Effects of interdiffusion on the band alignment of GeSi dots

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(Received 1 May 2001; accepted for publication 19 July 2001)

The interdiffusion effects on the band alignment of the GeSi dots embedded in Si matrix were studied by temperature- and excitation-power-dependent photoluminescence measurements. A different power-dependent behavior of the photoluminescence for the as-grown and the annealed samples was observed. It was suggested that the band alignments of the dots changed from type II to type I after annealing due to the Ge/Si interdiffusion. The decrease of the valence band offset, which was also induced by the Ge/Si interdiffusion, was observed from the temperature-dependent photoluminescence measurements. © *2001 American Institute of Physics.*
[DOI: 10.1063/1.1405152]

Recently, many studies have been focused on the growth mechanism, optical, and electrical properties of the self-assembled GeSi dots embedded in Si matrix.[1] The photoluminescence (PL) results showed that the band alignment for the as-grown dots is a type-II structure, which means that the conduction band of the dots is higher than that of the Si matrix ($\Delta E_c > 0$).[2–4] However, it is desirable to obtain the type-I dots which confine both electrons and holes within the dots for its many potential applications, such as single electron transistor and quantum computer.[5] It is worth noting that the band alignment of Ge_xSi_{1-x}/Si quantum well with x as low as 0.25 (Ref. 6) and 0.177 (Ref. 7) is type-I structure. This implied the possibility of reaching type-I GeSi dots with low Ge content. Since the Ge content in the as-grown GeSi self-assembly dots is around 50% although pure Ge atoms were deposited on the substrate during the dot growth,[1,8] it is important to find some ways to obtain type-I GeSi dots. Although it has been demonstrated that the thermal annealing could be a useful technique for tuning the optical properties of quantum structure,[9] few works were reported on the effects of interdiffusion on the band alignment of the GeSi dots.[10] In this letter, the effects of interdiffusion on the band alignment of the GeSi dots were studied. It will be shown that annealing is an effective method to modify the band alignment of the GeSi dots from type II to type I.

The sample was grown on Si (001) substrate by gas-source molecular beam epitaxy (MBE) with a Si_2H_6 gas source and a Ge effusion cell. After the growth of 100 nm Si buffer layers, ten layers of dots separated by Si spacer layers were grown at the temperature of 575 °C. The growth rates of Ge and Si were 0.38 and 4 nm/min, respectively. The thicknesses of the Ge and the Si spacer layer were 1.6 and 40 nm, respectively. Pieces of the sample were annealed for 5 min with temperatures varied between 650 and 900 °C by 50 °C steps using rapid thermal annealing in a nitrogen gas ambient.

The PL spectra of the as-grown and annealed samples measured at 4.5 K are shown in Fig. 1. In the PL spectrum of the as-grown sample, apart from the Si peaks, the spectrum consists of two separate components which are characteristics of the wetting layers (WL) and the GeSi dots, respectively. The broad PL peak of the dots could be deconvoluted into two Gaussian line-shaped peaks. After thermal annealing, the PL peaks shifted to higher energies due to the Ge/Si interdiffusion and the broad dots PL peaks evolved into two well separated peaks. For the sample annealed at 900 °C, only PL peaks from the dots and the Si substrate are observed. If the two deconvoluted Gaussian line-shaped PL peaks of the as-grown dots were due to the size distribution of the dots, the PL from the dots should become one narrower peak after annealing because the size of the dots be-

