Mat. Res. Soc. Symp. Proc. Vol. 737 © 2003 Materials Research Society E13.7.1

# Resonant Raman Scattering by Strained and Relaxed Ge Quantum Dots

Alexander G.Milekhin[1], Alexander I.Nikiforov[1], Mikhail Ladanov[1], Oleg P. Pchelyakov[1], Dmitri A.Tenne[1], Steffen Schulze, Dietrich R.T.Zahn
Institut für Physik, Technische Universität Chemnitz, D-09107, Chemnitz, Germany
[1]Institute of Semiconductor Physics, 630090 Novosibirsk, Russia

## ABSTRACT

Fundamental vibrations in Ge/Si structures with strained and relaxed Ge quantum dots (QDs) grown by molecular beam epitaxy were investigated using resonant Raman spectroscopy. Transmission electron microscopy experiments show that the strained Ge QDs are typical "hut clusters" with base size of 15nm and a height of 2nm. A two mode distribution in size (100-200nm and 3-6nm) is found for relaxed QDs. The Raman efficiencies of the Ge optical phonons as a function of excitation energy reveal maxima at 2.35-2.41eV attributed to the $E_0$ resonance in Ge QDs due to electronic confinement. The frequency positions of optical phonons localized in Ge "hut clusters" under non-resonant conditions correspond to fully strained Ge QDs while the frequency position of optical phonons in relaxed Ge QDs corresponds to the value in bulk Ge. With increasing excitation energy (2.5-2.7eV) the position of the Ge optical phonons shifts downwards due to size-confinement effect of optical phonons in strained and relaxed Ge QDs, indicating the presence of a QD size distribution in Ge dot structures.

## INTRODUCTION

Physical properties of semiconductor quantum dots (QDs) have recently attract much attention. The three-dimensional confinement of charge carriers and consequently the atomic-like electronic spectrum of such structures drastically influences the electronic and optical properties, which are much different from those of bulk solid materials [1-3]. Many exciting experiments have been performed in the field of e.g. luminescence and nonlinear optics revealing this novel state of matter with improved properties for potential applications in nanoelectronic and optoelectronic devices such as light-emitting diodes, photovoltaic cells and single-electron transistors [4]. From the point of view of potential device application Ge/Si and Ge/$SiO_2$ nanostructures are attractive candidates due to the high compatibility and possible integration with well-developed silicon technology. Despite a number of techniques known to fabricate QD structures a breakthrough has occurred through the employment of self-assembled growth using molecular beam epitaxy (MBE), chemical beam epitaxy (CBE), and metal-organic chemical vapor deposition (MOCVD) of a number of lattice mismatched semiconductors. This approach is based on the Stranski-Krastanov growth mode in which deposition of a material having a large lattice mismatch with respect to the substrate under certain conditions leads to spontaneous formation of high density arrays with strained coherent (dislocation-free) islands of nanometer size that exhibit excellent optical properties [5-7]. Recently the self-organising growth was also applied to form small relaxed QDs. For the Ge/Si system the introduction of an intermediate silicon oxide layer of nanometer thickness before Ge deposition is used to form relaxed Ge QDs with sizes less than 7nm [8]. A number of papers is devoted to investigation of Ge related nanostructures by Raman spectroscopy. Optical phonons are found to be a sensitive probe for study structure, built-in strain, atomic intermixing in Ge QDs [9-12].

In this paper we report on a study of self-organised nanostructures with strained and relaxed Ge QDs using resonant Raman scattering.

## EXPERIMENTAL DETAILS

Structures with Ge QDs were grown by molecular beam epitaxy (MBE) of Ge and Si layers on (001)-oriented Si substrates.

Ge/Si structures with strained Ge QDs were fabricated utilizing the Stranski-Krastanov growth mode. The growth temperature of the silicon layers was 800 and 500ºC before and after Ge deposition, respectively. The Ge quantum dot layers were grown at 300ºC. Control of thickness and structure of the growing film was performed by recording intensity oscillations of reflection high electron energy diffraction (RHEED) from the film surface. The set of samples under investigation consists of Ge and Si layers with nominal thicknesses $d_{Ge}$= 1.4 nm and $d_{Si}$= 37 nm. The period of repetition of the Ge and Si layer pair was 10. As it was shown previously the atomic intermixing for such a thickness is negligible [11].

