Ge/Si interdiffusion in the GeSi dots and wetting layers

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(Received 1 March 2001; accepted for publication 23 July 2001)

The Ge/Si interdiffusion in GeSi dots grown on Si (001) substrate by gas-source molecular beam epitaxy is investigated. Transmission electron microscopy images show that, after annealing, the aspect ratio of the height to base diameter increases. Raman spectra show that the Si–Ge mode redshifts and the intensity of the local Si–Si mode increases with the increase of annealing temperature, which suggests the Ge/Si interdiffusion during annealing. The photoluminescence peaks from the dots and the wetting layers show blueshift due to the atomic intermixing during annealing. The interdiffusion thermal activation energies of GeSi dots and the wetting layers are 2.16 and 2.28 eV, respectively. The interdiffusion coefficient of the dots is about 40 times higher than that of wetting layers and the reasons were discussed. © *2001 American Institute of Physics.*
[DOI: 10.1063/1.1403667]

Self-assembled quantum dots have attracted extensive interest due to their appealing properties and potential applications.[1–3] Many studies have been performed on the growth and optical properties of GeSi quantum dots.[1,2] Light emitting diode[4] and photodiode[5] based on the GeSi quantum dots grown on Si substrates have been fabricated. Normally device fabrication needs a high-temperature process and the operation involves high temperatures as well. In addition, thermal annealing could be a useful technique for tuning the optical properties of quantum structures.[6] Thus, it is necessary to study the thermal stability and the atomic interdiffusion of the quantum dots at high temperatures. However, although the interdiffusion in Si/Ge quantum wells at high temperatures has been widely studied,[7–12] little work has been done on the interdiffusion in the GeSi dots grown on the Si substrate except for the annealing effects on carbon-induced GeSi dots in Si.[13] In this communication, the Ge/Si interdiffusion in the GeSi dots was studied using transmission electron microscopy (TEM), Raman, and photoluminescence (PL) spectroscopy. The atomic interdiffusion coefficient and thermal activation energy were calculated from the PL peak shifts. In addition, the interdiffusion in the wetting layer (WL), which is an inevitable result of the Stranski–Krastanow growth mode upon reaching a strain-defined critical thickness, was studied and compared with that of the GeSi dots.

The sample was grown on Si (001) substrate by gas-source molecular beam epitaxy with a Si_2H_6 gas source and a Ge effusion cell. Ten layers of dots separated by Si spacer layers were grown at the temperature of 575 °C. 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 varying between 650 and 900 °C by 50 °C steps using rapid thermal annealing in a nitrogen gas ambient. The PL measurements were performed by excitation of an Ar^+ laser and with a liquid nitrogen cooled Ge detector.

Figure 1 shows two typical bright-field cross-sectional TEM images of the as-grown sample (sample A) and the sample annealed at 900 °C for 5 min (sample B). As shown in the images, the GeSi dots were still present and dislocation free after annealing. For the as-grown sample, the mean base and the height of the dots were 80 and 14 nm, respectively. For sample B, the mean base and the height of the dots changed to 100 and 30 nm, respectively. It was interesting to note that the base diameters of the dots increased slightly, but the height increased a lot and the aspect ratio of the height to base diameter of the dots increased from 0.18 to 0.30 after annealing.

The Raman spectra of the samples annealed at different temperatures are shown in Fig. 2. For the as-grown sample, besides a strong Si–Si vibrational mode at 520 cm^{-1}, three peaks were observed. The peak located around 300 cm^{-1} may be the sum of the Ge–Ge mode and the Si acoustic phonon. The peaks located at 437 and 415 cm^{-1} were ascribed to the local Si–Si and Si–Ge peaks, respectively. The local Si–Si peak was due to the localized Si–Si vibration in the neighborhood of one or more Ge atoms[14] in the dots and the WLs, which meant that the GeSi dots in our samples were the SiGe alloy. With increasing annealing temperature, these peaks showed different behaviors. The local Si–Si mode intensity increased, indicating that the amount of Si–Si bonds increased and the Ge content decreased in the dots and the WLs. The Si–Ge mode peak was observed to shift from 415 to 411 cm^{-1}, as seen in the inset, which could be attributed to the decrease of the Ge content in the dots and/or the WLs.[15]

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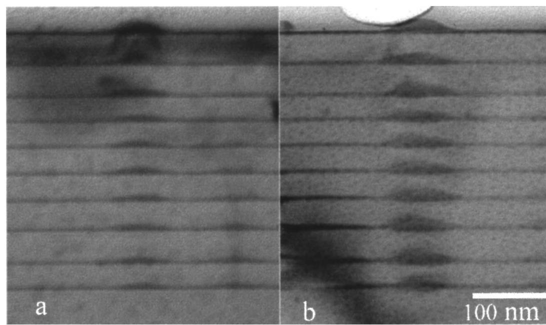

FIG. 1. Bright-field cross-sectional TEM image of ten stacked layers of GeSi dots grown on Si (001) substrate: (a) as-grown and (b) annealed at 900 °C for 5 min. TEM images show that the dots are dislocation free and the aspect ratios of the height to base diameter of the dots increase after annealing.

