Optical properties of Ge self-organized quantum dots in Si

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(Received 6 November 1997)

Small-size, high-density, and vertical-ordering Ge quantum dots are observed in strained Si/Ge short-period superlattices grown on Si(001) at low growth temperature by molecular-beam epitaxy. The photoluminescence (PL) peak position, the strong PL at room temperature, and the high exciton binding energy suggest an indirect-to-direct conversion of the Ge quantum dots. This conversion is in good agreement with the theoretical prediction. The characteristic of absorption directly indicates this conversion. The tunneling of carriers between these quantum dots is also observed. [S0163-1829(98)03515-2]

A major hurdle in the development of silicon optoelectronic integrated circuits has been the difficulty in fabricating efficient light-emitting devices. This is a direct consequence of the indirect energy gap of this material. Band-gap engineering of indirect-to-direct conversion structures using the Si/SiGe material system attracts considerable interest. In 1974, Gnutzmann and Clausecker[1] predicted the quasidirect band gap in the short-period superlattices of an indirect semiconductor. Due to the progress in silicon molecular-beam epitaxy (MBE), the research of Si_m/Ge_n short-period strained-layer superlattices (SLS's) on optical properties achieved encouraging developments.[2,3] Recently, the reports on the optical properties of porous Si suggest that this conversion may result in the formation of quantum confined structures that can and do emit strongly in the near-infrared and visible regions.[4,5] The apparent dimensionality of the confinement is zero-dimensional quantum dots (QD's). The QD research has attracted much attention from the fundamental physics viewpoint and from the potential application to optical devices. Takagahara and Takeda[6] and Ren[7,8] have reported theoretically that an indirect-to-direct conversion of the optical transition of GeSi QD's would occur whenever the size of the QD's is small enough. This is the so-called quantum size-dependent effect, which is in good agreement with the porous Si (Refs. 4 and 5) and the Ge OD's embedded in SiO_2 glassy matrices.[9] However, another kind of GeSi QD, which is epitaxially grown by self-organization, is more practical because it is very easily integrated. In this paper we report the direct optical transition in the Ge self-organized QD's grown by MBE. These QD's are the very small and dense Ge islands in Si.

GeSi island (also QD) formation on/in Si grown by MBE is very sensitive to the growth conditions. Generally, to relax misfit strain, dislocations are induced in the islands.[10,11] However, under certain conditions, dislocation-free Ge islands can be formed.[12] Concerning the islands formed by GeSi/Si superlattices, their size, density, and size uniformity are related to the structure of the superlattices.[13] The deposition of Sb can increase the density of nuclei of the islands.[14]

To grow Ge islands that are dislocation-free, dense, small sized, and as uniform as possible, we chose the structure as a SLS $\{[(Ge_4Si_4)\times 4+Si(5\ nm)]\times 2\}$, as shown in Fig. 1. The 5-nm Si layer between the two $(Ge_4Si_4)\times 4$ SLS's is used to reduce the strain energy. One monolayer of Sb was deposited to increase the number of nuclei of Ge islands. The growth process was monitored by reflecting high-energy electron diffraction (RHEED) *in situ*.

By RHEED, we observed that island growth agreed with the results of the high-resolution cross-section transmission electron microscopy (TEM) shown in Fig. 2. The analysis of the TEM results indicates that the growth is dislocation-free. The islands' diameter is predominately around 8 nm. The islands' density is more than 50 times higher than that reported.[12,13] The vertical ordering is also observed.

We can suggest that the island strain is partially relaxed by local elastic deformation as proposed in Ref. 12. The vertical ordering is formed due to the vertical propagation of the local strain's distribution. On the other hand, Sb atoms are deposited not only as the surfactant, but also as the nuclei of the islands. After 3 ML of Ge are deposited, in order to relax the misfit strain, the surface becomes rough by the formation of very small micropyramids,[16] which act as the nuclei of Ge islands. Then the island growth mode begins. This roughness may even be enforced in the presence of a surfactant[14] such as Sb. One monolayer of Sb can produce large numbers of such nuclei. Therefore, the density of the island must become very large and the size very small. Due to the large number of islands and the local elastic strain's relaxation, the misfit strain can be relaxed mostly without induction of misfit dislocation. Therefore, dislocation-free, very small, and dense Ge islands are expected.

