Effect of the insertion of an ultrathin AlP layer on the optical properties of GaAsP/GaP quantum wells

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We have systematically investigated the correlation between electronic states and optical properties in indirect GaAsP/GaP quantum wells (QW's) which have an ultrathin AlP layer inserted during fabrication. The insertion of 1 monolayer (ML) of AlP at the center of a 60-Å GaAsP QW drastically increased the photoluminescence intensity, and in particular the efficiency of the no-phonon (NP) transition. The NP intensity relative to its TO phonon replica was found to be greatly dependent on the structural parameters and was drastically reduced when the arsenic composition of the well region exceeded 15%. The relative NP intensity was found to increase sharply as the width of the AlP layer was increased above 2 ML's. These results suggest that the efficiency of the NP transition is improved when the X_z electrons are involved in radiative recombination rather than the X_{xy} electrons. [S0163-1829(99)10043-2]

I. INTRODUCTION

Indirect band-gap materials such as GaP-based and SiGe-based systems are of great practical importance since they have potential to operate in a range of desirable wavelengths and they provide an opportunity to integrate optical and electronic devices. Methods to obtain efficient light emission from these indirect semiconductors have been therefore pursued by many researchers. One well-known method is the introduction of an isoelectronic trap which relaxes the selection rule of momentum-conserving optical transitions by mixing the states of different k vectors. In particular, incorporating nitrogen into GaP-based systems as an isoelectronic substituent enabled us to fabricate visible light emitting devices with high efficiency.[1,2]

Recently, different approaches involving various kinds of heterostructures have been pursued. Due to the controllability of the band structures allowed by the recent progress of such growth techniques as molecular-beam epitaxy (MBE), new concepts based upon heterostructures have been proposed and their feasibilities have been assessed. It is theoretically expected that periodic superlattices composed of two indirect semiconductors might fold the conduction-band minima into the zone center, resulting in the formation of direct-gap superlattices from indirect-gap binary constituents.[3] Experimentally, attempts have been made at growing superlattices in the lattice-matched GaP/AlP system[4,5] as well as in the strained-SiGe/Si system.[6] In both systems, photoluminescence (PL) with an enhanced no-phonon (NP) transition has been observed at low temperatures, though the origin is likely to be localization of excitons at local potential minima caused by the inevitable fluctuations of the thickness and/or the alloy composition.[7] Optical properties of AlP/GaP type-II single quantum wells (SQW's) have been also investigated, and the observed high efficiency of the NP transition is also interpreted to result from localization of indirect excitons by fluctuations in the potential at the interfaces.[8] To enhance confinement of both electrons and holes in type-II heterostructures, the neighboring confinement structure (NCS), where electrons and holes are separately confined in neighboring quantum wells (QW's), was proposed.[9,10] The PL intensity of a NCS has been shown to be comparable to or even larger than that of superlattices.

Recently, we proposed a quantum structure that uses a heterostructure as a localization center for electrons. The structure consists of a monolayer of AlP at the center of a type-I indirect GaAsP/GaP QW.[11] We have reported preliminary results showing that insertion of a monolayer (ML) of AlP has enhanced NP transition efficiency, as well as a drastic increase in integrated PL intensity.[12] A similar wavefunction engineering has been proposed by Farad[13] in AlGaAs/GaAs system to enhance the energy shift due to the interdiffusion and to manipulate the intersubband transition energies. In this paper, we will apply the idea to control electronic states of indirect semiconductors and investigate the correlation between electronic states and optical properties. For this purpose, a photoluminescence study of samples with various arsenic compositions and AlP layer widths was carried out.

II. BAND STRUCTURE

The samples consisted of strained GaAsP/GaP QW's with or without an additional AlP layer inserted into the center of the well. In our experiment, the arsenic composition was varied up to 23%, and the AlP layer width was 0–3 ML's.