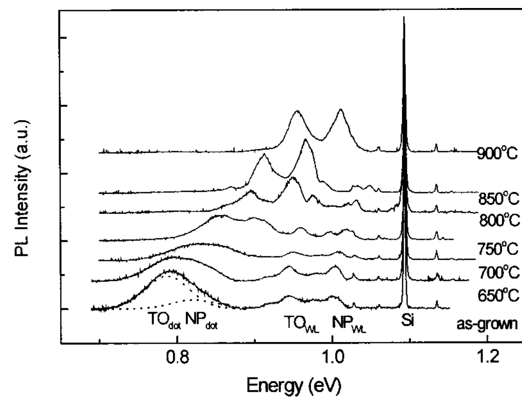

FIG. 3. PL spectra of multilayer GeSi dots annealed for 5 min at different temperatures. The PL intensities are normalized by Si TO peaks. The PL line shape and energy position for GeSi dots and the wetting layers changes after annealing.

The 4.5 K PL spectra of the as-grown and annealed samples are presented in Fig. 3. In the PL spectrum from the as-grown sample, apart from the Si peaks, two separate components which were characteristic of the WL and GeSi dots were observed. Two peaks located at 1.004 and 0.946 eV were attributed to the NP_{WL} transition and the TO_{WL} phonon-assisted transitions of the pseudomorphic wetting layers.[2] The broad PL peak located around 0.80 eV was assigned to the dots and it could be deconvoluted into two Gaussian line-shaped peaks at 0.822 and 0.780 eV, which were attributed to the NP_{dot} transition and the TO_{dot} phonon-assisted transitions of the dots. After thermal annealing, the PL peaks related to GeSi dots and the wetting layer shifted to higher energies. At the same time, the shape of the PL peak changed when the annealing temperatures increased and the broad dots PL peak evolved into two well separated peaks. For the sample annealed at 900 °C, only PL peaks from GeSi dots and Si substrate were observed.

The blueshift of the PL peaks with annealing arose from the change of the Ge content (band offset) and the shapes of the dots and wetting layers (confinement energy). Several models have been used to calculate the PL peak energies for the dot and the quantum well structures.[7–12] In our calculation, GeSi dots were simply treated as quantum boxes.[13] Because the base diameter of the GeSi dots (80 nm) were much larger than the heights (15 nm), the quantum confinement in the lateral direction was ignored. The wetting layers were treated as quantum wells. The excitonic luminescence energies of the wetting layers and the dots were calculated by using one-dimensional Schrödinger's equation for different well widths and box heights while keeping the total amount of Ge constant. In the calculation, we used the theoretical band offset given by Rieger and Vogl[16] and an empirical exciton binding energy.[10] The effective masses of the heavy hole were taken as $(0.278-0.07x)m_0$,[17] where m_0 and x are the free electron mass and Ge content, respectively. By fitting the excitonic luminescence energies of the dots and the wetting layers to the experimental data, we obtained the theoretical well width and box height for each annealing temperature. Then the diffusion coefficient Ds were calculated from the change of the well widths and the box heights.[3,9] The calculated Ds were plotted against $10^4/T$ as shown in Fig. 4. According to $D=D_0\exp(-E_a/kT)$ with the activation energy E_a, temperature T, and the prefactor D_0, the activation energies were fitted to be 2.16 and 2.28 eV for the dots and the wetting layers, respectively. D_0 was 1.48×10^{-6} and 1.06×10^{-7} cm^2/s for the dots and wetting layers, respectively. The activation energy of the wetting layer (2.28 eV) is close to the value 2.1–4.0 eV reported for the SiGe quantum well and superlattice structures.[7–12] However, the activation energy of the GeSi dots (2.16 eV) is higher than the reported data for cabon-induced GeSi dots in Si (1.6 eV) and the lower activation energy of the carbon-induced GeSi dots is due to the influence of the carbon atoms.[13]

