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Effects of thermal annealing on the emission properties of type-II InAs/GaAsSb quantum dots

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We report the effects of thermal annealing on the emission properties of type-II InAs quantum dots (QDs) covered by a thin $GaAs_{1-x}Sb_x$ layer. Apart from large blueshifts and a pronounced narrowing of the QD emission peak, the annealing induced alloy intermixing also leads to enhanced radiative recombination rates and reduced localized states in the GaAsSb layer. Evidences of the evolution from type-II to type-I band alignments are obtained from time-resolved and power-dependent photoluminescence measurements. We demonstrate that postgrowth thermal annealing can be used to tailor the band alignment, the wave function overlaps, and hence the recombination dynamics in the InAs/GaAsSb type-II QDs. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3062979]

Recently self-assembled InAs quantum dots (QDs) with a thin antimony-containing capping layer [e.g., (In,Al)GaAsSb] have attracted much attention because of its great capability of extending the emission wavelength toward 1.5 μm or beyond.[1–5] In particular, it was found that the $InAs/GaAs_{1-x}Sb_x$ QDs exhibit a type-II band alignment when the Sb composition exceeds ~14%.[1] Experimental evidences have been obtained from power-dependent photoluminescence (PL) (Ref. 3) and time-resolved PL (TRPL)[6,7] measurements. Due to the spatial separation of electrons and holes in the type-II QDs, the carrier lifetime should be much longer[6–10] than their type-I counterparts (i.e., InAs/GaAs QDs). Such spatially indirect excitons with long carrier lifetimes and the confinement of only one carrier species make the type-II QDs very promising for many applications, such as solar cells[11] and optical memory devices. Therefore, tailoring of the band alignment, the wave function overlaps and hence the carrier dynamics is necessary for practical applications. For the $InAs/GaAs_{1-x}Sb_x$ type-II QDs, these parameters can be tuned by varying the Sb composition in the GaAsSb layer.[1] An alternative approach is the use of postgrowth thermal annealing to smooth the valence band (VB) discontinuity at the InAs–GaAsSb interface by the annealing induced alloy intermixing.

In this letter, we employed PL and TRPL spectroscopes to investigate the emission properties of the $InAs/GaAs_{1-x}Sb_x$ type-II QDs after thermal annealing at temperatures ranging from 700 to 900 °C. The annealing induced changes in the band alignment, the carrier dynamics, and electronics structures due to the alloy intermixing were observed and discussed.

Self-assembled InAs QDs were grown by molecular beam epitaxy on GaAs substrates. The type-II QDs were formed by depositing 2.7 ML of InAs on a 200 nm thick GaAs buffer layer at 500 °C and subsequently capped by a 4.5 nm $GaAs_{1-x}Sb_x$ layer with a nominal $x=0.16$. A sample with GaAs covered InAs QDs was also grown as a reference of type-I QDs. Atomic force microscopy of uncapped samples reveals that the QDs are lens shaped, with an average height of $\approx 8(\pm 0.5)$ nm, a diameter of ≈ 20 nm, and a density of 3×10^{10} cm^{-2}. Finally, the QDs were capped by a 50 nm GaAs layer. Postgrowth rapid thermal annealing for the GaAsSb covered sample was performed at annealing temperatures T_A ranging from 700 to 900 °C for 20 s using GaAs proximity capping. PL was excited by an argon ion laser (488 nm), analyzed by a 0.5 m monochromator, and detected by an InGaAs photomultiplier tube. TRPL were performed using either a 200 fs Ti:sapphire laser (780 nm/80 MHz) or a 50 ps pulsed laser diode (405 nm/5 MHz). The decay traces were recorded using the time-correlated single photon counting technique with an overall time resolution of ~150 ps.

