Raman scattering of Ge/Si dot superlattices under hydrostatic pressure

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We have studied the self-organized Ge/Si quantum dots (QD's) by Raman scattering under hydrostatic pressure near resonance and off resonance with confined Ge-like E_1 transition. The Raman spectra of Ge-Ge, Si-Ge, and the Si acoustic phonon (Si-2TA) modes were obtained as function of pressures in the range 1–70 kbar. Our results show that the Ge-Ge and Si-2TA modes can be easily resolved at low pressure due to a high degree of compressive built-in strain in the Ge layers. The mode Grüneisen parameter of the Ge-Ge phonon mode in QD's is found to be $\gamma = 0.81 \pm 0.01$, which is smaller than the corresponding quantity in bulk Ge. Normalized Raman intensity profiles of Ge-Ge mode exhibit a resonance enhancement peak at ~32 kbar. The pressure coefficient α of this resonating electronic transition thus obtained is $\sim 5 \pm 1$ meV/kbar. This value is smaller than the pressure shift of the E_1 transition in bulk Ge.

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Self-assembled Ge/Si nanostructures have recently received considerable attention for their applications in optoelectronic[1,2] and electronic devices.[1,3] The Ge/Si islands nucleate in the Stranski-Krastanov growth mode as a result of strain accumulated due to the lattice mismatch.[4] The shape of the islands can change dramatically when Ge islands are overgrown with Si (Refs. 5 and 6) and only little is known about the resulting islands' strain and composition state. One of the most powerful methods to investigate built-in strain and quality of the interface in nanostructures is by Raman spectroscopy.

A lot of work has been put into studying of phonon modes in Ge quantum dots (QD's) by Raman scattering to predict the phonon confinement and strain effects due to size dependence at ambient pressure.[7,8] The application of pressure plays a major role in optical investigations of electronic states in quantum wells and superlattices.[9] Recently, high pressure in combination with laser excitation intensity has been used to infer a staggered type-II band alignment in carbon-induced Ge QD's.[10] On the other hand, Raman scattering at high pressure offers an attractive means for investigating phonon properties of solids.[11] In addition to the reduction of interatomic distances, the effect of pressure will also reduce the strain in Ge layers due to the difference between the bulk moduli of Si and Ge. Pressure can also tune the electronic transition through laser excitation energies resulting in resonance Raman scattering (RRS) in the Ge phonon mode.[11] Kwok *et al.*[8] utilized RRS to investigate Ge dot superlattices grown by molecular-beam epitaxy (MBE) at ambient pressure. They reported that E_1 excitions are weakly confined inside QD's. Recent optical absorption measurements on Ge QD's, deposited by pulsed-laser deposition on sapphire substrate, shows the excitonic nature of the E_1 transition is suppressed as the QD size decreases.[12] Although Raman studies on the effect of hydrostatic pressures have been reported on $Si_{1-x}Ge_x$ superlattices[13,14] and Ge_nSi_m multiple-quantum-wells,[15] there has been no investigation of RRS studies in Ge dot superlattices under pressure. In this paper, we report the results of pressure effects of Raman scattering of Ge QD's in strained Si/Ge short-period superlattices.

The sample for investigation was grown by MBE on a (001) Si substrate at 550 °C. In the sample 1 monolayer (ML) of Sb was deposited on the Si epitaxial layer to act as a surfactant. Afterwards two series of nominal Si_4Ge_4 superlattices, each with four periods and separated by a 5-nm Si buffer layer, were grown. Previous studies on the sample by high-resolution transmission electron microscopy shows that the typical diameter of the islands is ~8 nm, while their height is 1–2 nm. The islands density is $\sim 5 \times 10^{11}\,cm^{-2}$. The details of the growth technique and sample characteristics can be found in Ref. 16.

The pressure-dependent measurements were carried out using standard diamond anvil cell technique with a 4:1 mixture of methanol and ethanol as the pressure-transmitting medium. The applied pressures were monitored by the shift of the ruby $R1$ line.[17] Since with increasing pressure, the frequency of the first-order Si Raman peak (present in all spectra) blueshift with a pressure coefficient[18] of 0.52 cm^{-1}/kbar we can used it as an internal calibration of the pressure. The Raman spectra were taken in a backscattering geometry at room temperature using 514.5-nm (2.41-eV) and 488-nm (2.541-eV) lines from an argon-ion laser and the 632.8-nm (1.96-eV) line from a He-Ne laser. The scattered spectra were analyzed with a Jobin-Yavon T4600 micro-Raman system.

