Photoluminescence and Raman Studies of Nanocrystalline Silicon Enclosed in a $\text{SiO}_2$ Shell

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Spherical silicon-nanocrystals prepared by the thermal evaporation method were examined using Raman and photoluminescence measurements. The Raman analysis indicates that the content of the crystalline silicon decayed exponentially over time, which explains the reduction in size of the silicon-nanocrystals caused by oxidation. The visible photoluminescence spectra of silicon-nanocrystals are about the same. Although the size of the samples varied significantly, the temporal variation of the photoluminescence spectra was negligible, except for the very first day when samples were taken out from the growth chamber. Based on the Raman and photoluminescence results, we conclude that the red photoluminescence of silicon-nanocrystals near 680 nm is mainly attributed to defect states residing at the Si/$\text{SiO}_2$ interfaces.

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I. INTRODUCTION

Silicon has been widely used in the semiconductor industry for the past several decades. However, due to the indirect band gap in the electron energy structure, the light emission from crystal Si bulk is inefficient. About ten years ago, the bright photoluminescence (PL) from porous Si was first observed [1, 2]. Subsequently, the light emission from Si in low dimensional structures, such as the Si nanocrystals (Si-NCs) [3, 4], Si-NC/$\text{SiO}_2$ system [4–6], and porous Si [1, 7–9] was intensively studied. The mechanisms proposed can be divided into two major categories: the interface effect [4–9], and the quantum confinement effect [3, 10–16]. Although there are many reports concerning the light emission from porous Si, there are relatively few reports related to the light emission from other Si nanostructures, such as spherical Si nanocrystals.

In this article, we report on the temporal photoluminescence (PL) and Raman spectra of spherical Si-NCs, and the correlations of dot-size with the PL and Raman spectra are discussed. The spherical Si-NCs were prepared by the thermal evaporation method [15, 16], and the samples were preserved in a controlled environment after growth. As the natural oxidization process took place, the thickness of the oxidized shell increased while the volume of the nanocrystalline Si-core decreased. Several groups have successfully used Richter’s model [17, 18] to analyze the Raman spectra and to obtain the size of the nanoparticles [19, 20]. Richter’s model is also adopted here to reveal the average size of the spherical
Si-NCs during the oxidization process. Finally, the temporal PL and Raman data help us to determine the origin of the light emission of spherical Si-NCs at 680 nm.

II. EXPERIMENT

Spherical Si-NCs were prepared by the thermal evaporation method, for which we followed the same system as used by Liao et al. [21]. The Si source was heated on a Ta boat to about 1500 K, and the substrate (kept at 77 K) was exposed to the Si vapor for one minute. 7059-glass and sapphire (1120) served as substrates to grow the Si-NCs for Raman measurement, while samples grown on 7059-glass and Si(001) substrates are used for the PL measurement. The chamber was purged by argon gas, and the size of the Si-NCs is controlled by the argon gas pressure during growth. In order to grow Si-NCs with different sizes, samples were grown at pressures from 0.33 to 6.9 torr. In total 22 samples were grown, and examined by Raman scattering and PL after being taken out of the growth chamber. Samples were then preserved in a controlled environment, in which the humidity was 25% and the temperature was 25 °C.

Micro-Raman and PL measurements were performed at room temperature. Both Raman and PL signals were recorded by a DILOR XY-800 triple grating Raman spectrometer, which is equipped with a liquid-nitrogen-cooled CCD and an OLYMPUS BH-2 microscope. The 514.5 nm line of the Ar+ ion laser was used as the excitation source. The laser beam then was focused on the sample surface with a 100X objective. The focusing spot size was about 1 µm and back scattering light was collected. The obtained spectra had a resolution of about 0.6 cm⁻¹. To prevent the sample being heated, the laser output power was less than 2 mW on the sample surface.
FIG. 2: The average size of spherical Si-NCs analyzed using Richter’s model. The size depends on the argon gas pressure in the growth chamber. The hollow circles represent the samples grown on 7059-glass, and the solid squares are the samples on a sapphire substrate.

III. ANALYSIS

In the Raman spectra, the optical phonon peak of Si-NC was redshifted and broadened. Based on Richter’s model [17], the Raman intensity of the optical phonon of spherical Si-NC (< 20 nm) can be expressed as [18]:

\[
I(\omega) = \int_0^1 d^4q \frac{e^{-q^2d^4/4}}{(\omega - \omega(q))^2 + (\Gamma_0/2)^2},
\]

where \(\omega(q)\) is the dispersion relation of the TO phonon, and, for Si, \(\omega(q) = [A + B \cos(\pi q/2)]^{1/2}\), with \(A = 1.714 \times 10^5 \text{ cm}^{-2}\) and \(B = 1.000 \times 10^5 \text{ cm}^{-2}\) [23]. \(q\) is the wave vector of the phonon in \(2\pi/a_0\), and \(a_0\) (0.543086 nm for Si [22]) is the lattice constant. \(\Gamma_0\) is the natural linewidth (3.6 cm\(^{-1}\) for Si), and \(d\), in units of \(a_0\), is the average diameter of the spherical Si-NCs.

The measured Raman spectra were shown in Fig. 1. We found that the optical phonon intensity of Si-NCs increases with the Ar pressure, as shown in the inset of Fig. 1 (a) and (b). The measured Raman signal, i.e., the solid lines marked (1) in Fig. 1 (a) and (b), includes several features, such as the optical phonon peak (~ 515 cm\(^{-1}\)) as described by Eq. (1) (dash line), and an \(\alpha\)-Si peak (~490 cm\(^{-1}\)) as fitted by a Gaussian function (dotted line), also the signals from the substrate. A broad \(\alpha\)-SiO\(_2\) peak (~480 cm\(^{-1}\)) and a sapphire LO phonon peak at 418 cm\(^{-1}\) fitted by a Lorentzian function (dash-dot line) were also found for samples grown on sapphire substrate. The curves marked (2) in Fig. 1 (a) and (b) are the fitting results, which are compared with Raman curves (1) in Fig. 1(a) and (b). Therefore, the size information revealed from the fitting of optical phonons of Si-NCs is reliable.