Structures with relaxed Ge QDs were grown on an oxide layer formed on the substrates with a 50 nm buffer silicon layer grown at a substrate temperature of 600°C. The oxide layer was formed for 5 min at 500°C at an oxygen pressure of $2 \cdot 10^{-4}$ Pa in the chamber. According to Ref. [8] the Si (100) surface is oxidised under these conditions. Two samples with different nominal thickness (1 and 2 nm) of Ge QD layer were fabricated. In order to protect the island surface against oxidation in air the wafer was covered by a 10 nm layer of amorphous silicon.

The Raman scattering experiments were performed in $z(x,x)\bar{z}$ and $z(x,y)\bar{z}$ scattering geometry, where x, y, z refer to directions parallel to the [100], [010], [001] crystal axes, respectively. As excitation sources $Ar^+$, $Kr^+$ and HeNe lasers having lines in the range of 676.4-457.9nm (1.83-2.71eV) were used. 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 $cm^{-1}$.

## DISCUSSION

Structural parameters of Ge quantum dots were obtained from cross-sectional high resolution transmission electron microscopy (HRTEM) images shown in Fig.1. Ge/Si QDs are typical “hut” clusters with the dot base size of strained of approximately 15 nm with a QD height of about 1.5-2 nm. The density of the dots was estimated to be $3 \times 10^{11} cm^{-2}$. The dot uniformity is about 20%. Ge QDs grown on a $SiO_2$ layer have hemi-spherical shape with a base size of 4-6 nm and a height

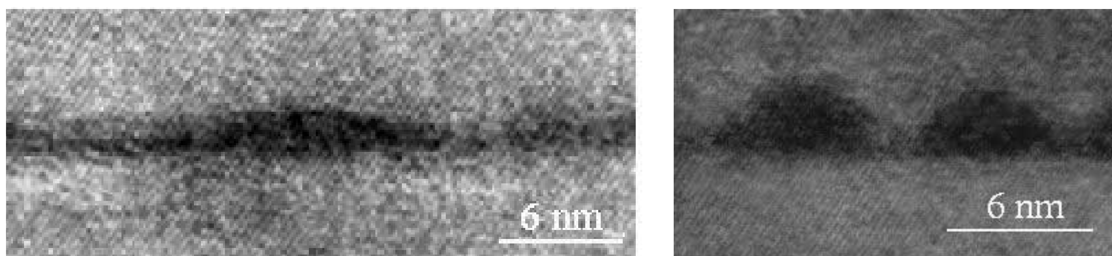


**Figure 1.** Cross-sectional HRTEM images of a)- a Ge/Si QD layer, b)- a Ge QD layer on $SiO_2$.

of 3-4 nm. The areal density of the islands was approximately $2{\cdot}10^{18}$ cm$^{-2}$. Formation of large-scale Ge islands (100-200nm) with an areal density of $7.3{\cdot}10^{7}$ cm$^{-2}$ was also established from transmission electron microscopy experiments (not shown in the figure).

Raman spectra of relaxed and strained Ge dot structures are shown in Fig.2. The strong peak in the spectrum of the structures with relaxed QDs observed at 297 cm$^{-1}$ corresponds to Ge optical phonons confined in the QDs (longitudinal and transverse optical (LO and TO) phonons are degenerated at the center of the Brullouin zone). Ge/Si structures reveal a peak at 315 cm$^{-1}$ which is attributed to longitudinal optical (LO) phonons in the pseudomorphic Ge QDs [13]. Features near 400 and 520 cm$^{-1}$ in the spectra are attributed to Ge-Si vibrational modes [9] and the Si phonon predominantly stemming from the substrate, respectively.

It was already discussed [14] that the bare (001)-oriented Si also exhibits a maximum at about 300 cm$^{-1}$ in the Raman spectrum due to second-order scattering by 2TA phonons originating from the X or (and) the Σ points of the Brillouin zone in Si and can lead to misinterpretation of the Raman spectra of the nanostructures with relaxed Ge QDs. From other side, interpretation of the Raman spectra of the structures with strained Ge QDs requires the influence of both confinement and strain on Ge phonon line to be distinguished. Phonon confinement causes a downward shift of the Ge optical phonon frequency with respect to its bulk value while strain in Ge QDs is responsible for an upward shift. One possible way to differentiate between contributions from Ge QDs and the Si substrate and to determine an influence of strain and confinement on Ge phonons is to perform resonant Raman scattering experiments.