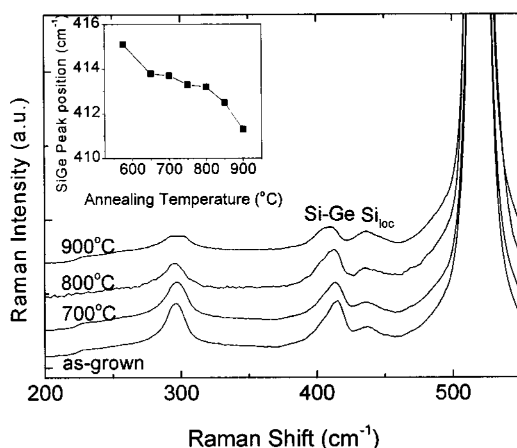

FIG. 2. Raman spectra of the multilayer GeSi dot samples annealed at different temperatures. With the increase of annealing temperature, the Ge–Si peaks show redshift and the intensity of the local Si–Si mode increases, which implies the Ge/Si intermixing during annealing.

It is noted that the interdiffusion coefficient for the GeSi dots is much higher (about 40 times) than that of the wetting layers. This difference is due to three reasons, as shown in the inset of Fig. 4: (1) The Ge content difference between the dots and the wetting layer. Investigations of single SiGe layer as well as superlattices indicated a significant enhancement of the interdiffusion for higher Ge concentrations.[11,12] For example, it was found that the diffusion coefficient at 900 °C of $Si_{0.54}Ge_{0.46}$ was about 1 order higher that of $Si_{0.8}Ge_{0.2}$.[11] It was theoretically calculated that the Ge con-

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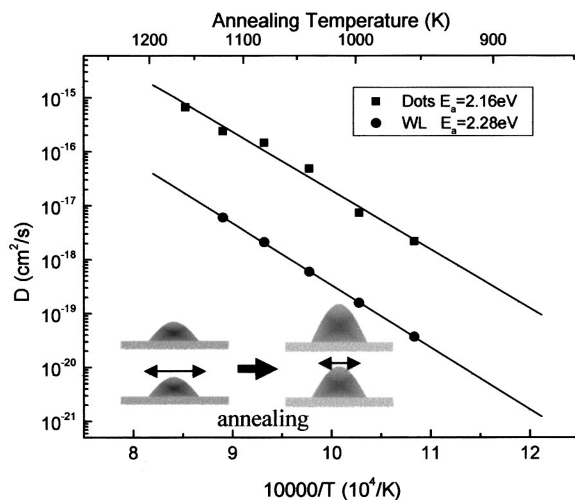

FIG. 4. Arrhenius plot of the interdiffusion coefficients D for the wetting layers and GeSi dots. The coefficient D of the dots is much higher than that of the wetting layers. The inset shows the schematic diagram of the annealing effect, showing the nonuniform Ge content in the dots and the wetting layers (darker shade of gray indicated higher Ge composition) and the tensile strain in the Si spacer layer (double-ended arrows).

tent in the GeSi dots is higher than that in the wetting layers, especially when the growth is limited by surface diffusion.[18] From the experimental point of view, it was also proposed that the Ge content in the dots is higher.[2] So the higher Ge content in the dots probably played an importment role on the enhancement of Ge/Si interdiffusion in the dots. (2) Nonuniform Ge content distribution inside the dots. It is suggested that the Ge content in the GeSi dots is not uniform and the dots have Ge-rich cores.[18] As the diffusion coefficient was proven to be strongly dependent on the local Ge concentration in the film,[8] the Ge/Si interdiffusion coefficient in the dots could be higher. (3) The tensile stain in the Si spacer on the top of the dots. For the GeSi dots, the Si spacer between the dots is tensily strained,[19] as indicated in the inset of Fig. 4. As observed in Fig. 1, after annealing the increase of the height was larger than that of the base, indicating the interdiffusion was mainly in the vertical direction. This implied that the tensile strain in the Si spacer layer also enhanced the Ge/Si interdiffusion.

In summary, the interdiffusion in the GeSi dots and the wetting layers grown on Si (001) substrate were studied by using TEM, Raman, and PL spectra. TEM images showed that the dots were dislocation free and the aspect ratio of the height to base diameter of the dots increased after annealing. The atomic intermixing during growth and annealing was also confirmed by Raman spectra, which showed the redshift of the Si–Ge mode and the increase of the local Si–Si mode intensity with the increase of annealing temperature. By fitting the blueshift of the PL from the dots and the wetting layers, the interdiffusion thermal activation energies for GeSi dots and the wetting layers were calculated to be 2.16 and 2.28 eV, respectively. The interdiffusion coefficient of the dots was much higher than that of the wetting layers and the reasons were discussed.

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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