PHYSICAL REVIEW B VOLUME 60, NUMBER 3 15 JULY 1999-I

Magnetophotoluminescence spectroscopy of AlGaP-based neighboring confinement structures

N. Usami, T. Sugita, T. Ohta, F. Issiki, and Y. Shiraki
Research Center for Advanced Science and Technology (RCAST), The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan

K. Uchida and N. Miura
Institute for Solid State Physics, The University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106-8666, Japan

(Received 18 March 1999)

Magnetophotoluminescence (PL) spectroscopy with field strengths of up to 40 T have been carried out on tensilely strained AlGaP-based neighboring confinement structures (NCS's), consisting of adjacent AlP and GaP quantum wells sandwiched between AlGaP barrier layers. With increasing magnetic field, an anomalous redshift of PL peak energy and an anomalous reduction of PL intensity, both of which were previously reported for AlP/GaP superlattices, were clearly observed in unstrained NCS's. As an unstrained NCS is a nonperiodic structure, this result reveals that folded conduction bands in superlattices are not important for this phenomenon and that localization of excitons is likely essential. Introduction of tensile strain to an NCS was found to drastically modify magnetic-field dependence. Above a certain magnetic-field strength, the anomalous behavior stopped and a spectral blueshift and an increase of PL intensity with increasing magnetic field were observed. A competition between the confinement by magnetic field and the degree of exciton localization would be the key to explaining the unique magnetic-field dependence of PL spectra of AlGaP-based NCS's.
[S0163-1829(99)13727-5]

I. INTRODUCTION

It is a challenging problem to synthesize luminescent semiconductor structures from materials with indirect band gaps. There are several different strategies to solve this problem. One method is based on a theoretical prediction that a periodic superlattice composed of two indirect-gap semiconductors provides the folding of the conduction-band minimum state into the zone center, which converts indirect semiconductors to direct ones.[1] After improvements of crystal-growth techniques such as molecular-beam epitaxy (MBE) and metalorganic vapor phase epitaxy (MOVPE), short-period superlattices with indirect semiconductors were grown for lattice-mismatched Si/Ge and lattice-matched AlP/GaP systems. The former attracts a great deal of interest due to the fact that Si-based light emission would lead to combining electronics and optics on the same Si substrate. New electronic transitions induced by superlattice symmetry were reported by several groups,[2–4] however there is no persuasive evidence to show that these transitions are direct. The latter system, AlP/GaP, is also intensively studied since its band gap is technologically important especially for optical devices. Also, technological barriers for crystal growth are expected to be low since the lattice constants of AlP and GaP are almost equivalent and there is no limitation in critical thickness, unlike the Si/Ge system. Several reports have already been done on optical characterizations of MOVPE-grown AlP/GaP superlattices, and the observed strong PL intensity and electroreflectance signal[5,6] were interpreted as pseudodirect transitions. However, strong PL intensity was found to be observed not only from AlP/GaP superlattices but also from nonperiodic AlP/GaP neighboring confinement structures (NCS's), which consist of adjacent AlP and GaP quantum wells (QW's) sandwiched by AlGaP barriers.[7] Therefore, localization of carriers is now recognized to be important for improvements of luminescence efficiency in indirect semiconductors.

Recently, Uchida *et al.* have observed an unusual phenomenon in the PL spectra of a series of AlP/GaP short-period superlattices under high magnetic fields.[8] In the Faraday configuration where magnetic fields are parallel to the growth direction of superlattices, PL intensity was found to decrease with increasing magnetic field. Also, the diamagnetic shift was absent and an anomalous redshift was observed. To explain this phenomenon, they proposed that a crossover between two closely located conduction bands, unfolded X_{XY} and folded $X_Z(\Gamma)$ states, might take place. On the other hand, they also pointed out that another interpretation based on the disordered interfaces would be possible. The first explanation requires the supperlattice symmetry, but the second is also applicable to nonperiodic samples such as NCS.

