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# Inelastic phonon scattering in long-range-ordered $(\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5})_{0.5}\mathrm{In}_{0.5}\mathrm{P}$

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Carrier relaxation and recombination in long-range-ordered $(\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5})_{0.5}\mathrm{In}_{0.5}\mathrm{P}$ have been studied by selectively excited photoluminescence (PL) spectroscopy. We observed sharp resonant PL peaks under near-resonant excitation. The set of resonant PL peaks evolves according to excitation energy. The excess excitation energies for the resonant PL peaks agree well with the LO-phonon energies related to the In-P, Ga-P, and Al-P bonds of the ordered sample. Furthermore, the LA resonance caused by zone-folding effects was observed. These resonant PL intensities show different excitation energy dependence, which precludes the possibility of resonant Raman scattering. High dense excitation reveals an excited state near the $X$ level. This suggests mixing of electron wave functions in the $\Gamma$ and $X$ states. Energy relaxation of excited carriers from the pseudodirect $X$ state to the $\Gamma$ ground state causes the resonant PL. Time-resolved spectroscopy was employed to study the carrier relaxation mechanism.

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Spontaneous CuPt-type ordering of $\mathrm{Ga}_{0.5}\mathrm{In}_{0.5}\mathrm{P}$ has been widely observed in vapor-phase epitaxy on a lattice matched GaAs (001) substrate.[1] This ordering has periodically stacked cation sublattices along the [111] or [111] direction, the two $\mathrm{CuPt}_B$ subvariants. All forms of deviation from perfect randomness profoundly affect material properties especially the electronic band structure. It has been shown experimentally and theoretically that atomic ordering causes a reduction of the band gap and a splitting of the valence band maximum,[1,2] which depend on the square of the order parameter. Similar effects are also found in $(\mathrm{Al}_x\mathrm{Ga}_{1-x})_{0.5}\mathrm{In}_{0.5}\mathrm{P}$ alloys.[1] Generally, ordered $(\mathrm{Al}_x\mathrm{Ga}_{1-x})_{0.5}\mathrm{In}_{0.5}\mathrm{P}$ $(0 \leqslant x \leqslant 1)$ alloys have crystal domains with different order parameters and different sizes. A statistical distribution of the order parameter in the epitaxial film and ''sequence mutations''[3] of the ordered atomic layer cause a fluctuation of the band-gap energy in real space. This explains the photoluminescence (PL) and its excitation (PLE) properties observed in ordered alloys.[4–6] In such a band structure an anomalously large Stokes shift in PL has been observed at low temperature. In this study we focus our attention on the energy relaxation process of photoexcited carriers in ordered $(\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5})_{0.5}\mathrm{In}_{0.5}\mathrm{P}$. The $(\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5})_{0.5}\mathrm{In}_{0.5}\mathrm{P}$ random alloy is an indirect gap material, while the optical transition in ordered $(\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5})_{0.5}\mathrm{In}_{0.5}\mathrm{P}$ is direct, because the $\Gamma$ conduction band energy is reduced and crosses the $X$ valley level.[7] We observed inelastic phonon scattering in this ordered $(\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5})_{0.5}\mathrm{In}_{0.5}\mathrm{P}$ alloy by selectively excited PL spectroscopy. Strongly modulated near-resonant excitation efficiency allows selective excitation of the ordered domains. Selectively excited PL spectra reveal sharp PL peaks due to phonon scattering. We discuss these phenomena from the point of view of energy relaxation of carriers from excited states to ground states.