Typical band discontinuities at GaP/GaAsP/AlP interfaces are illustrated in Fig. 1. Since the structures are grown on GaP(001) substrates, the GaAsP and the AlP layers are under biaxial compression which reduces the symmetry and splits degenerate bands. The band discontinuity at the GaAsP/GaP interface was calculated by using deformation potential theory including strain-induced band modifications. The band offset ratio at the Γ point was assumed to be 0.60.[14] The conduction band offset at the AlP/GaP interface was chosen to be 0.36 eV based on PL results of type-II AlP/GaP QW's with various AlP widths.[15] The resulting X conduction

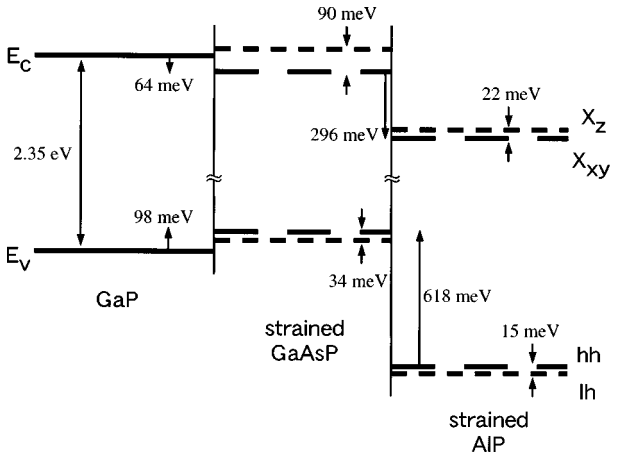

FIG. 1. The band lineups at GaP/$GaAs_{0.2}P_{0.8}$/AlP interfaces. The band discontinuity at the GaP/GaAsP interface was calculated by using deformation potential theory assuming that the band offset ratio at the Γ point is 0.60. The conduction-band offset at the AlP/GaP interface was chosen to be 0.36 eV.

band splits into a fourfold X_{xy} band and a twofold X_z band where z is parallel to the (001) growth direction. A detailed photoreflectance and PL study of GaAsP/GaP multiple QW's revealed that the band lineup of QW's with low arsenic compositions is type-I at both the X and Γ points, and that the conduction-band minima lie around the X point.[14] Since the X_z band lies above the X minimum of GaP, only the X_{xy} band participates in optical transitions in simple GaAsP/GaP type-I QW's. The efficiency of the NP transition in these QW's is, however, lower than that of a NCS or type-II superlattices. It is thought that the localization of excitons and the resulting Γ-X mixing effect are essential to the NP transition efficiency.[8,10] The insertion of AlP might bring about intentional quantum confinement of electrons as well as inevitable fluctuations of potential energy at the interfaces.

III. EXPERIMENTAL PROCEDURE

The GaAsP/GaP QW's with and without AlP layers were grown on GaP(001) substrates by gas-source MBE (VG-Semicon V80H) using AsH_3 and PH_3 as source gases. The source gases were introduced into the growth chamber from a pressure-controlled subchamber and cracking cells were operated at 1000 °C for thermal decomposition. The arsenic fraction was controlled by regulating the partial pressures of the source gases. Prior to growth, the surface of the substrate was thermally cleaned at 670 °C for 10 min. The samples consisted of a 3500-Å GaP buffer layer, a 60-Å strained GaAsP well layer with or without an ultrathin AlP layer at its center, and a 500-Å GaP cap layer. At all interfaces, a growth interruption of ~20 s was performed to obtain a stable flow rate of source gases. The growth temperature of 630 °C was used.

PL spectra were measured in a standard lock-in configuration. The samples were excited with the 325-nm line from a He-Cd laser and the PL signal was analyzed by a 0.3-m monochromator and detected by a photomultiplier. Typical incident power of the laser and beam diameter were 10 mW and 3 mm, respectively.

