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Phonons in Ge/Si quantum dot structures: influence of growth temperature

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Abstract

In this paper we present the results of a Raman study of Ge/Si quantum dot (QD) superlattices grown with different thicknesses of a Si interlayer and at different substrate temperatures. The built-in strain and atomic intermixing in the QDs are deduced from an analysis of optical phonon frequencies of the QDs obtained from Raman spectra of the structures.

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1. Introduction

Among structures with self-assembled quantum dots (QDs) the arrays of Ge QDs grown on Si substrates attracts special attention. Compatibility with a well-developed Si technology makes these structures very attractive for fabrication of optoelectronic and microelectronic devices. Multi-layered arrays of Ge QDs or Ge/Si QD superlattices are even more desired for optoelectronic applications [1,2]. Fabrication of the devices with superior performance requires knowledge of optical and electronic properties of QDs. At present, the influence of different interconnected QDs parameters (such as QD size, strain and composition in QDs) on the properties of QDs has been studied. While structural parameters (QD size and shape) have been determined by direct methods such as transmission electron microscopy (TEM), scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) [3–6] optical techniques (photoluminescence and Raman spectroscopy) have been applied to study electron and vibrational spectra which provide information on strain and composition of the structures [7–10]. Evaluation of strain and composition in Ge/Si QD structures using Raman spectroscopy is based on the dependence of Ge, Ge–Si and Si–Si optical phonons vs. strain tensor components and composition found for Ge/Si superlattices and Ge_xSi_{1-x} solid solutions, respectively. Nevertheless, it was shown that even for wavy GeSi/Si superlattices the strain influences the frequencies of Ge, Ge–Si and Si–Si optical modes in a different way [10]. While the Ge and Ge–Si mode frequencies

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Table 1
Structural parameters of the Ge QD superlattices

No.	T_g (°C)	d_{Si} (nm)	d_{Ge} (ML)	n	x_{Ge}	e_{xx}
1	300	10	10	10	0.85 ± 0.05	-0.034 ± 0.002
2	300	4.5	10	10	0.85 ± 0.05	-0.034 ± 0.002
3	300	2.5	10	10	0.80 ± 0.03	-0.032 ± 0.001
4	300	1.5	10	10	0.78 ± 0.03	-0.031 ± 0.002
5	300	50	8	10	0.82 ± 0.05	-0.033 ± 0.002
6	400	50	8	10	0.80 ± 0.02	-0.032 ± 0.001
7	500	50	8	10	0.67 ± 0.02	-0.027 ± 0.001
8	600	50	8	10	0.53 ± 0.02	-0.022 ± 0.002
9	650	40	7	7	0.46 ± 0.05	-0.019 ± 0.002

behaviour is similar to those in GeSi/Si planar superlattices the Si–Si mode reveals an opposite behaviour. Moreover, despite the bulk behaviour of Ge–Si mode in Ge_xSi_{1-x} solid solutions is usually used for determination of composition in the QDs, the presence of Ge–Si modes in Raman spectra of Ge/Si superlattices can manifest only the formation of atomic clusters at the interfaces of superlattices. Thus, utilization of several vibrational modes for determination of both strain and composition can lead to misleading results. To the best of our knowledge despite of a number of papers being devoted to Raman studies of Ge QDs, no systematic study of the influence of any parameter (growth temperature, thickness of Ge, Si layers etc.) on vibrational properties of the structures in a wide range has been performed yet. In our paper we present the Raman study of Ge/Si QD superlattices grown at a wide substrate temperature region (300–650°C) that causes dramatic changes in QD size, shape, as well as the strain and the composition in the QDs.

2. Experimental

Samples under investigation were grown by molecular beam epitaxy utilizing the Stranski–Krastanov growth mode on Si-(0 0 1) substrates at temperatures varying in the range of 300–650°C. The period of structures consisting of Ge and Si layers with a nominal thickness of 7–10 monolayers (MLs, 1 ML = 0.14 nm) and 1–50 nm, respectively, was $n = 7$–10. The structural parameters of the samples under investigation are summarized in Table 1.

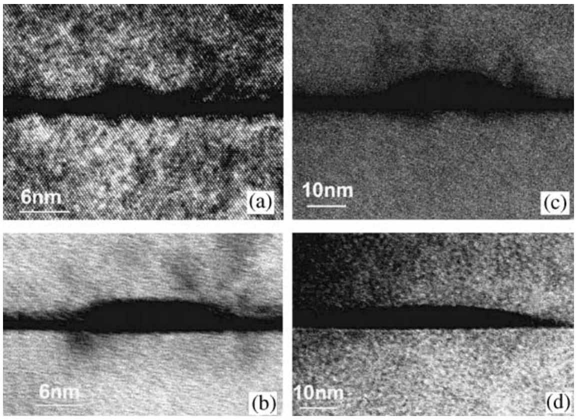

Fig. 1. Cross-sectional HRTEM images of Ge QD superlattices grown at different substrate temperatures: (a) 300°C, (b) 400°C, (c) 500°C, (d) 600°C.

