Substrate-induced stress in silicon nanocrystal/SiO_2 multilayer structures*

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A Raman frequency upshift in the nc-Si phonon mode is observed at room temperature, which is attributed to a strong compressive stress in the Si nanocrystals. The 10-period amorphous-Si(3 nm)/amorphous-SiO_2 (3 nm) layers are deposited by high-vacuum radio-frequency magnetron sputtering on quartz and sapphire substrates at different temperatures. The samples are then annealed in N_2 atmosphere at 1100 °C for 1 h for Si crystallization. It is demonstrated that the presence of a supporting substrate at the high growth temperature can induce different types of stresses in the Si nanocrystal layers. The strain is attributed to the difference in the thermal expansion coefficient between the substrate and the Si/SiO_2 SL film. Such a substrate-induced stress indicates a new method for tuning the optical and electronic properties of Si nanocrystals for strained engineering.

Keywords: stress, Raman spectrum, silicon nanocrystal, sputtering

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1. Introduction

Silicon nanostructures are currently under intensive study for both practical application and fundamental research. The low-dimensional form of silicon embedded in silica has great potential for use as an optical material.[1] There are lots of reports on the characterization of Si nanocrystals (NCs) focusing on the luminescence properties,[2−5] and the Si quantum dot solar cell, a very promising new-concept solar cell, is also attracting more attention for its potential high efficiency and low cost.[6] The main challenge is how to effectively transport and collect the carriers generated in Si nanocrystals embedded in the isolating matrix (SiO_2, etc).

Strained silicon has been widely used in electron devices with high electron mobility. This trend has rapidly extended to lower-dimensional structures such as silicon nanowires.[7] Several experiments have been conducted to study the effects of strain and quantum confinement on optical emission,[8] mostly in II–VI CdTe core/shell quantum dots.[9] Arguirov *et al.*[10] found the residual compressive stress in silicon NCs inside 2 nm thin layers embedded in a SiO_2 matrix, but the influence of strain on Si NCs is still poorly understood. In this work, we find a new method of forming Si NCs with large compressive and tensile strain by using high growth temperature and different substrate types, which is a new strategy for strained engineering.

2. Experimental details

The 10-period a-Si (3 nm)/a-SiO_2(3 nm) superlattice films were deposited on Si, quartz, and sapphire substrates, respectively, by radio-frequency magnetron sputtering of the Si and fused quartz targets in a computer-controlled KJLC Lab 18 system. The base pressure was 1×10^{-5} Pa, and the working gas pressure was 0.4 Pa. The growth temperature varied from 200 °C to 500 °C. The samples were then annealed in N_2 atmosphere at 1100 °C for 1 h to form the Si NCs.

The annealed samples were characterized in terms of their structural and optical properties. Cross-sectional high-resolution transmission electron microscopy (HRTEM) observation was performed by using a Tecnai G2 F20 S-Twin with an incident elec-

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tron energy of 200 kV. The transmission electron microscopy (TEM) samples were prepared by the standard mechanical and Ar ion thinning techniques. Micro-Raman scatting spectra were obtained to investigate the microstructure of the films by using the 488 nm line of an Ar ion laser produced by JY HR800. To avoid the unintended thermal effect of laser heating on the Si NCs, the laser power was reduced to a minimum below 2 mW. The laser spot size was focused into a size of around 3 μm. Samples on quartz and sapphire substrates were used for the Raman studies, while samples on Si wafer substrates were used for the TEM studies.

3. Results and discussion

The microstructures of the samples were investigated using HRTEM and micro-Raman scattering spectra. The HRTEM image of the sample grown at 500 °C on the Si substrate shows the existence of Si NCs with a size of around 2.8 nm and a density of 7.96×10^{11} cm^{-2}, as shown in Fig. 1.

