Luminescence efficiency measurements of silicon nanoclusters

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We present the results of what we believe to be the first study of the power efficiency of room temperature photoluminescence from thin films of silica containing silicon nanoclusters. Films were prepared by plasma enhanced chemical vapor deposition from silane and nitrous oxide precursors. Luminescence was excited using the 476 nm line of an argon-ion laser. We have measured power efficiencies for samples that exhibit luminescence solely due to radiative recombination of quantum confined excitons. Efficiencies around 0.04% are reported. © *1998 American Institute of Physics.*
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Following Canham's report of visible luminescence from porous silicon,[1] there has been an explosion of interest in light emission from novel forms of nanoscale silicon. There have been a number of reports in the literature of visible and near-IR emission from silicon nanoclusters.[2–6] Typically, such clusters lie in the sub-100-Å diameter regime and exhibit a broad red luminescence band similar to that reported from porous silicon. Reports have been published of nanoclusters deposited onto silicon substrates and embedded within dielectric matrices such as silica. There has been much debate over the nature of the luminescence mechanism in this material and contradictory reports of its optical properties, but there is a growing consensus that, in common with porous silicon, quantum confinement of excitons within the nanoclusters plays a significant role.[7–10] Previous work by this group has addressed the nature of the luminescence mechanism and has indicated the presence of two distinct processes: radiative recombination of confined excitons within the silicon nanoclusters and defect luminescence from the surrounding matrix.[7,8] A single unique mechanism does not provide a good enough explanation of the luminescence properties of nanoscale silicon. However, whatever the mechanism, this remains a technologically important material as it makes a significant contribution to the search for a silicon-based light emitting material. For this reason, it is imperative to obtain measurements of luminescence efficiency from nanoclustered silicon. To date, despite the number of reports of luminescence from silicon nanoclusters, there have been no reported studies of luminescence efficiency from this class of material.

In this letter we present the results of a study undertaken to measure photoluminescence power efficiencies of thin films of silica containing nanoclustered silicon. The films were produced by plasma enhanced chemical vapor deposition (PECVD): details of their growth can be found in Ref. 7. Films were 1–2 μm thick and were grown on silicon substrates. Photoluminescence was excited using the 476 nm line of an argon-ion laser, and for the purposes of recording spectra luminescence was dispersed through a single-grating Bentham M300 monochromator and detected using a photomultiplier tube. Spectra were corrected for the spectral response of the optical system and the whole apparatus was computer controlled.

For measurements of power efficiency, the total incident laser power was measured using an optical power meter, the specular laser reflection was measured directly, and diffuse laser scatter estimated by measuring the laser light intensity away from the specular reflection, knowing the area of the power meter head and film-to-detector distance, and hence calculating the total scattered power. Account was taken of the reflection of laser scatter at the thin film/silicon interface by measuring the reflectivity of a clean silicon wafer at the laser wavelength.

Photoluminescence from the silicon nanoclusters was collected using a BK7 glass lens which focused the light onto the power meter head through a filter which served to remove the laser scatter. The transmission factors of the lens and the filter were measured at 820 nm using a gallium arsenide semiconductor laser. This wavelength was chosen as being representative of the peak of the photoluminescence band from silicon nanoclusters, and could therefore be used to estimate losses in the lens and filter. Once again, the reflectivity of the silicon substrate was taken into account in order to calculate the total luminescence yield, including that emitted into the substrate.

Figure 1 details the geometry of the measurements and the luminescence collection arrangement.

Figure 2 illustrates a photoluminescence spectrum typical of a silica film containing silicon nanoclusters. Indicated are the two bands which we ascribe to quantum confinement (low energy band) and defect luminescence (high energy band). Further details of these assignments can be found in Ref. 7. For this study, it was proposed to measure the luminescence efficiency of the quantum confinement band in isolation, as this is the more useful of the two luminescence mechanisms and the only one that can be assigned to the presence of silicon nanoclusters. For this reason, the samples selected were those that exhibited very little or no defect luminescence. We have shown in previous work that it is possible to control the relative intensities of the two luminescence bands through careful choice of deposition and post-processing parameters.[7] Consequently, the samples studied

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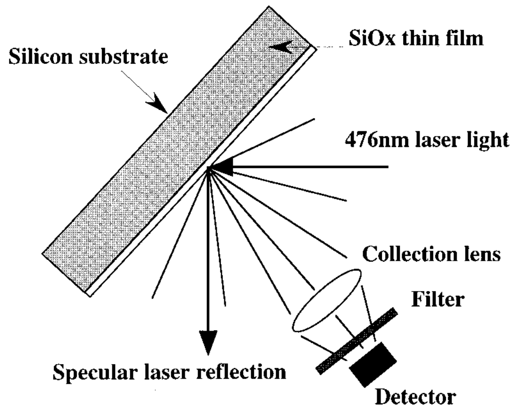

FIG. 1. Geometry of efficiency measurements. The setup illustrated is for measurement of luminescence. Reflection and scatter of the laser light is measured by moving the detector and removing the filter used to remove laser scatter from the luminescence measurement.

here were either deposited at high temperature (NEL10, deposited using a substrate temperature of 350 °C) or annealed at a sufficient temperature to remove defects (SS27, annealed in nitrogen at 1000 °C for 90 min).

