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Optical Characterization of Ge Quantum Dots Grown by Using Rapid Thermal Chemical Vapor Deposition

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The optical properties of multi-stacked Ge quantum dots (QDs) grown on Si (100) by using rapid thermal chemical-vapor deposition have been studied by using photoluminescence (PL), high-resolution transmission electron microscopy (HRTEM), and atomic force microscopy (AFM). The HRTEM images demonstrate vertically ordered Ge QDs and full contrast between the Si spacer and the Ge QDs. With increasing growth temperature, the size and the height of the dots increase, but the dot density decreases, as confirmed by using AFM. The Ge QDs had a bimodal shape distribution with domes and pyramids coexisting at specific growth conditions. The two major emission bands observed in the PL spectra are attributed to non-phonon (NP) and transverse-optical (TO) phonon replica of the Ge QDs and they are blue-shifted with decreasing thickness of the Si spacer. The interdiffusion or intermixing effects of Ge QDs have been studied by annealing the samples at various temperatures. As the excitation power increases, the NP energy of the Ge QDs is shifted to higher energy, and a plot of PL intensity vs excitation power shows a sublinear behavior with powers of 0.68 and 0.75 for the NP and the TO PL peaks, respectively. The experimental results are discussed with reference to possible emission mechanisms of Ge QDs/Si.

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I. INTRODUCTION

Recently, self-assembled Ge QD structures have been of strong interest for their potential applications in optoelectronic devices such as light-emitting diodes and infrared photodetectors [1, 2]. Ge QDs usually arrange vertically on top of each other in subsequent layers and such vertical stacking is important for device applications. The structural and the optical properties of Ge QDs are greatly influenced by their arrangement [3, 4], which is associated with the strain controlled mostly by the thickness of the Si spacer and the growth temperature. Size distribution of QDs and their uniformity are also crucial for practical application. Systematic variations in the deposition parameters can lead to an understanding of the mechanisms controlling dot formation, thereby allowing uniform dots of the desired size to be obtained. One of the interesting observations is a bimodal distribution of Ge dots corresponding to two different shapes, pyramids and domes under certain growth conditions. Kamins *et al.* [5] have studied the formation of dome and pyramid shapes and the effect of annealing on the Ostwald ripening and size distribution. Several models have been proposed to explain the bimodal growth of Ge QDs [6, 7]. The variation of the composition in Ge QDs by intermixing during growth is one of the important issues in such materials because it can change the structure-property relationship of QDs [8]. The intermixing or interdiffusion behaviors have been studied through the annealing effects on photoluminescence (PL) [9]. It has been suggested that the band alignments of the dots change from type II to type I after annealing due to Ge/Si interdiffusion. The power dependence of

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the PL is also closely related with the band alignment [9,10].

In this paper, we report PL properties depending on the spacer thickness, the annealing temperature, and the excitation power for 10-stacked Ge QD layers grown by using rapid thermal chemical vapor deposition (RTCVD). We also discuss the experimental results with reference to possible emission mechanisms based on a type-II band structure of QDs.

II. EXPERIMENT

Ten-stacked Ge QDs with Si spacers of different thicknesses were grown on p-type (100) Si substrates by using RTCVD with SiH_4 and GeH_4 as source gases. The samples were grown on a Si buffer layer in the temperature range of 470 to 750 °C. The growth pressure was changed in the range of 100 to 200 mTorr. The QD multilyers consisted of 10 bilayers, each of which was composed of 6.5 monolayers of Ge and a Si-spacer layer of 15 to 100 nm in thickness. The samples underwent the following growth procedures: after baking at 1000 °C in hydrogen, a Si buffer layer of 210 nm was deposited on the Si substrate at 850 °C and self-assembled Ge QDs were then grown on top of the Si buffer layer. Atomic force microscopy (AFM) and high-resolution transmission electron microscopy (HRTEM) revealed that the Ge QDs had an average height of ∼16 nm and an average base length of ∼110 nm. The average density of the dots was estimated to be approximately 2×10^8 cm^{-2}. Annealing was done in a rapid thermal annealing (RTA) apparatus for 3 min by changing the temperature from 800 to 1050 °C in 50 °C steps.

All photoluminescence (PL) spectra were measured using the 488-nm line of an Ar-ion laser as the excitation source. For PL measurements, the specimen was mounted on the cold finger in the vacuum chamber (pressure $< 10^{-5}$ Torr) of a closed-cycle refrigerator. Emitted light was collected using a lens and analyzed using a single monochromator with 1-m focal length and a liquid nitrogen cooled Ge detector. Standard lock-in detection techniques were used to maximize the signal-to-noise ratio.

