Formation of Silicon Nanoclusters during the Reaction of β-Ionone with Tetrachlorosilane

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The chemical reaction between β-ionone and tetrachlorosilane yields silicon nanoclusters entrapped in a polysiloxane matrix along with a cyclized product of β-ionone as a side product. The IR spectrum observed in the entire region of 1000−1200 cm^{-1} indicates the polymer chain length, while UV absorption at 320 nm shows the presence of extended π-conjugation in the system. Photoluminescence spectrum shows a broad band with a maximum at 724 nm and is qualitatively similar to that of porous silicon and related q-particles. Transmission electron microscopy and selected area electron diffraction analysis show the presence of embedded nanocrystalline Si particles of average particle size 50−60 nm. ESR spectrum shows a sharp signal with a g value of 2.0138 due to the dangling bonds of silicon clusters, while cyclic voltammetry gives a reversible peak with $E_{1/2}$ at +1.92 V and an irreversible peak at −0.48 V vs saturated calomel electrode (SCE) confirming the mechanism of reductive silylation of the conjugated ketones.

Introduction

After the remarkable discovery of the light-emitting nature of the porous silicon in 1990,[1,2] there has been a great deal of interest in the synthesis and optical properties of various silicon-based materials. In particular, nanocrystalline silicon[3] and porous silicon thin films have received continued attention because they exhibit visible light emission (PL) at room temperature. Recent studies regarding quantum confinement have elicited a strong response from the synthetic perspective, and the inherent nature of these materials allows the selective formation of unique electronic components and mechanical nanoclusters with great practical utility. For example, several attractive applications realized in recent years include optoelectronics,[4] high-field electron emission source,[5] chemical sensing microstructure,[6] ion-selective membrane,[7] and finally electrochromic materials to be used in flat-screen full-color displays.[8]

As a consequence of this tremendous technological importance, several approaches have been made to artificially design nanostructures based on silicon.[9] One general and expedient method to form nanostructures is the electrochemical etching of silicon in HF-based electrolytes to form an interconnected network of small Si crystallites with a typical size of few tens of angstroms; but there stability is rather poor due to gradual surface degradation in air. Quantum-size Si particles have been synthesized from silanes using different approaches, such as slow combustion, microwave heating, and chemical vapor deposition,[10] and the stabilization has been achieved by spatial confinement in polymers, glass matrixes, zeolites, etc. More recent examples include emission of blue light from amorphous silicon carbide by controlled hydrogenation of the lattice[11] and polymer-coated colloidal silicon suspension in solution.[12] In addition to these, organosilicon compounds containing clusters, chains, rings, or three-dimensional structures of unsaturated silicon atoms [silenes, disilenes, siloxenes[13,14]] are also especially significant for their optoelectronic properties reflecting the exceptionally facile delocalization of σ- and π-electrons. They also find suitable applications such as synthesis of polymer magnets[15] and precursors for high-temperature ceramic powders and fibers of SiC and Si_3N_4, which are of interest as ceramic plastics and metal matrix composites.[16,17]

We have recently reported the photoluminescence of a gel obtained from the reaction between acetone and tetrachlorosilane,[18] where the origin of the photoluminescence was attributed to the chemical nature of the resulting polymer. There was no positive evidence for the formation of Si-q particles by TEM of the gel. In contrast, in this study we report a novel synthesis of the silicon-q particles embedded in a functionalized siloxane polymer obtained by the reaction between

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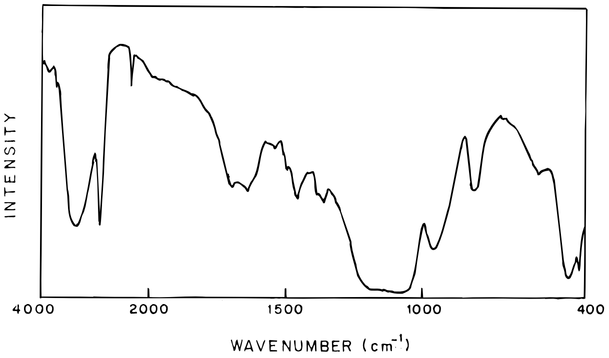

Figure 1. Infrared spectrum of the β-ionone/$SiCl_4$ gel recorded as a thin film on a KBr pellet.

tetrachlorosilane and β-ionone; β-ionone is selected because of its inherent π-conjugated lattice along with an active carbonyl group which may play a crucial role in modulating the optoelectronic properties of the resulting material. The material thus obtained is characterized by infrared spectroscopy (IR), ultraviolet spectroscopy (UV), electron spin resonance spectroscopy (ESR), and transmission electron microscopy (TEM). The light-emitting properties are studied by photoluminescence spectroscopy (PL).

