9 K. In the recent report about long-range ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$, T_0 is 7.5 K.²⁴ Those two values for ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}_y$ and $\text{Ga}_x\text{In}_{1-x}\text{P}$ are almost the same. The inset shows a plot of $\ln I$ as a function of $100/T$. The solid line is a least-squares fit to a linear function, yielding an activation energy of 47 meV at >70 K. This activation energy shows a magnitude of the potential fluctuations.

IV. CONCLUSIONS

We carried out ER and PL spectroscopic studies for ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(001) and GaAs(115) A. When the Al composition in $(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}\text{P}$ random alloy is larger than ~ 0.4 , the optical transition is indirect, and the conduction-band minimum is at X_{6c} . The ER and PL spectra show that the alloys on GaAs(001) and GaAs(115) A are strongly and weakly ordered, respectively. Because of the band-gap reduction by long-range ordering, the $\Gamma_{6c}-\Gamma_{4v}, \Gamma_{5v}$ energy of the strongly ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ is low rather than $X_{6c}-\Gamma_{4v}, \Gamma_{5v}$. Then, the $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(001) is optically direct. A strong anisotropy of the ER-polarization spectra appeared in the strongly ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$. The anisotropy relates to the selection rule for electronic-dipole transitions between the CBM and the split VBM. The PL decay of the $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(115)A includes two components related to the indirect transition. The fast and slow components correspond to the relaxation processes of exciton localization and the intrinsic PL decay, respectively. Furthermore, phonon replicas for LA and AIP-like LO appeared in the PL spectrum of the $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(115)A. A coupling between excitons and AIP-like LO phonons at the Γ point is caused by the localization of the excitons. When sample temperature increases, the PL intensity of the $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(115)A shows a rapid decrease. The relative PL intensity of the strongly ordered alloy to the weakly ordered one reaches 100 at 50 K. The temperature dependence of $I_0/I(T) - 1$ for the strongly ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ is proportional to the relative probabilities for nonradiative and radiative recombinations given by $\exp(T/T_0)$. The obtained T_0 is 6.9 K. Above 70 K, the temperature dependence shows an Arrhenius-type trend with an activation energy of 47 meV. This activation energy indicates a magnitude of the potential fluctuations in long-range ordered epitaxial film.

The direct optical transition was observed in long-range ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$. This result suggests that atomic ordering in alloy semiconductors will open a new field of optoelectronic applications of indirect-gap materials.

ACKNOWLEDGMENTS

The authors would like to thank Dr. S. Minagawa of Hitachi, Ltd. for sample preparation. This work was supported in part by Iketani Science and Technology Foundation (T.K.). This work was partly supported by the Photonics Materials Laboratory Project of the Graduate School of Science and Technology at Kobe University.

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