

The observation of silicon nanocrystals in siloxene

R. F. Pinizzotto, H. Yang, and J. M. Perez

Center for Materials Characterization and Physics Department, University of North Texas, Denton, Texas 76203

J. L. Coffey

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

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We report the direct observation of silicon nanocrystals in unannealed siloxene using high resolution transmission electron microscopy. The microstructure consists of an amorphous matrix plus silicon crystallites with dimensions of a few nanometers. This is additional evidence that the photoluminescence of silicon-based materials is due to quantum confinement.

I. BACKGROUND

Observations of the visible photoluminescence of many silicon-based materials have recently been reported. The materials include anodically etched or "porous" silicon,^{1,2} silicon nanocrystals,^{3,4} silicon-rich SiO₂,⁵ *a*-Si:H,⁶ polysilane,⁷ and siloxene.^{8,9} There is strong interest in understanding the basic luminescence mechanisms from a fundamental physics perspective and for optoelectronic applications.

Generally, the optical properties of these materials are attributed to quantum confinement effects due to the presence of silicon nanocrystals;¹⁰ that is, small crystalline regions with dimensions on the order of a few nanometers. However, some researchers have proposed alternative models based on surface passivation (Si-H/Si-OH bonds),^{11,12} molecular orbitals confined to Si rings or chains due to the presence of oxygen in a planar array of silicon atoms, similar to siloxene,¹³ or amorphous material.¹⁴⁻¹⁶ The many similarities of the optical properties of these materials are strong indications of a common photoluminescence mechanism, as has been pointed out by others.^{8,17} However, this is difficult to justify if the microstructures of the materials are vastly different, such as Si nanocrystals synthesized in the gas phase versus siloxene synthesized in concentrated hydrochloric acid.

Si nanocrystals have been observed previously using transmission electron microscopy for materials fabricated in the gas phase¹⁸ and in solution.¹⁹ Nanocrystals have also been observed in porous silicon.^{10,20} Annealed Si-rich SiO₂ is known to consist of a mixture of stoichiometric SiO₂ and crystalline silicon particles. Recently, Jung *et al.* have reported that porous silicon synthesized from amorphous silicon is not photoluminescent (PL), whereas porous silicon synthesized from recrystallized amorphous silicon is photoluminescent, and that PL activity coincides with the formation of silicon microcrystallites.²¹ All of these experimental observations are consistent with a quantum confinement mechanism.

Brandt *et al.*⁸ have pointed out that siloxene-based materials have been known for many decades to have unique fluorescence properties.²² They have attributed this to silicon rings or chains that are isolated from each other by Si-O linkages.^{8,13} They have also used the similarities of the optical properties of siloxene and porous silicon to argue that a

similar bonding mechanism is responsible for the photoluminescence of both materials. The implicit assumption is that silicon nanocrystals are not present in siloxene to any appreciable extent.

However, as far as we are aware, there are no published high resolution transmission electron microscopy (HREM) data on the microstructure of siloxene. We have used HREM to examine siloxene and have observed the presence of silicon nanocrystals with dimensions on the order of a few nanometers embedded in the material. This observation is additional evidence that the photoluminescence properties of all Si-based materials are due to quantum confinement effects.

II. EXPERIMENTAL DETAILS

Siloxene was prepared by reacting CaSi₂ powder (Fluka Chemika) with concentrated hydrochloric acid (38%) according to a standard preparation method described in the literature.²³ The mixture was allowed to react for approximately 5 h and then vacuum dried. The resulting material is a greenish-white powder.

HREM samples were prepared by dispersing the powder in methanol by ultrasonic agitation for 15 min. One or two drop aliquots were placed on amorphous carbon films supported by standard copper TEM grids. The samples were allowed to air dry on filter paper. HREM was performed using a Hitachi H-9000 TEM operating at 300 kV. This instrument is equipped with a top-entry stage and has a demonstrated lattice resolution of 0.1 nm. Lattice imaging was performed using an aperture that allowed all diffracted beams for lattice spacings greater than 0.15 nm to contribute to the image. Electron diffraction studies were performed using the H-9000 and a JEOL 200CX scanning transmission electron microscope (STEM) operating in conventional mode at 200 kV. We routinely observe that lower accelerating voltages result in electron diffraction patterns with better signal-to-noise ratios; hence, they are easier to analyze.