Figure 1(a) shows the PL spectra for the as-grown and the annealed QD samples measured at 10 K under a low excitation power of 0.5 mW. The PL spectrum for the type-I InAs/GaAs QDs is also shown for comparison. With the increasing T_A, a blueshift and a narrowing of the QD's emission peak were observed.[12–17] The energy blueshift is caused by the alloy intermixing between the QDs and barrier materials, which shallows the QD's confining potential due to the

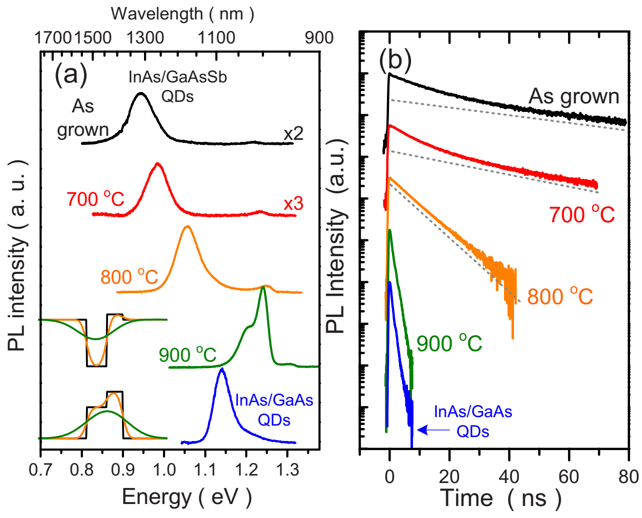

FIG. 1. (Color online) PL spectra (a) and TRPL decay traces (b) for the as-grown and annealed InAs/GaAsSb QDs, together with the reference InAs/GaAs QDs.

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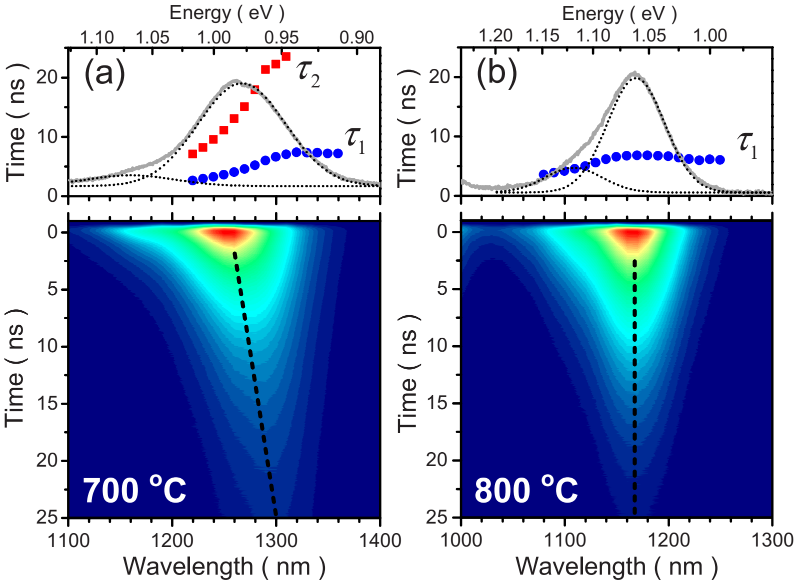

FIG. 2. (Color online) Energy dependent carrier lifetimes and time evolution of the PL spectra for the samples annealed at (a) 700 °C and at (b) 800 °C.

incorporation of more Ga atoms into the InAs QDs.[12–17] For the as-grown sample, it has been confirmed in our previous study[7] that the InAs/GaAs$_{0.84}$Sb$_{0.16}$ QDs exhibited a type-II band lineup, where the radiative recombination occurs between the electrons confined in the QDs and the holes in the GaAsSb layer. Annealing induced alloy intermixing also tends to smooth the VB discontinuity at the InAs–GaAsSb interface. Therefore, the electron-hole wave function overlaps and hence the radiative recombination rate is expected to be enhanced or even changed gradually to type-I transitions after thermal annealing.

To understand the effects of thermal annealing on the recombination dynamics in the type-II QDs, TRPL measurements have been performed and the results are shown in Fig. 1(b). The PL decay time was found to decrease with the increasing T_A, indicative of a more penetrated hole wave function into the InAs QDs due to the reduced VB offset caused by alloy intermixing at the InAs–GaAsSb interface. In particular, we found that the decay transient for the 900 °C annealed QDs became as fast as the InAs/GaAs type-I QDs. This implies that the QD structure has been changed to a type-I band alignment after high-temperature annealing.

