Phonon bottleneck in self-formed $In_xGa_{1-x}As/GaAs$ quantum dots by electroluminescence and time-resolved photoluminescence

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We demonstrate experimentally that a photon bottleneck for carrier relaxation does exist in self-formed $In_xGa_{1-x}As/GaAs$ quantum dots. With time-resolved photoluminescence, we measured the carrier relaxation lifetime and radiative recombination lifetime in five discrete levels as a function of temperature. We found that the higher the temperature and the level were, the shorter the relaxation lifetime was (1 ns–10 ps). The radiative recombination lifetime measured was about 1 ns and was found to be independent of temperature. We also simulated electroluminescence spectra at 77 and 300 K with the measured lifetimes. We found that the first, second, and third levels could not be fully filled with injected carriers. [S0163-1829(96)50332-2]

After the zero-dimensional (0D) semiconductor structure (quantum dots) was shown to be promising for optoelectronic application,[1–3] the physics of the carrier relaxation between subband levels in the 0D system has been intensively studied. According to Bockelmann, the electron-phonon scattering rate is reduced drastically (to below $10^7\ s^{-1}$) in the 0D system due to the δ-function-like state density of the levels (the ''phonon bottleneck'' effect).[4] If the phonon bottleneck exists, practical application of quantum dots will be extremely limited. Benisty predicted that the low scattering rate in the 0D system will result in a long carrier relaxation lifetime between the levels (nanoseconds or longer), and that the slow relaxation rate will enhance the nonradiative recombination process.[5,6] Comparatively shorter lifetimes have been predicted with other theoretical approaches. Bockelmann stated that the lifetime may be in the picosecond order considering the Auger process[7] and electron-hole interaction.[8] Inoshita examined the LA±LO phonon process and reported that the lifetime can decrease drastically (to the subpicosecond order) when level spacing matches LO phonon energy.[9]

Due to the lack of high-quality semicondcutor microcrystals, the phonon bottleneck has not been closely examined experimentally. Reduction of photoluminescence (PL) intensity in III-V compound semiconductor dots prepared by lithography and regrowth was reported and used as a demonstration of the existence of phonon bottleneck effect.[10] However, defects introduced during the nanofabrication process require a more complex picture for PL intensity analysis. Low defect density has been achieved with the recently developed self-formed quantum dots via Stranski-Krastanow mode (the S-K dots).[11] Due to the low uniformity, however, carrier dynamics among subband levels in the dots has not yet been investigated. We have developed highly uniform self-formed $In_xGa_{1-x}As/GaAs$ quantum dots.[12] Our quantum dots are grown by alternate supply of precursors using the atomic layer epitaxy (ALE) technique while the ordinal S-K dots are grown by molecular-beam epitaxy (MBE) and metal-organic vapor-phase epitaxy (MOVPE). We have succeeded in observing the multiple discrete subband levels of the dots with measurement of PL (Ref. 13) and electroluminescence (EL).[14]

In this study, we examined the carrier relaxation lifetime and radiative recombination lifetime of five discrete levels in our self-formed $In_xGa_{1-x}As/GaAs$ quantum dots. By time-resolved photoluminescence (TR-PL), we measured the temperature dependence of the lifetime in five levels. The higher the temperature and the level were, the shorter the relaxation lifetime was. We simulated EL spectra with measured lifetime values, and our simulation collaborates well with the measured spectra.

Our $In_{0.5}Ga_{0.5}As$ quantum dots formed on a (001)-GaAs substrate during alternate supply of precursors using a supply sequence of ALE, instead of a short-periodic layer.[12,15] Their size is about 20 nm in the in-plane direction and 10 nm in the growth direction. There are some unique characteristics of these dots that cannot be found in the ordinal S-K dots. Our dots were involved within the $In_{0.1}Ga_{0.9}As$ quantum-well layer, which has almost the same thickness as the dots do ($\sim$10 nm). The band gap in the dots can be reduced to 0.8 eV—narrower than that of S-K dots ($\sim$1.1 eV). The full width at half maximum of PL spectra is 30–40 meV—suggesting the high uniformity (the typical value for S-K dots is 80–100 meV). In this study, we prepared two types of samples. Our ALE chamber is designed for pulse jet epitaxy where a high-speed stream of source gases is supplied in pulses. We used trimethylindium-dimethylethylamine adduct (TMIDMEA), trimethylgallium (TMGa), and arsine (AsH_3) to grow the quantum dots. The 18-cycle intermittent supply of (TMIDMEA)-(TMGa)-(AsH_3) with a H_2 carrier gas was administered to grow a quantum-dot layer that consists of the quantum dots and the quantum well surrounding the dots.[15] The growth temperature was 460 °C. Type-*A* samples have a simple structure and were used in every measurement for this study except for the EL measurement. A quantum-dot layer formed on a 0.5-μm-wide GaAs buffer layer, and was overlaid with a 0.1-μm-wide GaAs layer. The type-*B* sample was for EL measurement and was grown by three pieces of equipment to ensure sample quality. First, an *n*-type layer was grown in a conventional MOVPE chamber at 650 °C. Then, the quantum-dot layer and two sandwiching GaAs layers were grown in the ALE chamber. Finally, *p*-type layers were grown in an MBE chamber at 550 °C.