We have used different polarization configurations to distinguish the signals from the dot sample and the Si substrate.[19] Figure 1(a) shows the spectrum taken from the backside of the sample (Si substrate) in the $001(110,110)00\bar{1}$ backscattering geometry that enhances the Si acoustic-phonon peak (abbreviated as Si-2TA) at ~303 cm^{-1}. The peak at 434 cm^{-1} is identified to be the Si local mode. In the $001(100,010)00\bar{1}$ configuration as shown in Fig. 1(b), the spectrum taken from the sample shows that the Si-2TA and

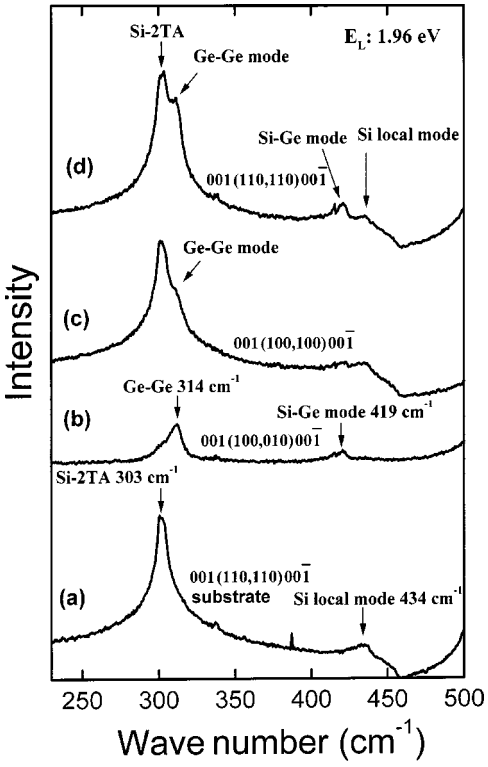

FIG. 1. Raman spectra of Ge QD's under different polarization configurations with a laser excitation energy of $E_L \sim 1.96$ eV. (a) Substrate, 001(110,110)00$\bar{1}$; (b) sample, 001(100,010)00$\bar{1}$; (c) sample, 001(100,100)00$\bar{1}$; and (d) sample, 001(110,110)00$\bar{1}$.

Si local modes are suppressed while the Ge-Ge mode at 314 cm^{-1} can be clearly observed. The peak at 419 cm^{-1} is identified as the Si-Ge interface phonon mode localized at the surfaces of Ge quantum structures.[8] Figure 1(c) shows the spectrum taken from the sample in the 001(100,100)00$\bar{1}$ configuration. The signals from the Ge wetting layers are forbidden in this geometry, according to the selection rules.[20] Therefore, the observed Ge-Ge modes are mainly from their Ge dots rather than Ge wetting layers. Figure 1(d) shows the spectrum taken in the 001(110,110)00$\bar{1}$ backscattering geometry from the sample in order to enhance the Si acoustic-phonon peak. The Si-2TA, Ge-Ge, Si-Ge, and Si local modes can be clearly distinguished.

It is well known in Ge QD's and nanocrystals that a compressive built-in strain can lead to a blueshift of the Ge-Ge mode frequency, while confinement effect can cause a redshift.[21] For pseudomorphically grown Ge on an Si substrate, the lattice mismatch between Si and Ge gives rise to ~3.8% of compressive strain in the Ge layer. In QD's, this lattice-mismatch-induced strain is partially reduced and nonuniform across the structure as a result of island formation.[22] Our result shows that the Ge-Ge mode frequency in QD's is ~314 cm^{-1} as compared to 300 cm^{-1} in bulk Ge at ambient pressure. If we neglect the confinement effect, a biaxial strain[23] of about 3.4% is estimated to cause a frequency shift by 14 cm^{-1}.

Figure 2 shows the Raman spectra of Ge QD's at various pressures under the laser excitation energy E_L of 2.541 eV.