In principle, the recombination lifetime can be quantitatively deduced from the measured PL decay transients. However, the determination of recombination lifetime is not straightforward for a type-II system. One complication arises from the effect of nonequilibrium carriers: as the carriers recombine continuously, the PL shifts to lower energies due to the reduced VB bending surrounding the QDs.[3–10] Therefore, the decay transient recorded at a given wavelength does not reflect the true lifetime since the PL decay arises not only from the carrier recombination but also from the temporal PL shift. For the InAs/GaAsSb material system, the carrier dynamics is further complicated by the presence of localized hole states in the GaAsSb layer due to alloy fluctuations and/or Sb clustering.[7] The redistribution of holes among these localized states also significantly influences the overall carrier dynamics, particularly at low temperatures.[7] In order to clarify the role of both effects (i.e., the nonequilibrium carriers and the localized states) in the PL transients, energy dependent TRPL has been performed. The results for the 700 and 800 °C annealed QDs are shown in Figs. 2(a) and 2(b), respectively. For the 700 °C annealed QDs, a clear temporal PL redshift can be observed. Since the excitation power was kept low, the effect of nonequilibrium carriers is expected to be less significant. In fact, an even more pronounced temporal PL shift was observed for the as-grown sample. Thus we ascribe the temporal PL redshift to the effect of hole localizations in the GaAsSb layer. On the contrary, the temporal PL redshift was absent for those QDs annealed at $T_A \geq 800$ °C. This indicates that the localized hole states have been removed by the annealing induced alloy intermixing. The temporal PL redshift is closely related to the nonsingle-exponential decay observed in PL transients shown in Fig. 1(b). Investigations of all samples revealed that the temporal PL redshift can be observed only when the decay transient is nonsingle exponential. By using a double exponential function $I(t)=A_1e^{-t/\tau_1}+A_2e^{-t/\tau_2}$ to fit the PL decay recorded at each wavelength, the decay time constants τ_1 and τ_2 for the faster and the slower decay components can be obtained. The fitted results are shown in the upper panel of Fig. 2, along with its time integrated PL spectrum. For the 700 °C annealed QDs, both τ_1 and τ_2 show strong energy dependences, indicative of hole transfers among localized states in the GaAsSb layer.[7] For the 800 °C annealed QDs, we found that τ_1 is almost unchanged across the ground state emission band.

The energy dependent lifetime can be described by $\tau(E)=\tau_{\mathrm{rad}}/\{1+\exp[(E-E_{\mathrm{me}})/E_0]\}$, where τ_{rad} is the radiative lifetime, E_0 describes the localization depth, and E_{me} is the energy similar to the mobility edge.[18] Figure 3 shows the radiative recombination rate $(\tau_{\mathrm{rad}}^{-1})$ deduced from the energy dependent lifetime for all annealed samples. The measured τ_{rad}^{-1} increases slightly from 0.095 ns^{-1} for the as-grown sample to 0.15 ns^{-1} after annealing at $T_A=800$ °C, but still about an order of magnitude lower than the InAs/GaAs type-I QDs (1.25 ns^{-1}). The low recombination rates indicate that their band lineups remain type-II, with an electron-hole wave function overlap of only ~28%–35% of the type-I QDs. As T_A was increased to 900 °C, the recombination rate increases dramatically to $\tau_{\mathrm{rad}}^{-1}=1.2$ ns^{-1}, which is

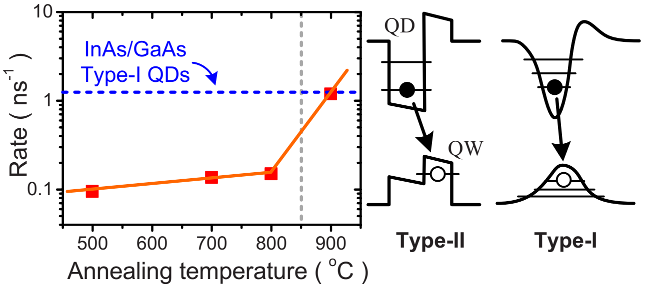

FIG. 3. (Color online) Radiative recombination rate τ_{rad}^{-1} as a function of the annealing temperature. The data from the as-grown sample are plotted at 500 °C.

very close to that of the type-I QDs, and confirms the band alignment change after annealing.