Below is detailed the efficiency calculation for one of the samples studied, SS27. This sample had been annealed at 1000 °C in a dry nitrogen atmosphere and exhibited bright luminescence with a peak around 1.55 eV (800 nm). Figure 3 shows the photoluminescence spectrum of SS27. It should be noted that the silicon clusters within this sample are thought to be amorphous. X-ray diffraction studies of similar films have shown no significant degree of crystallization, and it is the consensus opinion that nanoclustered silicon only crystallizes following annealing at temperatures in excess of 1050 °C.[11]

Given that the diameter of the collection lens was 75 mm and the lens-sample distance was 95 mm, we can calculate the total laser scatter and total emitted photoluminescence as follows:

(i) Ratio of light through lens to total light emitted into a sphere of radius equal to focal length of lens: approximated by ratio *Area of sphere/Area of lens* (Table I)

$$R=\frac{4\pi(95)^2}{\pi(37.5)^2}=25.7. \tag{1}$$

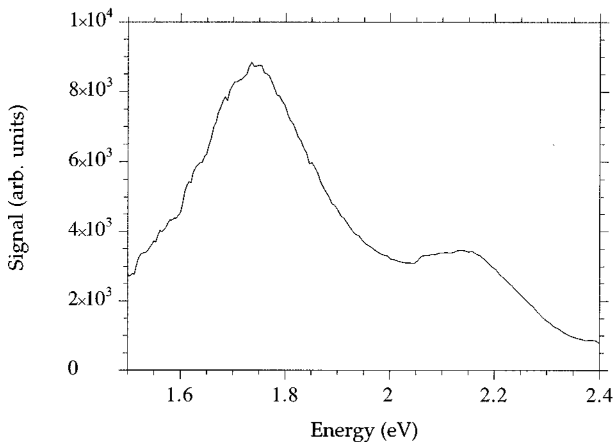

FIG. 2. Typical photoluminescence spectrum of silicon-rich silica sample showing two luminescence bands centered at around 2.1 and 1.7 eV.

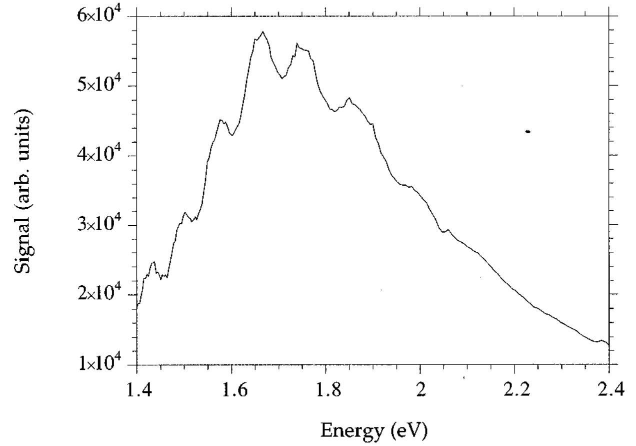

FIG. 3. Photoluminescence spectrum of sample SS27 following 1000 °C anneal. Note the absence of the high energy defect luminescence band.

(ii) Total scattered laser light is given by

$$L=\frac{R}{T_{l476}(1+\rho_{476})}S. \tag{2}$$

(iii) Total luminescence power is given by

$$P_l=\frac{R}{T_{l820}\times T_{f820}\times(1+\rho_{820})}\times(P_{\mathrm{det}}-P_b). \tag{3}$$

(iv) The total laser power absorbed is given by

$$A=(\rho_{476}\times P_{476})-P_{\mathrm{ref}}-L. \tag{4}$$

(v) Finally, the power efficiency is

$$Q=\frac{P_l}{A}. \tag{5}$$

Putting in the values quoted for sample SS27, we obtain

$$Q=\frac{P_l}{A}=\frac{2.15\ \mu\mathrm{W}}{5.28\ \mathrm{mW}}=4.1\times10^{-4}\ (0.041\%). \tag{6}$$

We estimate the error on this figure to be around ±10%.

