A Raman scattering study of self-assembled pure isotope Ge/Si(100) quantum dots

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Use of self-assembled Ge/Si(100) quantum dots (QDs) grown from pure isotope ^{70}Ge and ^{76}Ge sources provides a unique possibility to experimentally deconvolute contributions from Ge QDs and Si substrate into the Raman spectrum. We demonstrate that raw Raman spectra of Ge/Si(100) QDs are dominated by the Si substrate. We further show that intermixing in the QDs depends on the dot size and is stronger in smaller dots, and that the Ge-rich area exists as a core of the dots. It is also shown that the amplitude of the Raman peak is *not* directly proportional to the number of the corresponding bonds. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1521261]

The lattice mismatch between the substrate and the overgrown layer allows the formation of self-assembled quantum dots (QDs) through the Stranski–Krastanov mechanism, and this technique has been successfully applied to various semiconductor systems. Interest in Ge/Si QDs is additionally driven by the conjecture that the size reduction results in a change in the electron band structure and leads to a significant increase in the efficiency of optical transitions.[1]

The local structure of the grown QDs is, however, not definitely known. Raman scattering is routinely used to characterize the structure. However, the Si two-phonon acoustic peak, located at almost exactly the same frequency as the Ge peak, usually dominates the Raman spectrum, making it difficult to draw definite conclusions.[2]

In order to check the applicability of Raman scattering to the characterization of Ge/Si self-assembled QDs, and to determine the location of the Ge-rich phase in the QDs, we have used pure ^{70}Ge and ^{76}Ge isotopes whose Raman peak positions are shifted by about 11 cm^{-1} with respect to each other. Raman scattering has previously been successfully applied to the study of bulk Ge isotopes[3] and ^{70}Ge/^{76}Ge superlattices.[4] The samples for this study were grown on Si(100) with a Si buffer layer using a solid source molecular beam epitaxy, a growth temperature of 350 °C, and a nominal thickness of ~10 monolayers. An atomic force microscopy (AFM) image of the uncapped sample is shown in Fig. 1. The formed nanostructures, all dome-shaped, possess two

characteristic sizes. The smaller ones have a base diameter ~100 nm, a height ~20 nm, and an areal density of 4×10^8 cm^{-2}. The larger ones have the base of up to 500 nm, a height of up to 50 nm, and a density of $\sim 2 \times 10^7$ cm^{-2}. We subsequently refer to the former as ''smaller QDs'' and to the latter as ''larger islands.'' The Ge QDs were either left uncapped on the sample surface or capped with 6 nm of Si.

Raman spectra were taken in the back-scattering geometry at room temperature using a Renishaw System 1000. Two different excitation wavelengths, namely, 633 and 488 nm, have been used, with a power of ~20 mW and the spot size on the sample ~10 μm. Figure 2(a) shows Raman spectra of the uncapped ^{76}Ge QDs samples together with the Raman spectra of the Si wafer. Due to the isotope effect, the Ge peak (287 cm^{-1}) is now shifted from the Si peak (301 cm^{-1}) and is clearly seen. Use of polarized Raman scattering in the $Z(XY)Z$ configuration, which suppresses the two-
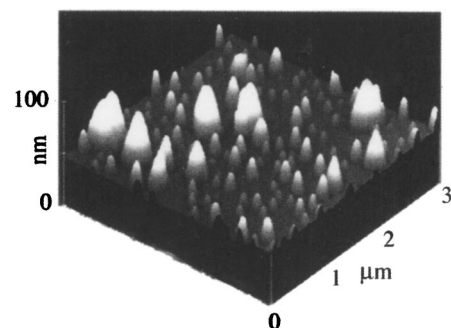

FIG. 1. An AFM image of the grown uncapped sample.