Epitaxial films of $(\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5})_{0.5}\mathrm{In}_{0.5}\mathrm{P}$ alloys were grown on GaAs(001) and GaAs(115)$A$ substrates by organometallic vapor-phase epitaxy. The film thickness was 1.8 μm. Detailed sample growth conditions were reported in Refs. 6 and 7. The ratio of Al to Ga was confirmed by measuring the optical band gap of a Zn-doped random alloy on GaAs(001).[7] The estimation error of the Al mole fraction is about $\pm 0.02$. Transmission-electron diffraction of $(\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5})_{0.5}\mathrm{In}_{0.5}\mathrm{P}$ on GaAs(001) shows superreflection spots of CuPt type 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 show clear superlattice diffraction, although optical anisotropy caused by the ordering was observed.[7] This indicates that the atomic ordering on GaAs(115)$A$ is weak. In this paper the samples grown on GaAs(001) and GaAs(115)$A$ are called the ordered sample and the weakly ordered sample, respectively.

For PL experiments the samples were mounted in a cryostat at 10 K. A tungsten lamp dispersed by a 0.27 m single grating monochromator served as a tunable low-excitation-density light source. The excitation density was about 10 $\mu\mathrm{W/cm}^2$. The diameter of the excitation light at the sample was about 1 mm. The time-resolved PL measurements were performed in a He-gas-flow cryostat at 2.8 K using 250 fs pulses from the second harmonic of a mode-locked Ti:sapphire laser with a repetition rate of 4 MHz. The excitation laser wavelength and initial density are 440 nm and $2 \times 10^{11}\ \mathrm{cm}^{-2}$, respectively. The laser spot diameter was about 100 μm. The PL was dispersed in a 0.25 m monochromator and detected with spectral and temporal resolution of 0.15 nm and about 2 ps, respectively, by a streak camera with two-dimensional readout. Raman scattering measurements were performed at room temperature in a backscattering configuration along the [001] direction, using the 514.5 nm line of an Ar ion laser.

A proven method to demonstrate the dominant carrier relaxation process is the observation of hot exciton relaxation, revealing phonon resonances in PL and PLE spectra.[8] A

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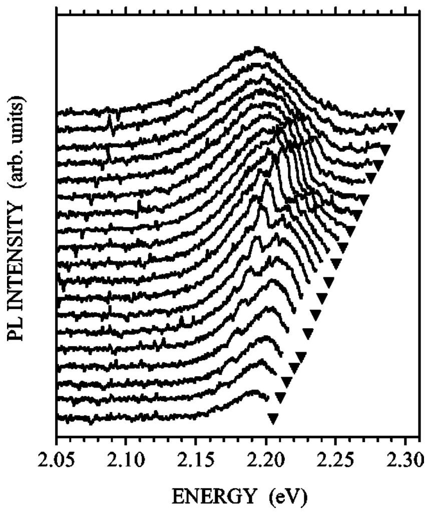

FIG. 1. Selectively excited PL spectra of a partially ordered sample. The triangles indicate the excitation energies.

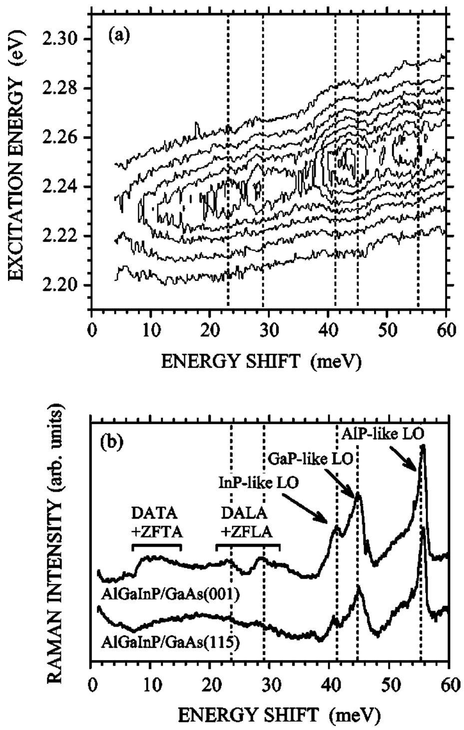

FIG. 2. Contour plot of selectively excited PL. Dashed lines mark constant phonon resonances (a). Raman scattering spectra of the ordered sample and the weakly ordered sample are compared with the PL data (b).