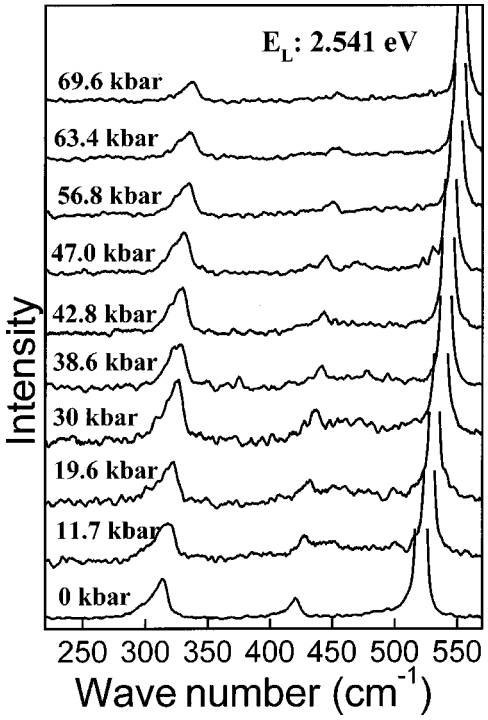

FIG. 2. Raman spectra of Ge QD's at various pressures under the laser excitation energy of $E_L \sim 2.541$ eV.

Spectra are normalized to silicon substrate phonon intensity. With increasing pressure, the Ge-Ge, Si-Ge, and the first-order Si Raman modes shift to higher frequencies. Similar Raman spectra are also obtained with $E_L \sim 2.41$ eV (not shown). The rates of frequency shift of these modes with pressure are shown in Fig. 3(a). The solid curves correspond to the least-square fits to the experimental data as given by

$$\omega_{\mathrm{Si}}(P) = (521.2 \pm 0.2) + (0.50 \pm 0.01)P, \tag{1}$$

$$\omega_{\mathrm{Ge}}(P) = (314.4 \pm 0.1) + (0.34 \pm 0.01)P, \tag{2}$$

$$\omega_{\mathrm{Ge\text{-}Si}}(P) = (419.5 \pm 0.2) + (0.50 \pm 0.01)P, \tag{3}$$

where P is in kbar and frequencies ω are measured in cm^{-1}. We use the following relation to calculate the mode Grüneisen parameter γ_i:

$$\gamma_i = \frac{B}{\omega_i}\frac{d\omega_i}{dP}, \tag{4}$$

where B is bulk modulus of Ge [750 kbar (Ref. 24)] at room temperature and ω_i is the phonon frequency of mode i. From the linear pressure coefficient $d\omega/dP$ of Eq. (2), we obtain a value of $\gamma = 0.81 \pm 0.01$ in our Ge QD's. This value is about 27% smaller than the corresponding quantity found in the bulk Ge (1.12).[25] If we assume that the Ge QD's are constrained by the Si host so that the bulk modulus of Ge becomes the same as that of Si (978.8 kbar),[26] we obtain $\gamma = 1.06$, which is only about 5% smaller than the accepted value. This clearly shows the Ge QD's are restricted by the Si lattice so that they almost deformed like the surrounding Si host.

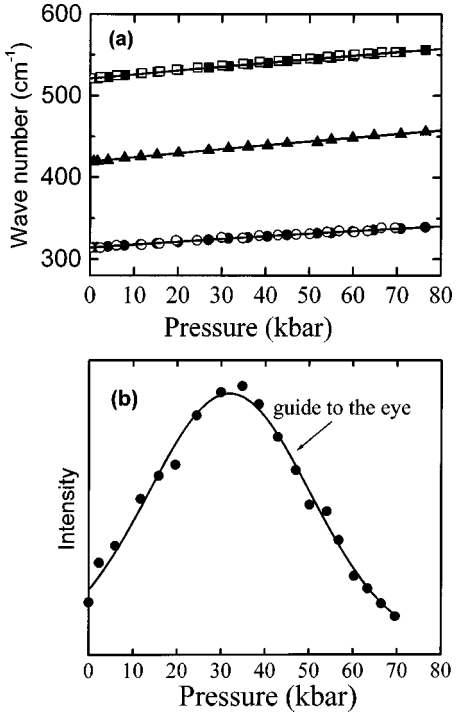

FIG. 3. (a) Raman shifts as function of pressures, using $E_L = 2.41$ eV: Si substrate (solid squares), Si-Ge mode (solid triangles), and Ge-Ge mode (solid circles). For $E_L = 2.541$ eV, Si substrate (open squares) and Ge-Ge mode (open circles). The solid curves correspond to the least-square fits to the experimental data. (b) Normalized intensities of the Ge-Ge mode versus pressure. The solid curve is a guide to the eye.