Fig.3 shows the Raman spectra of relaxed and strained Ge QD structures measured in $z(x,y)\bar{z}$ scattering geometry at different excitation energies. One can see from the figure that the position of Ge phonon in the QDs shifts towards lower frequencies with increasing excitation energy while the Raman line broadens. Strain distribution in the QDs of different sizes can also affect the frequencies of optical phonons in QD's. Nevertheless, calculations of the spatial strain distribution show that the strain in Ge QD's does not significantly depend on the QD size [15]. This effect can be entirely excluded in Raman scattering experiments under resonant conditions

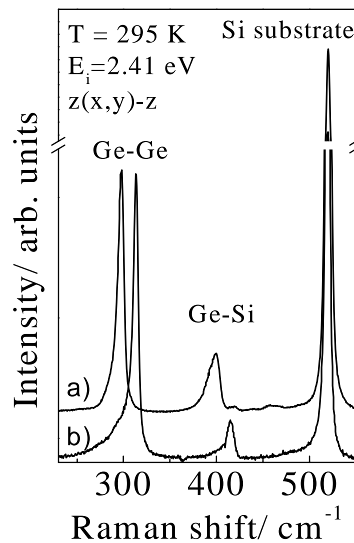


**Figure 2.** Raman spectra of a Ge QD structures grown on a) a thin silicon oxide layer and on b)-silicon layer measured in $z(x,y)\bar{z}$ scattering geometry at an excitation energy $E_i$=2.41 eV

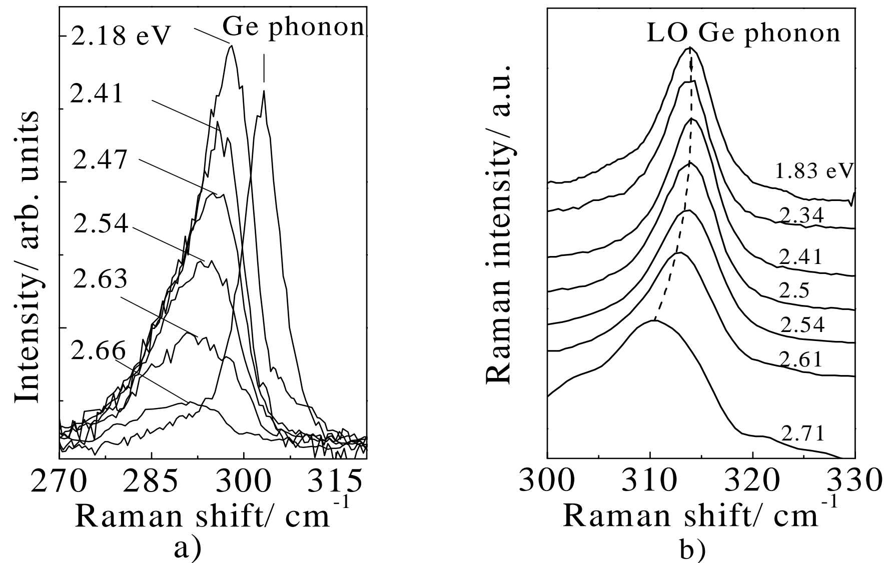


**Figure 3.** Raman spectra of a)-relaxed and b)- strained Ge QD structures (Ge coverage of 1 nm) measured in $z(x,y)\bar{z}$ scattering geometry at different excitation energies. The frequency position of Ge optical phonons in the Raman spectrum of Ge bulk is shown by the vertical line. The dashed line is a guide to the eye.

using relaxed Ge QDs. Thus, the low frequency shift of optical phonons vs excitation energy is entirely determined by confinement in the QDs.

Fig.4 shows the Raman efficiencies and the frequency positions of the LO Ge phonon as a function of excitation energy derived from Fig.3. 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 unambiguous assignment of the Ge peak. The frequency positions of optical phonons localized in Ge "hut clusters" under non-resonant conditions correspond to fully strained Ge QDs while the frequency position of optical phonons in relaxed Ge QDs corresponds to the value in bulk Ge. The position of the optical phonons localised in Ge QDs shifts towards lower frequency with increasing excitation energy (from 2.5 to 2.7 eV). This shift amounts to 4-5 cm$^{-1}$ (about 10 cm$^{-1}$) for the structures with strained (relaxed) QDs and indicates the presence of a QD size distribution in the Ge dot nanostructures.