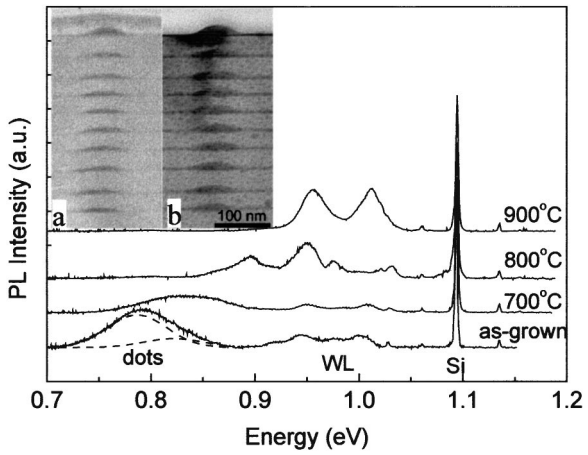

FIG. 1. PL spectra of the multilayer GeSi dots samples annealed at different temperatures. The PL intensities are normalized by Si TO peak. The PL line shapes and peak positions of the dots and the wetting layers change after annealing. The inset shows the cross-sectional TEM images of the as-grown sample (sample A) and the sample annealed at 900 °C for 5 min (sample B). TEM images show that the dots are still present after annealing. The scale in the images is 100 nm.

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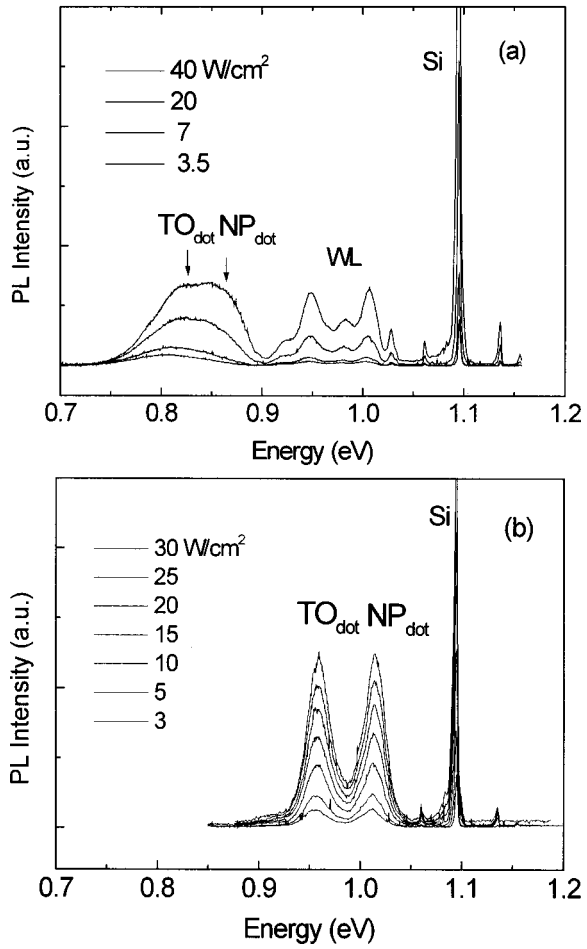

FIG. 2. Typical power-dependent PL spectra of (a) sample A and (b) sample B. The PL peak positions of the dots show different power-dependent behaviors for samples A and B.

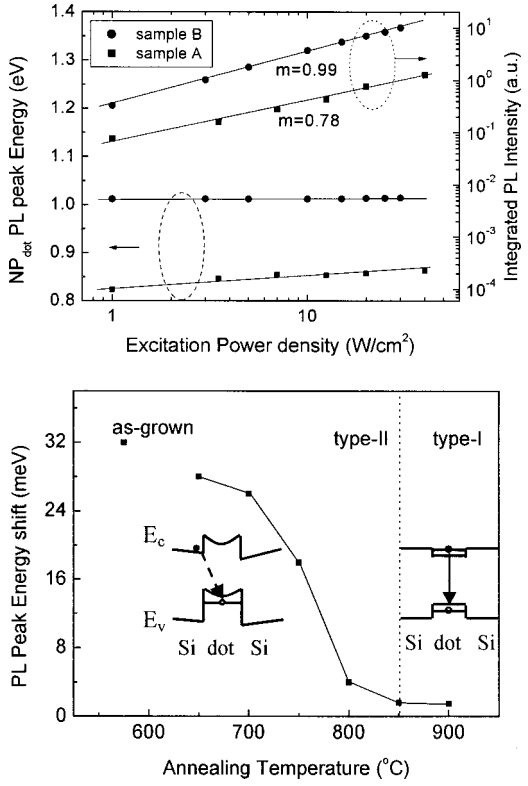

FIG. 3. (a) Power dependence of PL peak (NP_{dot}) energies and integrated PL intensity from the dots of samples A and B. (b) The power-dependent PL peak blueshifts (with the excitation power increased from 1 to 30 W/cm^2) for the as-grown and the samples annealed at different temperatures. The decrease of blueshift. indicates the decreasing band-bending effect after annealing. After 850 °C annealing, the band alignment of the dots changes to type I from type II.