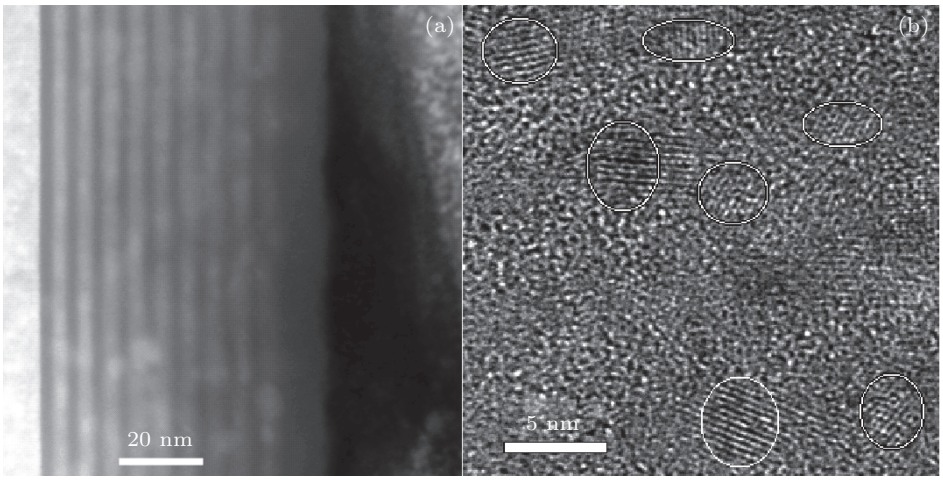


Fig. 1. (a) STEM and (b) HRTEM images of the sample grown at 500 °C on Si substrate annealed in N_2 atmosphere at 1100 °C for 1 h. The circles indicate some crystalline grains in the Bragg conditions, showing their crystallinities.

To calculate the Raman shift and the peak broadness values accurately, all the spectra are compared with those obtained on crystalline Si (c-Si). Figure 2 shows the Raman spectra of samples grown at 200 °C and 500 °C on quartz and sapphire substrates normalized to the same arbitrary value.

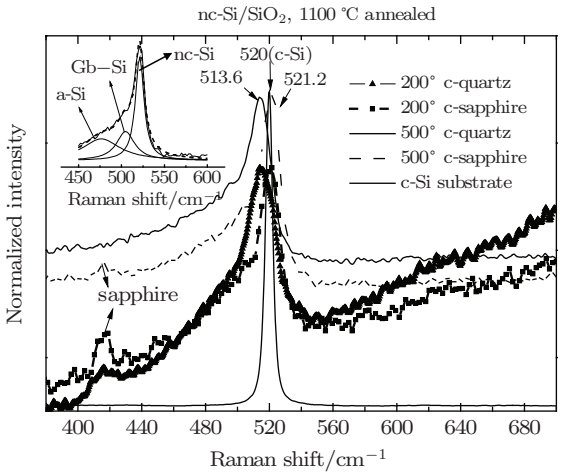


Fig. 2. The Raman spectra of samples grown at different growth temperatures and substrates.

The Raman intensities of the samples grown at 200 °C are larger than that of the sample grown at 500 °C, and apparent high backgrounds exist, which are caused by the stronger photoluminescence (PL) emission intensities. According to Ref. [11], the Raman peak of Si NCs can be deconvoluted into three peaks: the nano-crystalline component peak at around 520 cm^{-1}, the amorphous component peak at around 480 cm^{-1}, and the intermediate component peak at 494–507 cm^{-1}, which is associated with the bond dilation at the grain boundary. The total crystalline volume fraction and the grain boundary volume fraction, X_c and X_{gb}, are estimated from $X_c = (I_c + I_{gb})/[I_c + I_{gb} + y(D)I_a]$ and $X_{gb} = I_{gb}/[I_c + I_{gb} + y(D)I_a]$,[12,13] respectively, where I_c, I_a, and I_{gb} are the integrated intensities of crystalline, amorphous, and intermediate peaks, respectively, and y is the ratio of the cross section for the amorphous phase to that for the crystalline phase, which varies with grain size D as

$y(D) = 0.1 + \exp[-(D/250)]$. As the Raman scattering cross section for Si NC is strongly dependent on the size of the NC, it is not possible to determine exactly the absolute volume fraction of nc-Si if D is unknown. Using the D value obtained in the HRTEM at 500 °C on the Si substrate, we can estimate the crystalline volume fraction X_c. The results are listed in Table 1 with the value of y taken to be 1.09.

Table 1. Fitting and calculated parameters from the Raman spectra.