IV. RESULTS AND DISCUSSION

The 5-K PL spectra of the QW's with and without the presence of a 1-ML AlP layer are contrasted in Fig. 2. The arsenic fractions of the samples are ~9%, and ~19%. The spectrum of the sample without an AlP layer consists of four main peaks. They are assigned as an NP line and its transverse acoustic (TA), longitudinal acoustic (LA), and transverse optical (TO) phonon replicas from the higher energy side, respectively.[16] It is very likely that the TO phonon replica overlaps the longitudinal optical (LO) phonon replica. The prominent phonon replicas show that the indirect transition is dominant in these samples. This figure clearly demonstrates that the spectral features are considerably changed by the insertion of 1 ML of AlP. The AlP layer increases the integrated PL intensity drastically. In particular, the efficiency of the NP transition is conspicuously improved, which is firm evidence of an enhanced Γ-X mixing effect due to the localization of electrons around the AlP layer. Effective isolation of excitons from nonradiative pathways would also contribute to the increase of PL intensity.

Figure 3 shows the PL spectra dependence versus the arsenic composition for the samples with 1 ML of AlP. As the arsenic composition increases, the NP peak shifts towards lower energy and the relative NP intensity decreases. Figure 4 shows the NP intensity relative to its TO phonon replica versus the arsenic composition of the well region. The thickness of the AlP layer was 1 ML. It is seen that the relative NP intensity is drastically reduced when the arsenic compo-

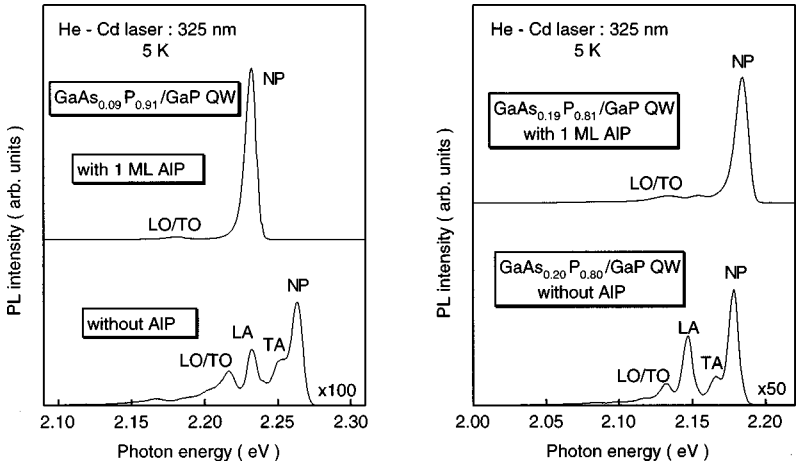

FIG. 2. PL spectra of GaAsP/GaP QW's with and without 1 ML of AlP at the center of the well. The AlP layer drastically enhanced the PL intensity, especially the NP peak.

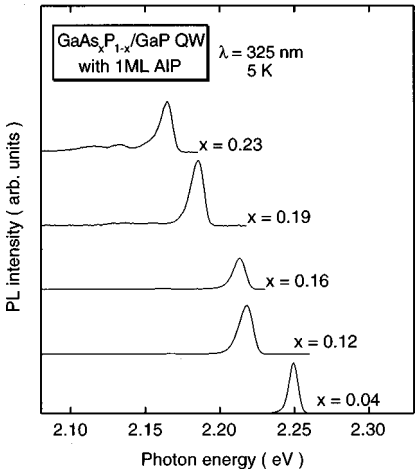

FIG. 3. Arsenic composition dependence of the 5-K PL spectra of the samples with 1 ML of AlP. As the arsenic composition of the well region increases, the NP peak shifts toward lower energy. The variation of the relative NP intensity is also seen.

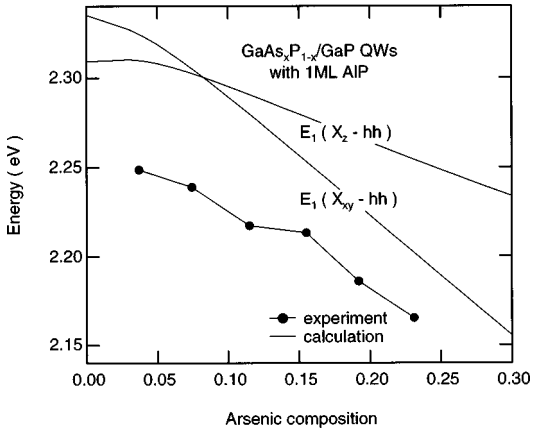

FIG. 5. Arsenic composition dependence of the NP peak energy of the samples with 1 ML of AlP. Calculated transition energies between the ground state of X electrons and heavy holes are also depicted. Around an arsenic composition of ~10%, a changeover of the lowest electron states between the X_z and the X_{xy} is anticipated by the calculation.