came uniform after annealing, which is not our case. So the two deconvoluted PL peaks of the as-grown dots were attributed to the NP transition and TO replica (TO_{dot} and NP_{dot}). The insets in Fig. 1 show the typical bright-field cross-sectional transmission electron microscopy (TEM) images of as-grown sample (sample A) and the sample annealed at 900 °C for 5 min (sample B). It is observed that the dots are still present after annealing. For the as-grown sample, the average base and the height of the dots are 80 and 14 nm, respectively. After annealing in sample B, due to the Ge/Si interdiffusion, the average base and the height of the dots increase to 100 and 30 nm, respectively.

Typical PL spectra measured at 4.5 K with different excitation powers for samples A and B are shown in Fig. 2. Figure 3(a) shows the excitation-power dependence of NP_{dot} PL peak energies of sample A and sample B. For sample A, the NP_{dot} peaks show a linear blueshift of 32 meV with increasing excitation power from 1 to 30 W/cm^2. For sample B, the PL peak blueshift is only 1.5 meV with the same excitation power increment.

The power-dependent PL measurements were widely used to study the band alignment of the GeSi quantum dots,[2–4] SiGe/Si quantum well,[11,12] and III–V heterostructures.[13] In the type-II band alignment quantum structure, a band bending occurs at the interfaces due to the Hartree potential, as seen in the insets of Fig. 3(b). At higher excitation power, more photon induced electrons and holes result in a higher Hartree potential, and the potential upshifts the relative energies of electrons and holes states and results in the blueshift of PL band.[11] So, the significant PL blueshift of sample A indicates that the band alignment of the as-grown dot is type II, which is consistent with former studies on GeSi dots.[2–4]

In contrast to sample A, the NP_{dot} PL peak blueshift (1.5 meV) of sample B is much smaller than the value usually observed in Ge_xSi_{1-x}/Si type-II system. For example, even when the excitation power density increases from 1 to 4 W/cm^2, the blueshift was as large as ~3.6 meV, in a 3-nm-type-II $Ge_{0.3}Si_{0.7}$/Si quantum well.[12] This NP_{dot} PL peak blueshift (1.5 meV) of sample B is similar to the blueshift of the GeSi wetting layer, whose band alignment is type I,[4] so, the band alignment of sample B could be reasonably explained by a type-I band alignment and the blueshift is due to the band filling effect,[11] which is due to the finite density of states of the GeSi dots layer. The power dependence of the integrated PL intensities of the dots as shown in Fig. 3(a) further support the type-I band alignment of sample B. According to the formula $I \propto P^m$, where I represents the PL intensity and P the excitation power,[3] the coefficient m is found to be 0.78 and 0.99 for samples A and B, respectively. The sublinear power dependence of PL intensity of sample A is due to a typical saturation effects of the type-II alignment. In type-II alignment, the indirect excitons are first localized at the interfaces, and then recombine. As the interface state

