Resonant Raman scattering of relaxed Ge quantum dots

A G Milekhin, A I Nikiforov, O P Pchelyakov
Institute of Semiconductor Physics, 630090 Novosibirsk, Russia

J C Galzerani
Departamento de Fisica, Universidade Federal de Sao Carlos, C.P.676, 13565-905 Sao Carlos, SP, Brasil

S Schulze, D R T Zahn
Institut für Physik, Technische Universität Chemnitz, D-09107, Chemnitz, Germany

Abstract. This paper presents the results of an investigation of fundamental vibrations in self-organised Ge/Si structures with a single layer of relaxed Ge quantum dots performed using resonant Raman spectroscopy. A two mode distribution of quantum dots in size in the ranges of 100-200 nm and 3-6 nm is evident from the plan-view and cross-sectional high resolution transmission electron microscopy experiments. Raman spectra measured in the vicinity of E_0 resonance in Ge QDs show that the position of the Ge phonon localized in QDs shifts towards lower frequencies with increasing excitation energy indicating the presence of a QD size distribution.

1. Introduction

Recently, it has been demonstrated that under certain growth conditions dislocation-free pseudomorphic Ge quantum dots (QDs) of various QD sizes (a lateral size of 8-95 nm and a dot height of 1-7 nm) can be fabricated [1-5]. Their vibrational properties have been intensively investigated by Raman spectroscopy [1-3,6-11]. In the low frequency region, the Ge QD superlattices behave very similar to planar superlattices exhibiting a number of low frequency phonon oscillations in the Raman spectra [8,10,11].
Optical phonon frequencies in such structures undergo shifts due to both strain and confinement. The built-in strain and Ge-Si intermixing in Ge QDs have been determined using the frequency positions of optical phonons in the QDs [1,6-9]. The strain field in self-assembled QDs was shown to depend very little on the dot size [12], while confinement strongly influences the frequency position of phonon lines. Influence of confinement effect on the frequencies of optical phonons in Ge QDs has been studied by resonant Raman scattering [1,6].
In particular cases the self-organising growth provides an opportunity to form small relaxed QDs where only confinement affects the optical phonon frequencies. For the Ge/Si system the introduction of an intermediate SiO_2 layer of nanometer thickness

before Ge deposition is used to form Ge QDs with sizes less than 7nm [13]. In this paper we report on a study of optical phonons in relaxed Ge QDs using resonant Raman scattering.

2. Experimental

Samples were grown by MBE on silicon (100) wafers misoriented by less than 0.5°. An oxide layer was formed on the substrates with a 50 nm buffer silicon layer grown at a substrate temperature of 600°C. The oxide layer was grown for 5 min at 500°C at an oxygen pressure of $2 \cdot 10^{-4}$ Pa in the chamber. Oxygen was fed into the MBE chamber using a leak valve at a turned-on ion pump. According to Ref. [13] the Si (100) surface is oxidised under these conditions. After oxygen was pumped out and the chamber pressure reached 10^{-7} Pa, Ge was deposited at a rate of 0.3 nm/min. Two samples with different nominal thickness (1 and 2 nm) of Ge QD layer were fabricated. Weak smeared out reflections assigned to the island film were observed against a strong diffuse background in the post-deposition diffraction pattern. The last stage of germanium island formation was an annealing process at a temperature of 900°C for 3 min. After this procedure a sharp diffraction pattern containing clear reflections due to bulk diffraction from 3D islands was recorded. In order to protect the island surface against oxidation in air, part of the wafer was covered by a 10 nm layer of amorphous silicon.

Characterisation of structural parameters of QDs was performed using a transmission electron microscope (TEM) CM20 FEG Philips with Gatan imaging filter GIF 200. The Raman scattering experiments were performed using lines of Ar^+, Kr^+ and HeNe lasers in the range of 676.4-457.9nm (1.83-2.71eV). The scattered light was analyzed in backscattering geometry using a Dilor XY triple monochromator equipped with a CCD camera for multichannel detection. The monochromator slits were set to a spectral resolution of 1.5 cm^{-1}. The scattering geometries employed were z(xx)-z and z(xy)-z in macro-Raman experiments, where the labels x, y, z refer to directions parallel to the [100], [010], [001], respectively.