In order to examine whether the QDs are still present after high-temperature annealing, rather than evolving into a quantum-well-like structure, we have also measured the power-dependent PL spectra for the annealed samples. Figure 4 shows a comparison among the power-dependent spectra for the QDs annealed at 700, 800, and 900 °C. With the increasing excitation power (P_{ex}), higher energy peaks become observable for all samples due to the state-filling effect, which is a feature specific to a zero-dimensional system.[13,15–17] This demonstrates unambiguously that the annealed structures remain as QDs even after 900 °C annealing. The peak energy shifts in the power-dependent spectra also provide evidences for the band alignment changes after thermal annealing. For the 700 °C annealed QDs, the QD peaks shift linearly with $P_{\text{ex}}^{1/3}$, i.e., a fingerprint of type-II transitions.[3] This feature is not observed for the QDs annealed at 900 °C, confirming their type-I alignment. The most interesting is the case annealed at 800 °C, where the peak blueshift is observed at lower excitation powers but becomes nearly unchanged for $P_{\text{ex}} > 5$ mW. This behavior can be explained by an evolution from the type-II to type-I recombination induced by the large VB bending surrounding the QDs. After 800 °C annealing, the VB offset at the InAs-GaAsSb interface has been reduced by the alloy intermixing. To confine holes around the QDs and retain a type-II recombination, the VB bending should be weak and the excitation power must be low. When a large amount of nonequilibrium electrons was injected into the QDs by a higher P_{ex}, a very strong VB bending will exhibit in the QD surrounding. This makes the small VB offset unable to support confined hole states in the QD surrounding, leading to a gradual evolution from a type-II to a type-I transition.

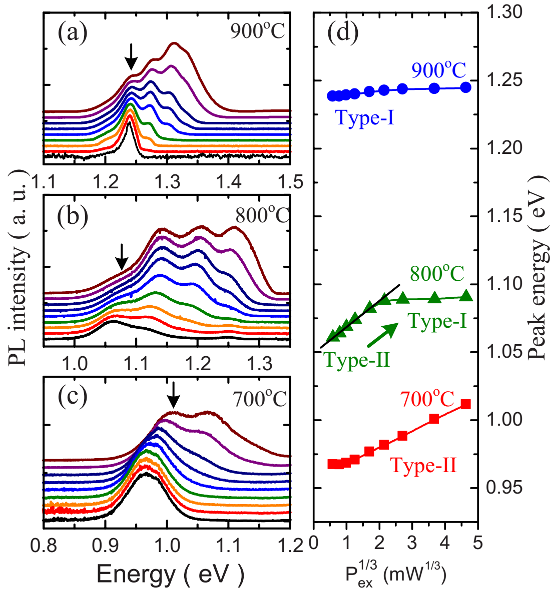

FIG. 4. (Color online) Power dependent PL spectra for the samples annealed at (a) 900 °C, (b) 800 °C, and (c) 700 °C. (d) The peak energy of QD ground state as a function of $P_{\text{ex}}^{1/3}$.

In summary, the emission properties of the InAs/GaAs$_{1-x}$Sb$_x$ type-II QDs after thermal annealing have been investigated. Apart from large blueshifts and a pronounced narrowing of the QD emission peak, alloy intermixing also lead to enhanced recombination rates and reduced localized states in the GaAsSb layer. The type-II QD structure has evolved into a type-I alignment after 900 °C annealing. We found that it is possible to manipulate between type-I and type-II recombinations in annealed QDs by using different excitation powers. We demonstrated that postgrowth annealing can be used to tailor the band alignment, the wave function overlaps, and hence the recombination dynamics in the InAs/GaAsSb type-II QDs.