The samples were investigated using a cross-sectional and plan-view high-resolution transmission electron microscopy (HRTEM). The cross-sectional HRTEM images of the samples are presented in Fig. 1. They show dramatic changes of QD size and shape of Ge QDs. One can see that hut clusters are predominantly formed only at the growth temperature of 300°C (Fig. 1(a)) while dome-like QDs occur at elevated temperatures (Fig. 1(b–d)). An average dot base size was found to be approximately 15 (20–100) nm with a QD height of 2 (4–6) nm for hut clusters (domes). A planview HRTEM image of sample 1 (Table 1) shows a single Ge QDs (Fig. 2). Here, despite the fact that QD is clearly seen an accurate determination of QD size from the image seems to

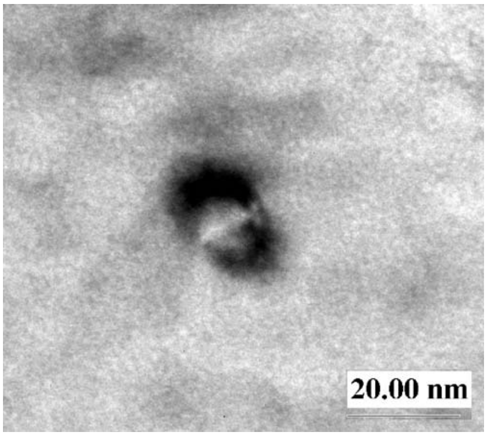

Fig. 2. Plan-view image of Ge QD superlattice grown at substrate temperature of 300°C (sample 1 in Table 1).

be a rather sophisticated problem, while HRTEM is sensitive to both the composition and the strain.

The Raman spectra were measured in a backscattering geometry using a Dilor XY triple spectrometer equipped with a micro-Raman setup. The Raman scattering experiments were performed using 514.5 nm (2.41 eV) line of an Ar^+ laser. The scattering geometries employed were $z(y,x)\bar{z}$, $z(x,x)\bar{z}$, $y'(x',x')\overline{y'}$ and $y'(z,x')\overline{y'}$ with x, y, z, x', y' parallel to the [1 0 0], [0 1 0], [0 0 1], [1 $\bar{1}$ 0] and [1 1 0] directions, respectively. For the study of TO phonons a microscope was employed to focus the light to the 1 μm spot on a cleaved (1 1 0)-oriented sample edge. The resolution was 2 cm^{-1} over the whole spectral range.

3. Results and discussion

The zone-center optical phonons in Ge are triply degenerated due to the cubic symmetry of the crystal. Strain reduces the symmetry and lifts the degeneration. Biaxial strain induces a splitting of the zone-center optical phonons into a doublet and a singlet for modes with atomic displacements in the (0 0 1) plane and normal to plane, respectively. For biaxial strain along the (0 0 1) plane, $\varepsilon_{xx} = \varepsilon_{yy}$ and ε_{zz} are the strain tensor components perpendicular and parallel to the [0 0 1] direction. The strain-induced shifts of optical phonons propagating along the [0 0 1] direction in pseudomorphic Ge/Si superlattices grown on a (0 0 1)-oriented Si substrate can be obtained using the following equations [11]:

$$p\varepsilon_{zz} + q(\varepsilon_{xx} + \varepsilon_{yy}) = \omega^2 - \omega_0^2 \tag{1}$$

for LO phonons and

$$p\varepsilon_{xx} + q(\varepsilon_{yy} + \varepsilon_{zz}) = \omega^2 - \omega_0^2 \tag{2}$$

for TO phonons. Here ω_0 is the frequency of the zone-center optical phonon in the absence of strain, p, q, r are the phonon deformation potentials taken from Ref. [12].

Using Eqs. (1) and (2) the shifts of LO and TO phonon frequencies in pseudomorphic Ge layers are determined as $\Delta\omega_{\mathrm{LO}} \approx 17\ \mathrm{cm}^{-1}$ and $\Delta\omega_{\mathrm{TO}} \approx 12\ \mathrm{cm}^{-1}$. In the case of the Ge–Si solid solution the frequency ω_0 is to be substituted by $\omega_0(x) = 280.8 + 19.37 \times x$ [10]. The frequency positions of LO and TO phonons are mostly determined by composition in Ge QDs while their splitting value depends only on the magnitude of the strain tensor components. Recently, it was shown [13] that a conventional backscattering from a (0 0 1) plane of Ge/Si QD superlattice allows only LO phonons localized in Ge QDs to be observed. The observation of TO phonons in Ge QDs requires the application of backscattering from the (1 1 0) cleavage surfaces ($y'(z,x')\overline{y'}$ scattering geometry in Porto notations) [13].