strongly modulated near-resonant excitation efficiency allows selective excitation of domains with ground state transition energy below the excitation energy. Figure 1 shows selectively excited PL spectra of ordered $(Al_{0.5}Ga_{0.5})_{0.5}In_{0.5}P$. The solid triangles indicate the excitation energy for each spectrum. For excitation energy above 2.28 eV an inhomogeneous broad peak was observed, indicating nonselective excitation. Since the ordered sample comprises inhomogeneous ordered domains, nonselective excitation causes such broad luminescence consisting of the ground state PL from the ordered domains. Under near-resonant excitation, on the other hand, we found a set of sharp PL peaks together with the inhomogeneous broad PL. With decreasing excitation energy the set of sharp PL peaks evolves. For excitation energy below 2.20 eV the sharp peaks disappear and the inhomogeneous broad PL only was observed. The resonance phenomenon was not observed in weakly ordered $(Al_{0.5}Ga_{0.5})_{0.5}In_{0.5}P$ grown on GaAs(115)A.

Figure 2(a) is a contour plot of the selectively excited PL intensity as a function of the energy shift from the excitation energy. The dashed lines indicate the positions of the sharp PL peaks. It is found that the energy shifts of these PL peaks are independent of excitation energy. These excess excitation energies lie in the range of typical phonon energies of the $(Al_{0.5}Ga_{0.5})_{0.5}In_{0.5}P$ alloy. We compare the sharp PL with Raman scattering spectra obtained from the ordered sample and the weakly ordered sample in Fig. 2(b). The sharp PL agrees well with the Raman scattering peaks of the LO phonons related to In-P, Ga-P, and Al-P bonds[9–11] of the ordered sample. Also, we found signals near 24 meV and 29 meV in the PL and Raman scattering spectra of the ordered sample. These structures can be attributed to LA-phonon modes caused by zone-folding effects, i.e., zone-folded LA (ZFLA), in the long-range atomic ordering, and to a disorder-activated LA-phonon (DALA) band.[9,10,12] The low-frequency Raman scattering of the weakly ordered sample is weak. Similarly, the Raman signal near 10 meV in the ordered sample is due to ZFTA and DATA phonons, not observed in the PL measurements. These bands represent the corresponding broadened density of phonon states of $(Al_{0.5}Ga_{0.5})_{0.5}In_{0.5}P$. It is considered that the ordered domain structure, e.g., domain boundaries, enhances the intensity of the DATA and DALA signals. Since the LA-phonon energy at *X* is larger than that at *L*, the Raman signals near 24 meV and 29 meV are due to DALA bands related to *L* and *X*, respectively. Moreover, the ZFLA signal caused by the long-range ordering is superposed on the 24 meV signal.

The relative intensity of the sharp PL depends on excitation energy, which reflects the density of domains with a matching ground state transition energy. Figure 3 plots the excitation energy dependence of the sharp PL intensities corresponding to the LA (29 meV), InP- and GaP-like LO, and AlP-like LO resonances. In the resonant PL, the InP- and GaP-like LO modes were not resolved. These profiles show different resonance energies. Peak separations between the (a), (b), and (c) profiles are indicated by $\Delta E_1$ and $\Delta E_2$ in Fig. 3. $\Delta E_1$ and $\Delta E_2$ nearly coincide with the differences in energy between the corresponding phonons. These results preclude the possibility of resonant Raman scattering. Therefore, we consider that inelastic phonon scattering in the energy relaxation of excited carriers causes the observed resonant phenomena in PL. Since spatial localization of excited carriers in ordered domains suppresses carrier-carrier scattering, and the localized density of states drastically restricts phonon scattering, it is considered that localization in the fluctuating potential enhances such inelastic phonon scattering processes.