We measured the photoluminescence excitation (PLE)

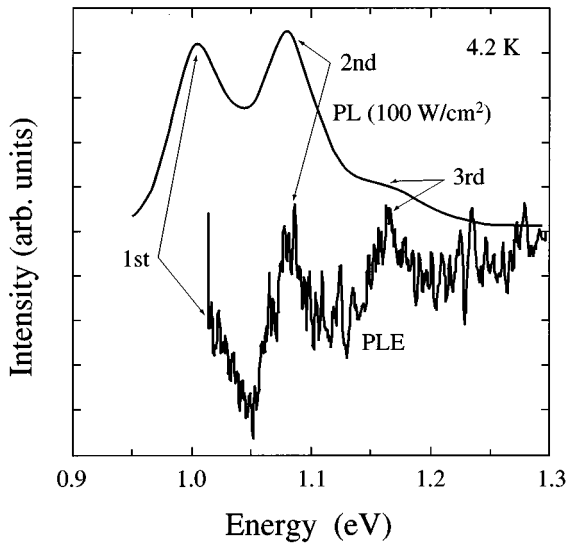

FIG. 1. PLE and PL spectra at 4.2 K. Discrete levels up to the third level were observed.

spectra of type-*A* samples at 4.2 K (Fig. 1). In the PLE measurement, we used a halogen lamp as the exciter. The excitation wavelength was controlled by a monochromater, and luminescence from the sample surface was monochromed and detected by a Ge detector. We monitored the luminescence at 1235 nm—the wavelength of the lowest-energy peak in the PL spectra (superimposed in Fig. 1). In PLE spectra, we can see two more peaks in addition to the lowest one. These peaks are at the same energy position as those in the PL spectra. We thus conclude that these peaks correspond to the subband levels in the dots. An additional argument can be found in our previous study where it had been demonstrated that, as the dot size decreases, the energy position of the first and the second peaks moves up towards the high-energy direction and the energy interval between the peaks also increases.[14] The size dependence suggests a quantum size effect at work. Note that the peak intensity of the PLE spectra does not suggest the state density of each level since the intensity depends on the carrier relaxation rate between levels. We think that the peak width is the result of the variation in size and composition among the dots, even though every dot has the δ-function-like emission spectra.

We studied the EL spectra of the type-*B* sample at 300 and 77 K [Figs. 2(a) and 2(b)]. In the measurement, luminescence parallel to the sample surface was dispersed and detected with a lock-in technique using an $In_xGa_{1-x}As$ photomultidetector kept at -70 °C. The electrode size was 20×900 μm^2, and injected current was spread to an area of $(150–200)\times 900$ μm^2 in the quantum-dot layer (estimated from the near field pattern). Three peaks corresponding to subband levels appeared at 300 K as the injected current was increased while five peaks appeared at 77 K. At both temperatures, emission from the levels appeared first in the low-energy position then gradually moved upward as the current increased. In other words, higher-level emission appeared before emission intensity of the lowest level reached the maximum value. The phenomena suggests the presence of bottleneck effect in this system. By comparing the spectra from the two temperatures, we can see that high-energy

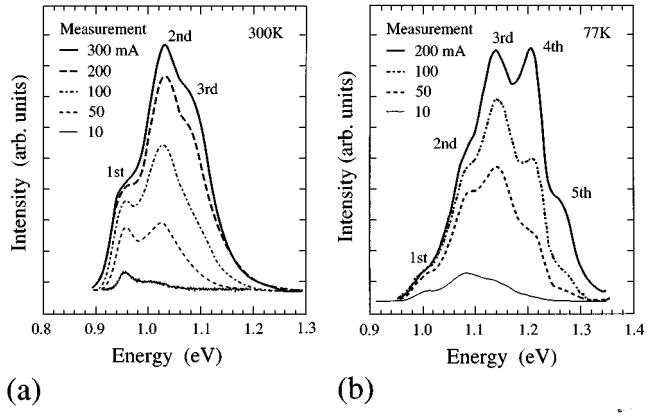

FIG. 2. Measured EL spectra at (a) 300 K and (b) 77 K.

peaks appeared earlier for 77 than for 300 K as the current increased. For instance, when the emission intensity of the first level reached half maximum, the intensity of the second level was stronger than that of the first level at 77 K (10 mA), but almost equal at 300 K (50 mA).