III. RESULTS AND DISCUSSION

Figure 1(a) shows cross-sectional HRTEM image of 10-stacked Ge QDs with a Si spacer thickness of 59 nm, which demonstrates vertically-ordered Ge dots as dark features between two-dimensional wetting layers. Thus, the growth mode in which the Ge QDs were fabricated is Stranski-Krastanov (SK) mode. In this figure, a vertical correlation also appears, and the lateral size of Ge QDs gradually increases from layer to layer due to a reduction in the strain coupling between different dot layers [11]. The growth conditions of Ge QDs depend mainly on the growth temperature, the gas pressure, and the thickness of the Si spacer. These factors were varied to find optimum preparation conditions. Here, the coexistence of two typical shapes of Ge QDs, domes and pyramids, is evident at growth temperatures >650 °C, as shown in the AFM image of Figure 1(b). For such bimodal formation of dots, the pyramids and the domes have been suggested to correspond to two minimum-energy configurations of strained islands, with an activated transition from pyramids to domes [7]. One the other hand, the films can also be dominated by domes after long-time annealing at low temperatures [12]. This indicates that in the competition between the different kinetic processes responsible for the pyramid and the dome formations, the domes require a higher activation energy and grow slower.

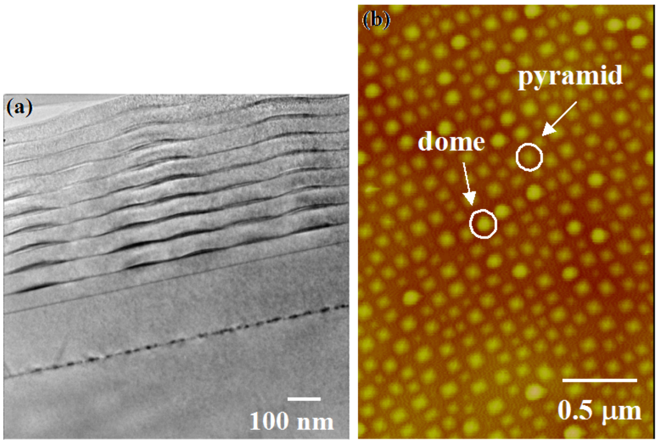

Fig. 1. (a) Cross-sectional HRTEM image of 10-stacked Ge QDs with a Si spacer with a thickness of 59 nm and (b) AFM image of the self-assembled Ge QDs showing a bimodal growth of domes and pyramids.

Figures 2(a) and (b) show plots for the size and the density of Ge QDs as functions of the growth temperature. As Figure 2 (a) shows, the lateral dot size increases gradually with increasing growth temperature while the height of the dots increases up to 650 °C and above which it saturates. A higher growth temperature produces larger-height dots because of temperature-enhanced surface diffusion. The height saturation is thought to be associated with a critical thickness of Ge QDs. In Figure 2(b), the dot density decreases rapidly with increasing growth temperature up to 600 °C, but it decreases more slowly for temperatures above 600 °C. The two different slopes in Figure 2(b) are thought to be associated with the dome and the pyramid shapes of the QDs, respectively. The Si content in the islands increases with temperature with the same trend as the average island volume does [12]. This means that, in addition to the effect of the temperature-enhanced surface diffusion, Si-Ge

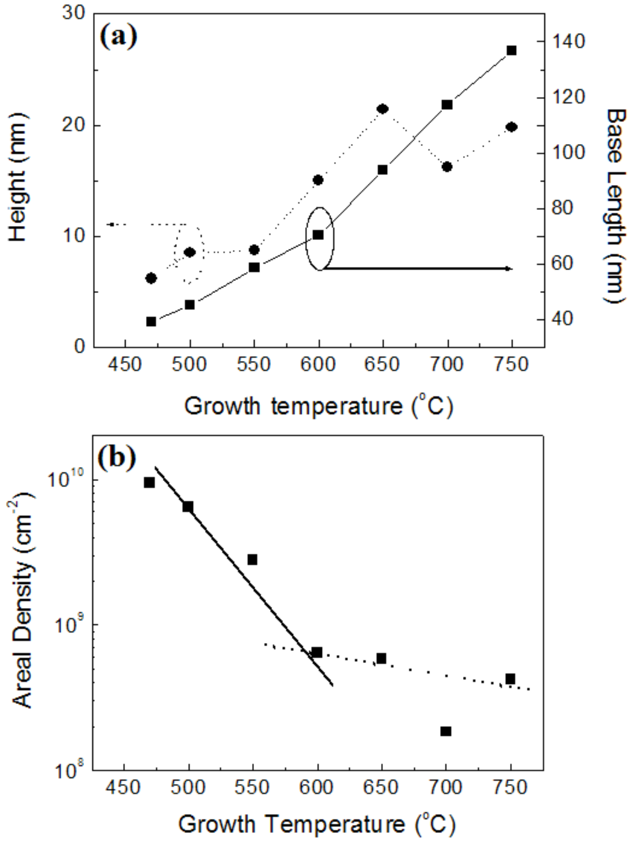

Fig. 2. (a) Height and base length of Ge QDs and (b) their areal density as functions of growth temperature.

