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Photoluminescence from metastable states in long-range ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$

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We have investigated photoluminescence of long-range ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ grown by metalorganic vapor-phase epitaxy on GaAs(001) and GaAs(115)A. Photoluminescence spectra were measured as functions of temperature and delay time. The fundamental edge luminescence from $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(001) shifts to the lower-energy side about 120 meV at 11 K due to the long-range ordering, relative to the luminescence from the Γ conduction-band valley in the disordered alloy. The Γ luminescence of $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ appears at lower energy than the indirect luminescence from the X valley. These observations give clear evidence that the ordering causes the band gap to change from indirect to direct. In the temperature dependence of the photoluminescence (PL) peak energy, there are three regions divided by a local minimum and a local maximum. Below the temperature showing the local minimum, the temperature dependence of the PL intensity is characteristic of the localization of photoexcited carriers. The origin of the localization is the band-gap fluctuation. The temperature dependence of the PL intensity shows thermal activation between the temperatures showing the local minimum and the local maximum in the PL energy. The activation energy is proportional to the energy shift at the local minimum. In time-resolved PL measurements at low temperatures, we observed a delayed emission due to the electrons trapped at metastable states. The delayed component was only observed below 15 K and the delay time varies with temperature. [S0163-1829(97)12107-5]

I. INTRODUCTION

Many alloy semiconductors spontaneously form superlattice structures when grown epitaxially.¹ In particular, the electronic band structures in long-range ordered $(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$ alloys have been investigated by optical measurements and theoretical calculations.¹⁻¹⁹ CuPt-type long-range ordering appears in $(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$ alloys grown on GaAs(001) substrates by metalorganic vapor-phase epitaxy (MOVPE). The 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 ordering depends on growth conditions, such as growth temperature, gas-flow ratio of column V and III sources, and substrate orientation. In the ordered superlattice, the conduction-band minimum (CBM) at the L point is folded into the Γ point, because of the doubling periodicity along the $[1\bar{1}1]$ or $[\bar{1}11]$ direction. A coupling between the Γ and the folded band, $\Gamma(L)$, reduces the band-gap energy. The magnitude of the band-gap reduction (BGR) is a function of order parameter η that is defined as $(\text{Al}_x\text{Ga}_{1-x})_{0.5+\eta/2}\text{In}_{0.5-\eta/2}\text{P}/(\text{Al}_x\text{Ga}_{1-x})_{0.5-\eta/2}\text{In}_{0.5+\eta/2}\text{P}$. For $\eta=1$, the completely ordered case, the structure is $(\text{Al}_x\text{Ga}_{1-x})\text{P}/\text{InP}$, the cation sublattice is composed of alternating $(\text{Al}_x\text{Ga}_{1-x})$ and (In) planes. For $\eta=0$, the completely random case, each plane of the cation sublattice has the composition $(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}$. The energy of the $\Gamma(L)$ band in ordered $(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}\text{P}$ alloys with $x<0.6$ is higher than that of the Γ band.¹⁻¹⁹ By utilizing the BGR in ordered alloys, we can produce a new direct gap $(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}\text{P}$, when the energy of the reduced Γ band crosses the X band.¹⁹

On the other hand, it is well known that epitaxially grown

ordered alloys are comprised of many domains with varying values of the order parameter.²⁰⁻²⁶ A distribution of the order parameter in the epitaxial film causes a fluctuation of the band-gap energy in real space. In recent reports, photoluminescence (PL) properties related to this band-gap fluctuation were observed in long-range ordered $\text{Ga}_x\text{In}_{1-x}\text{P}$.²⁰⁻²⁶ The PL-peak energy shifts to higher energy, when the excitation intensity is increased.²⁰ This is caused by band-filling effects within the fluctuating band structure. It was found in time-resolved PL measurements that a long lifetime component ($\sim 8 \mu\text{s}$) appears even in direct-gap $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ because of the recombination between spatially separated centers.²¹ At low temperatures ($<30 \text{ K}$), the temperature dependence of the PL-peak energy shows a local minimum,²² because the photoexcited carriers are localized at metastable states caused by the fluctuating band structure. Grossmann *et al.* clearly observed a fluctuating band structure in partially ordered $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$ by using picosecond four-wave mixing experiments.²³ The magnitude of the fluctuation depends on the order parameter and is maximum at an order parameter of 0.5.²⁴ For example, a fluctuation of order parameter was estimated to be about ± 0.05 in $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ with order parameter of 0.58.²⁵