We also measured luminescence decay of the five levels as a function of temperature by the TR-PL system. In the measurement, the exciter was a mode-locked 532-nm Nd:YAG laser beam having a 200-ps pulse width. Luminescence from the sample surface was dispersed by a monochromater and time resolved with a streak camera (Streak Scope C4334, Hamamatsu Photonics). Samples were set in a temperature-controlled cryostat. Examples of the decay curves obtained are shown in Fig. 3. We found that the higher the temperature is, the faster the decay progresses, and that the lower the order of a level is, the more the decay progresses slowly.

In analyzing the decay curves, we assumed that the decay curves can be analyzed using a double-exponential curve fitting equation: $[\exp(-t/\tau_r)+\exp(-t/\tau_{0i})]$, where τ_r is the radiative recombination lifetime and τ_{0i} is the relaxation lifetime for the ith level. The second term is neglected in the

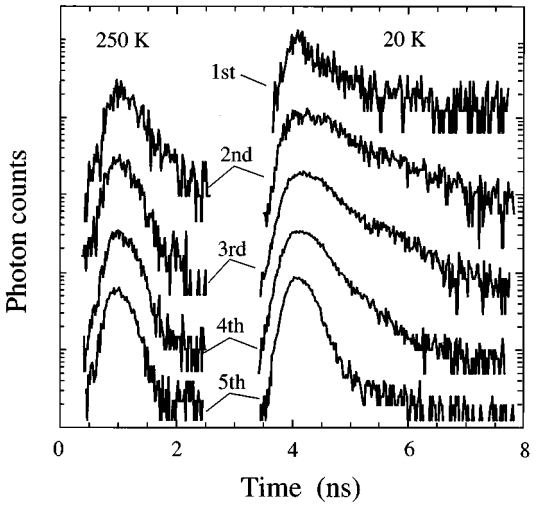

FIG. 3. Decay curves for the five subband levels in TR-PL at 250 and 20 K. The emission decay for the first level at 250 K was outside the detectable range of the measurement.

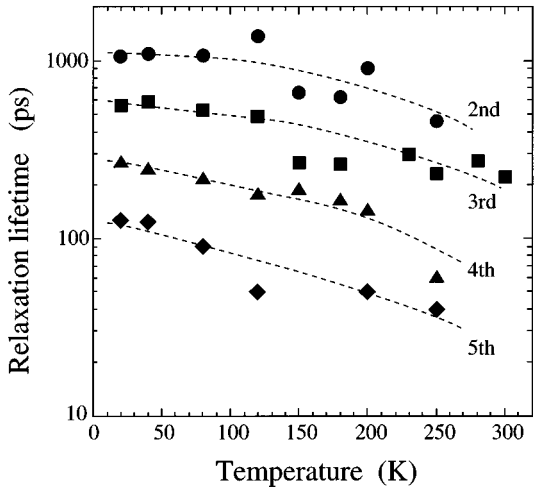

FIG. 4. Relaxation lifetime for the second to the fifth levels in quantum dots as a function of temperature.

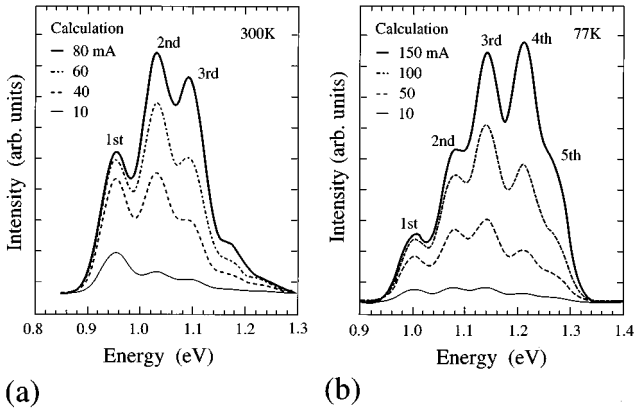

FIG. 5. Calculated EL spectra for (a) 300 K and (b) 77 K.