Raman efficiency of the nanostructures reveals the broad resonance peak near 2.2-2.4eV. The large broadening of the resonant peak (0.4 eV) can be explained by contributions of several resonances. The maximum of the Raman efficiency for relaxed QDs at 2.35 eV (1nm of nominal Ge coverage) is attributed to the $E_0$ transition in Ge QDs. The energy of the $E_0$ resonance in Ge bulk amounts to 0.9 eV while in Ge QDs it reaches a value of about 2.5 eV due to electronic confinement [17]. With a larger nominal thickness of the Ge QD layer (2 nm) the position of the maximum shifts towards higher energy (2.42 eV) indicating formation of QDs with a smaller size. The shoulder located at about 2.2 eV is likely due to the $E_1$ transition in relaxed Ge QDs.

In strained Ge quantum dots the maximum of Raman efficiency is very close to the resonance at 2.34 eV observed in Ref. [9] and assigned to the $E_1$ transition. Due to the biaxial compressive strain the energy of the $E_1$ transition is increased by 0.16 eV from its bulk value (2.23 eV). At the

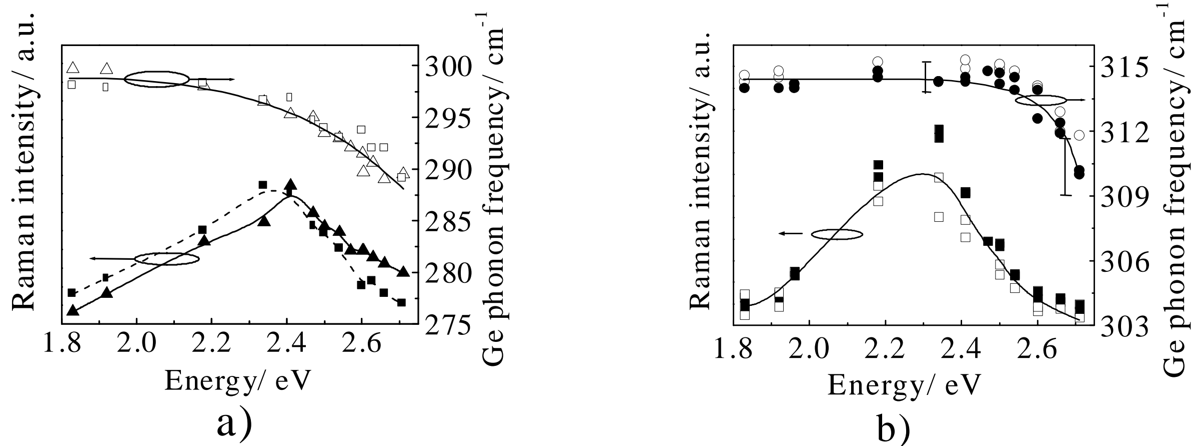


**Figure 4.** Raman intensity and frequency positions of Ge phonons for a)-a Ge QD structure with a nominal Ge coverage of 1nm (squares) and 2nm (triangles) grown on a thin silicon oxide layer measured in $z(x,y)\bar{z}$ geometry and for b)-Ge/Si QD structure measured in $z(x,y)\bar{z}$ (open) and $z(x,x)\bar{z}$ (solid) geometry. Error bars are given for resonance and non-resonance conditions. Solid lines are guides to the eye.

low energy part (2.0-2.2 eV) the $E_0$ resonance in the wetting layer can contribute to the resonance profile [16] while the $E_0$ resonance in Ge QDs is responsible for the peak broadening at higher energy (2.4-2.6 eV).

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 optical phonon in relaxed (strained) Ge QDs under non-resonant conditions amounts to 300 $cm^{-1}$ (315 $cm^{-1}$) at 1.83 eV and corresponds to the value of relaxed Ge bulk (pseudomorphic Ge). Since Ge QD in the structures under investigation are distributed in size, it is most probable that the large Ge islands 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 Ge QDs leads to a decrease of the phonon frequency position with increasing excitation energy. This shift in relaxed Ge QDs exceeds the corresponding value in strained Ge QD superlattices due to the significantly smaller size of the relaxed QDs**.**

The frequency positions of optical phonons confined in Ge QDs allow the QD size to be determined. The Ge optical phonons reflect elastically at the Ge/Si interface of two faces of pyramidal Ge/Si QDs and a dot base creating a resonator [17]. Using dispersion relation of LO phonons in bulk Ge a wavevector corresponding to the observed optical phonons confined in the resonator is found to be $q=(0.25\pm0.05)/a$ . The first mode confined in QD should satisfy the following equation: $2\cdot h\cdot \cos\alpha=\pi/q$ , where h and $\alpha$ are the dot height and the angle between the dot base and pyramid faces. The QD height obtained from this relation amounts to $(0.9\pm0.2)$ nm. Thus, the smallest QDs which are involved to Raman scattering process have a height of 0.7 nm and a lateral size of 9nm.