Figure 4 shows a photoluminescence spectrum for sample NEL10: this sample had been grown at a higher temperature than SS27 and had not been annealed. There are clearly two luminescence bands in this spectrum, though it is not clear what their assignments are. The higher energy band is at too low an energy to be due to luminescence from the nonbridging oxygen hole centers as customarily seen in such material (this band typically lies around 2.0–2.3 eV).[7] It may

TABLE I. Experimental results.

Quantity	Value
Total laser power at sample surface (P_{476})	14.0 mW
Specular laser reflection (P_{ref})	6.0 mW
Diffuse laser scatter into collection lens (S)	6.1 nW
Luminescence collected by lens (P_{det})	44.0 nW
Background noise level of detector[a] (P_b)	2.1 nW
Transmission of collection lens at 476 nm (T_{l476})	89.2%
Transmission of collection lens at 820 nm (T_{l820})	93.5%
Transmission of filter at 820 nm (T_{f820})	74.6%
Reflectivity of silicon at 476 nm (ρ_{476})	97.6%
Reflectivity of silicon at 820 nm (ρ_{820})	7.9%

[a]Includes any residual 476 nm light not blocked by the filter.

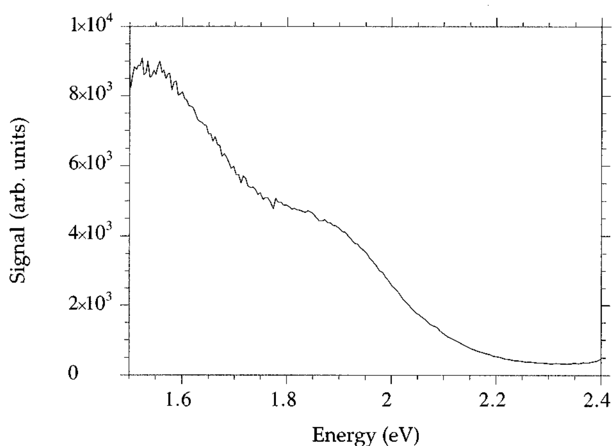

FIG. 4. Photoluminescence spectrum of sample NEL10.

be that there are two peaks in the size distribution of clusters in this film. However, measurements of this sample yield a power efficiency of 0.025% for the total luminescence band.

No reports have been published of efficiency measurements on this material: the only figure we have found in the literature quotes an efficiency of 0.011% for PECVD-produced silica measured by comparing luminescence from the film with a reference ruby sphere of known quantum efficiency.[12] However, the material produced was not silicon rich, and the authors ascribed the luminescence solely to defects. Their luminescence spectra exhibit a peak around 2.3 eV which shows no annealing-related redshift, and there is no evidence of silicon clusters from either x-ray photoelectron spectroscopy (XPS) or x-ray diffraction studies. This is in excellent agreement with our assignment of the upper luminescence band in silicon-rich silica to defect luminescence. We have been careful in our study to exclude defect luminescence from the efficiency measurements, and we are therefore confident that this study represents the first set of measurements of luminescence efficiency of nanoclustered silicon.

The quantum efficiencies measured for the silicon-rich silica films studied here are of the same order of magnitude as reported for early work on porous silicon. Following several years of effort, efficiencies quoted for porous silicon are currently around the 10% mark for photoluminescence and 0.1% for electroluminescence.[13] Given the state of research into nanoclustered and nanocrystalline silicon, there is every reason to expect that the efficiencies quoted in this study can be greatly improved. As bulk silicon effectively exhibits no luminescence at room temperature, these results demonstrate luminescence enhancement due to the quantum confinement effects seen in nanoscale material. The contamination problems that plague luminescent devices fabricated using porous silicon are not encountered in silicon-rich silica; the silica matrix serves as a very effective barrier between the luminescent silicon nanoclusters and the environment.

In this and previous studies we have demonstrated that silicon-rich silica may be conveniently fabricated by PECVD, overcoming some of the processing complexities associated with porous silicon (principally drying and protecting the fragile surface). Through a careful choice of deposition parameters and postprocessing, it is possible to minimize the defect contribution to luminescence in this material, and the peak emission wavelength of the quantum confinement band exhibits a marked dependence on silicon nanocluster size. By tailoring the production process appropriately, it would in principle be possible to manufacture material with a peak emission tailored to the desired application. Furthermore, there have been reports of luminescence from silicon nanoclusters doped with luminescent centers that exhibit fast narrow-band luminescence via an excitation exchange process from the silicon nanoclusters.[2,8,14] As yet there are no efficiencies quoted for such material, but work in our group is progressing in this direction. There have also been a small number of demonstrations of electroluminescence from films of silicon-rich silica:[8,15–17] This material does not suffer from the problems of poor surface contact encountered in porous silicon; opening up the way for the development of luminescent devices based on silicon nanoclusters.

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