In this paper, we report on a magneto-PL study with field strengths of up to 40 T on a series of AlP/GaP NCS's with and without built-in tensile strain. Anomalous redshifts of PL peak energy and reductions of PL intensity, which are very similar to the phenomena observed in AlP/GaP superlattices, were observed in unstrained NCS with increasing magnetic field. Introduction of tensile strain to NCS drastically modified magnetic-field dependence of PL spectra. The redshift was quenched at a certain magnetic field, and the usual diamagnetic shift was observed. A crossover from a decreasing to an increasing PL intensity was also observed at the same magnetic field. Since the tensile strain is expected to modify the degree of exciton localization through potential fluctuations due to interface and/or strain randomness and also through a changeover of ground states from heavy hole to light hole, a competition between the confinement of carriers

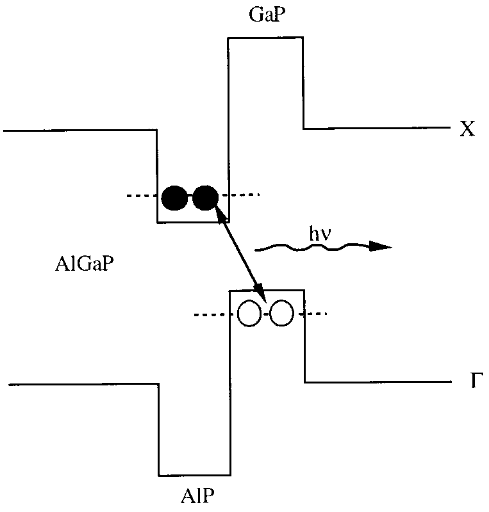

FIG. 1. Band structure of AlGaP-based NCS. Electrons and holes are separately confined in adjacent quantum wells.

induced *externally* by magnetic fields and *internally* by the potential geometry is likely the key for the explanation of the experimental observations.

II. NEIGHBORING CONFINEMENT STRUCTURE WITH TENSILE STRAIN

An NCS consists of adjacent QW's to separately confine electrons and holes as shown in Fig. 1. This quantum structure was originally proposed by Issiki *et al.* to improve luminescence efficiency of AlGaP-based semiconductor heterostructures.[7] Since the AlP/GaP heterointerface is type-II where the conduction-band edge of AlP is located below that of GaP, AlP (GaP) QW's with GaP (AlP) barriers confine only electrons (holes). However, by adopting NCS, both carriers can be confined in neighboring QW's. In spite of the spatial isolation of carriers, an appropriate choice of sample structure results in an overlap of the envelope functions which is comparable to type-I QW's. Moreover, strong Γ-X mixing effects can be expected by inserting a pair of AlP/GaP QW's, which leads to a breakdown of translational symmetry and therefore efficiently relaxes the selection rule of optical transitions. In fact, PL intensity of a single pair of NCS is reported to be comparable to AlP/GaP superlattices with a few hundred periods. NCS's have also been successfully applied to another indirect semiconductor system, SiGe/Si, and a remarkable enhancement of PL intensity and no-phonon dominant PL spectra have been reported.[9]

Recently, Ohta *et al.* have applied tensile strain to AlGaP-based NCS's by using relaxed-InGaP buffer layers for further improvement of luminescence efficiency.[10] Deformation-potential theory predicts that the introduction of tensile strain brings two beneficial modifications. The first is the enhancement of the Γ-X mixing effect through the different sign of hydrostatic deformation potentials of Γ and X points. Another is the increase of spatial overlap of envelope functions of electrons and holes through the decrease of the band offset at AlP/GaP interface. As expected, Ohta *et al.* observed an enhancement of PL intensity by the introduction of an appropriate amount of tensile strain. Unexpectedly, they observed the increase of the activation energy against thermal quenching in the strained NCS in spite of the decrease of the band offset. The formation of the deep bound states in the strained NCS was pointed out to be a possible explanation for the increase of the activation energy.

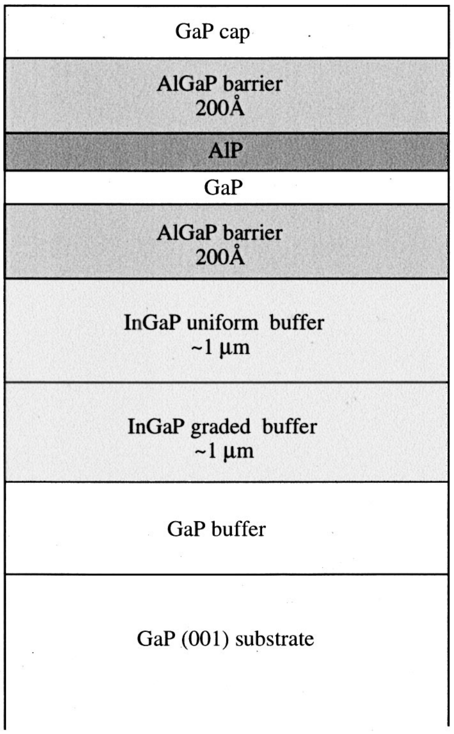

FIG. 2. Sample structure of AlGaP-based NCS with tensile strain. The amount of the tensile strain is controlled by In composition of strain-relaxed InGaP pseudosubstrates.