In this study, we investigated localization effects of photoexcited carriers due to fluctuating band structures of ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ alloys on GaAs(001) and GaAs(115)A by PL and time-resolved PL spectroscopies. The temperature dependence of the PL intensity reveals localized states caused by the fluctuating band structure. The magnitude of the fluctuation depends on the order parameter. From the temperature dependence of PL intensity, we found that long-range ordering enhances quantum efficiency of

transitions from localized states. From time-resolved PL measurements, we found a delayed emission relating to electrons trapped at metastable states corresponding to the $\Gamma_{6c}-\Gamma_{4v,5v}$ PL peak. The delay time increases with decreasing temperature below 15 K.

II. EXPERIMENT

Epitaxial thin films of $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ were grown on n^+ -type GaAs(001) and GaAs(115)A substrates by MOVPE. Source gases for the group-III elements were trimethylaluminum, triethylgallium, and trimethylindium. The source gas for P was phosphine. The growth temperature and the total gas pressure were 670 °C and 30 Torr, respectively. The V/III ratio of the source gases was 122. The Al/Ga composition ratio of the films was determined by tuning the gas-flow ratio of trimethylaluminum and triethylgallium. Since films on GaAs(001) and on GaAs(115)A were grown simultaneously in each deposition, the Al/Ga ratio in the films was the same in both samples.¹⁹ The Al/Ga ratio was verified by measuring the optical band gap of a Zn-doped random alloy on GaAs(001). The film thickness was 1.8 μm . From analyses of double crystal x-ray diffraction, the horizontal lattice mismatch was within $\Delta a/a=0.1\%$, where Δa and a are $|a(\text{GaAs})-a[(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}]|$ and $a(\text{GaAs})$, respectively. a is the horizontal lattice constant. The degree of atomic ordering was controlled by the orientation of the substrate. In ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$, it was confirmed that the degree of ordering depends on the substrate tilt angle from the (001) plane by measurements of the PL peak energies.¹² The PL peak energy monotonically increases when the tilt angle is increased from the (001) to the [111]A direction. From transmission-electron diffraction (TED) observation, $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(001) shows super-reflection spots at $(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$. These spots correspond to the CuPt-type ordered structure. On the other hand, in the TED observation of $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}/\text{GaAs}(115)\text{A}$, such super-reflection spots do not appear, though the electroluminescence (ER) spectrum does show a valence-band splitting.¹⁹ In this paper, we call the $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ alloys on GaAs(001) and GaAs(115)A strongly ordered (so) $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ and weakly ordered (wo) $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$, respectively.

We measured time-resolved PL spectra and PL intensities with a gated photon-counting system. The gate width was 30 ns. The measurement temperature was 11 to 300 K. The excitation light source was the 488 nm line of an Ar^+ laser. In the time-resolved PL measurements, an acousto-optic modulator was used to generate pulse excitation. The pulse width and repetition frequency were 30 ns and 2.5 kHz, respectively. The exciting energy per pulse of the Ar^+ laser was $\sim 350 \text{ nJ/cm}^2$ ($8.6 \times 10^{11} \text{ photons/cm}^2$). This energy is low enough to avoid heating the specimen.²⁷

III. RESULTS AND DISCUSSION

A. Temperature dependence of PL spectra

Figure 1 shows PL spectra of wo- and so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ alloys at 11 K. The PL from the wo- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ in Fig. 1(a) shows two peaks at 2.28 and 2.31 eV labeled by X and Γ , respectively. Since the

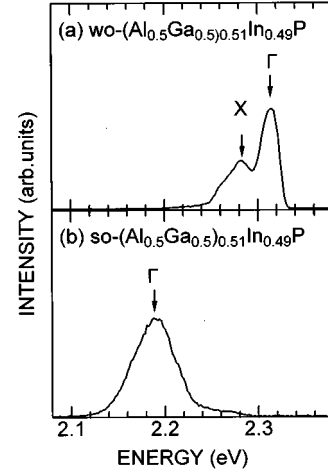


FIG. 1. PL spectra of $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on (a) GaAs(115)A and (b) GaAs(001). Measurement temperature is 11 K. The arrow labeled by X or Γ shows the PL component due to the X or Γ conduction band, respectively.