To confirm the island nucleation effect of Sb, a similar structure except for 1 ML of Sb was grown at the same

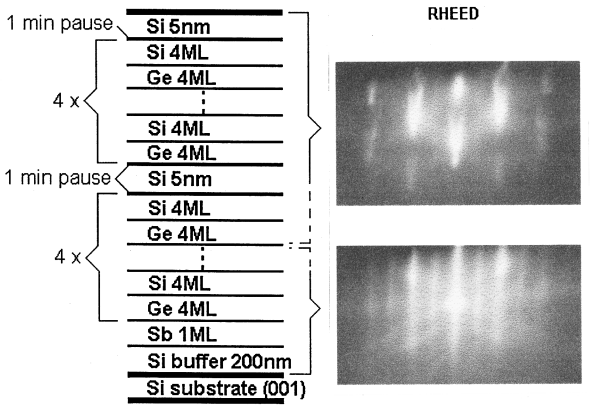

FIG. 1. Layer structure and the RHEED pictures. The growth temperature of the SLS's is 550 °C and that of the buffer layer is 850 °C. The RHEED shows that the SK growth begins gradually from the third Ge ''4 ML.''

growth condition and the surface morphology was characterized by an atomic force microscope (AFM). In Fig. 3 a significant difference is observed. Moreover, when the photoluminescence (PL) measurement temperature was at 77 K, only a very weak transverse-optical (TO) phonon replica peak of the Si substrate was observed from the sample without the Sb adlayer.

Figure 4 shows the PL spectra of the QD's and quantum wells (QW's). The 488-nm line with an intensity of 8 mW of the Ar^+ laser was used for the excitation. Concerning each

FIG. 2. High-resolution cross-section TEM image. From the analysis of the TEM results, the real thickness of layers is larger than the design, the Ge islands are free of dislocation, the density is about 5×10^{11} cm^{-2}, the island's diameter is predominately around 8 nm while very few scattered distributions from 4 to 11 nm, and the height is 1–2 nm.

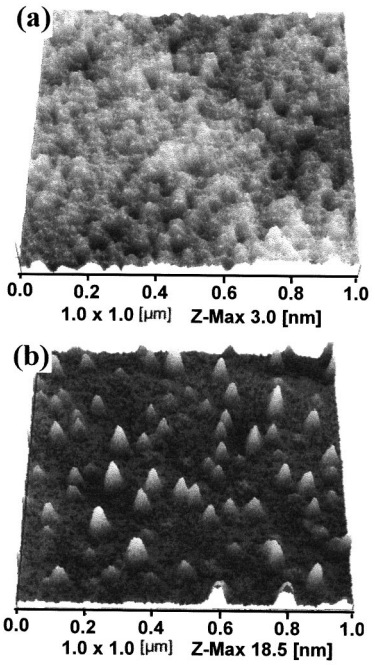

FIG. 3. AFM analysis of the effect of Sb surfactant on the formation of Ge islands: (a) 1-ML Sb adlayer and (b) non-Sb adlayer. A significant difference is observed in that the size of the non-SM islands is from 40 to 90 nm ($\sim$10 times larger), the maximum height is 18.5 nm ($\sim$6 times higher), and the density is 1.5×10^{-10} cm^{-2} ($\sim$30 times lower).

spectrum shown in Fig. 4(a), the lower energy peak is the Si TO one and the higher one is from the Ge QD's. Gaussian fitting was carried out to separate the PL of the QD's from the whole PL spectrum (dotted lines). The conventional SiGe/Si QW PL, which is the indirect band-gap optical transition, was also carried out. The intensity of PL from QD's is more than 500 times higher [Fig. 4(a), left inset]. At the measured temperature from 77 K to room temperature, the Ge QD's PL peak position shifts from 1224 to 1165 meV. From the temperature dependence of the integrated intensity of the PL of the QD's, it is deduced that the exciton binding energy is about 52 meV, which is much higher than that in conventional Si/SiGe QW's.

Figure 5 shows the room-temperature Ge QD's absorption spectrum that was obtained from the deduction of the absorption of the Si substrate from the whole of the QD's sample. The absorption coefficient α reaches to the order of 10^3 cm^{-1}, which is much larger than the indirect band-gap absorption of the bulk of Ge and Si ($10-10^2$).[17] The energy dependence of α is different between the optical direct and indirect transitions. In a small range over the absorption edge, this difference is

$$\alpha = C_d(h\nu - E_0)^{1/2} \quad \text{for the direct transition,} \qquad (1)$$

$$\alpha = C_i(h\nu - E_0)^2 \quad \text{for the indirect transition,} \qquad (2)$$

where C_d and C_i are constants, $h\nu$ is the photon energy, and E_0 is the absorption edge. In the inset of Fig. 5 the relation of α^2 *Vs* $h\nu$ and $\alpha^{1/2}$ *Vs* $h\nu$ is shown. Obviously, the spec-

