APPLIED PHYSICS LETTERS **87**, 213110 (2005)

# H-sensitive radiative recombination path in Si nanoclusters embedded in $SiO_2$

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(Received 25 April 2005; accepted 27 September 2005; published online 16 November 2005)

The room-temperature photoluminescence (PL) from silicon nanocrystals embedded in a $SiO_2$ matrix fabricated by electron cyclotron resonance plasma-enhanced chemical vapor deposition and subsequent annealing in Ar and $(Ar+5\%H_2)$ was studied. In addition to strong increases of the integrated PL intensity (factors of ~4 to 10), the selective enhancement of contributions to the PL spectra at long wavelengths was observed for $(Ar+5\%H_2)$ annealings. The selective H passivation of Si dangling bonds in disordered Si nanoclusters where radiative recombination proceeds through disorder-induced shallow states is proposed as a possible explanation for the observed effects. *© 2005 American Institute of Physics.* [DOI: 10.1063/1.2135382]

Silicon nanocrystals (Si-nc) embedded in $SiO_2$ is a very promising system for silicon-based photonics.[1] Efficient photoluminescence (PL) in the visible whose intensity and energy depend on the Si-nc size has been observed and explained in terms of quantum confinement (QC) effects.[1–3] However, there is increasing evidence that the optical properties of this material are strongly influenced by electronic states in the Si-nc/$SiO_2$ interface region.[4–6] The interplay between QC and interface states is a matter of active debate in the literature. Bonds are likely to break at the Si-nc/$SiO_2$ interface to reduce stress, thus forming dangling bonds (db). A single db in a Si-nc is sufficient to deactivate light emission from it as a result of the large electron-hole capture cross section of this defect.[7] Hence, the observation of light emission in Si-ncs implies by itself that passivating configurations, such as the Si═O double bond,[8] play an important role. Alternatively, H can also passivate dbs and produce other chemical changes at the Si-nc/$SiO_2$ interface.[9,10]

In this letter, we study this question in annealed silicon-rich-silicon oxide (SRSO) films by comparing the shape of PL spectra from Si-ncs obtained from films annealed in inert (Ar) and hydrogen containing $(Ar+5\%H_2)$ gas. We find that the annealing in $(Ar+5\%H_2)$ selectively activates contributions to the PL at long wavelengths. The selective H passivation of Si dbs in disordered Si quantum dots where radiative recombination proceeds through band-gap states is proposed to explain the results.

2 $\mu$m thick SRSO films were deposited on (100) crystalline-silicon substrates held at 120 °C using an electron cyclotron plasma-enhanced chemical vapor deposition reactor described elsewhere.[11] The silane (30% in Ar) and oxygen (10% in Ar) flow rates were chosen so as to produce films with 36 at. % and 42 at. % Si (Ref. 12) as determined by Rutherford backscattering measurements. Annealing of the film samples cleaved from the same wafer after growth was performed in a quartz tube furnace under either Ar or $(Ar+5\%H_2)$ atmospheres for times from 30 min to 3 h and at temperatures between 800 °C and 1100 °C. PL measurements were carried out at room temperature using the 325 nm line of a He–Cd laser and an Ocean Optics spectrometer. The effective power density of the laser beam on the surface of samples was ~0.64 W/cm$^2$. All PL spectra were corrected for the detection system response. X-ray diffraction (XRD) scans were performed using the Cu $K_\alpha$ line in a Bede D1 diffractometer at a fixed beam incidence angle (2.5° with respect to the film surface).

As in a previous study,[2] we find that after the annealing of SRSO films at temperatures between 900 and 1100 °C, broad PL bands in the 600–900 nm wavelength range appear. The observed effects can be attributed to the precipitation of the excess Si and the formation of Si nanocrystals in an amorphous $SiO_2$ matrix.[2] The PL peak shifts to longer wavelengths with increasing Si content and annealing temperature, consistent with a reduced QC effect resulting from a corresponding increase of the Si-nc mean size.