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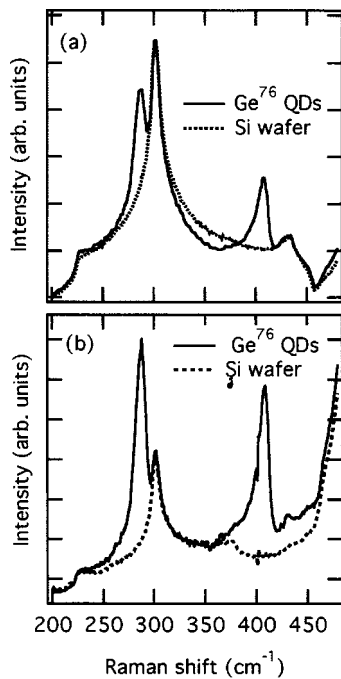
FIG. 2. (a) Unpolarized and (b) polarized Raman spectra of ^{76}Ge QD sample and of the Si wafer taken with the 633 nm light.

phonon acoustic features, makes the Ge peaks relatively stronger [Fig. 2(b)].

Figure 3 shows the result of subtraction of the substrate contribution from the total signal. The obtained spectrum has a line shape totally different from that of the Si substrate (and also from the spectra often attributed in literature to Ge nanostructures[5]). The other peak, located at ~ 410 cm^{-1}, is due to the Ge–Si vibrations.

In the subtracted spectra we do not observe any feature at 225 cm^{-1}, which is characteristic of the two-phonon acoustic vibrations in Si.[6] We argue, based on this result, that this feature is entirely due to the substrate and not to vaguely defined "Ge-related components"[7] or to "threefold bonded Ge".[8]

Figure 4 shows the Raman spectra of the ^{70}Ge and ^{76}Ge samples measured with the 488 nm light. One can see that the relative intensity of the Ge peak is much stronger and this wavelength should be the wavelength of choice for investigation of Ge/Si QDs. The spectra for ^{76}Ge and ^{70}Ge exhibit an isotope shift in frequencies of both ~ 300 cm^{-1} (287
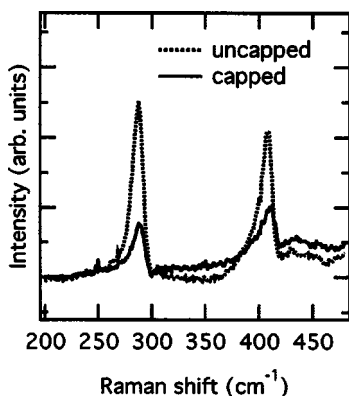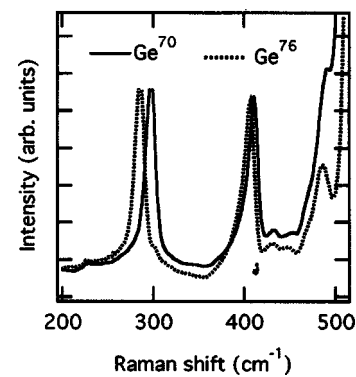

FIG. 4. Raman spectra of ^{70}Ge and ^{76}Ge samples taken with the 488 nm light.

cm^{-1} for ^{76}Ge and 298 cm^{-1} for ^{70}Ge, and ~ 410 cm^{-1} (407 cm^{-1} for ^{76}Ge and 413 cm^{-1} for ^{70}Ge) features, which is direct and unambiguous evidence that the observed two peaks are due to Ge.

The Ge–Ge peak positions in the dot samples are shifted by ~ 9 cm^{-1} to lower wave numbers with respect to the peak position of bulk Ge (296 cm^{-1} for ^{76}Ge and 308 cm^{-1} for ^{70}Ge). The peak shift may generally be caused by the size effect, strain, or presence of Si in the QDs. However, the diameter of the QDs in our case is quite large and the effect of lateral confinement can be neglected (although confinement in the direction of growth is possible). The compressive strain shifts the Ge–Ge peak to higher wave numbers, and therefore this cannot be the main reason for the observed peak shift.

The presence of Si in the QDs should indeed shift the peak to lower wave numbers and, assuming that this is the only mechanism for the shift the concentration of Si in the QDs, is estimated (from the peak position) to be around 50%.[9–11] This result agrees with recent extended x-ray absorption fine structure studies of the local structure of Ge QDs[12,13] and also with the observed position of the Ge–Si peak.