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[1] H. Y. Liu, M. J. Steer, T. J. Badcock, D. J. Mowbray, M. S. Skolnick, P. Navaretti, K. M. Groom, M. Hopkinson, and R. A. Hogg, Appl. Phys. Lett. **86**, 143108 (2005).

[2] J. M. Ripalda, D. Granados, Y. Gonzalez, A. M. Sanchez, S. I. Molina, and J. M. Garcia, Appl. Phys. Lett. **87**, 202108 (2005).

[3] C. Y. Jin, H. Y. Liu, S. Y. Zhang, Q. Jiang, S. L. Liew, M. Hopkinson, T. J. Badcock, E. Nabavi, and D. J. Mowbray, Appl. Phys. Lett. **91**, 021102 (2007).

[4] W.-S. Liu, D. M. T. Kuo, J.-I. Chyi, W.-Y. Chen, H.-S. Chang, and T. M. Hsu, Appl. Phys. Lett. **89**, 243103 (2006).

[5] P.-C. Chiu, W.-S. Liu, M.-J. Shiau, J.-I. Chyi, W.-Y. Chen, H.-S. Chang, and T.-M. Hsu, Appl. Phys. Lett. **91**, 153106 (2007).

[6] Y. D. Jang, T. J. Badcock, D. J. Mowbray, M. S. Skolnick, J. Park, D. Lee, H. Y. Liu, M. J. Steer, and M. Hopkinson, Appl. Phys. Lett. **92**, 251905 (2008).

[7] W.-H. Chang, Y.-A. Liao, W.-T. Hsu, M.-C. Lee, P.-C. Chiu, and J.-I. Chyi, Appl. Phys. Lett. **93**, 033107 (2008).

[8] U. E. H. Laheld, F. B. Pedersen, and P. C. Hemmer, Phys. Rev. B **52**, 2697 (1995).

[9] C.-K. Sun, G. Wang, J. E. Bowers, B. Brar, H.-R. Blank, H. Kroemer, and M. H. Pilkuhn, Appl. Phys. Lett. **68**, 1543 (1996).

[10] F. Hatami, M. Grundmann, N. N. Ledentsov, F. Heinrichsdorff, R. Heitz, J. Böhrer, D. Bimberg, S. S. Ruvimov, P. Werner, V. M. Ustinov, P. S. Kop'ev, and Zh. I. Alferov, Phys. Rev. B **57**, 4635 (1998).

[11] R. B. Laghumavarapu, A. Moscho, A. Khoshakhlagh, M. El-Emawy, L. F. Lester, and D. L. Huffaker, Appl. Phys. Lett. **90**, 173125 (2007).

[12] R. Leon, Y. Kim, C. Jagadish, M. Gal, J. Zou, and D. J. H. Cockayne, Appl. Phys. Lett. **69**, 1888 (1996).

[13] S. Malik, C. Roberts, R. Murray, and M. Pate, Appl. Phys. Lett. **71**, 1987 (1997).

[14] S. J. Xu, X. C. Wang, S. J. Chua, C. H. Wang, W. J. Fan, J. Jiang, and X. G. Xie, Appl. Phys. Lett. **72**, 3335 (1998).

[15] R. Leon, S. Fafard, P. G. Piva, S. Ruvimov, and Z. Liliental-Weber, Phys. Rev. B **58**, R4262 (1998).

[16] S. Fafard and C. Nì. Allen, Appl. Phys. Lett. **75**, 2374 (1999).

[17] T. M. Hsu, Y. S. Lan, W.-H. Chang, N. T. Yeh, and J.-I. Chyi, Appl. Phys. Lett. **76**, 691 (2000).

[18] S. F. Chichibu, T. Onuma, T. Sota, S. P. DenBaars, S. Nakamura, T. Kitamura, Y. Ishida, and H. Okumura, J. Appl. Phys. **93**, 2051 (2003).