Figure 1(a) shows PL wavelength spectra obtained for SRSO samples with 36% Si annealed for 3 h at 1100 °C using Ar and $(Ar+5\%H_2)$ atmospheres. Also shown is the

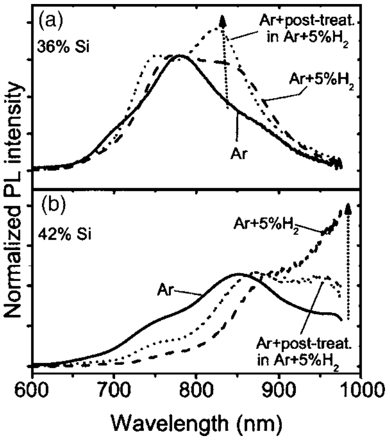

FIG. 1. PL spectra obtained from SRSO samples having a Si content of (a) 36 and (b) 42 at. % annealed at 1100 °C for 3 h in Ar (solid lines), and $(Ar+5\%H_2)$ (dashed lines). The spectra for samples annealed in Ar (1100°, 3 h) and subsequently posthydrogenated in $(Ar+5\%H_2)$ at 1000 °C for 2 h are also shown as dotted lines in (a) and (b). Actual PL intensities are very different for different Si content and thermal treatments; spectra were normalized to allow appreciation of shape variations. The data corresponding to solid line in (b) were smoothed for clarity.

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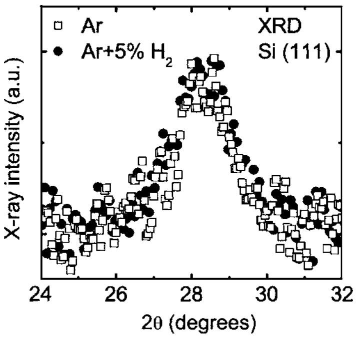

FIG. 2. XRD pattern showing the Si (111) diffraction peaks from Si-ncs observed for SRSO samples having a Si content of 42 at. % annealed at 1100 °C for 3 h in Ar (squares) and $(\mathrm{Ar}+5\%\mathrm{H}_2)$ (dots) atmospheres.

PL spectrum obtained for a sample annealed first in pure Ar (3 h at 1100 °C) and subsequently posthydrogenated for 2 h at 1000 °C in $(\mathrm{Ar}+5\%\mathrm{H}_2)$. It can be seen that both annealing treatments in $(\mathrm{Ar}+5\%\mathrm{H}_2)$ produce significant changes in the spectral shape of the PL band in that additional contributions appear at wavelengths above the peak wavelength of about 780 nm observed for samples annealed in pure Ar. This effect is accompanied by the enhancement of the absolute integral PL intensity by a factor of about 4 (not shown), probably due to passivation by hydrogen of nonradiative recombination pathways, such as Si dbs.[13] The oscillatory structure observed in the PL spectra is probably due to interference effects.[14] Similar data as those shown in Fig. 1(a) are presented for the 42% Si samples in Fig. 1(b). As can be seen in the figure, the PL peaks in this case are all shifted to longer wavelengths as compared to the spectra in Fig. 1(a). The corresponding PL intensities, in addition, are considerably lower (not shown). Both trends are expected from the QC effect as a result of the larger Si-nc size resulting from the larger excess Si concentration.[2] As can be also noted in Fig. 1(b), annealing in $(\mathrm{Ar}+5\%\mathrm{H}_2)$ again produces significant enhancements of the PL band in the long-wavelength region. As for the case shown in Fig. 1(a), this behavior is also accompanied by a strong increase (a factor of $\sim 10$) of the integral PL intensity. Comparisons of the PL spectra for various samples annealed in Ar and $(\mathrm{Ar}+5\%\mathrm{H}_2)$ at other temperatures and for various times show qualitatively similar effects.