Photoluminescence spectra were recorded at room temperature using a SPEX Fluorolog-2 system with double emission monochromator and a constant excitation wavelength of 375 nm. All emission spectra were corrected for fluctuations in photomultiplier tube response.

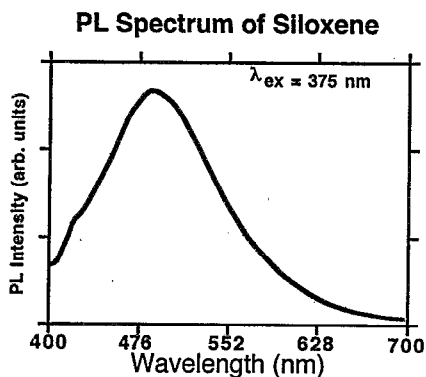


FIG. 1. A typical photoluminescence spectrum for unannealed siloxene.

III. RESULTS AND DISCUSSION

Figure 1 illustrates a typical photoluminescence spectrum of this material. This particular siloxene derivative has not been annealed and demonstrates a broad PL maximum near 490 nm (2.5 eV). The yellow-green emission of this sample is similar to that of $\text{Si}_6\text{H}_5(\text{OH})\text{O}_3$ ²⁴ and contrasts with the 690 nm emission of Kautsky's siloxene reported by Brandt *et al.*⁸ However, Brandt *et al.*'s sample was thermally annealed at 400 °C. It has been previously shown that both preparative conditions and environmental/thermal history play an extremely sensitive role in the observed luminescent and microstructural properties of such silicon-based materials.²⁵⁻²⁷ Given recent accounts demonstrating that thermal annealing can affect the presence of nanocrystals in porous silicon (both stain etched and anodic etched),^{21,28} it is possible that such treatments have a concomitant effect on the position and intensity of the photoluminescence of siloxene as well. It is also important to point out that Brandt *et al.* noted that the similarities of the infrared spectra of porous silicon and siloxene cannot rule out the possibility of silicon nanocrystals in siloxene.⁸

Figure 1 demonstrates that the siloxene used for our HREM characterization is similar to the original Kautsky unannealed siloxene. It is thus reasonable to assume that the microstructure reported here is similar to the microstructure of siloxene produced elsewhere.

Figure 2 is a typical HREM lattice image of siloxene. The microstructure consists of an amorphous matrix with nanoparticles embedded throughout the material. Several nanocrystalline regions are indicated with arrows. Lattice fringes with 0.314 nm spacing are visible. This is consistent with the {111} lattice spacing of silicon.²⁹ We have found it difficult to obtain HREM images which include {220} crossed lattice fringes due to time-dependent electron beam charging of the siloxene sample. To ensure that the imaging difficulties were due to the sample, we obtained crossed lattice fringes for [110] oriented single crystal silicon samples immediately before and after examination of the siloxene. The 0.314 nm {111} and the 0.192 nm {220} fringes were clearly visible. In addition, we routinely obtain HREM images of nanocrystals within porous silicon with both the {111} and {220} fringes.

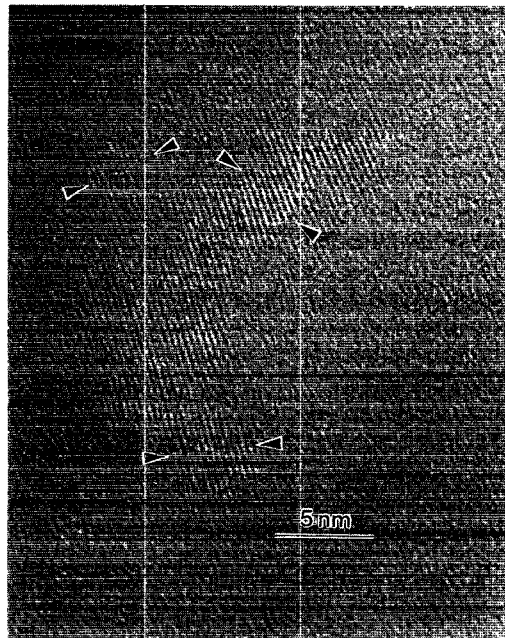


FIG. 2. A high resolution transmission electron micrograph demonstrating the presence of silicon nanocrystals in siloxene. Several nanocrystals are indicated with arrows.