3. Results and discussion

The existence of Ge QDs was evident from TEM experiments. Figure 1 presents the plan-view TEM images of the structure with relaxed Ge QDs. A two mode distribution of QDs in size is clearly observed from the images taken at different resolution. The typical lateral sizes of the QDs determined from the images are 100-200 and 3-6 nm.

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A typical Raman spectrum of such a Ge dot structure is shown in Fig.2. Strong peaks in the spectrum are observed at 295, 406 and 520 cm^{-1} in the spectra and attributed to Ge-Ge, Ge-Si vibrational modes [1] and the Si phonon predominantly stemming from the substrate, respectively. The broad feature near 480 cm^{-1} corresponds to local Si-Si vibrations and indicates Ge-Si intermixing at the interface [14]. Phonon confinement causes a downward shift of the Ge optical phonon frequency with respect to its value in Ge bulk (303 cm^{-1} at 295K). It is worth mentioning that the Raman spectrum of the bare (001)-oriented Si also exhibits a maximum at about 300 cm^{-1} due to second-order scattering by 2TA phonons originating from the X or (and) the Σ points of the Brillouin zone in Si [15]. Possible misinterpretation of the phonon lines was already discussed in Ref. [16]. One possible way to differentiate between contributions from Ge QDs and the Si substrate is to perform resonant Raman scattering.

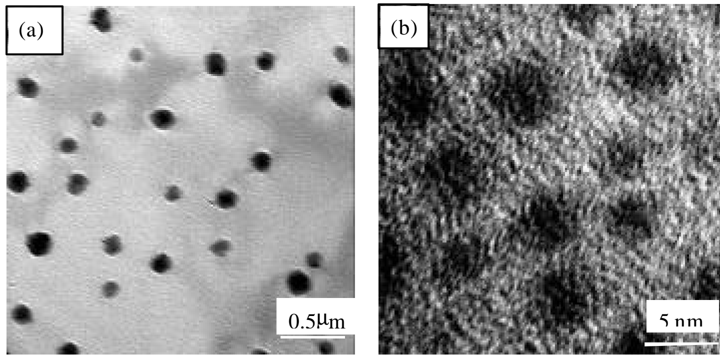

Figure 1. The plan-view TEM images of a sample with Ge QDs (1nm of nominal Ge coverage) grown on a thin silicon oxide layer. a)- a low resolution image, b)- HRTEM

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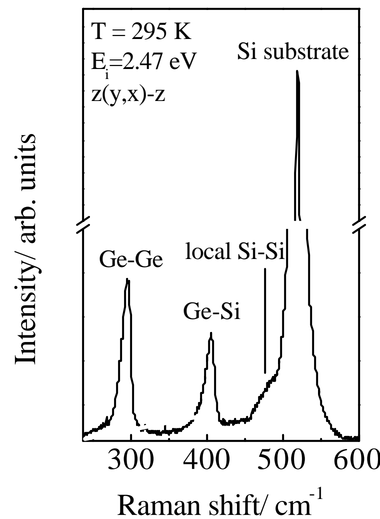

Figure 2. Raman spectrum of a Ge QD structure grown on a thin silicon oxide layer measured in $z(y,x)\bar{z}$ scattering geometry at an excitation energy E_i=2.47eV.

Resonant Raman scattering spectra of the structures with relaxed Ge QDs measured with different laser excitation energies (Fig.3) in the vicinity of E_0 resonance in Ge QDs show that the position of the Ge phonon shifts towards lower frequencies with increasing excitation energy while the Raman line broadens. This behavior is found to be typical for the QDs whose constituent materials have a negative dispersion of optical phonons [17]. Figure 4 shows the frequency positions of the Ge phonon and the Raman efficiencies vs. excitation energy for samples with relaxed Ge QDs. The values presented in Fig.4 were normalised to those of the Si phonon feature observed in the same Raman spectra. The observed dependence of Raman intensity of Ge phonon scattering and the frequency positions on excitation energy allows to make an unambiguous assignment of the Ge peak. The maximum of the Raman efficiency at 2.42 eV (1nm of nominal Ge coverage)