Figure 4 shows excitation-density-dependent PL spectra of the ordered sample. The spectra are normalized and

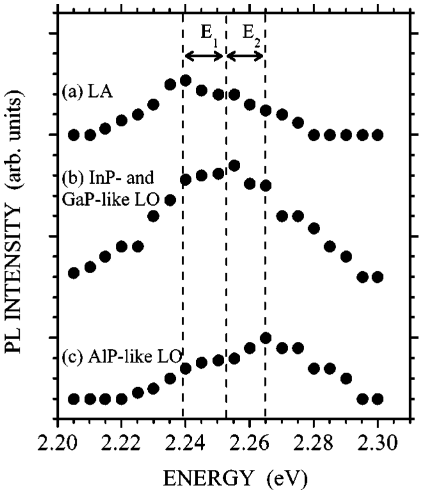

FIG. 3. Excitation energy dependence of the resonant PL intensities of LA (29 meV) (a), InP- and GaP-like LO (b), and AlP-like LO (c) resonances. The vertical lines represent resonant peaks.

shifted in the *y* direction for clarity. The excitation power of the cw Ar ion laser was changed from 0.3 mW/cm$^2$ to 0.3 W/cm$^2$. With increased excitation power, the ground state PL near 2.18 eV shows a blueshift. This indicates a band filling effect in the fluctuating band lineup of the ordered sample. At 0.3 mW/cm$^2$ only ground state PL is evident, and above 6 mW/cm$^2$ the spectral shape saturates, revealing an emission band from *excited* states about 70 meV above the ground state transitions. Let us consider two scenarios for the origin of the excited states: (1) a low-dimensional system giving the required discrete energy level and (2) pseudodirect *X* states resulting from Γ-*X* mixing. The domain size in ordered $(\mathrm{Al}_x\mathrm{Ga}_{1-x})_{0.5}\mathrm{In}_{0.5}\mathrm{P}$ can vary from micrometers to nanometers, depending on growth conditions and substrate orientation. Thus, sufficiently small domains in the inhomogeneous domain ensemble, which may behave like a low-dimensional system giving the required discrete energy level, can contribute to such resonance. Transmission electron microscopy, however, did not confirm that the dominant domain size is indeed sufficiently small to give the required discrete energy level structure. On the other hand, scenario (2) originating from the *X* states is an important candidate. In a previous paper,[7] we observed *X* band luminescence near 2.25 eV in a weakly ordered sample. This energy position is close to the emission band observed in Fig. 4. In contrast to the Γ level, the *X* level energy is not so sensitive to ordering.[13] Even in the weakly ordered sample we observed a strong zero-phonon PL band of the *X* exciton consisting of the *X* electron and Γ heavy hole.[7] Also, a localization of the exciton causes coupling between the exciton and the phonon at the Γ point. Therefore, the observed excited state is considered to be a pseudodirect type of transition of the *X* states with a finite oscillator strength resulting from the Γ-*X* mixing in the conduction band. Scattering effects at domain boundaries play an important role in the Γ-*X* mixing.[15]

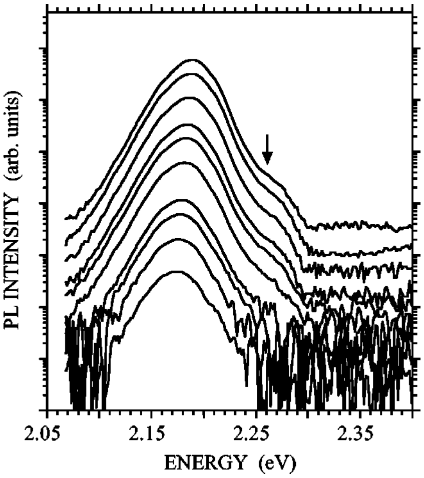

FIG. 4. Excitation-density-dependent PL spectra for the ordered sample. The spectra are normalized and shifted in the *y* direction for clarity.

