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Raman scattering from Ge nanocrystals on Si substrates: problems and solutions

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1. Introduction

Recent years have witnessed growing interest in Ge and Si nanostructures. A number of groups have reported the formation of Ge nanocrystals embedded in SiO₂ by different methods such as annealing of Ge-containing oxides [1, 2], ion implantation [3], UV-assisted oxidation [4] and intense photoluminescence around 2 eV has been observed [2, 4].

The technique most often used to characterize the structure of the nanocrystals is Raman scattering. However, as some of us have argued earlier [5], in many cases the experimentally observed peak attributed to Ge is in fact coming from the Si substrate (See Fig. 1). The three upper curves represent Raman spectra of Ge nanocrystals formed in SiO₂ by different methods [1, 3, 4]. The lower curve is a Raman spectrum of a silicon wafer [6]. The striking line shape similarity of the “Ge nanocrystal” samples with that of the Si wafer and one-to-one correspondence of features located at 229, 300 and 435 cm⁻¹ clearly demonstrate that the reported spectra are strongly dominated by the two-phonon acoustic Si peak. It is thus very important that the Ge signal be separated from the Si peak and below we present results of different approaches to achieve his goal.

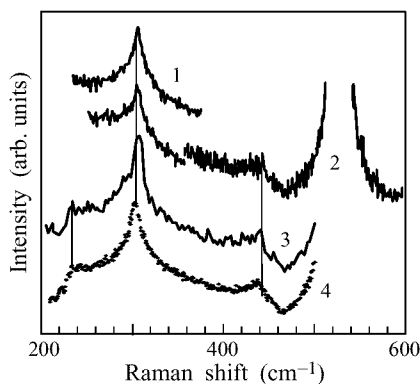


Fig. 1. Raman spectra from Ge nanocrystals samples prepared through different techniques (curves 1–3, respectively after Refs) and that from a Si wafer (4).

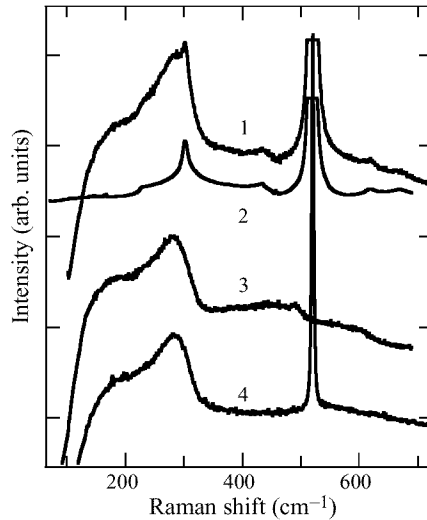


Fig. 2. Raman spectra of as-made samples containing 60.2 mol.% Ge deposited onto Si (1) and quartz glass (3). The dotted line (2) is a Raman spectrum of the Si wafer. At the bottom, HY-polarized spectrum (4) is shown. The excitation light is a 633 nm line from a He–Ne laser. The spectra obtained under the non-polarized and polarized conditions are normalized.

2. Experimental details

The samples were prepared by co-deposition of Si and Ge oxides onto Si(001) substrates by magnetron sputtering. The Ge concentration varied from 25 to 60 mol.%. After deposition, the samples were annealed for 1 h at 800 °C in an argon atmosphere which produced nanocrystals with a characteristic size of 6–8 nm. More details can be found elsewhere [2].

Raman spectra were taken at room temperature in the back-scattering geometry. A YAG:Nd³⁺ laser ($\lambda = 1064$ nm), a He–Ne laser ($\lambda = 633$ nm) and an Ar-ion laser ($\lambda = 488$ nm) were used as excitation light source. The temperature dependence was studied using the He–Ne excitation in the temperature range from ~ 77 K to 300 K. In the case of polarized measurements, a thin film polarizer was placed at the entrance slit of the monochromator.

The X-ray absorption measurements were performed at BL13B station at the Photon Factory using a 27-pole wiggler magnet inserted in a 2.5 GeV storage ring. More details can be found elsewhere [7].

3. Experimental results

Figure 2 shows Raman spectra for an as-made sample (60.2 mol.% Ge) together with the signal obtained from the back side of the same Si substrate under the same conditions. The excitation source is a He–Ne laser. The origin of features located at 229, 300, and 435 cm^{-1} is obvious: they come from the substrate. The only contribution from Ge is a broad feature located below 300 cm^{-1} . This is further evidenced by the spectrum of an identical sample deposited onto a quartz glass substrate.

One possible way to decrease the contribution from the substrate is to make use of resonant Raman scattering. We found that indeed if an Ar-ion laser is used (the dielectric constant, ϵ_2 , of Ge reaches maximum at around 2.3 eV) the signal from the substrate is

considerably suppressed. Use of 1064 nm light did not result in improvement of the Ge/Si peak ratio.

Since the Si peak located at 300 cm^{-1} is a two-phonon peak while that of Ge is a single phonon peak, they should have different temperature dependencies. Our measurements show that while the intensity of the Si peak does decrease at lower temperatures it still remains significant.

Finally, we used various scattering configurations. It is known [6, 8] that the acoustic two-phonon peak disappears in the configuration when the polarisation planes of the incident and scattered beams are parallel to each other. Curve 4 in Fig. 1 shows the polarised Raman spectrum. The spectrum does not contain the contribution from the Si substrate: the features at 229, 300 and 435 cm^{-1} disappear and the remaining broad peak is very similar to the one detected in the sample on a quartz substrate (curve 3).

4. Discussion

The above results allow us to conclude that the most efficient way to suppress the relative intensity of the Si two-phonon signal is to use an Ar-ion laser as the excitation source and/or utilize an appropriate scattering configuration.

Based on the peak position and line shape we conclude that the Ge peak observed in as-made samples is due to amorphous Ge present in the matrix. Upon annealing, Ge nanocrystals are formed. The formation of Ge crystals was checked by Raman spectroscopy. The line shape of the observed peak is asymmetric as should be for nanocrystals. The formation of nanocrystals was also verified by HR-TEM.

In order to confirm these conclusions we have also performed EXAFS (extended X-ray absorption fine structure) measurements. We found no peaks above the first Ge–Ge neighbour which confirms our conclusion that Ge is mainly present in the amorphous phase. After annealing the Ge–Ge peak gets stronger and peaks corresponding to higher shells emerge which is another evidence of crystallisation. Details of this work will be published elsewhere [9].

In samples with lower Ge concentration we were not able to observe any Ge-related features in the Raman spectra although our TEM and EXAFS studies indicated the formation of Ge nanocrystals.

At present we do not completely understand why there are no Ge-related peaks in the Raman spectra containing 25 and 40 mol.% Ge. A possible explanation is that in the case of lower Ge concentration the formed nanocrystals are much smaller (our TEM data) and the line broadening due to the size distribution can be more significant. Further studies are needed and are currently underway.

5. Conclusion

We have demonstrated that in many cases the experimentally observed peak at $\sim 300\text{ cm}^{-1}$ is in fact originating from the Si substrate. We have found that the most promising ways to tackle this problem are (1) use of resonant Raman and/or (2) use of polarized Raman scattering. The former is more efficient to excite the Ge nanoclusters but also results in stronger photoluminescence which can make the measurement more difficult.

Our results also demonstrate that Raman scattering can be used as an efficient probe only if Ge concentration exceeds a certain value.

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