!!!! According to fig. 4 1nm = squares, then maximum = 2.35 eV!!!!

is attributed to the E_0 transition in Ge QDs. The energy of the E_0 resonance in Ge bulk

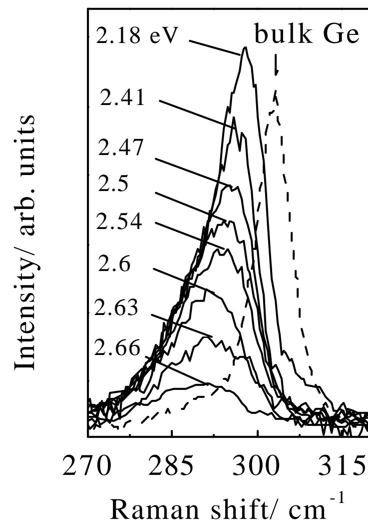

Figure 3. Raman spectra of a Ge QD structure (Ge coverage of 1 nm) measured in $z(y,x)\bar{z}$ scattering geometry at different excitation energies. The frequency position of Ge optical phonons in Ge bulk is shown by the dashed line.

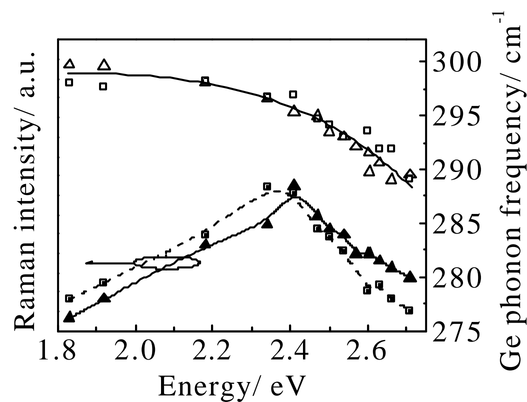

Figure 4. Raman intensity and frequency positions of Ge phonons for a Ge QD structure with a nominal Ge coverage of 1nm (squares) and 2nm (triangles) grown on a thin silicon oxide layer measured in $z(x,y)\bar{z}$ geometry. Solid and dashed lines are guides to the eye.

amounts to 0.9 eV while in Ge QDs it reaches a value of about 2.5 eV due to electronic confinement [9]. There seems to be a shoulder located at about 2.2 eV likely being due to the E_1 transition in relaxed Ge QDs. The maximum of the Raman efficiency with a larger nominal thickness of the Ge QD layer (2 nm) shifts towards lower energy (2.35 eV)

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!!!! see comment above there is a mistake in assignment!!!!

. The Raman intensity for small-sized QDs, in which electronic states lie at higher energies, increases when the excitation line approaches the E_0 energy. The frequency position of the Ge optical phonon under non-resonant conditions (300 cm^{-1} at 1.83 eV) corresponds to the bulk value of relaxed Ge. Since the QD structures under investigation have a two mode size distribution of QDs, it is most probable that the large Ge islands (see Fig.1. a) for which the confinement effect is negligible contribute effectively to the Raman scattering. With increasing excitation energy (above 2.3 eV) the smaller QDs are more involved in the scattering process. Size-selective Raman scattering by optical phonons in relaxed Ge QDs leads to a decrease of the phonon frequency position with increasing excitation energy. This shift is about 10 cm^{-1} thus exceeding the corresponding value in strained Ge QDs (about 5 cm^{-1}) [6] due to the significantly smaller size of the relaxed QDs**.**

The maximum of the Raman efficiency with a larger nominal thickness of the Ge QD layer (2 nm) shifts towards higher energy (2.42 eV) and indicates the formation of small-sized Ge QDs.

!!!! Once again this is not in accordance with fig. 4!!!!

In conclusion, MBE growth of relaxed Ge QDs on a silicon oxide layer of a nanometer thickness has been demonstrated. Two mode distribution of Ge QDs in size was evident from transmission electron microscopy experiments. Resonant size-selective Raman scattering allows to make unambiguous assignment of optical phonons localized in the relaxed Ge QDs.

Acknowledgements

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