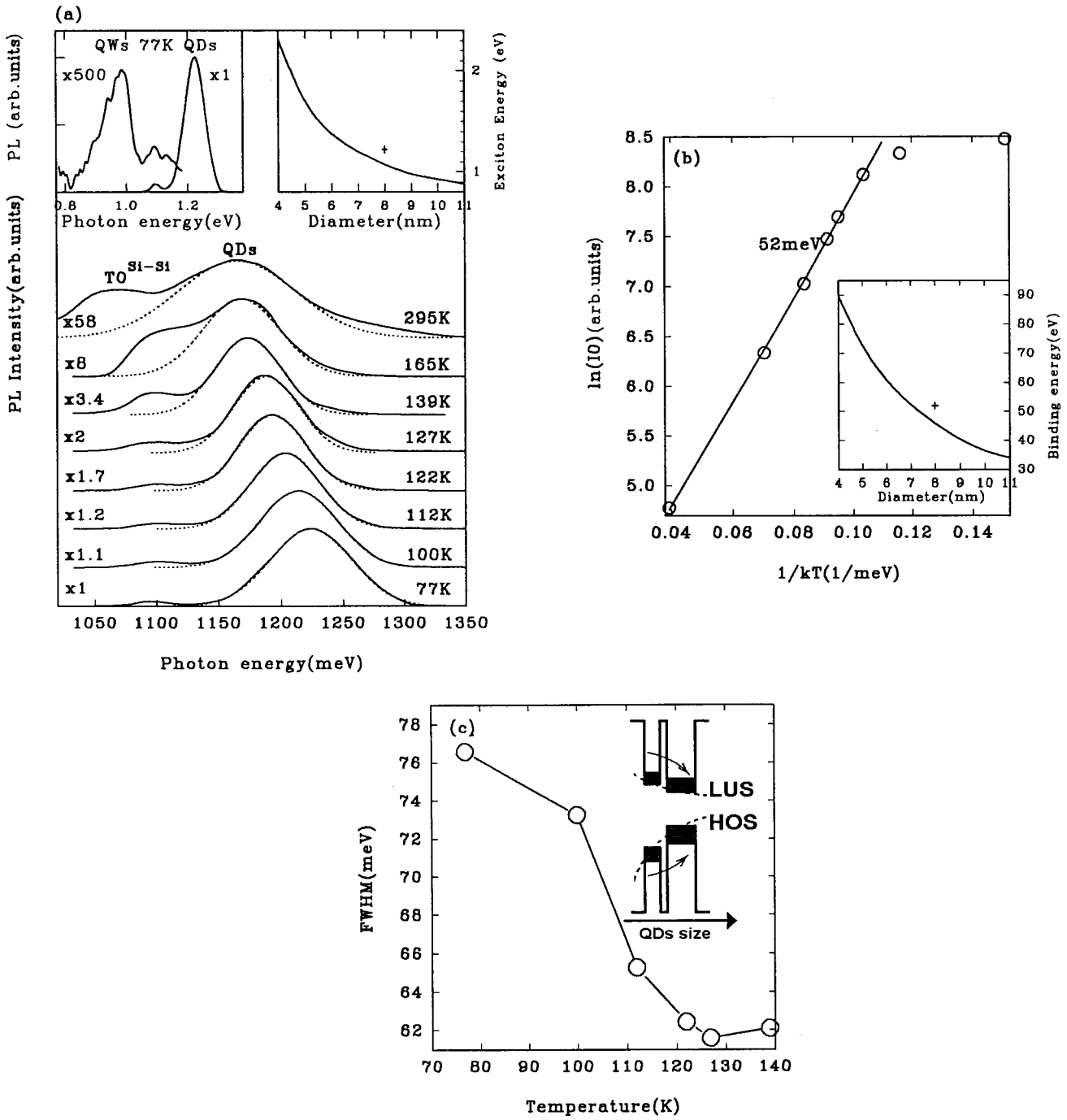

FIG. 4. (a) PL spectra from 77 K to room temperature. The dotted line is the Gaussian fitting of the PL of Ge QD's. The left inset is the comparison of the PL spectra of QW's and QD's. The QW's are (20 nm Si+3 nm $Ge_{0.3}Si_{0.7}$)×5 grown at 550 °C. The right inset is the theoretical calculation (Ref. 6) of the exciton energy of Ge QD's (solid line) and the experiment result (plus). (b) Temperature (T) dependence of integrated intensity ($I0$) of PL from QD's (open circles). The slope (solid line) shows the exciton binding energy (52 meV) in the Ge QD's. The inset is the theoretical calculation (Ref. 6) of the exciton binding energy of the Ge QD (solid line) and the experiment result (plus). (c) Temperature dependence of the FWHM of the PL peak from the Ge QD's. The inset shows the free carriers tunneling between the QD's of different sizes.

trum agrees quite well with Eq. (1), rather than with Eq. (2). This suggests that the direct transition occurs in the Ge QD's. In the low-energy range below the absorption edge, there is an exponential decrease of α. This is the Urbach absorption tail[17] because the sample was heavily doped by Sb.