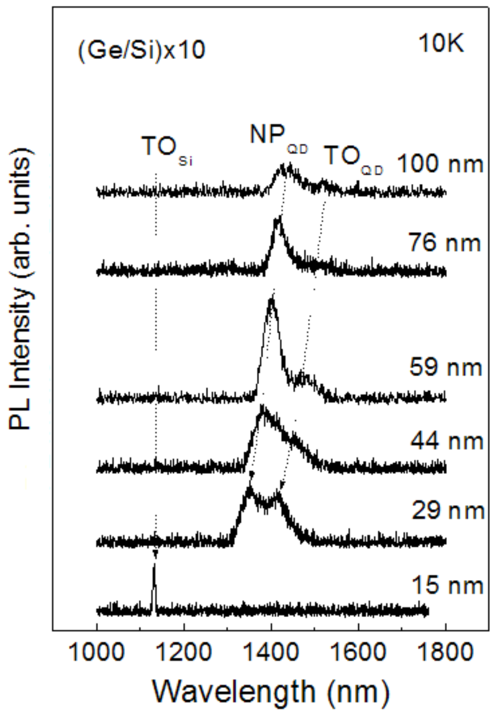

Fig. 3. PL spectra of 10-stacked Ge QDs for various thicknesses of the Si spacer.

intermixing plays a role in increasing the island volume (decreasing the density). A higher growth temperature will lower the strain energy of the growing film due to Si-Ge intermixing, which will result in the appearance of the domes.

The arrangement of Ge QDs and the degree of correlation between them have been found to strongly depend on the thickness of the Si spacer (d) [13,14], which has a great influence on the optical properties of Ge QDs [3,14]. The amount of strain transferring from the buried Ge dots into the Si spacer is also determined by the spacer thickness in the stacked Ge dot layers. Figure 3 shows PL spectra of 10-stacked Ge QDs as a function of d. When d = 100 nm, two major peaks are observed, one at 0.86 eV and the other at 0.82 eV, which are widely attributed to no phonon (NP) and transverse-optical (TO) phonon replica of the Ge QDs, respectively [9]. These peaks are blueshifted to 0.92 and 0.88, respectively, by decreasing d down to 29 nm. The energy shifts can be associated with the strain between the Si barrier and the Ge QDs. When d decreases, more strain is transferred from the Ge QDs into the Si spacer due to an enhanced vertical correlation between the layers. The PL blueshift is also known to originate from SiGe material intermixing due to a strain field superposition of buried dots during overgrowth [14].

In order to study the interdiffusion behaviors of the Ge QDs and the Si spacer or the Si substrate, we performed RTA in an Ar atmosphere. As Figure 4 shows, the annealing temperatures was changed from 750 to 1000 °C in 50 °C steps for 2 samples of different thicknesses. After thermal annealing, the NP and the TO PL peaks were blue-shifted from 0.856 to 0.917 eV and from 0.820 to 0.871 eV, respectively. The shift of the two peaks can be attributed to the interdiffusion of Ge and Si, thereby changing the Ge concentration in Ge QDs and, as a result, shifting the confined energy levels in the Ge QDs to the conduction band of Si. The total energy shift with annealing temperature is higher for thicker samples, as shown in Figures 4 (a) and (b). This indicates that the interdiffusion between the Ge QDs and the Si spacer mainly occurs in the vertical direction, and the diffusion length of Ge depends on the Si spacer thickness. On the other hand, the annealing effect can be associated with a variation in the Ge concentration. The interdiffusion of Ge and Si takes place at the interface of the QDs/Si spacer, leading to a change in Ge concentration, which plays an important role in changing the band structure.