ER energy matches the peak at 2.31 eV,¹⁹ the 2.31-eV signal corresponds to $\Gamma_{6c}-\Gamma_{4v,5v}$ luminescence. The PL peak at 2.28 eV corresponds to a zero-phonon line of the $X_{6c}-\Gamma_{4v,5v}$ luminescence. For the so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$, the PL energy at 2.19 eV labeled by Γ in Fig. 1(b) matches the ER peak.¹⁹ The $\Gamma_{6c}-\Gamma_{4v,5v}$ transition energy is reduced about 120 meV by long-range ordering in the so alloy. These results show that the $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ changes to a direct-gap material because of the ordering-induced BGR at the Γ point. The full widths at half maximum of the $\Gamma_{6c}-\Gamma_{4v,5v}$ luminescence are about 24 and 55 meV for wo- and so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$, respectively. The width is larger for so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$. The width increases with increasing ordering, which is also observed in $\text{Ga}_3\text{In}_{1-x}\text{P}$. The increase in the width is caused by band-gap fluctuations in the ordered films.^{20,24,26}

Figure 2 shows the temperature dependencies of the PL-peak energies corresponding to the transition from Γ_{6c} to the valence-band maximum (VBM). Closed and open circles denote the data for wo- and so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$, respectively. Each dependence shows a local minimum and a local maximum. These trends are the same as the case in ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$.^{22,24,26} However, the magnitude of the energy shift at the local minimum in Fig. 2 is large even for the wo alloy. For both samples, there are three regions divided by the local minimum and maximum. The regions are shown in Fig. 2. The local minimum for wo- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ is at 25 K. On the other hand, the minimum for so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ is at 60 K. As discussed below, the PL in region I shows behavior of characteristic luminescence from localized states caused by a spatial band-gap fluctuation. In the temperature range from the local minimum to 50 K for wo- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ [to 120 K for so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$] (region II), the localized carriers populate higher-energy states. The PL peak energy follows the well-known temperature dependence of the band gap above 50 and 120 K for wo- and so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$, respectively (region III). The solid and dashed lines in Fig. 2 are the band-gap energies estimated for wo- and so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ by nonlinear least-squares fitting of

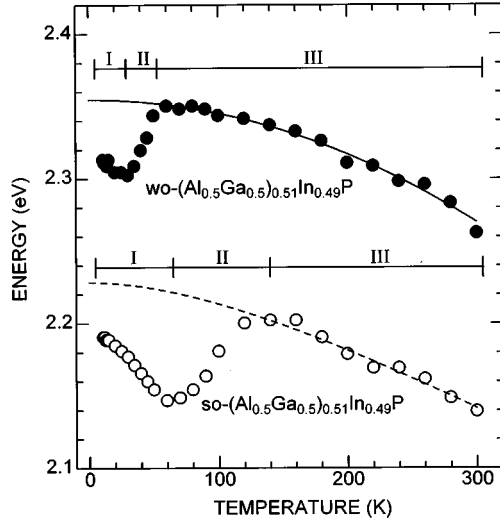


FIG. 2. Temperature dependences of PL-peak energies for $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(115)A (closed circle) and GaAs(001) (open circle). Solid and dashed lines are calculated by least-squares approximations of $E_{g0} - aT^2/(b+T)$.

our data by the function $E_g(T) = E_{g0} - aT^2/(b+T)$. Here, E_{g0} the band-gap energy at 0 K, a , and b are fitting parameters. The band-gap fluctuation causes the PL peak energy to deviate from the $E_{g0} - aT^2/(b+T)$ function form. The redshift energy, which is defined as the difference between the observed PL peak and $E_{g0} - aT^2/(b+T)$ at the local minimum, is 48 (75) meV for wo (so) $-(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$. This result shows that the band-gap fluctuation increases with increasing order parameter.

