

Photoluminescence of chemically vapor deposited Si on silica aerogels

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We have prepared *in situ* porous Si by the decomposition of SiH_4 at 500 °C on an aerogel substrate. Electron microscopy studies indicate that the as-deposited Si is primarily amorphous while the sample annealed in Ar at 800 °C has various nanometer-sized crystalline Si particles. Visible photoluminescence (PL) can be observed only from the annealed sample and the PL peak red shifts with the annealing temperature from 800° to 1000 °C. The results support the quantum confinement theory as the luminescence mechanism in porous Si.

Recently, visible photoluminescence (PL) has been reported from porous Si (PS) prepared by electrochemical or chemical etching of Si wafers in HF-based solution.^{1,2} The discovery of the PL has stimulated significant interest in Si for optoelectric applications. However, the origin of the luminescence in PS remains in dispute because bulk Si, being an indirect-gap semiconductor, is only weakly luminescent in the near-infrared region of the optical spectrum. Recent studies³⁻⁷ indicate that, among the several proposed mechanisms, quantum confinement effects appear to play a key role in the light emission from PS. The quantum confinement theory attributes the visible PL in PS to the increased band-gap energy of crystalline Si arising from the presence of isolated small Si features of a few nanometers.³⁻⁵

Besides the wet etching technique, alternative methods to fabricate luminescent Si have been attempted. Takagi *et al.*⁴ observed visible PL from ultrafine Si particles prepared by a plasma-enhanced chemical vapor deposition process and then oxidized under high humidity conditions. In another study, a spark-erosion technique was used to make porous Si with the PL characteristics similar to that etched in HF solution.⁸ We report here on a new method of preparing luminescent Si films by chemical vapor deposition (CVD) on a porous substrate. Silica aerogels appear to be an ideal substrate for depositing porous Si because of their high porosity, high surface area, and small particle size.⁹⁻¹² Aerogels are transparent microporous materials prepared using sol-gel processing and supercritical solvent extraction. In the sol-gel process, silicon alkoxide, e.g., tetraethylorthosilicate (TEOS), when catalyzed by an acid or base, undergoes a series of hydrolysis and condensation reactions, leading to the formation of a crosslinked solid called an alcogel. An aerogel is obtained after liquid in the voids is extracted from the alcogel under supercritical conditions. Silica aerogels studied in this letter were prepared using the CO_2 substitution process from base-catalyzed TEOS gels and their microstructures have been characterized.^{10,13}

Si was deposited on the surface of small aerogel bars in a quartz-tube furnace by the thermal decomposition of silane.¹⁴ Dilute silane gas (0.48% SiH_4 in argon) was introduced into the reaction chamber at a flow rate of 400 cc/min. The deposition of Si took place typically at 500 °C for a period of 1 h. After the deposition, the surface of the aerogel was covered with a thin layer of metallic Si, some of which

extended a short distance into the pores in the aerogel. The Si-deposited aerogels were annealed in a flowing argon atmosphere at a temperature ranging from 750° to 1000 °C. As-deposited Si layers do not have noticeable PL under an UV lamp, while those that were annealed emit red light visible to the naked eye. PL measurements were made on annealed samples using a commercial spectrofluorometer at an excitation wavelength of 320 nm. The sample was positioned so that the incident beam penetrated the Si layer from the aerogel side at an approximate angle of 45° in order to achieve the maximum PL intensity, which generally varied less than 10% from one position to another. PL spectra of all samples were recorded from 500 to 800 nm at an interval of 10 nm.

Since silica aerogels are highly porous (96% porosity), the deposition of Si will not be homogeneous on a microscopic scale. Because of the high surface area of the aerogel ($\sim 900 \text{ m}^2/\text{g}$), silica acts as a catalyst for the thermal decomposition of silane. Silane molecules tend to adsorb and decompose on the silica network, creating tiny Si columns that resemble the morphology and structure of the underlying aerogel substrate. As more Si layers are deposited, these separate columns or rods may form a loosely interconnected pattern with a characteristic size in the same range as that of silica particles in the aerogel (2–5 nm). Figure 1(a) illustrates a high-resolution electron microscopy (HREM) image of as-prepared Si-deposited aerogel powders. The main feature here is that Si appears predominantly amorphous as indicated by the lack of crystallinity in electron diffraction patterns. Admittedly, a very small number of crystalline Si particles were identified in certain areas of the sample (not shown here). After annealing, numerous crystalline Si particles a few nanometers in size emerged, as shown in Fig. 1(b) for a sample annealed in an argon ambient at 800 °C for 10 min.