An average size of relaxed QDs contributing to Raman scattering at particular excitation energy was estimated supposing the QDs have a spherical shape. The phenomenological model [18] was used to calculate the Raman spectra and determine the QD size from the best fitting of

theoretical spectra to experimental ones. The Ge QDs with an average size of 7.5; 5.4;3;2.2 and 2 nm are predominantly contribute to the Raman spectra measured at an excitation energy of 2.18; 2.41; 2.47; 2.54; 2.63 and 2.66 eV, respectively.

## CONCLUSIONS

MBE growth of strained Ge/Si QD structures and relaxed Ge QDs on a silicon oxide layer of a nanometer thickness has been demonstrated. Size and shape of Ge QDs in size was derived from transmission electron microscopy experiments and Raman data. Resonant size-selective Raman scattering allows to make unambiguous assignment of optical phonons localized in the relaxed Ge QDs. Influence of confinement effect and strain in the QDs on the vibrational spectrum of Ge QD structures can be studied using resonant Raman scattering.

## ACKNOWLEDGEMENTS

The present study was supported INTAS (grant 01-0444) and RFBR (02-02-17746).

## REFERENCES

1. U. Woggon, *Optical properties of Semiconductor quantum dots*, Springer Tracts in Modern Physics v. 136 (Berlin, Heidelberg, 1997).
2. P. Beaumont and C. N. Sotomayor-Torres eds., *Science and Engineering of One-and Zero-Dimensional Semiconductors*, v. 214 (New York: Plenum Press, 1990).
3. D. Bimberg, M. Grundmann, and N. N. Ledentsov, *Quantum Dot Heterostructures* (Wiley, New York, 1999).
4. A. P. Alivisatos, *MRS Bulletin/February,* 18 (1998).
5. B.Voigtlaender, *Surf.Sci.Reports* **43**, 127 (2001).
6. F.Liu, M.G.Lagally, *Surf.Sci.* **386**, 169 (1997).
7. C. S. Peng, Q. Huang, W. Q. Cheng, J. M. Zhou, Y. H. Zhang, T. T. Sheng and C. H. Tung, *Phys.Rev.* **B57**, 8805 (1998).
8. A. A. Shklyaev, M. Shibata and M. Ichikawa, *Phys. Rev.* **B62**, 1340 (2000).
9. C. H. Kwok, P. Y. Yu, C. H. Tung, Y. H. Zhang, M. F. Li, C. S. Peng and J. M. Zhou *Phys.Rev.***B59**, 4980 (1999).
10. H. K. Shin,D. J. Loockwood and J.-M. Baribeau, *Solid St.Comm.* ***114*,** 505 (2000).
11. A. G. Milekhin, A. I.Nikiforov, O. P. Pchelyakov, S. Schulze and D. R. T. Zahn, *Eur. Phys. J.* **B16**, 355 (2002).
12. C. Guedj, A. Beyer, E. Mueller and D. Gruetzmacher, *Appl. Phys. Lett.* **78**, 1742 (2001).
13. A. Milekhin, S. Schulze, D. R. T. Zahn, N. Stepina, A. Yakimov and A. Nikiforov, *Appl.Surf.Sci.* **175-176**, 629 (2001).
14. A. V. Kolobov, *J. Appl. Phys.* **87** 2926 (2000).
15. A. V. Nenashev and A. V. Dvurechensky, *JETP* **91**, 497 (2000).
16. R. Schorer, G. Abstreiter, S. de Gironcoli, E. Molinari, H. Kibbel and H. Presting, *Phys. Rev.* **B49**, 5406 (1994).
17. A. B. Talochkin, V. A. Markov, A. I. Nikiforov and S. A. Teys, *JETP Lett.* **70**, 288 (1999).
18. I. H. Campbell and P. M. Fauchet, Solid State Commun. **58**, 739 (1986).