We believe that the magnitude of the redshift at the local minimum of the PL in region I is mainly determined by the band-gap fluctuation. However, other effects such as valence-band splitting and the spatial fluctuation of the Al/Ga mole fraction can also contribute to the redshift. A periodic crystal field in the ordered superlattice splits the fourfold degenerate Γ_{8v} at the VBM into two doubly degenerate bands represented by $\Gamma_{4v,5v}$ and Γ_{6v} . Therefore, the PL peak energy depends on the population of photogenerated holes at the $\Gamma_{4v,5v}$ and Γ_{6v} points. In our recent study of the valence-band splitting (VBS) of $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ using ER measurements, the VBS energies of wo- and so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ are about 30 and 50 meV, respectively.¹⁹ Though the VBS energies are larger than thermal energies in these experiments, the potential fluctuation may produce a contribution of the valence-band splitting to the redshift. The Γ_{6c} energy is more sensitive to the relative mole fraction of Al/Ga than the X_{6c} energy.¹⁹ If the spatial fluctuation of the mole fraction were large, then the spectral line width of the Γ_{6c} luminescence would be larger than that of the X_{6c} luminescence. However, the experimental results shown in Fig. 1(a) do not show an increased linewidth for the Γ_{6c} peak. Therefore, the fluctuation of the Al/Ga mole fraction does not appear to contribute to the redshift.

To investigate the temperature dependence of the PL intensity in region I, we used an $I_0/I(T) - 1$ versus T plot, where $I_0/I(T) - 1$ corresponds to the relative probability of nonradiative to radiative recombination and can be fitted within some temperature range to $\exp(T/T_0)$.²⁸ T_0 is a char-

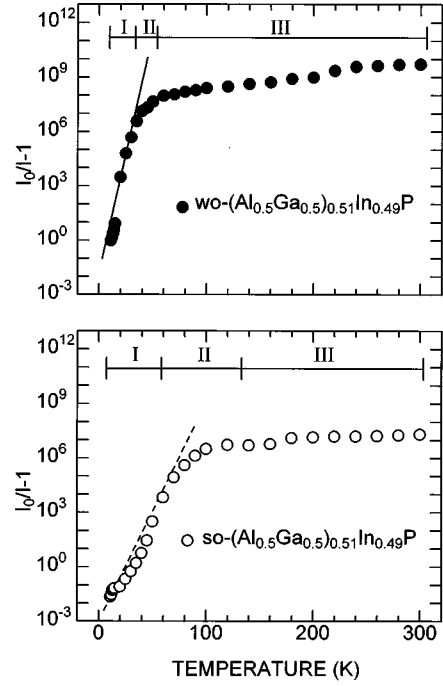


FIG. 3. Temperature dependence of $I_0/I(T) - 1$, where $I(T)$ and I_0 are the measured intensity and the intensity at the low-temperature limit, respectively. Closed and open circles correspond to $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(115)A and GaAs(001), respectively. Solid and dashed lines are calculated by least-squares approximations of $I_0/I(T) - 1$.

acteristic temperature reflecting a temperature dependence of quantum efficiency of transitions from localized states. $I(T)$ is the PL intensity at a temperature T and I_0 is the intensity at the low-temperature limit.²² In this plot, a linear relationship between T and $\ln\{I_0/I(T) - 1\}$ denotes the localization of photoexcited carriers. Figure 3 plots $I_0/I(T) - 1$ as a function of T for wo- and so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$. The $I_0/I(T) - 1$ curves for both wo- and so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ follow $\exp(T/T_0)$ in the region I. The PL in this region comes from localized states caused by the fluctuating potential. T_0 for wo- and so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ estimated from Fig. 3 is 1.6 and 3.6 K, respectively. This result indicates that radiative recombination is enhanced by the long-range ordering. For ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$, it was reported that $I_0/I(T) - 1$ is proportional to $\exp(T/T_0)$ below 30 K, and that T_0 is 7.5 K.²² Since T_0 relates to degree of ordering, the change of T_0 is caused by the different localized states in the wo and so alloys. The reason why T_0 of ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ is larger than that of $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ alloys is that the Γ (direct-gap) conduction-band minimum is much lower than the X (indirect-gap) conduction-band minimum in $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$, while the energies of Γ and X minima are similar in the $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ alloys. Therefore, X -band luminescence is significant in the $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ alloys but negligible in $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$. The X -band luminescence is quenched by nonradiative recombination at lower temperature (smaller value of T_0) than is the Γ -band luminescence.

