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Resonant Raman scattering of a single layer of Si nanocrystals on a silicon substrate

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We report Raman spectra of a single layer of silicon nanoparticles, spatially ordered in SiO₂ at a tunneling distance from a silicon substrate. This is achieved by exploiting effects which enhance the nanocrystal signal, while suppressing the substrate one. The method is applied to investigate the structure of ion-implantation-produced Si nanoparticles annealed under different conditions. The results, which are in good agreement with transmission electron microscopy data, are used to explain photoluminescence measurements. © 2004 American Institute of Physics.

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The study of materials and devices containing silicon nanocrystals (NCs) has been extremely active, since they display intense light emission offering new possibilities for Si-based optoelectronics. Recently, it was also found that Si NCs could have applications in microelectronics, for example as storage elements within the gate oxide of non volatile memory devices.¹ In order to optimize the electrical properties of such devices the structural characterization of the nanoparticle layer is indispensable. Most commonly, transmission electron microscopy (TEM) is employed^{2,3} but the differentiation between amorphous Si, crystalline Si, and SiO₂ remains a very challenging task. The development of other characterization methods is therefore highly desirable.

A powerful nondestructive method for the characterization of Si nanostructures is Raman spectroscopy. It allows differentiation between amorphous and crystalline phases^{4,5} and stress measurements.⁶ Size measurements of Si NCs (Refs. 4, 7, and 8) exploit phonon confinement effects in the NCs which lead to a size-dependent down shift and broadening of the optical phonon peak.^{8,9} Generally Raman spectroscopy of Si nanostructures has to be performed on thick layers or multilayers and preferably without Si substrate since it can mask the signal arising from the Si nanostructures. These constraints rendered the technique unusable for the structural characterization of Si NCs at a tunneling distance from a Si wafer, the channel of nonvolatile memory devices. In this paper we present a method that allows the detection of the Raman signal of a single layer of Si NCs embedded in a thin oxide on a Si substrate. We apply this method to investigate thin Si implanted SiO₂ layers annealed under different conditions. The Raman spectra are also correlated to TEM and photoluminescence (PL) measurements.

The Si NCs were produced by low energy ²⁸Si ion implantation (1 keV, dose $2 \times 10^{16} \text{ cm}^{-2}$) into a 10 nm thin SiO₂ layer on a Si (100) wafer followed by thermal anneal-

ing in N₂ or N₂+1.5% O₂ at 950 °C for 30 min. The samples were imaged by TEM. Cross sectional images (Fig. 1(a)) were taken with a CM30 Philips TEM operating at 300 keV using strongly underfocused bright-field imaging (Fresnel contrast).¹⁰ The layer of Si excess (thick black line) is extremely well depth localized and forms a quasi two-dimensional array of NCs 3 nm in thickness. Spatially resolved electron energy loss spectroscopy using the spectrum-imaging mode of a scanning TEM (Ref. 11) was performed on plane-view specimen to measure the size distribution and surface density of the NCs population¹² (Figs. 1(b) and 1(c)).

The Raman scattering experiments were performed at room temperature using a UV-specified Dilor XY spectrometer equipped with a liquid nitrogen-cooled charge-coupled-device (CCD) detector. The light was focused to a spot of about 50 μm in diameter with the laser power being 400 mW (20 times less on the sample surface). No laser heating effects should occur under such conditions. The spectrometer was calibrated using a monocrystalline Si wafer as a reference. We also measured the photoluminescence of the samples. The spectra were recorded using a Dilor XY Raman spectrometer equipped with a liquid-nitrogen-cooled

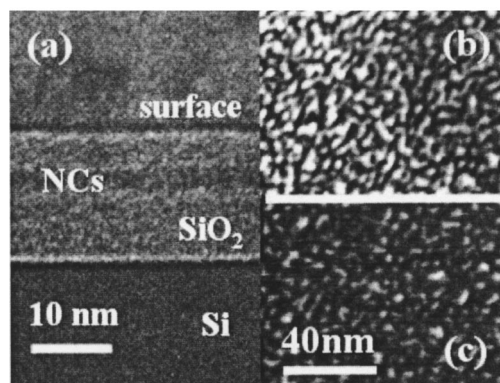


FIG. 1. Bright field cross section (left) and plane-view spectrum (right) TEM images of Si NCs annealed in (a,c) N₂+O₂ and (b) N₂ atmosphere.