Experimental Details

The gel samples studied here were all prepared by adding tetrachlorosilane (Merck) to a benzene solution of β-ionone (Aldrich) in 1:1 ratio in an argon-filled glovebox with stirring for 72 h. After the removal of benzene, the resulting viscous and oily material was washed with petroleum ether (60−80 fraction). The resulting shining brown solid was subject to various physicochemical analyses. Elemental analysis of the solid gave 39.34% C, 5.3% H, 14.1% Cl, 19.82% Si, and 20.0% O.

IR spectra of the samples were recorded in a Nicolet 60 SXB spectrometer in the form of pressed KBr pellets in the range between 400 and 4000 cm^{-1}. The UV spectra of the reaction mixture in benzene were recorded in a Shimadzu (Model UV 2101 PC) spectrophotometer. The ESR spectrum of the sample (at room temperature) was recorded in a JEOL Model ESR spectrophotometer. A JEOL Model 1200EX electron microscope operating at 120 kV was used for the transmission electron microscopy (TEM) measurements. The samples were ultrasonically dispersed in isopropyl alcohol before deposition on the holey carbon film of the TEM specimen grid. The PL spectra were recorded at room temperature using an argon ion laser (488 nm lines) as an excitation source, monochromator grating of 1 μm, with a LP filter 0.515 μm, slit 2 mm, and a silicon photodiode with a lock-in amplifier as the detector.

Cyclic voltammetric experiments were carried out in 0.1 M solution of tetrabutylammonium tetrafluoroborate (TBFAB) in acetonitrile using a platinum electrode of geometric area 0.02 cm^2 as a working electrode in a three-electrode, single-compartment setup with a saturated calomel reference electrode and a platinum foil counter electrode. All the experiments were conducted using a PAR 173 potentiostat coupled with a PAR 175 function generator, and the data were recorded on a RE0091 X-Y recorder in an argon atmosphere at a temperature of 25 ± 1 °C controlled by a thermostat.

Results and Discussion

Infrared Spectra. The IR spectrum of the gel recorded in the form of a pressed KBr pellet is shown in Figure 1. It clearly indicates a broad band in the region 1000−1200 cm^{-1} which is the characteristic band corresponding to the bulk interstitial Si−O−Si stretching of a siloxane polymer with the possibility of infinite chain length.[19] Other major bands are observed at 3500 cm^{-1} corresponding to the O−H stretching vibration. This indicates that some of the Si−Cl bonds are hydrolyzed and terminated as Si−OH bonds. Interestingly, a sharp peak is observed at 2200 cm^{-1} corresponding to the Si−Si stretching vibrations reported in earlier studies for silicon nanostructures. This is specially significant as the IR absorption observed corresponding to Si−O−Si cannot be used unambiguously to discriminate between the presence of polysiloxane or silica. IR spectrum also shows the presence of C═O (1720 cm^{-1}) and C═C (1640 cm^{-1}) groups in the polymer. These peaks are highly broadened, which indicates the presence of extended π- or σ-conjugation in the system. A small amount of Si−Cl is evidenced by its stretching vibration at 662 cm^{-1}, in agreement with the results of the elemental analysis. Symmetric stretching vibration of the C−H groups is observed at 2890 cm^{-1} while the antisymmetric stretching vibration is observed at 1460 cm^{-1}. The symmetric deformation of this group is observed at 1206 cm^{-1}. Thus the IR spectrum clearly indicates that the polymer obtained is a functionalized siloxane polymer with embedded silicon nanoparticles.

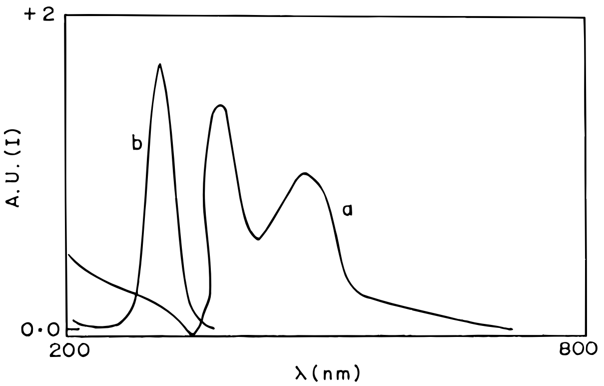

Figure 2. Ultraviolet spectra of the reaction mixture in benzene just before cross-linking: (a) acetone/$SiCl_4$; (b) β-ionone/$SiCl_4$.

It is interesting to compare the IR results with that obtained for the gel produced as a result of acetone/$SiCl_4$ reaction.[18] The basic pattern of the spectrum is the same in both the cases, except for the 2200 cm^{-1} corresponding to Si−Si stretching vibration, indicating that functionalized siloxane polymer is formed during both the reactions.