Figure 4 shows Arrhenius plots of the PL intensities. Closed and open circles indicate data for wo- and so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$, respectively. The plots are proportional to $1/T$ in region II. An activation energy in this plot

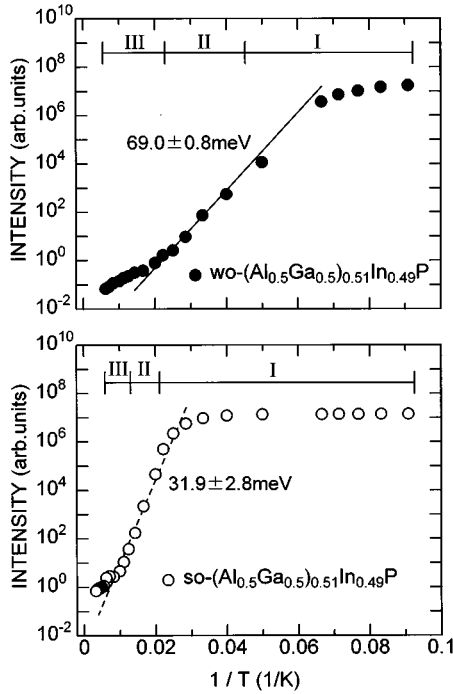


FIG. 4. Arrhenius plots of PL intensities. Closed and open circles correspond to $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(115)A and GaAs(001), respectively. Solid and dashed lines are calculated by least-squares approximations of $\exp(E/kT)$.

corresponds to the magnitude of potential fluctuation. Fitted activation energies for wo- and so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ are 31.9 ± 0.9 and 69.0 ± 2.8 meV, respectively. We believe that the differences between the fitted activation energies from Fig. 4, and the redshifts at the local minimum of the PL from Fig. 2, correspond to the effects of the valence-band splitting. The temperature dependence of the intensity has an Arrhenius form only in region II, not in regions I and III. In region I, the photoexcited carriers are localized at lower-energy states in the fluctuated band as indicated by Fig. 2. In region III the photoexcited carriers completely escape from the localized states.

B. Time-resolved PL spectra

Figure 5 shows time-resolved PL spectra of (a) wo- and (b) so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ at 11 K. We observed decays of the intensities of the PL components shown in Figs. 1(a) and 1(b). The decays at 2.28 and 2.31 eV in Fig. 5(a) correspond to the X and Γ PL peaks, respectively, in wo- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$. Both decays in Fig. 5(a) show long lifetime components corresponding to indirect transitions. Moreover, we found a delayed component around 2 μs in the decay profile 2.31 eV, but not in the 2.28-eV decay profile. The decay of so- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ in Fig. 5(b), on the other hand, shows a fast lifetime which is smaller than the instrumental time resolution of 30 ns in this experiment. The fast lifetime is evidence for the direct characters of the luminescence transition. The decays at 2.28 and 2.31 eV in Fig. 5(a) can be fitted to a double-exponential function given by $A_f \exp(-t/\tau_f) + A_s \exp(-t/\tau_s)$,²⁷ except for the delayed component mentioned above. Here, τ_f and τ_s are the decay lifetimes of the fast and slow components, respectively. τ_f

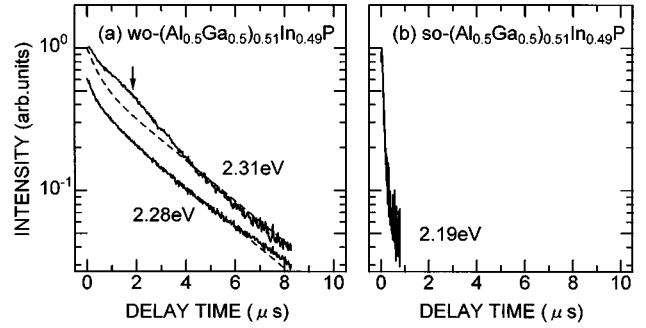


FIG. 5. Time-resolved PL spectra of $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on (a) GaAs(001) and (b) GaAs(115)A at 11 K. Detected energies correspond to the PL-peak energies shown in Fig. 1. Dashed line is a double-exponential function.

(τ_s) obtained by a least-squares approximation is 0.46 (3.06) μs . The dashed lines are the calculated double-exponential functions. Since the photoexcited electron lifetime at the Γ point is much shorter than that at the X point, excited electrons at the Γ point relax rapidly to the X point. Therefore, in general we would not expect to observe the Γ -to-valence-band luminescence in the indirect-gap semiconductors. However, if there is mixing between the Γ and X electronic states, then carriers will be excited and/or scattered from the X point to the Γ point. In this case, Γ -to-valence-band luminescence will be produced by carriers transferred from the X band, and the Γ -luminescence lifetime will be almost the same as the lifetime of the indirect X-band luminescence. The observed long lifetime of the Γ (2.31 eV) luminescence thus reveals the presence of Γ -X mixing in wo- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$. The optical property of Γ_{6c} decay is similar to X_{6c} . We observed a phonon replica of the longitudinal-optical phonons at the Γ point at the lower-energy side of the 2.28-eV band.¹⁹ This indicates that Γ -X scattering occurs in wo- $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$, because of mixing between the X_{6c} and Γ_{6c} bands.