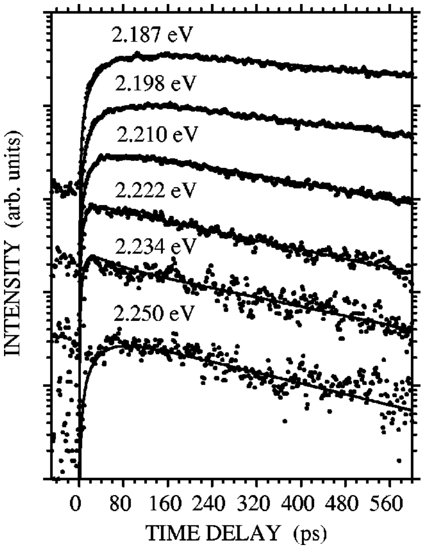

FIG. 5. PL decay profiles measured at various detection energies excited at 440 nm with an initial carrier density of $2\times10^{11}$ cm$^{-2}$.

We performed time-resolved PL measurements to investigate the dynamic process of energy relaxation. Decay profiles detected at various detection energies are summarized in Fig. 5. Solid lines plot least-squares fits of the PL data. Each PL decay curve obeys a double-exponential profile consisting of fast and slow components. The PL decay profile at 2.250 eV corresponds to the excited state PL. A slow rise profile was found at this energy. This phenomenon also precludes the possibility of scenario (1) above. The estimated rise time constant is about 40 ps. On the other hand, PL profiles at 2.234 eV and 2.222 eV show a steep rise of less than 10 ps and a fast decay of about 35 ps. The fast decay time is almost independent of the detection energy. This corresponds to the well-known cooling process of excitons near Γ states.[14] Below 2.210 eV, a slow increase of the PL intensity appears after the excitation. The rise time constant of these profiles is about 50 ps, which indicates the relaxation process of excitons in the fluctuating band gap. The estimated slow decay times at 2.250, 2.234, 2.222, 2.210, 2.198, and 2.187 eV are about 300, 350, 350, 400, 600, and 850 ps, respectively. The slower decay at lower detection energy indicates localization effects of the exciton. The PL spectra indicate that the distributed $\Gamma$ states in the ordered domain structure overlap in energy with the $X$ states. This indicates the presence of lower-ordered domains with the $X$ ground level. Therefore, the $\Gamma$ and $X$ states are confined in different domains; i.e., the respective wave functions are spatially separated. We consider that the real space $\Gamma$-$X$ transfer between them causes the slow rise profile observed at 2.250 eV. The rise time of about 40 ps corresponds to the scattering time. In the case of GaAs/AlAs short-period superlattices,[16] it was reported that the $X \rightarrow \Gamma$ electron scattering time is about 30 ps, that is, larger than the $\Gamma \rightarrow X$ scattering time (subpicoseconds). The estimated scattering time (about 40 ps) of our sample is of the same order as this $X \rightarrow \Gamma$ scattering time. In spite of the excited states due to $X$, the observed decay time of about 300 ps is very fast. Electrons in the $X$ state near $\Gamma$-$X$ resonances can escape into the $\Gamma$ state, and therefore the lifetime of the excited state PL decreases drastically.[17,18] Further investigations of, for instance, the temperature dependence of the dynamics are needed to investigate the scattering process in detail.

In summary, we have investigated carrier relaxation and recombination in ordered $(\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5})_{0.5}\mathrm{In}_{0.5}\mathrm{P}$ by selectively excited PL spectroscopy. In the selectively excited PL spectra, we observed LA-phonon resonances as well as LO-phonon resonances. The LA-phonon resonances are phonon modes caused by zone-folding effects and alloy disordering effects in the ordered alloy. High dense excitation reveals excited states near the $X$ level. This indicates mixing of electron wave functions in the $\Gamma$ and $X$ bands. The energy relaxation of excited carriers from the pseudodirect $X$ state to the $\Gamma$ ground state causes such resonances. Time-resolved spectroscopy was employed to study the carrier relaxation mechanism.

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