III. EXPERIMENTS

The samples were grown by gas-source MBE (VG-Semicon V80H) with phosphine (PH_3) for group-V sources and solid Al, Ga, and In for group-III sources. PH_3 was introduced to the growth chamber through a cracking cell at 1000 °C for thermal decomposition. The sample structure is illustrated in Fig. 2. The samples consist of a 3000-Å GaP buffer layer, 1-μm-graded and 1-μm-uniform $In_xGa_{1-x}P$ buffer layers ($x=0.053$ to 0.25), 10-Å-GaP/10-Å-AlP QW's embedded between 200-Å-AlGaP barrier layers, and a 50-Å-GaP cap layer. Since the lattice constant of InGaP is larger than that of AlGaP, all the layers on relaxed InGaP are tensilely strained. The amount of strain was controlled by changing In composition in the relaxed-InGaP buffer. The growth temperature was chosen as 630 °C for the NCS to obtain good crystal quality, and that of the $In_xGa_{1-x}P$ buffer layer was lowered to 550 °C for $x=0.093$ and 500 °C for $x=0.13$ and 0.26 to avoid reevaporation of In atoms. The composition of relaxed InGaP was measured by double-crystal x-ray diffraction.

Magneto-PL was performed under pulsed magnetic fields up to approximately 40 T at 4.2 K. The excitation was provided by an argon ion laser of 351 nm. PL spectra were collected with an optical multichannel analyzer (EG&G PARC OMA III) with exposure time of 1 ms at the top of the 12-ms field pulse. Since the variation of magnetic fields dur-

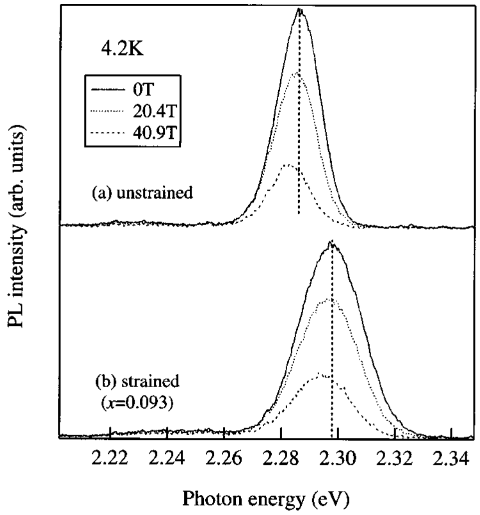

FIG. 3. PL spectra of (a) unstrained NCS and (b) strained NCS ($x=0.093$) with three different magnetic fields of 0, 20.4, and 40.9 T.

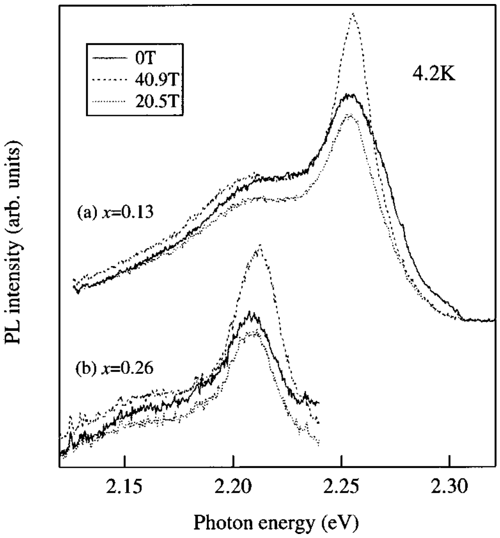

FIG. 4. PL spectra of highly strained NCS (a) $x=0.13$ and (b) $x=0.26$ with three different magnetic fields of 0, 20.4, and 40.9 T.

ing this exposure is typically less than 1%, it would be reasonable to believe that PL spectra were measured at a constant magnetic field. More detailed description of the instrumental setup can be found elsewhere.[8]

IV. RESULTS AND DISCUSSIONS

Figure 3 shows the PL spectra of (a) an unstrained NCS and (b) a strained NCS ($x=0.093$) with three different magnetic fields of 0, 20.4, and 40.9 T. All the spectra are dominated by no-phonon transitions, and phonon replicas are barely identifiable. The spectral features show that the selection rule of optical transitions is efficiently relaxed by the potential geometry of an NCS. The spectral linewidth of the strained sample is larger than that of unstrained sample, showing that significant inhomogeneity was induced by the strain. With increasing magnetic field, two drastic changes can be clearly observed. The PL peak shifts to lower energies and the PL intensity decreases. It is worth mentioning that the observed tendency is quite similar to the recent results reported by Uchida *et al.* for AlP/GaP superlattices.[8] Although they speculate that a crossover between the folded and unfolded conduction bands is responsible for this anomalous phenomenon, it should be emphasized that our sample contains only a single pair of AlP/GaP and the folding of the conduction bands cannot be expected.