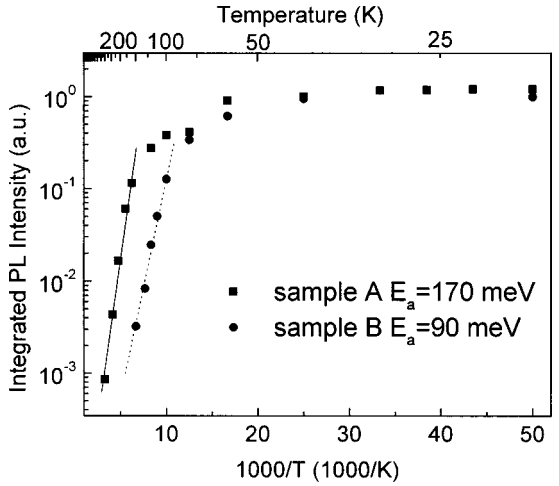

FIG. 4. Temperature dependence of integrated PL intensities from the dots of samples A and B. The fitted lines are also shown, from which the thermal activation energy E_a is determined. The lower thermal activation energy of sample B indicates that the valence band offset decreases after annealing.

density is finite, the PL intensity quickly saturates and $m<1$.[3,4] For sample B, $m\sim1$ and the linear relationship without saturation confirms the type-I band alignment.

The power-dependent PL peak blueshifts (with the excitation power increased from 1 to 30 W/cm^2) for the as-grown and the samples annealed at different temperatures are shown in Fig. 3(b). It is observed that the magnitude of the blueshift decreases with the increase of the annealing temperature. The decrease of the magnitude of the blueshift in the type-II quantum well structure has two possible reasons: one is the decrease of the well width and another one is the decrease of the conduction band offset.[8] In our samples, the height of the dots (compared with the well width in type-II quantum well structure) increased after annealing, so the decrease of the conduction band offset ΔE_c is the only reason for the decrease of the magnitude of the blueshift.

The decrease of the conduction band offset is induced by the Ge/Si interdiffusion during annealing. With the increase of the annealing temperature, due to the Ge/Si intermixing, the Ge content in the dots decreases. As a result, the conduction band offset ΔE_c decreases because ΔE_c decreases with the decrease of Ge content.[14–16] The Ge content in the as-grown dots grown by our gas-source MBE was determined to be 0.42 by using x-ray diffraction techniques.[8] After annealing, the Ge content in the GeSi dots would decrease due to the Ge/Si interdiffusion.[10] For sample B, the volume of the dots increases about 3.3 times (calculated from TEM data), so the average Ge content in the dots is estimated to be $\sim$0.13. For the Ge_xSi_{1-x}/Si quantum well structure with similar Ge content, the experiments showed that band alignment was type I for $x=0.25$ (Ref. 6) and $x=0.177$.[7] So the type-I band alignment of the dots annealed above 850 °C is reasonable.

The normalized integrated PL intensities from the dots as the function of measurement temperatures for samples A and B are shown in Fig. 4. According to the formula $I(T)=I(0)/[1+A(T)\exp(-E_a/kT)]$, where I is intensity, T is temperature, $A(T)$ is the coefficient, E_a is an activation energy, and k is Boltzmann's constant, the slopes of the straight lines at higher measurement temperature give the thermal activation energy E_a, which is related to the depth of the dot confining potential.[9] In GeSi dot/Si system, since the conduction band offset of the GeSi on Si is small, this activation energy at higher measurement temperature mainly reflects the valence band offset between the dots and the Si matrix (and/or the wetting layer). The activation energies for samples A and B are fitted to be 170 and 90 meV, respectively, as shown in Fig. 4. The smaller activation energy in sample B indicates the decrease of the valence band offset caused by the Ge/Si interdiffusion.

In conclusion, the interdiffusion effects on the band alignment of the GeSi dots were studied. The TEM image showed that the dots were dislocation-free and the dots still present after annealing. For the as-grown GeSi dots, the PL peaks of the dots showed a large blueshift (32 meV) when the excitation power increased from 1 to 30 W/cm^2. After annealing, the magnitude of the blueshift decreased. For the samples annealed above 850 °C, the blueshift decreased to 1.5 meV. The different power-dependent PL behavior indicated that the band alignment of the dots changed from type II to type I due to the decrease of the Ge content in the dots. The decrease of the valence band offset was observed from the temperature dependent photoluminescence measurements.

The authors acknowledge partial support by ARO and Semiconductor Research Corporation. The Australian Research Council is also acknowledged for their financial support.

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