We now turn to the process of the Ge QD formation. Figure 5 compares Raman spectra taken from an area containing a large island with an area that only contains small QDs. One can see that while the smaller QDs layer consists predominantly of the intermixed Ge–Si phase, the larger islands do have a Ge-rich phase. A similar conclusion has been also drawn in Ref. 14. We also notice that the Ge–Si peak is

FIG. 3. A Raman spectrum of the uncapped and Si-capped QDs with the substrate contribution being subtracted.
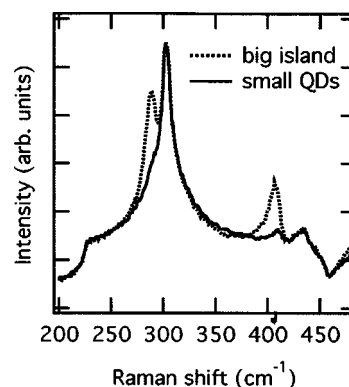

FIG. 5. Comparison of Raman spectra from large islands and the small QDs.

shifted to higher wave numbers in the spectrum for the smaller QDs. Most likely, this represents the excess strain in the smaller dots compared to the intermixed region in the larger islands.

Detection of the intermixed GeSi region in the QDs does not provide enough information on the spatial location of the Ge-rich phase. Two possibilities exist: the Ge-rich phase may be a core of the QDs, or it may be located at the upper part of the dot, with the lower part of the dot being intermixed with Si and thus accommodating the strain. In order to distinguish between these possibilities, we have capped the Ge QDs with Si. In the case of Ge phase being located at the upper part of the island, one would expect further Ge–Si intermixing as a result of capping, while for the case of the Ge core the intermixing resulting from the Si capping should be negligible. The results are shown in Fig. 3. One can see that the Ge peak intensity is substantially reduced in the Si-capped sample, and one may be tempted to conclude that significant Ge–Si intermixing takes place during the capping. However, comparison of the intensities of the Ge–Si peaks in the uncapped and Si-capped samples demonstrates that the intensity of the Ge–Si peak *also decreases* as the result of the Si capping. This result is very unusual since, first, Ge–Si mixing should have resulted in an increase in the intensity of the Ge–Si peak and, second, the simultaneous decrease in the intensity of both Ge and Ge–Si peaks may lead to a conclusion that the amount of Ge in the sample is decreased after the Si capping, which is not the case (the amount of Ge in both samples has been measured by x-ray fluorescence).

We believe that the observed decrease in the peak intensities is related to a change in the surface roughness and possibly also to changes in QDs size as a result of capping. An AFM image of the Si-capped sample (not shown) demonstrates that, indeed, the height of the "hills" on the sample surface was reduced by about a factor of 4.

It is known that the Raman scattering intensity from rough Si surfaces and from Si nanostructures may be significantly stronger than that from bulk Si.[15] Increased Raman efficiency for Ge nanocrystals embedded in SiO_2 has also been reported.[16] We believe, however, that the *ratio* of the peak intensities *does* represent the relative number of Ge–Ge and Ge–Si bonds.[11] The fact that this ratio does not change significantly after the capping indicates that the Ge phase exists as a core of the QDs.

It should also be noticed that while the Ge–Ge peak position remains effectively unchanged after the capping, the Ge–Si peak shifts to higher wave numbers, possibly due to increased strain as a result of the capping.

In conclusion, use of pure Ge isotopes for the QDs fabrication allowed us to unambiguously deconvolute the contribution from the Ge QDs and from the Si substrate into the Raman spectrum and demonstrated that the raw spectrum is dominated by the two-phonon features from the Si substrate. We found that the smaller QDs that exhibit a higher degree of intermixing with Si are more strained. The Ge-rich phase in the islands exists as a core of the dots encapsulated by the intermixed phase. It is also shown that the absolute intensity of the Raman peaks cannot be used as a measure of Ge–Ge or Ge–Si bonds number in the sample.

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