The relation of size deduced from Raman analysis and the growth pressure are shown in Fig. (2) for Si-NCs grown on both 7059-glass and sapphire substrates. We found that
FIG. 3: The $I_0/I_\alpha$ ratio is plotted. The fitting result marked in the solid line is an exponentially decaying function. The lifetime of the oxidation process of the spherical Si-NCs is about 46 days. The inset is the Raman spectra of the 0.5 torr sample measured at different dates.

The average size of Si-NCs depends strongly on the growth pressure, and the properties of the substrate are not relevant. The reason for the negligible influence of amorphous or crystalline substrates on the Si-NC's growth may due to the low substrate temperature, i.e., 77 K. This indicates that the migration of Si atoms during growth is negligible for a low-temperature substrate. The average size of the spherical Si-NCs dramatically increases for pressure increasing from $\sim 0.3$ to 3 torr, and reaches 7.2 nm for pressures higher than 4 torr.

The oxidation process of Si-NCs was observed and monitored by using the Raman scattering and PL measurements. Raman spectra were taken at time periods of 0 to 443 days. We found that the intensities of the optical phonon of Si-NCs decreased with time, and the lineshape became broader. The intensity of the optical phonon peak ($\sim 515 \text{ cm}^{-1}$) of nanocrystalline Si decreases quite slowly, and this phenomenon is mainly due to oxidization of the crystalline Si in the Si-NC’s core. The ratio of the integrated intensity of the optical phonon near $\sim 515 \text{ cm}^{-1}$, $I_0$, to the integrated intensity of the amorphous Si peak near $\sim 485 \text{ cm}^{-1}$, $I_\alpha$, can be used to analyze the contents of Si-NC enclosed in the Si-oxidized shell. As shown in Fig. 3, the contents of the Si-NC’s core decay exponentially with time, when the samples are preserved in a controlled environment, with a humidity of 25 % and a temperature of 25 °C. The spherical Si-NCs started to oxidize when they were removed from the growth chamber, and the size of the Si-NCs became smaller as a function of time. The fitting result, i.e., the solid line in Fig. 3, shows an exponential decay function and time constant of the slow oxidization process of about 46 days. Though the samples’ growth conditions were different, such as substrate and Ar pressure, the time constant of oxidization is about the same. The slow down of the oxidizing rate can be explained by the self-limitation of the oxidization process [24]. However, at the end of the oxidation process, the average size of the Si-NCs still depends on the initial growth conditions.

The temporal PL spectra of samples were measured during a 41-day period. In Fig. 4(a) and (b), temporal PL spectra for the average size of about 5 nm and 3 nm, i.e.,
FIG. 4: PL spectra of Si-NCs measured at different dates. (a) The PL spectra of the sample with 1.0 torr argon gas pressure, which had an average size of fresh Si-NCs of about 5 nm. (b) The PL spectra of a sample with 0.52 torr argon gas pressure, which had an average size of fresh Si-NCs of about 3 nm. The energy of the PL spectrum was about 1.82 eV.

growth Ar pressure being 0.52 torr and 1.0 torr, respectively, are shown. The intensity of the PL peak near 550∼750 nm of a fresh Si-NC sample was very weak for all samples, while the PL intensity near 680 nm (~1.82 eV) measured on the second day was significantly increased. Although the average sizes of the spherical Si-NCs were different, as shown in Fig. 4(a) and 4(b), the differences in the PL peak were negligible at a later date. From the Raman results, we know that the sizes of the spherical Si-NCs become smaller due to oxidization. The results revealed from the temporal Raman and PL measurements indicate that the origin of the PL at ~680 nm of spherical Si-NCs mainly arises from to the oxidized effect. In fact, the oxidized shell of a fresh sample was not well-formed, in other words, the surface of spherical Si-NCs has not been passivated by oxygen, and the intensity of the PL spectrum was weak. After the samples were preserved in controlled air for one day, the oxidized shell formed and the intensity of the PL peak increased. After a couple days, although the size of the Si-NCs is shrinking, the PL peak intensities and shapes are about the same for samples grown under different conditions, as we found in Fig. 4(a) and (b). Based on these results, we think the structure of the Si-O single-bond interface remained invariant during oxidization, while the size of the Si-NCs continues to reduce.
IV. CONCLUSION

Raman spectra have been used to determine the average size of the spherical Si-NCs prepared by the thermal evaporation method. The average size of fresh Si-NCs is controlled by adjusting the argon gas pressure in the growth chamber. The substrate, such as 7059-glass or sapphire (1120), does not have significant influence on the sample growth when it is kept at 77 K. The oxidation process of Si-NCs was also observed by Raman measurements. The size of the Si-NCs decays exponentially as a function of time. The time constant for the oxidation process is about 46 days in each sample. Although the size of samples varied significantly, the temporal PL spectra are found to be about the same, as described above. Our results are similar to the result of Wolkin [5], which was done with porous Si. The PL and Raman data of the Si-NCs shown in this work supports the theory that the origin of red light emission near 700 nm for spherical Si-NCs is most likely defect states residing at the Si-NCs/SiO$_2$ interfaces. There should be a significant concentration of defects at the interface of amorphous SiO$_2$ and Si-NCs.

References

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