The delayed emission in the decay profile at 2.31 eV was observed only below 15 K, i.e., in region I, where the electrons are localized by the band-gap fluctuations. If we assume that the delayed component comes from metastable states, an escape probability P_e is given by $P_e = 1/\tau_D = \nu \exp(-E_D/kT)$.²⁹ Here, τ_D is the delay time as indicated by the arrow in Fig. 5(a), ν is the attempt-to-escape frequency, and E_D is the mean energy separation between the metastable states. As shown in Fig. 6, E_D and ν obtained from a least squares fit are 1.24 ± 0.03 meV and $1.52 \times 10^6 \text{ s}^{-1}$, respectively. These results indicate that electrons transfer from the X_{6c} CBM to the Γ_{6c} CBM via the metastable states with the mean energy separation of 1.24 meV.

IV. CONCLUSIONS

A systematic investigation of photoluminescence in long-range ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ alloys grown by MOVPE on GaAs(001) and GaAs(115)A has been performed. PL spectra indicate that $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ alloys on GaAs(001) and GaAs(115)A are strongly and weakly ordered, respectively. The fundamental edge luminescence from $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(001) shows BGR about

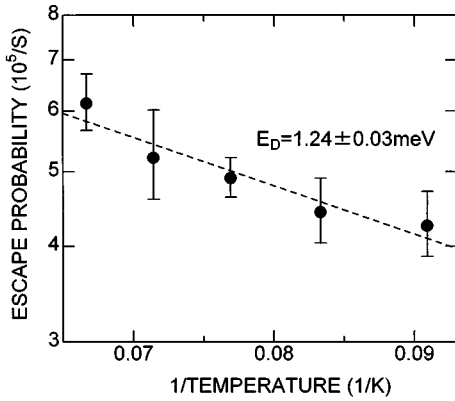


FIG. 6. Temperature dependence of escape probability of $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ on GaAs(115)A. The vertical axis shows logarithm of escape probability. The probabilities were estimated by the delay time indicated by an arrow in Fig. 5. Dashed line is calculated by a least-squares approximation of $P_e = 1/\tau_D = \nu \exp(-E_D/kT)$.

120 meV at 11 K due to the long-range ordering. This luminescence appears at the lower energy than the indirect luminescence from the X valley. In the temperature dependence of the PL-peak energy, there are three regions divided by a local minimum and a local maximum. Below the temperature showing the local minimum, $I_0/I(T)-1$ is proportional to $\exp(T/T_0)$, where $I(T)$ is the luminescence intensity. This result is explained by the localization of photoexcited carriers. The origin of the localization is potential fluctuations in the epitaxial films due to the ordering. Estimated values of

T_0 for the weakly and strongly ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ are 1.6 and 3.6 K, respectively. This result indicates that the quantum efficiency is enhanced by the long-range ordering. The PL intensities show thermal activation between the temperatures showing the local minimum and maximum of the peak energies. In the thermally activated region, the activation energies for the weakly and strongly ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$ are 31.9 ± 0.9 and 69.0 ± 2.8 meV, respectively, similar to the energy shift of the PL-peak energy at the local minimum.

In the time-resolved PL measurements for the weakly ordered $(\text{Al}_{0.5}\text{Ga}_{0.5})_{0.51}\text{In}_{0.49}\text{P}$, the decays at the X and Γ PL peaks show long lifetime components corresponding to indirect transitions. This result indicates that photoexcited electrons at the Γ_{6c} band are populated from the X_{6c} band. Furthermore, we observed a delayed emission which was not observed in ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ and is attributed to electrons trapped at metastable states. The delayed component was only observed below 15 K, and the delay time increases with decreasing temperature. The temperature dependence of the delay time suggests that electrons transfer from the X_{6c} CBM to the Γ_{6c} CBM via the metastable states with a mean energy separation of 1.24 meV.

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