Figure 2 shows a series of PL spectra for a Si-deposited sample which was annealed in Ar for 10 min at a temperature ranging from 750° to 1000 °C. As a control, pure silica aerogels were subjected to the same heat treatment and found to have no or insignificant PL as expected. It can be seen from Fig. 2 that the PL intensity increases dramatically with the annealing temperature, reaching a maximum at 910 °C. The PL peak initially shifts toward shorter wavelengths (blue shift) from 750° to 800 °C and then red shifts at temperatures

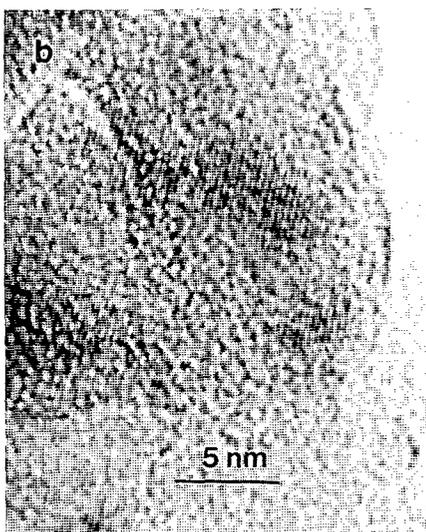
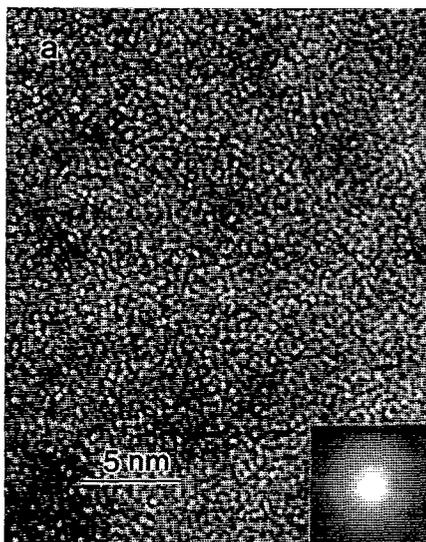


FIG. 1. HREM micrographs and electron diffraction patterns of CVD Si (a) as-deposited and (b) annealed at 800 °C in Ar. The samples were taken from the portion of the aerogel substrate containing Si and prepared as fine powders.

higher than 800 °C. The position of the PL peak varies between 720 and 760 nm for all samples measured. The PL spectrum has a typical peak width of 150–160 nm, which is comparable to that of HF-etched PS.⁵

Silica aerogels make possible *in situ* deposition of porous Si without the usual etching step in HF, which may introduce impurities and complicate the interpretation of the luminescence mechanism. It is reasonable to suggest that the PL observed here originates from the same mechanism as that of HF-etched PS. The fact that as-deposited Si is primarily amorphous and has no PL indicates that amorphous Si, as suggested by some,¹⁵ cannot be the dominant luminescent material in PS. Some degree of crystallinity appears to be necessary for efficient PL, as confirmed by the presence of numerous small Si particles in the annealed sample. Another interesting observation is that visible PL can be seen only

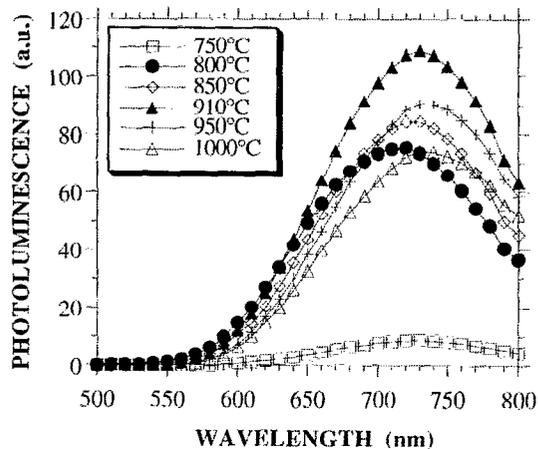


FIG. 2. PL spectra of a Si-deposited aerogel sample which was repeatedly annealed at higher temperatures in Ar. Note that the PL peak red shifts with the annealing temperature from 800° to 1000 °C.

from the region of the Si layer very close to the aerogel substrate though the location and thickness of this emitting layer are difficult to characterize. Based on this observation, we believe that *a*-Si:H¹⁶ and various silicon hydrides¹⁷ cannot be responsible for the observed visible luminescence as it is difficult to imagine that certain parts of the Si layer happen to have the right chemical composition while all other parts do not. Further evidence against the hydrogen-related mechanisms comes from the observation that visible PL could be seen from samples which had been annealed in Ar as high as 1000 °C, by which temperature hydrogen should have long been dissociated from the silicon hydride compounds.^{18,19} For the same reason, luminescence from siloxene and its derivatives²⁰ is insignificant or unlikely in our samples, considering that these compounds become less stable with temperatures and will not survive as high as 1000 °C. Thus the quantum confinement model is the only viable mechanism to account for luminescence we have seen from the annealed CVD Si on the aerogel surface.