Band alignment of Ge/Si QDs can be studied by measuring the excitation-power dependence of PL [9,10]. Figure 5 shows a plot of the PL intensity of 10-stacked Ge QDs as a function of the excitation power for powers ranging from 0.6 to 70 mW. The height of the QDs and the thickness of the Si spacer are 16.2 and 59 nm, respectively. As the excitation power is increased, the NP energy of the Ge QDs is shifted to high energy, and the total energy shift is about 4 meV. This suggests a type-

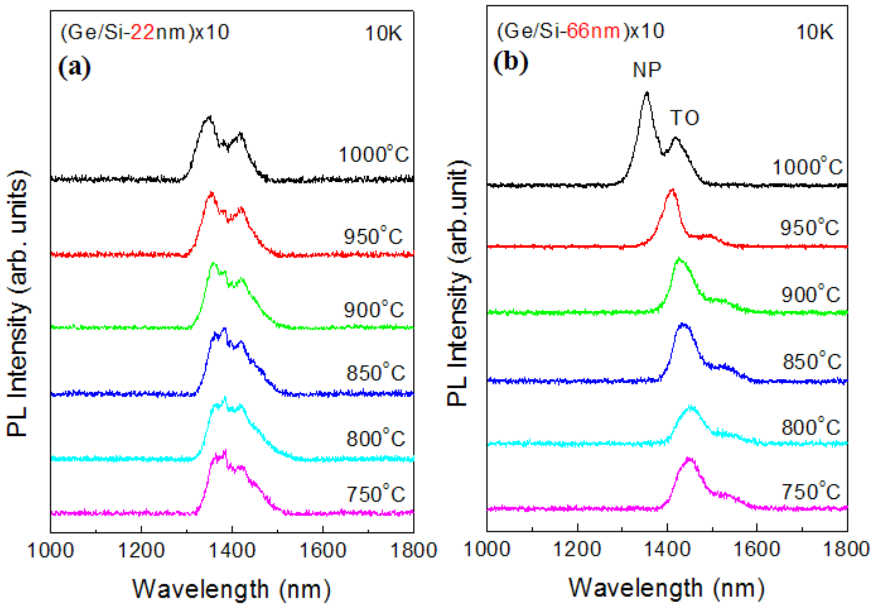

Fig. 4. PL spectra as a function of annealing temperature for 10-stacked Ge QDs with Si-spacer thicknesses of (a) 22 and (b) 66 nm thickness.

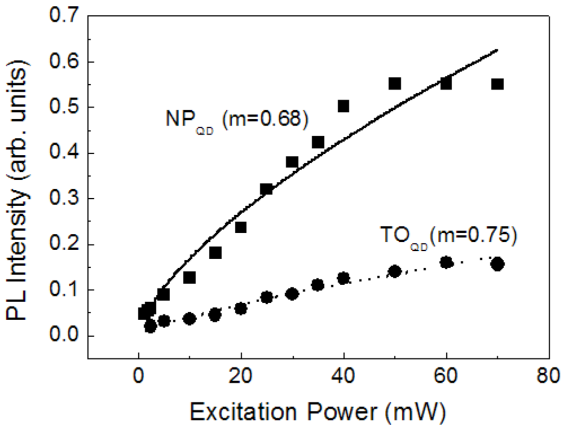

Fig. 5. Plot of the intensity vs excitation power for the NP and TO PL peaks of 10-stacked Ge QDs with a Si spacer of 59 nm.

II band structure, in which photo-induced holes are confined in the Ge dots while electrons are confined outside. Then, a band bending will occur at the interfaces due to the Hartree potential [9,10,15]. Since more electrons and holes are supplied at higher excitation powers, the electrons and holes will be at higher energy [16], resulting in a blueshift of the PL peak. In this type-II band, the PL depends on the excitation power (P) according to the equation $I = P^m$, where I is the normalized PL intensity, P is the excitation power, and m is a coefficient. In Fig. 5, the m values for the NP and the TO PL peaks are calculated as 0.68 and 0.75, respectively. This sublinear power dependence is typical in a type-II band structure. In contrast, in a type-I band alignment, the PL shows an almost linear dependence on the excitation power [9,10].

IV. CONCLUSIONS

PL, AFM, and HRTEM were employed to study the optical properties of multi-stacked Ge quantum dots (QDs) grown on Si (100) by the RTCVD. The HRTEM images demonstrated vertically ordered Ge QDs and full contrast between the Si spacer and the Ge QDs. The size/height of the dots and their density strongly depended on the growth temperature, as confirmed by using AFM. A bimodal growth of Ge QDs, domes and pyramids, was found under specific growth conditions. Two major PL emission bands, one each being attributed to the NP and the TO phonon replica of the Ge QDs, were blue-shifted with decreasing thickness of the Si spacer. Annealing experiments were performed to study the interdiffusion or intermixing effects of Ge QDs. As the excitation power was increased, the NP energy of the Ge QDs was blue-shifted with a total energy shift of about 4 meV. The dependence of the PL on the excitation power exhibited a sublinear behavior with m values of 0.68 and 0.75 for the NP and the TO PL peaks, respectively. These results were explained with reference to possible emission processes based on a type-II band structure of Ge QDs/Si.

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