decay of the first level. This assumption is based on the following observation. Since level spacing in each dot is comparatively larger than the value of kT and the physical distance between the dots is too long (several–ten nanometers) for carriers to tunnel, carriers in one dot cannot move to another dot and each decay curve is the sum of decay in individual dots. Now, the carrier relaxation rate in one dot strongly depends on the number of carriers in the dot. Carriers cannot relax when the lower levels are filled (case 1). Relaxation is supposed to be faster than recombination when the lower levels are empty (case 2) since the lowest-energy peak was dominated at low carrier density in PL at every temperature. Considering that each level is fully filled with a few carriers, the decay process in each dot can be accordingly categorized into the above-mentioned two cases. After deconvoluting the decay curves with excitation pulse spectra by the double-exponential equation, we determined the lifetimes. We found that the two lifetimes in each level can be characterized as follows. One is relatively longer (0.7–1.8 ns) and independent of level order and temperature. The other is shorter (10 ps–1 ns), varies among the levels, and is temperature dependent (Fig. 4). We denote the former the radiative recombination and the latter the relaxation as described below.

The near-one-nanosecond lifetime and the temperature independence match well with predicted characteristics of the radiative recombination lifetime for quantum dots. In a previous study, we proposed a theory on the spontaneous emission lifetime of excitons in quantum dots and predicted that as the in-plane diameter of an exciton decreases to several nanometers, the lifetime will increase to a few nanoseconds.[16] Spontaneous emission rate is not very temperature dependent since the excitons in the quantum dots have discrete energy states. Experimentally, Wang *et al.* found the decay time for ground-state spontaneous emission of $In_xGa_{1-x}/GaAs$ quantum dots to be ~1 ns (Ref. 17), which is in good agreement with our results in this study.

Relatively shorter lifetime can be explained well if we treat it as a relaxation lifetime. As the order of the level increased from the second to the fifth, the lifetime decreased by one order in magnitude (Fig. 4). Since relaxation rate can be expressed in terms of the sum of all possible transitions between the levels, the relaxation lifetime of a level should decrease as the state density increases. Now, the state density is expected to be larger in higher levels.[14] In fact, we have observed in EL spectra that the maximum intensity increases as the level order increases. We also saw in the experiment that lifetime decreased as the temperature was raised from 20 to 300 K. This observation agrees with the increase in the number of phonons predicted by the Bose distribution function: $[\exp(\hbar\omega/kT)-1]^{-1}$.

We simulated EL spectra basing on the measured lifetimes with the following simplified model. We considered five discrete levels of electrons, and assumed that the hole quantization energies are so small due to the heavy mass that the thermalization of holes is achieved within some kT and radiative decay in all electron levels is allowed.[4] We then assumed that electron relaxation mainly occurs toward the neighboring level and that other types of relaxation are negligible. We also ignored the upward movement of electrons to other levels since the level spacing is much larger than the value of kT in this case. We assumed that the relaxation rate of one electron in the ith level (τ_i^{-1}) is proportional to the filled proportion of the $(i-l)$th level ($f_{i-1}; 0 \leqslant f_{i-1} \leqslant 1$): $\tau_i^{-1}=(1-f_{i-1})\tau_{0i}^{-1}$, where τ_{0i}^{-1} is the intrinsic relaxation rate in the ith level. Considering that the recombination lifetime τ_r is common to all levels, and neglecting nonradiative recombination, we calculated EL spectra at 300 and 77 K using the rate equations in five levels [Figs. 5(a) and 5(b)].[14] In the calculation, we used an in-plane dot area ratio of 5%, a broadening factor of 50 meV, $\tau_r=1$ ns, and $N_i=2i$ ($i=1$ to 5) taking the spin into consideration. The intrinsic relaxation lifetimes used were $\tau_{02}=400$, $\tau_{03}=200$, $\tau_{04}=50$, $\tau_{05}=20$ ps for 300 K, and $\tau_{02}=1000$, $\tau_{03}=500$, $\tau_{04}=200$, $\tau_{05}=90$ ps for 77 K.

Results of the calculation correlate very well with measured EL spectra. We can see that the relaxation lifetime is short enough to allow the dominance of the emission intensity for the first level at a small injected current. As the number of injected carriers increases, emission from the higher levels cannot be eliminated during carrier cascade toward the first level since the carrier relaxation rate τ_i^{-1} proportional to the filled proportion of the $(i-1)$th level. Since the intrinsic relaxation lifetime is closer to the radiative recombination lifetime at 77 K than at 300 K, the emission from higher levels appeared at comparatively smaller current

at 77 K. At 300 K, though the trend of relative peak intensities has been explained, the values of current obtained from calculation are much smaller than the measured values. This discrepancy in current values worsens when the injected current is large. We suspect that this discrepancy is attributable to the nonradiative recombination process. Carriers may have been trapped in defects in the quantum well surrounding the dots where the indium atoms are missing. High current injection increases local temperature and may, as a result, promote the nonradiative recombination process. At 77 K, there is a good agreement in current value between calculation and measurement which suggests a rather negligible influence on the nonradiative process.