We graph in Fig. 3(b) the integrated intensity profile of Ge-Ge mode versus pressure for $E_L \sim 2.541$ eV. The Si Raman intensity is used as an internal standard for normalization of Ge-Ge intensity. It is evident that the Ge-Ge mode shows clear enhancement at ~32 kbar. It has been known that the optical-phonon Raman-scattering efficiency of bulk Ge exhibits a resonance peak at 2.23 eV. This has been attributed to the E_1 transition.[27] We interpret the enhancement for the Ge-Ge mode in our Ge QD's to be resonance scattering within the Ge layers as pressure tune the electronic transition through $E_L \sim 2.541$ eV. Previous resonant Raman-scattering studies on this sample has shown an enhancement peak at 2.38 eV at ambient pressure as a result of resonance with an E_1 exciton.[8] The following relation, in which the pressure tuned the electronic transition in resonance with the E_1 transition, is a linear function of pressure P:

$$E_1 = E_L - \alpha P, \tag{5}$$

where α is the pressure coefficient of the electronic transition at resonance. By substituting $E_1 \sim 2.38$ eV, $E_L \sim 2.541$ eV, and $P \sim 32$ kbar at resonance, we estimate α to be $\sim 5 \pm 1$ meV/kbar. This α value is about 33% smaller than the value found for E_1 transition in bulk Ge (7.5 meV/kbar).[28] The corresponding pressure coefficient of 4 ± 1 meV/kbar has been obtained in Ge_nSi_m multiple-quantum-wells (MQW's).[15] We note that the in-plane lattice constant of Ge layers is compressed to match that of the surrounding Si lattice. For a given applied pressure, the Ge layers will show a smaller change in the in-plane lattice constant than the Si since Ge has a smaller bulk modulus than Si. This leads to a smaller in-plane deformation as compared to the bulk Ge for the same applied pressure. In the case of Ge QD's the lattice dilation for the Ge layers along the growth direction will also be constrained by the surrounding Si lattice. Therefore, the Ge QD's may exhibit a smaller deformation than the bulk Ge when subjected to the same pressure. This could possibly explain the smaller pressure coefficient in our Ge QD's.

It is known that the frequency of the Si-Ge mode in bulk Si-Ge alloys depends on the alloy composition, while the frequency of Si-Ge mode at the interface can depend further on strain and interface roughness.[29] At ambient pressure the linewidth of the Si-Ge mode (~10 cm^{-1}) in our sample is much sharper as compared to those found in both bulk Si-Ge alloys and superlattice Si-Ge, which has a typical linewidth larger than 20 cm^{-1}. Under the effect of pressure, the linewidth of the Si-Ge mode remains approximately constant and the line shape remains slightly asymmetric. All these factors indicate the Ge/Si interface is quite smooth. With the frequency of the Si-Ge mode at 419 cm^{-1}, it can be estimated that the biaxial strain compressive of Ge bonds at the Ge/Si interface is ~3.2%.[21] In addition, the pressure effect shows the rate of frequency shift for the Si-Ge mode follows closely with that of Si substrate. This result further suggests that the strain variation at Ge/Si interface is rather small.

In many Raman scattering studies of Ge nanostructures grown on silicon substrates, the line shape and position of the Ge-Ge mode are found to be similar to those of the silicon wafer.[30] In our Ge QD's, due to a high degree of compressive built-in strain in the Ge layers, the Ge-Ge and Si-2TA modes can be clearly distinguished at ambient pressure. Figure 4 shows the Raman spectra of Ge QD's measured at various pressures using the off-resonance $E_L \sim 1.96$ eV excitation. The Si-2TA mode at 303 cm^{-1} can be clearly distinguished from the Ge-Ge mode at 314 cm^{-1}. It is well known that the major peak in the acoustical-overtone spectra of Si is bounded by the critical points 2TA(Σ;1) and 2TA(X).[18] At atmospheric pressure the critical point 2TA(Σ;1) and 2TA(X) are separated by only ~2 cm^{-1}. The frequency splitting of these two singularities increases with pressure and they are clearly resolved at high pressure. The results obtained are consistent with those reported in Ref. 18. In Fig. 5, the frequency shifts of various modes are plotted as a function of pressure. The measured pressure coefficients for 2TA(Σ;1) and 2TA(X) are 0.36 ± 0.02 and 0.54 ± 0.02 cm^{-1}/kbar, respectively. For the first-order Si Raman mode and Ge-Ge mode, the pressure coefficients are consistent with those obtained in Fig. 3(a).