sition exceeds 15%. This indicates that electrons are more strongly localized at AlP layer for smaller arsenic compositions. This result is in good agreement with the band alignment shown in Fig. 1. In particular, the splitting of the X conduction minima might be responsible for this behavior. In samples with high arsenic compositions, the lowest electron state is the X_{xy} state because of the large strain-induced splitting. However, in samples with a sufficiently small arsenic composition the quantized X_z ground state is the lowest-lying electron state. This is because the effective mass of the X_z electron (longitudinal effective mass) is heavier than that of the X_{xy} electron (transverse mass). Therefore a changeover between the X_z and the X_{xy} states is expected at an intermediate arsenic composition, which is related to the drastic reduction of the relative NP intensity. The changeover between the X_z and the X_{xy} states was initially discussed for AlAs/GaAs systems where a significant change in the ratio of the intensities of NP line to its phonon replica was observed.[17]

We calculated the electron ground state by using the envelope function approach and a discussion of the correlation between electronic states and optical properties in the QW's follows. In Fig. 5, the NP peak energy dependence on arsenic composition is shown. Calculated X_z electron-heavy hole (hh) and the X_{xy} electron-hh transition energies as a function of arsenic composition are also depicted, and the changeover of the lowest-lying X electron states is anticipated at an arsenic composition of ~10%. The redshift behavior of the NP peak is correctly reproduced by the calculation. However, a significant deviation is also seen to exist between the experimental and calculated results. The calculated exciton binding energy was found not to fully explain this difference and an additional binding energy due to the fluctuation of the potential at the interface might be responsible.

The arsenic composition dependence of the calculated envelope function of the lowest lying electron state is described in Fig. 6. It is noted in this figure that strong localization of electrons in the AlP layer occurs in samples with lower arsenic compositions since the lowest-lying electron state is at

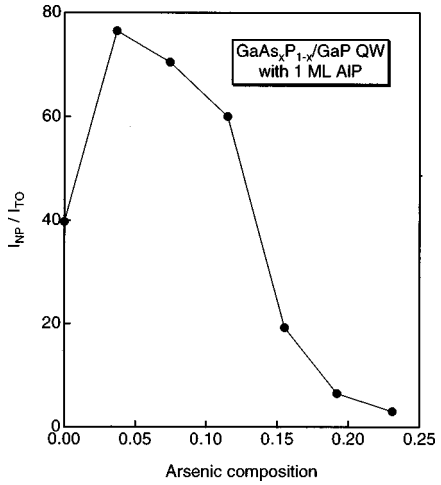

FIG. 4. Arsenic composition dependence of the NP intensity relative to its TO phonon replica. The relative NP intensity is drastically reduced when the arsenic composition exceeds 15%. This indicates that electrons are more strongly localized in the AlP layer for smaller arsenic compositions.

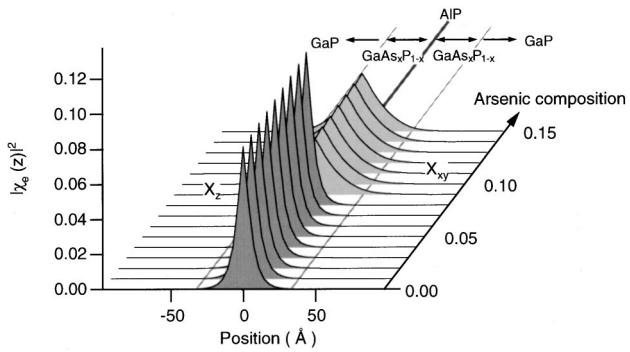

FIG. 6. The arsenic composition dependence of the envelope function of electrons. Strong localization of electrons in the AlP layer occurs in samples with lower arsenic compositions. At these compositions the lowest-lying electron state is at the X_z point.