In comparison to QW's and quantum wires, there exist several interesting features inherent in QD's only. The translational symmetry is broken in all directions in QD's; the concept of quasimomentum of the exciton gas and electron-hole plasma evidently fails in small QD's. Therefore, the energy structure of the ''indirect-gap'' QD's should be analyzed along with the probabilities and selection rules for optical transitions. Generally, a great increase is expected in the transition probability accompanied by the decrease of the QD's size. According to Ren,[7,8] when the size of QD's de-

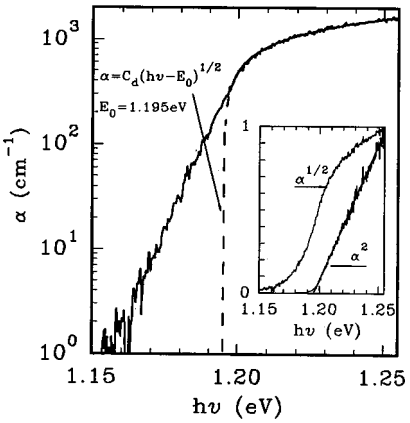

FIG. 5. Room-temperature optical absorption of Ge QD's. The dashed line is the direct transition fit according to Eq. (1). The inset is the relationship of α^2 *Vs* $h\nu$ and $\alpha^{1/2}$ *Vs* $h\nu$. The vertical axis value is normalized.

creases, the state distribution expands, the bands become flatter, and the intervalley coupling between different conduction-band minima in the bulk increases. All these lead to an increase of the ''average effective mass'' and state spreading in other bands: Even the ones with a curvature of different sign can have a significant contribution in small QD's. The highest occupied state (HOS) draws close to the lowest unoccupied state (LUS) in the **k** direction. The smaller the size, the more obvious the effects mentioned above. Therefore, the direct transition between the HOS and the LUS will happen if the size of QD's becomes smaller than a certain critical value. Ren estimated that the critical size of Ge QD's is Nc (>3109) (Ref. 8) atoms. The predominant size of our Ge QD's as shown in the TEM images is smaller than 3100 atoms. Therefore, a direct transition in our Ge QD's would exist.

The calculated exciton energy and exciton binding energy in such Ge QD's (Ref. 6) are shown as a function of the QD diameter in the right inset of Fig. 4(a) and the inset of Fig. 4(b). The plus denotes the experimental data that agree well with the theoretical calculation. According to this theoretical predication, a direct transition would also occur. A slight deviation from the experiment may be due to the simplified theoretical mode, such as the detail of the shape of the QD's and the strain distribution.

In Fig. 4(c) a remarkable effect is observed in the plot of the full width at half maximum (FWHM) of the Ge QD's PL as a function of temperature. The FWHM anomalously decreased from 77 to 130 K. This can be explained as follows. When the temperature increases, more free carriers generated by the exciton thermal dissociation in smaller QD's tunnel into the nearby larger ones because the confinement potential of larger QD's is deeper. Moreover, the high density of the QD's and the short space between them also make the tunneling easy. This is schematically shown in the inset of Fig. 4(c). The size of QD's that act in PL becomes more uniform. Consequently, we should expect a reduction of the FWHM in the QD's PL emission as the temperature increases. In the self-organized InAs QD's, a similar tunneling process was also observed.[15] It suggests that the PL peak near 1.2 eV is surely from the QD's.

In summary, we have described the fabrication of Ge self-organized QD's in Si by MBE and their optical properties. They are small, dense, dislocation-free, and vertical ordering. The PL of the QD's is about 500 times stronger than that of QW's. Both the PL and absorption spectra show a transition energy near 1.2 eV. The exciton binding energy is 52 meV. The peak of the PL, the absorption edge, and the exciton binding energy agree well with the theoretical calculation, which predicates an indirect-to-direct conversion. The characteristic of the Ge QD's absorption spectrum also shows the direct optical transition. The carrier tunneling between the QD's also has been observed.

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