An electron diffraction pattern of the siloxene obtained using 200 kV electrons is shown in Fig. 3. A spot pattern rather than a ring pattern is observed because the density of nanoparticles is relatively small. The lattice spacings derived from Fig. 3 are consistent with crystalline silicon (Table I). {200} diffraction is not observed because the nanoparticles are too small to produce significant double diffraction effects.³⁰ We observe similar diffraction patterns for Si nanocrystals in porous silicon.

The experimental lattice spacings measured from the diffraction patterns are not consistent with CaSi_2 , the precursor used to synthesize the siloxene (Table I).³¹ As a check, CaSi_2 TEM samples were prepared from the precursor powder us-

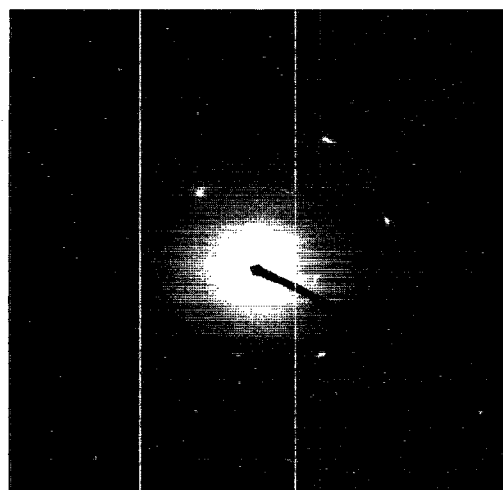


FIG. 3. A selected area electron diffraction pattern of siloxene.

TABLE I. Experimental selected area electron diffraction results compared to silicon, CaSi_2 , and graphite. Note: Some diffraction lines with relative intensities less than 10% have been omitted.

Si nanocrystals in siloxene (experiment)	Si (standard) ^a	CaSi_2 (experiment)	CaSi_2 (standard) ^b	Graphite (standard) ^b
		3.32	3.31	3.35
3.11	3.13	3.11	3.08	
			2.66	
		2.51	2.55	
		2.15	2.13	2.13
1.92	1.92	1.92	1.92	2.03
				1.80
1.63	1.63	1.65	1.64	1.67
			1.55	1.54
			1.47	
			1.43	
	1.36		1.36	1.32
1.25	1.24		1.25	1.23
1.11	1.11			1.15

^aReference 27.

^bReference 29.

ing the same methodology as described above. In this case, the electron diffraction patterns are consistent with CaSi_2 . Additionally, no evidence was found for the presence of silicon nanocrystals in the starting material. The d spacings observed for the siloxene sample are also inconsistent with those of graphite, which could be present in the amorphous carbon support film (Table I).³²

The above data conclusively demonstrate that crystalline silicon is present in amorphous siloxene, and that the crystals are only a few nanometers in size. These results are consistent with the small angle x-ray scattering observation of quantum size particles in siloxene reported by Franz *et al.*³³

IV. CONCLUSION

In conclusion, we have used high resolution transmission electron microscopy and electron diffraction to directly observe silicon nanocrystals in unannealed siloxene prepared using conventional chemical synthesis. The photoluminescence of siloxene may be due to quantum confinement effects within these nanocrystals rather than to confinement within silicon rings or chains separated by oxygen linkages. This observation is consistent with the striking resemblance of the optical properties of siloxene, porous silicon, and other photoluminescent silicon-based materials. The relationship between material properties and microstructure is a cornerstone of materials science. The observations reported here stress the underlying importance of HREM evaluation of all photoluminescent silicon-based materials to fully understand the nature of this phenomenon.

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