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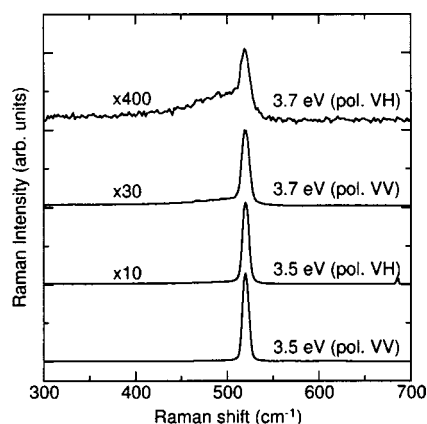


FIG. 2. Raman spectra of a single layer of Si nanocrystals on a silicon substrate for different excitation conditions.

CCD detector. The excitation wavelength was 488 nm using a power of 0.1 mW. A 100 \times objective was used to focus the incident laser light on the sample and to collect the light.

In order to detect the weak Raman signal arising from a single layer of Si NCs on a Si substrate both, the enhancement of the signal from the Si NCs and the minimization of the Si substrate signal, are crucial. Firstly, Raman selection rules can be exploited as illustrated in Fig. 2. Since the substrate signal is highly polarized it is greatly reduced when the spectra are recorded in the backscattering configuration and crossed polarizations for incident and scattered light with respect to the (001) Si substrate.¹³ The signal of the NCs is nearly unaffected due to their random orientation. Second, resonance conditions are applied to enhance the Raman scattering cross section. Resonant conditions occur when the excitation energy coincides with a direct electronic transition. Bulk silicon has a resonance at 3.4 eV corresponding to the E'_0 band gap¹⁴ and it has been demonstrated⁷ that excitation at this energy already results in a large increase of the Raman signal of Si NCs deposited on an alkali halide substrate. In the case of an underlying Si substrate, however, the resonant Raman signal of the substrate can still mask the signal of the NCs, especially if the optical absorption of the NC layer is not sufficient to absorb all incident photons. Fortunately, it is still possible to obtain a signal from the NCs since the electronic transitions of NCs (and therefore their Raman resonance) are expected to be shifted to higher energies due to the quantum confinement effect. Such a shift of the Raman resonance has indeed been observed for Ge nanocrystals.¹⁵ For Si NCs no such data are available but optical absorption experiments show a blueshift of the absorption edge with decreasing cluster size.¹⁶ We therefore used an excitation energy of 3.7 eV which is resonant with the NCs. Moreover, this energy presents the additional advantage that the Raman cross section of bulk Si is decreased by two orders of magnitude.¹⁴ By combining these three phenomena (maximum Raman scattering cross section of the NCs and minimum Raman scattering cross section of bulk Si for an excitation energy of 3.7 eV, as well as use of selection rules), the substrate signal is so strongly reduced that the signal from the NC layer is clearly discernible (Fig. 2).

We applied this method to investigate Si implanted SiO_2

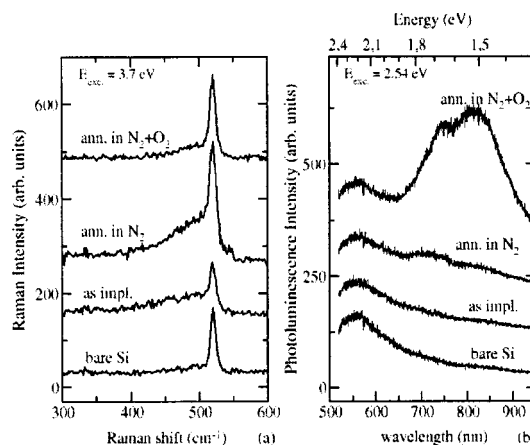


FIG. 3. (a) Raman and (b) PL spectra of Si implanted SiO_2 layers for different annealing conditions.

layers annealed under different conditions. Figure 3(a) presents typical Raman spectra obtained. A spectrum of an unimplanted Si substrate is also shown for comparison. The as-implanted sample shows a broad Raman band centered at 480 cm^{-1} and a small peak arising from the Si substrate. The broadband is typical for amorphous Si and indicates that the as-implanted Si rich layer is amorphous. After annealing at 950 $^{\circ}\text{C}$ in N_2 the amorphous band is still present while the peak arising from crystalline Si is about twice as intense as the Si peak from the bare Si substrate. This peak is also significantly broadened but it is not noticeably shifted with respect to the bulk reference. Annealing in an oxidizing atmosphere results in a reduction in the intensity of the amorphous band. The crystalline Si peak is also reduced but still more intense than the Si reference. Again, it is broadened but not shifted.