Sample	Fitting parameters		Calculation from model		
	$\Delta\omega$/cm^{-1}	FWHM/cm^{-1}	X_c/%	X_{gb}/%	D_Z/nm
200 °C-sapphire	+0.6	13.1	63	25	–
200 °C-quartz	–3.6	13.6	64	32	3.2
500 °C-sapphire	+1.2	12.1	65	26	–
500 °C-quartz	–6.4	13.6	63	25	2.2 (2.8*)

Table 1 shows the peak shift, the full-width at half-maximum (FWHM), and the crystalline volume fraction. The Si NC sizes are calculated from the Raman shift values using Zi's confinement model (D_Z),[14] which gives

$$\Delta\omega = \omega(D_Z) - \omega_0 = -A(a/D_Z)^\gamma,$$

where $\omega(D_Z)$ is the frequency of the Raman phonon in a nanocrystal with size D_Z, ω_0 (520 cm^{-1}) is the frequency of the optical phonon at the zone center for bulk crystal Si, and a is the lattice constant of Si (0.543 nm). The parameters A and γ used to describe the vibration confinement due to the finite size in the nanocrystal are 47.41 cm^{-1} and 1.44, respectively. Therefore, the Si NC size is estimated to be 3.2 nm for the sample grown at 200 °C on quartz. However, the Raman peaks of the samples grown on sapphire at 200 °C and 500 °C unexpectedly shift to a higher frequency around 522 cm^{-1}. The Raman shift induced by the phonon confinement due to the finite size of NCs shifts to a lower frequency of 520 cm^{-1}, and the thermal effect on the nanostructures, like nanowires and nanotubes, can also make the Raman frequency shift downward. The only explanation for this is the strain effect. Furthermore, only the compressive stress can make it shift upward, while the tensile stress makes it shift downward. To further rule out the possibility from the other effect and the system error, we carefully examine the Raman spectra by using minimum laser power to avoid the thermal effect, repeating the experiments more than 10 times to reduce the system error, and using a higher resolution grating of 1800 lines instead of that of 600 lines used before. The Raman shift is still around 522 cm^{-1} for the samples grown on sapphire, which indicates an obvious compressive stress in them.

On the other hand, the calculated smaller size of NC in the 500 °C-quartz sample also indicates the strong tensile stress in it. For Si material, the relation between the stress and the Raman shift can be estimated from the following formula:[15]

$$\sigma = -434\Delta\omega \text{ (MPa)},$$

where σ is the compressive when $\Delta\omega$ is positive, and it is the tensile when $\Delta\omega$ is negative. Since it is impossible to calculate the absolute stress if the size of the Si NC is not known, we can only estimate the relative stress between the samples. The Raman shift between the sample grown on quartz at 200 °C and that at 500 °C is 2.8 cm^{-1}, indicating a relative tensile stress of 1215 MPa. Similarly, the relative compressive stress between the samples grown on sapphire at 200 °C and 500 °C is estimated to be 258 MPa. The strain may be attributed to the difference in the thermal expansion coefficient between the substrate (sapphire: 5×10^{-6} K^{-1}, quartz: 0.5×10^{-6} K^{-1}) and the nc-Si/SiO_2 SL film (Si: 2.6×10^{-6} K^{-1}) at the high growth temperature. With the growth temperature increasing, the thermal expansion between the substrate and the SL film increases, and the stress also increases. The thermal expansion coefficient of the sapphire substrate is larger than that of the SL film, making the SL film under a compressive strain, while the smaller thermal expansion coefficient of quartz makes the SL film under a tensile strain during the cooling stage of the growth.

However, as shown in Table 1, the strain induced by the substrate has little effect on crystallinity, which is determined mainly by the annealing temperature, and the FWHM of the Si Raman peak is barely influenced by the stress.

4. Conclusion

Compressive and tensile strained Si NCs are demonstrated and revealed by micro-Raman spectra. The strain is attributed to the difference in the thermal expansion coefficient between the substrate and the Si/SiO_2 SL film at the high growth temperature. Such a substrate-induced strain has little effect on the optical bandgap of Si NC and its crystallinity. However, many other effects of strain on the nanometer scale remain to be explored, and the influences of strain on the electronic properties of Si NCs, especially the effect on the electron mobility, still need to be investigated further. This is very important for carrier transport in Si quantum dot solar cells.

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