Figure 4 shows that magneto-PL spectra of highly strained NCS, (a) $x=0.13$ and (b) $x=0.26$. In contrast to PL spectra in Fig. 3, phonon replicas can be clearly observed, indicating that the degree of localization of carriers is smaller than that in NCS with smaller tensile strain. This would be due to the fact that the changeover of ground states from heavy hole to light hole takes place at around $x=0.10$ (Ref. 10) and the wave function of holes in the growth direction is significantly expanded. PL spectra of an NCS with excess tensile strain can be seen to show quite different magnetic-field dependence. With increasing magnetic field from 0 to 20.5 T, the PL intensity slightly decreases and the PL peak shows almost no shift. However, a further increase of magnetic field up to 40 T results in a drastic increase of PL intensity, and spectral blueshift is clearly seen.

Figures 5 and 6 summarize the NP peak energy and the normalized PL intensity as a function of magnetic field. It is apparent that the four samples measured here are divided into two groups as symbolized with circles and triangles. The solid ($x=0$) and dotted lines ($x=0.13$) are calculated results based on a standard perturbation treatment of magnetic field for free excitons[11] where the heterointerfaces are assumed to be perfectly smooth and the magnetic field is treated like a harmonic confinement potential. The envelope functions of electrons and holes in the growth direction were obtained by numerically solving the Schrödinger equation with the potential geometry of the NCS deduced by the model solid theory.[12] Then, the binding energy of excitons was variationally calculated with a hydrogenlike $1S$ trial function with one variational parameter, λ,

$$\phi_{\mathrm{ex}}(r)=\left(\frac{2}{\pi}\right)^{1/2}\frac{1}{\lambda}e^{-r/\lambda},$$

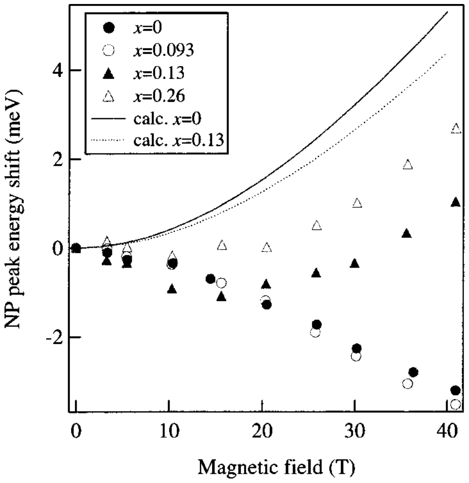

FIG. 5. Magnetic-field dependence of NP peak energy of NCS samples with various amounts of tensile strain. Calculated results based on a standard perturbation theory for free excitons are also shown.

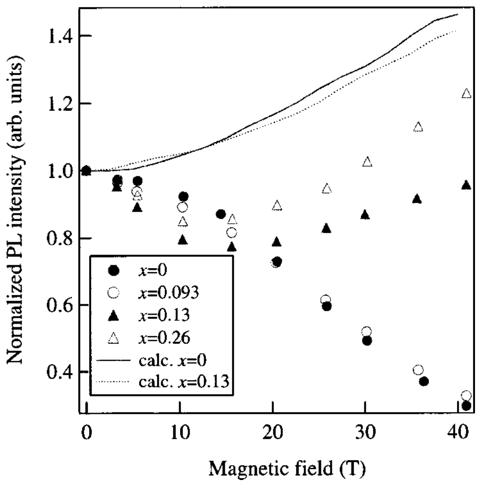

FIG. 6. Magnetic-field dependence of PL intensity of NCS samples with various amounts of tensile strain. The PL intensity was normalized by that without magnetic field.

where λ corresponds to the two-dimensional exciton radius. The PL intensity was calculated by assuming that it is proportional to $|\phi_{\mathrm{ex}}(0)|^2$. As can be seen in Figs. 5 and 6, this free-exciton picture predicts that the PL peak monotonically shifts to higher energies and PL intensity increases with increasing magnetic field.