It should be noted that the linewidth of the Ge-Ge mode obtained using different excitation sources is different for the same sample. In the present case, it is more appropriate to obtain the linewidth of Ge-Ge mode under off-resonance condition. The inset of Fig. 5 shows the linewidths of Ge-Ge and Si-2TA modes as function of pressures. Here, we take the total linewidth of the Si-2TA mode to be the sum of 2TA(Σ;1) and 2TA(X). While the linewidth of Si-2TA mode shifted linearly with pressure at a rate of 0.1 cm^{-1} kbar^{-1},

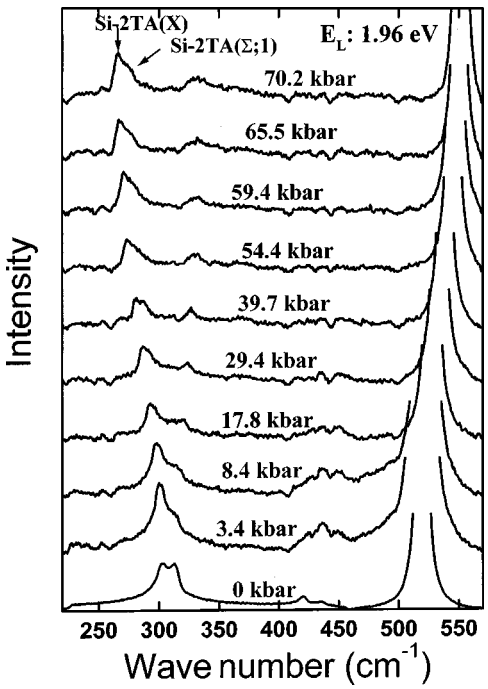

FIG. 4. Raman spectra of Ge QD's at various pressures using $E_L \sim 1.96$ eV.

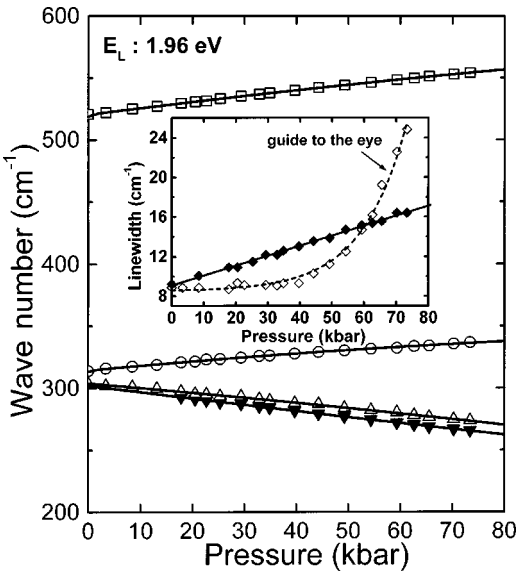

FIG. 5. (a) Raman shifts as function of pressures using $E_L \sim 1.96$ eV. Si substrate (open squares), Ge-Ge mode (open circles), 2TA(X) (open triangles), and 2TA(Σ;1) (solid triangles). The inset shows the linewidth of Ge-Ge (open diamonds) and Si-2TA modes (solid diamonds) as functions of pressures. The solid curves correspond to the least-square fits to the experimental data and the dash curve is a guide to the eye.

the Ge-Ge mode exhibits a nonlinear broadening in linewidth as the pressure increases. If we assume the strain inhomogeneity increases linearly with pressure, we would expect a large linear pressure coefficient in linewidth for the Ge-Ge mode, which is not observed in our results. A plausible explanation is given as follows. For $P \leqslant 32$ kbar the linewidth of the Ge-Ge mode is approximately constant (~ 9 cm^{-1}). This could be due to the fact that the Ge-Ge mode changes it shape since at low pressure the Ge-Ge mode overlaps partially with the Si-2TA mode, so that initially its linewidth appears not to change much. Thus, the linear pressure coefficient is abnormally small at low pressure. However, for pressure $P \geqslant 32$ kbar, the Ge-Ge and Si-2TA modes can be easily resolved without difficulty. Thus, at high pressure the line shape of the Ge-Ge mode does not seem to change much while the linewidth increases.

In summary, the effects of pressure on the Raman spectra of Ge QD's are examined. The mode Grüneisen parameter of the Ge-Ge phonon mode is obtained to be $\gamma = 0.81 \pm 0.01$, which is slightly smaller than the value found in bulk Ge. We also observed resonance effects with the confined Ge-like E_1 transition. The pressure coefficient obtained for this transition is $\sim 5 \pm 1$ meV/kbar. This value is lower than the corresponding quantity found in bulk Ge. Pressure-induced phonon shifts clearly resolved the Ge-Ge and Si-2TA modes at low pressure under off resonance with the E_1 transition. This allows us to unambiguously obtain the actual linewidth of the Ge-Ge mode in QD's.

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