Fig. 3 shows the Raman spectra of the samples under investigation measured in $z(y,x)\bar{z}$ and $y'(z,x')\overline{y'}$ scattering geometries in the spectral range of Ge optical phonons. One can see that both TO and LO phonons localized in Ge QDs are clearly observed in the Raman spectra. The frequency positions of the phonons observed exceed the value of Ge optical phonon in bulk Ge (300 cm^{-1} at $T = 300$ K) indicating the presence of compressive strain in the QDs. The confinement of optical phonons in the structures under investigation under the experimental condition used can cause a 1–2 cm^{-1} shift towards lower frequency [14]. An asymmetrical shape of the Raman lines is due to the distribution of the Ge QDs in size [14,15]. Using Eqs. (1) and (2) the strain component ε_{xx} in the sample 1 with Si interlayer thickness ($d_{\mathrm{Si}} = 10$ nm) grown at a low growth temperature ($T_{\mathrm{g}} = 300$°C) is estimated as −0.034. The content of Ge in QDs is determined to be 85%. With

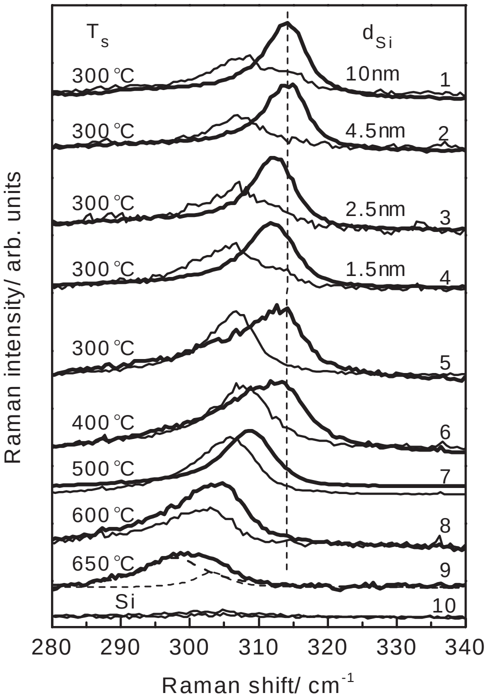

Fig. 3. Raman spectra of Ge QD superlattices grown with different thicknesses of Si interlayer at $T_g = 300°C$ (samples 1–4 and corresponding curves of the same numbers) and structures grown at different substrate temperatures $T_g = 300–650°C$ (samples 5–9). Raman spectra of a Si substrate measured under the same experimental conditions are shown for comparison. The dashed vertical line is a guide to the eye.

decreasing Si layer thickness the strain is elastically relaxed that is confirmed by an absence of misfit dislocations in HRTEM images of the structures. For a Si layer thickness of $d_{Si} = 2.5$ and $d_{Si} = 1.5$ nm in samples 3 and 4 the strain components of the partially relaxed structures amount to -0.032 and -0.031, respectively. A partial strain relaxation is induced by atomic Ge–Si intermixing in the QDs. The content of Ge is decreased up to 78% for sample 4 which has a Si layer thickness of 1.5 nm. Thus, decreasing Si layer thickness in Ge QD superlattices induces elastic strain relaxation and increasing Si content in the QDs.

Drastic changes occur in Raman spectra of Ge QD superlattices grown at different substrate temperatures ($T_g = 300–650°C$) shown in Fig. 3 (curves 5–9). With increasing growth temperature the frequency positions of Ge optical phonons and the LO–TO splitting value decrease. This manifests an elastic strain relaxation and increasing Si content in the Ge QDs. The content of Ge is about 50% for the samples grown at $T_g = 600–650°C$ (Table 1). It is worth mentioning that the LO–TO splitting is not resolved for sample 9. The frequency of Ge optical phonon was determined by decomposition of the phonons feature situated at about 300 cm^{-1} in two lines: a proper Ge optical phonon and the 2TA phonon. Ge–Si intermixing causes a disorder-induced second-order Raman scattering in Si layers (2TA phonon) of the structure. The contribution of 2TA obtained as well as Ge optical phonon line are shown in Fig. 3 by dashed lines.

4. Conclusion

We performed an experimental study of vibrational spectrum of Ge QD superlattices using Raman spectroscopy. The positions of LO and LO phonons confined in the Ge QDs observed in Raman spectra were used to calculate both strain and composition in the QD. It was found that the strain in QDs relaxes elastically and the Si content increases with decreasing Si interlayer thickness and increasing growth temperature of the structures.

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