The high intensity and the broadening of the crystalline Si Raman peaks indicates the presence of Si NCs. However, phonon confinement in Si NCs should lead not only to broadening but also to a size-dependent downshift of the optical phonon peak^{8,9} which is readably observed in Si/ SiO_2 systems.^{4,5} Filtered images (Figs. 1(b) and 1(c)) showed Si NCs with an average size of 9.3 nm and 6 nm in the samples annealed in N_2 and N_2+O_2 , respectively. NCs of this size display shifts to lower frequencies by 0.6 cm^{-1} and 1.1 cm^{-1} ,⁸ respectively. We also performed Raman scattering on thick layers of Si NCs similar in size where a contribution from the Si substrate can be excluded and also found no downshift of the Raman peak position. The absence of the shift can be explained by an isotope effect as reported in the case of Ge NCs.¹⁷ Since the diffusivity of Si in SiO_2 is very low¹⁸ and the implanted Si excess very high, the NCs are formed here by spinodal decomposition¹² and thus consist mainly of ^{28}Si , the isotope implanted. The Raman peak of ^{28}Si is shifted by about 1 cm^{-1} to higher frequencies¹⁹ with respect to our natural Si reference. This effect compensates the downshift from the quantum confinement effect.

We also measured the photoluminescence of the samples. The spectra are shown in Fig. 3(b)). All samples, even the Si substrate, showed a band centered at 560 nm which probably arises from transitions in the oxide layer.^{2,20} Here, we are interested in the PL in the red to infrared region

which is generally observed from Si nanostructures. As-implanted samples showed no photoluminescence in this region. After annealing at 950 °C in N₂ two very weak PL bands centered at about 730 nm and 828 nm appear. These bands increase strongly in intensity for annealing in an oxidizing atmosphere.

The PL measurements can be understood via the Raman and TEM results. The Raman spectrum shows that the as-implanted Si is amorphous and the absence of PL from this sample confirms this finding (though red PL from amorphous Si has been reported^{2,5} the results were obtained on thick layers and the intensity was low). The Raman spectrum and TEM imaging show that in the sample annealed in N₂ Si NCs are present. This is confirmed by the appearance of PL in the infrared region which is commonly linked to Si NCs.^{2,3,7,21} The origin of the red PL band at 1.7 eV, however, is less clear. It is commonly observed from Si/SiO₂ systems^{2,3,5,20,21} and has been ascribed to an oxygen related defect,⁵ an Si-O vibration assisted transition at the interface of Si nanocrystals and Si oxide,^{3,20} cluster-cluster interactions,²¹ and small amorphous Si clusters.² The Raman spectrum of the sample annealed in N₂ also shows that besides the Si NCs there is still a considerable amount of amorphous Si present. This explains the very low PL intensity of this sample. Due to their large size and the large amounts of amorphous Si, the NCs are not well separated but form percolation paths (Fig. 1(b)) resulting in low confinement and a large number of nonradiative recombination sites. After annealing in N₂+O₂ our Raman data shows that the excess amorphous Si has been oxidized. This leads to better separated Si NCs (Fig. 1(c)) and therefore results in higher photoluminescence intensity in the infrared region.

In summary, using Raman spectroscopy we have detected a single layer of Si nanocrystals embedded in a thin silicon oxide on top of a Si substrate. This is achieved by exploiting resonance and polarization conditions which suppress the Si substrate signal and enhance the signal arising from the Si NCs. We apply this method to investigate Si implanted SiO₂ layers annealed under different conditions. The Raman spectra show that the sample annealed in N₂ still contains a large amount of amorphous Si which is greatly

reduced by annealing in an oxidizing atmosphere. The results are in excellent agreement with TEM and can explain the PL measurements.

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