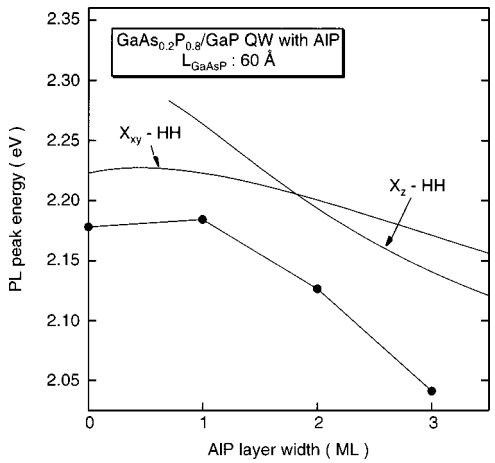

FIG. 7. The dependence of the NP peak energy on the AlP layer width. The arsenic composition is 20%. The changeover between the X_{xy} and the X_z states occurs at an AlP layer width of ~2 ML's.

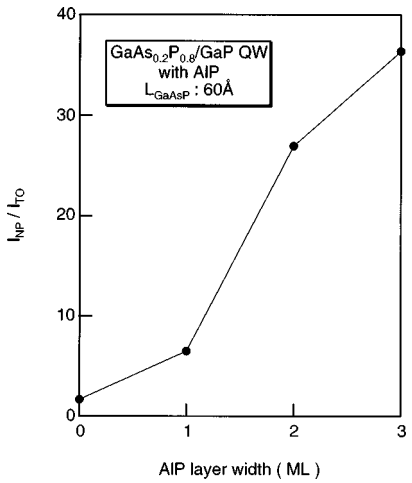

FIG. 8. The dependence of the relative NP intensity on the AlP layer width. The relative NP intensity is larger in the samples with AlP layer widths thicker than 2 ML's, where the lowest electron state is the X_z.

the X_z point. This is because GaAsP layer acts as a relatively higher barrier for X_z electrons and prevents the electrons from leaking outside the AlP layer. Therefore especially high efficiency NP transitions are obtained in samples with sufficiently low arsenic compositions.

To confirm the correlation between the relative NP intensity and the electronic state which participates in optical transitions, we carried out a PL study on samples with different AlP layer widths. Figure 7 shows the dependence of the NP peak energy on the AlP layer width. The X_{xy} electron-hh and the X_z electron-hh transition energies were also calculated for an arsenic composition of 20%. It is clear that the experimental data closely matches the results of our calculation including the changeover between the X_z and the X_{xy} states at the AlP layer width of ~2 ML's.

The dependence of the relative NP intensity on the AlP layer width is shown in Fig. 8. It is also seen in this figure that the relative NP intensity is larger in the samples with AlP layer widths thicker than 2 ML's, where the lowest electron state is the X_z. This supports our idea that the enhancement of the NP transition is achieved when the X_z electrons are involved in the optical transitions.

Although smaller arsenic composition and larger AlP width are favorable to obtain the efficient NP transition, one must consider the immunity of PL against thermal quenching, which is also greatly dependent on the structural parameters. In fact, the activation energy derived from the integrated PL intensity slope at higher temperatures was found to roughly correspond to the thermal escape of carriers from the QW, and increases with increasing arsenic composition.[18] Therefore the structural parameter should be carefully chosen to obtain the efficient NP transition and the good stability against temperature.

V. CONCLUSION

We have studied the optical properties of the GaAsP/GaP QW's with an ultrathin AlP layer inserted to increase electron localization and found significant enhancement of the luminescence, especially the NP peak. The arsenic composition dependence of the NP transition efficiency was shown to closely reflect the envelope function of electrons calculated by including the effect of strain and the resultant splitting of the X conduction minima. An especially high NP transition efficiency was obtained in samples where the lowest-lying electron state is X_z. This is because the X_z conduction-band edge in GaAsP is higher than the X_{xy} band edge, preventing electrons from leaking outside the AlP layer.

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