According to the quantum confinement theory, Si nanoparticles are responsible for visible PL through enhanced radiative recombination of electrons and holes. Annealing of amorphous Si results in its crystallization beginning at 600 °C or higher temperatures depending on the deposition condition and the substrate used.^{21,22} Annealing in an inert atmosphere has the advantage of not altering the Si surface which has been demonstrated to affect the luminescence process to a large degree.²³ With increasing annealing temperature, more and more Si crystallites are created from the Si layers deposited on the aerogel substrate. The appearance of the small Si particles increases the probability of interband radiative recombination and therefore the PL intensity. In the meanwhile, some of these particles may grow in size, which is responsible for the shift of the PL peak to longer wavelengths (see Fig. 2). It is not clear why the PL peak blue shifts initially from 750° to 800 °C upon annealing. It could be due to the nucleation of more small Si crystallites at 800 °C than at 750 °C, which means a higher intensity in the shorter wavelength region of the PL spectrum. At higher an-

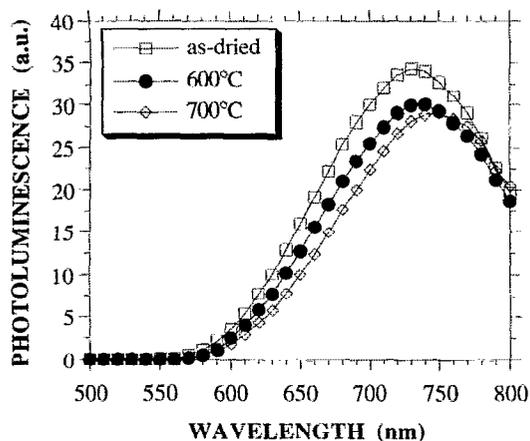


FIG. 3. PL spectra of Si deposited on aerogels presintered to different temperatures. The samples were annealed in Ar at 820 °C after the deposition of Si.

nealing temperatures, fewer new sites are available for the creation of Si crystallites and the rate of particle growth takes precedence over that of crystallization. Consequently, there are fewer small crystalline Si particles with an increased average particle size. It may be reasoned that there are more defects or nonradiative paths for the electron-hole recombination processes in large Si particles than in smaller ones. Using this argument we can explain the lowering of the PL intensity and further red shift of the peak with annealing temperature above 910 °C.

Another way to vary the size of Si particles is to modify the microstructure of the aerogel substrate before the CVD process. Aerogels are so porous that the porosity and the surface area can be easily reduced by heating them at an intermediate temperature. Partial sintering results in coarsening of the aerogel structure due to fusion or coalescence of adjacent silica particles or networks. As the substrate material can largely influence how films are deposited on it, Si deposited on the presintered aerogel is expected to have a characteristic dimension larger than Si on the as-dried aerogel. In accordance with the quantum confinement model, the PL spectra should red shift with the temperature at which the aerogel substrate was pretreated. This is the case as shown in Fig. 3 for Si deposited on three aerogel substrates pretreated at various temperatures. The samples were all annealed in Ar at 820 °C for 12 h after the deposition of Si. It can be seen that the PL peak shifts from 730 to 750 nm, with the peak intensity decreasing slightly, as the aerogel substrate is pretreated up to 700 °C. The result from the PL measurements of Si deposited on the presintered aerogels provides further evidence in support of the quantum confinement model.

In conclusion, we have developed a new method of making luminescent Si by chemical vapor deposition on porous aerogel substrates. The rationale of this method lies in that silica aerogels consist of small silica particles having roughly the same dimension as the luminescent Si features expected to be dominant in PS. The porous Si layer has been created *in situ* on the aerogel surface without further etching in HF as generally required. Light emission in red, visible to the

naked eye, has been observed from Si deposited on the aerogel and annealed in an inert atmosphere at 750 °C or higher. Changes in the PL spectra have been associated with the crystallization and growth of small Si particles upon annealing. The PL peak red shifts with the annealing temperature from 800° to 1000 °C with its maximum intensity at 910 °C. The red shift of the PL peak has also been realized by presintering the aerogel substrate before depositing Si in the CVC process. The results from the PL measurements on the annealed as well as presintered samples support the quantum confinement theory as the cause of luminescence in porous Si. Other proposed models including amorphous Si, silicon hydride, and siloxene have been ruled out based on unique characteristics of the PL spectrum.

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