We claim that the phonon bottleneck exists. As a result of the simulation, we found that the first, the second, and the third levels could not be fully filled, and that the maximum filled proportion of these levels depended on temperature. The maximum for the first and the second levels was about 80% at 300 K and 60% at 77 K, and for the third level it was 90% at 300 K and 80% at 77 K. When the emission from the first level was dominant, the filled proportion for the first level was 60% at maximum for 300 K. Where application to optical devices is concerned, the suppression of carrier filling extremely limits laser operation at the ground state. On the other hand, laser operation at a higher level is attainable since the relaxation lifetime at the fifth level is comparable to the carrier-capture time in $In_xGa_{1-x}As/GaAs$ quantum wells.[18] In fact, we have accomplished pulse laser operation at the sixth level with the same dots studied in this report.[19] The practical carrier relaxation lifetime matches the relatively shorter lifetimes predicted theoretically.[7–9] The dot-size dependence of the lifetime is one interesting subject which can be examined as a continuation of this study. If the drastic decrease of relaxation lifetime is attainable owing to the LO phonon as claimed by Inoshita,[9] further understanding of carrier behavior in an 0D system and promotion of this material to device application are expected.

To summarize, we have demonstrated experimentally that a phonon bottleneck for carrier relaxation exists in self-formed $In_xGa_{1-x}As/GaAs$ quantum dots. By TR-PL, we measured the carrier relaxation lifetime and radiative recombination lifetime in five discrete subband levels as a function of temperature. We found that the higher the temperature and the order of a level were, the shorter the relaxation lifetime was. The measured relaxation lifetimes were comparable to the measured radiative recombination lifetime even at 300 K. By EL spectra simulation, we showed that long relaxation lifetime caused emission from higher levels during carrier cascade toward the lowest energy level.

[1] Y. Arkawa and H. Sakaki, Appl. Phys. Lett. **40**, 939 (1982).
[2] L. Brus, IEEE J. Quantum Electron. **22**, 1909 (1986).
[3] D. S. Chemla and D. A. B. Miller, Opt. Lett. **11**, 522 (1986).
[4] U. Bockelmann and G. Bastard, Phys. Rev. B **42**, 8947 (1990).
[5] H. Benisty, C. M. Sotomayor-Torres, and C. Weisbuch, Phys. Rev. B **44**, 10 945 (1991).
[6] H. Benisty, Phys. Rev. B **51**, 13 281 (1995).
[7] U. Bockelmann and T. Egeler, Phys. Rev. B **46**, 15 574 (1992).
[8] U. Bockelmann, Phys. Rev. B **48**, 17 637 (1993).
[9] T. Inoshita and H. Sakaki, Phys. Rev. B **46**, 7260 (1992).
[10] K. Brunner, U. Bockelmann, G. Abstreiter, M. Walther, G. Bohm, G. Trankle, and G. Weimann, Phys. Rev. Lett. **69**, 3216 (1992).
[11] D. Leonard, M. Krishnamurthy, C. M. Reaves, S. P. DenBaars, and P. M. Petroff, Appl. Phys. Lett. **63**, 3203 (1993).
[12] K. Mukai, N. Ohtsuka, M. Sugawara, and S. Yamazaki, Jpn. J. Appl. Phys. **33**, L1710 (1994).
[13] K. Mukai, N. Ohtsuka, and M. Sugawara, Jpn. J. Appl. Phys. **35**, L262 (1996).
[14] K. Mukai, H. Shoji, N. Ohtsuka, and M. Sugawara, Appl. Phys. Lett. **68**, 3013 (1996).
[15] N. Ohtsuka and K. Muaki, in *Wavelength Controlability of InGaAs/GaAs Quantum Dots Emitting at 13 μm Region*, Proceedings of the 7th International Conference on InP and Related Materials (IEEE, New York, 1995).
[16] M. Sugawara, Phys. Rev. B **51**, 10 743 (1995).
[17] G. Wang, S. Fafard, D. Leonard, J. E. Bowers, J. L. Merz, and P. M. Petroff, Appl. Phys. Lett. **64**, 2815 (1994).
[18] L. Davis, Y. L. Law, Y. C. Chen, J. Singh, and P. K. Bhattacharya, IEEE J. Quantum Electron. **30**, 2560 (1994).
[19] H. Shoji, K. Mukai, N. Ohtsuka, M. Sugawara, T. Uchida, and H. Ishikawa, IEEE Photonics Technol. Lett. **7**, 1385 (1995).