PL spectral shape changes could result from artifacts associated with optical interference phenomena through refractive index changes.[14] As in a previous study,[2] we found the refractive index (from ellipsometry measurements) to decrease by as much as 3% with increasing annealing time and temperature in the whole studied ranges, however no differences were detected between samples annealed in Ar and $(\mathrm{Ar}+5\%\mathrm{H}_2)$. Therefore, the H-induced effects as shown in Fig. 1 cannot be attributed to refractive index changes.

The question as to whether the Si-nc size distribution is affected by the $(\mathrm{Ar}+5\%\mathrm{H}_2)$ annealing was addressed by performing XRD measurements. The Si diffraction peaks could be detected in the samples having 42 at. % Si but not in the 36 at. % samples, probably due to the much lower excess Si expected in the latter. Figure 2 shows the Si (111) diffraction peak for samples with 42 at. % Si content and annealed in Ar and $(\mathrm{Ar}+5\%\mathrm{H}_2)$. From the width of the peaks, no significant difference in the mean Si-nc size between materials annealed under Ar and $(\mathrm{Ar}+5\%\mathrm{H}_2)$ is detected. This observation is consistent with recent theoretical predictions[9] and experimental results[15] of negligible size modifications in Si-ncs upon H passivation.

The results above indicate that the effects observed in Fig. 1 are likely to be related to H-induced chemical modifications at the Si-nc/SiO$_2$ interface and not to Si-nc size effects. We note that the replacement of passivating Si$=$O double bonds at the Si-nc oxidized surface by Si–H bonds during annealing in $(\mathrm{Ar}+5\%\mathrm{H}_2)$ should result in a blueshift of the PL peak.[8] A blueshift is also expected from recently predicted H alloying effects in Si-ncs.[10] However, this is not what we observe in Fig. 1; the PL bands are actually skewed to the infrared after the H treatments.

A possible reason for the activation of PL contributions at long wavelengths in $(\mathrm{Ar}+5\%\mathrm{H}_2)$ treated samples (Fig. 1) could be excitonic transitions at energies lower than the Si-nc band gap involving shallow traps at the Si-nc/SiO$_2$ interface. The participation of shallow traps in radiative recombination and in light amplification in Si-ncs has been discussed in the literature.[16] A disordered region in the Si cluster would indeed be rich in strained bonds and prone to exhibit dbs because Si $sp^3$ bonds are destabilized when sufficiently strained.[17] Theoretical predictions[18] and experimental evidence[19] of noncrystalline Si quantum dots in coexistence with Si-ncs within a SiO$_2$ matrix have been reported recently. Distorted and broken bonds in disordered nanoclusters would be energetically favorable sites for thermal H$_2$ dissociation and bond passivation. This fact, together with the expected presence of states in the Si-nc band gap due to strained Si bonds,[20] provides a consistent picture to explain both, the H sensitivity and the high wavelength position of the PL contributions activated in the $(\mathrm{Ar}+5\%\mathrm{H}_2)$ annealed samples.

An alternative explanation for the increased long-wavelength contributions would consider preferential H passivation of dbs in the larger Si-ncs present in the samples,[13] as these should emit light at longer wavelengths.

In conclusion, we find that the annealing of SRSO samples in $(\mathrm{Ar}+5\%\mathrm{H}_2)$ produces a large improvement of the integrated PL intensity and a selective enhancement of contributions to the PL at long wavelengths. We propose that these effects are due to the selective H passivation of dbs in disordered Si quantum dots where radiative recombination proceeds through disorder-induced band-gap states.

The authors gratefully acknowledge Professor W. Lennard for Rutherford backscattering measurements, J. Wojcik and E.A. Irving for growing the SRSO samples, M. Flynn and T. Roschuk for fruitful discussions, G. Pearson for assistance with the XRD measurements, and J. Garrett for help with the annealing furnace. This work has been funded by the Ontario Research and Development Challenge Fund (ORDCF) under the Ontario Photonics Consortium (OPC) and by Ontario Centres of Excellence (OCE) Inc.

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