These predictions are totally different from the experimental results and only describe the nature of the PL spectra of an NCS with large strain (triangles) and high magnetic field larger than 20 T. It is reasonable that excitons in an NCS with smaller strain (circles) are strongly localized, as can be imagined from the no-phonon dominant spectral shape. On the other hand, excitons in a highly strained NCS (triangles) are less localized since the PL spectra contain phonon replicas. Therefore, to fully explain the experimental results, it is important to consider excitons which are localized due to the interface roughness and/or the strain randomness. This is especially necessary for an NCS with small strain.

Recently, Kobayashi *et al.* calculated the PL intensity and the exciton binding energy of AIP/GaP superlattices in a magnetic field by considering bound excitons.[13] Their model includes a two-dimensional square well along the interface due to the interface roughness, and an assumption that the electrons are trapped in the well and bound excitons are formed through Coulomb interactions. By using an infinite barrier for the in-plane QW's and products of a Gaussian as a trial function, they deduced that the binding energy increases with increasing magnetic field. They also succeeded in reproducing the reduction of the PL intensity with increasing magnetic field. This was brought by the decrease of the spatial overlap of wave functions of electrons and holes since they assumed that the in-plane electron charge distribution is determined by the lateral size of the well and only holes experience lateral shrinkage with application of magnetic fields. The superlattice potential is included in the Hamiltonian for the variational calculation, however the resultant wave function in the growth direction is not spread out through the whole superattices but localized almost in a single period. Therefore, the same tendency is expected to be obtained by using the potential geometry of an NCS. However, an in-plane square well with an infinite barrier is unlikely to be formed by the interface roughness since 1-ML roughness gives change of the quantized energy of around a few tens of meV, which is much smaller than the band offset in the growth direction. Therefore, it is not appropriate to apply their model directly to our experimental results, but it does support the conclusion that the localization of excitons plays an important role for both superlattices and NCS's. To explain the experimental results of highly strained NCS's, it would be necessary to develop a model to describe an intermediate state between localized and free excitons.

V. SUMMARY

Magneto-PL spectroscopy with field strengths of up to 40 T was performed on a series of nonperiodic AlP/GaP NCS with and without built-in tensile strain. With increasing magnetic field, an anomalous redshfit of PL peak energy and an anomalous reduction of PL intensity, both of which were previously observed in AIP/GaP superlattices, were observed in unstrained NCS's. In highly strained NCS's, a crossover from a decreasing to an increasing of PL intensity and from a redshift to a blueshift of PL peak energy was observed at a certain magnetic field. It was pointed out that localized excitons are likely to play an important role to predict the experimental results.

ACKNOWLEDGMENTS

The authors would like to thank H. Kamimura, Y. Kobayashi, and K. Kouzu for fruitful discussions, R. Ferguson for his critical reading of this manuscript, and S. Ohtake for his technical support. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

---

[1] U. Gnuntzmann and K. Clausecker, Appl. Phys. **3**, 9 (1974).
[2] T. P. Preasall, J. M. Vandenberg, R. H. Hull, and J. C. Bonar, Phys. Rev. Lett. **63**, 2104 (1989).
[3] K. Asami, K. Miki, K. Sakamoto, T. Sakamoto, and S. Gonda, Jpn. J. Appl. Phys., Part 2 **29**, L381 (1990).
[4] J. Engvall, J. Olajos, H. Grimmeiss, H. Presting, H. Kibbel, and E. Kasper, Appl. Phys. Lett. **63**, 491 (1993).
[5] A. Morii, H. Okagawa, K. Hara, J. Yoshino, and H. Kukimoto, J. Cryst. Growth **124**, 772 (1992).
[6] K. Asami, H. Asahi, T. Watanabe, S. Gonda, H. Okumura, and S. Yoshida, Surf. Sci. **267**, 450 (1990).
[7] F. Issiki, S. Fukatsu, and Y. Shiraki, Appl. Phys. Lett. **67**, 1048 (1995).
[8] K. Uchida, N. Miura, J. Kitamura, and H. Kukimoto, Phys. Rev. B **53**, 4809 (1996).
[9] N. Usami, F. Issiki, D. K. Nayak, Y. Shiraki, and S. Fukatsu,

Appl. Phys. Lett. **67**, 524 (1995).

[10] T. Ohta, N. Usami, F. Issiki, and Y. Shiraki, Semicond. Sci. Technol. **12**, 881 (1997).

[11] M. Sugawara, N. Okazaki, T. Fujii, and S. Yamazaki, Phys. Rev. B **48**, 8848 (1993).

[12] C. G. Van de Walle and R. M. Martin, Phys. Rev. B **34**, 5621 (1986).

[13] Y. Kobayashi, K. Kouzu, and H. Kamimura, Solid State Commun. **109** 583 (1999).