Ultraviolet Spectra. UV spectrum of the reaction mixture diluted in benzene is shown in Figure 2a. It shows a sharp peak with a maximum at 322 nm possibly arising due to a σ−σ* transition which normally occurs around 305−320 nm. In contrast, the β-ionone molecule is known to absorb at two wavelengths, 228 and 295 nm.[20] Further, the UV spectrum shows a very high time dependence, i.e., these peaks corresponding to β-ionone which are initially present in the system subsequently disappear as the siloxane polymer forms. Interestingly, normal siloxanes are not UV-active and any absorption of even functionalized siloxanes are not reported so far in this range. The synergetic effect arising from both

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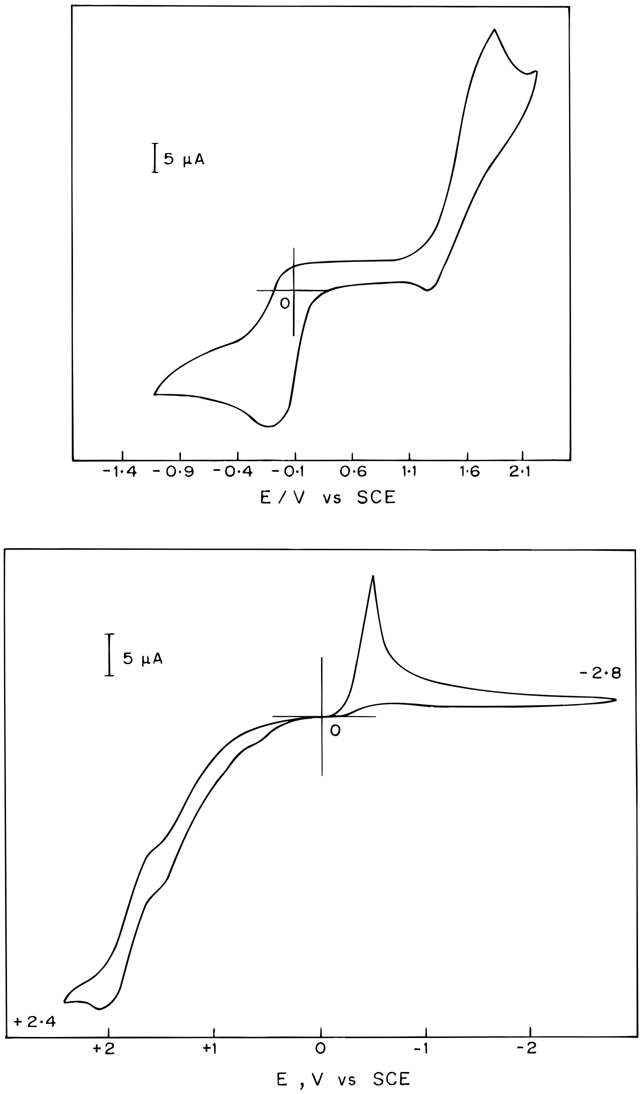

Figure 3. Cyclic voltammogram of the reaction mixture in acetonitrile containing 0.1 M tetrabutylammonium fluoroborate: (a, top) acetone/$SiCl_4$; (b, bottom) β-ionone/$SiCl_4$.

the inherent extended π-conjugation of the β-ionone molecule and the properties of Si makes the optical properties of the system interesting. The possible contribution of delocalization of the n-electrons of siloxane polymer may also play a crucial role. Another plausible explanation is the electron−hole recombination in the π-backbone of the polymer as supported by the unusual sharpness observed in the spectrum. In contrast, the gel obtained from the reaction between acetone and $SiCl_4$ shows a sharp maximum at 329 nm and also an additional peak at the initial stages of reaction at 415 nm. This may be arising from the intermediate formed, which may undergo a homolytic cleavage and form siloxane network with subsequent hydrolysis.

Cyclic Voltammetry. Electrochemical properties of the siloxane polymer before cross-linking are studied due to their relevance in electroluminescence and in understanding their electron-transfer properties leading to photoluminescence. In addition crucial information could be gained regarding the mechanism of Si−Si or C−Si bond formation and the possible intermediates. The CV of the gel before cross-linking in acetonitrile containing 0.1 M TBAFB shows (Figure 3b) a reversible peak at +1.92 V along with an irreversible peak at −0.480 V. The peak observed at +1.92 V is due to the oxidation of the ketonic group. Although the oxidation of aliphatic carbonyl groups occurs at a very positive potential, it is found to decrease significantly with silyl substitution.[21] This is because in the case of alkyl silanes since the C−Si bond and the oxygen lone pair are fixed in the same plane, they can always interact quiet effectively, facilitating the oxidation to occur at lower thermodynamic potentials. The irreversible peak at −0.480 V is due to the carbanion formation from Si−CH_2−, where the irreversibility is arising from the stabilization of the radical anion by the inherent π-conjugation of the β-ionone molecule.

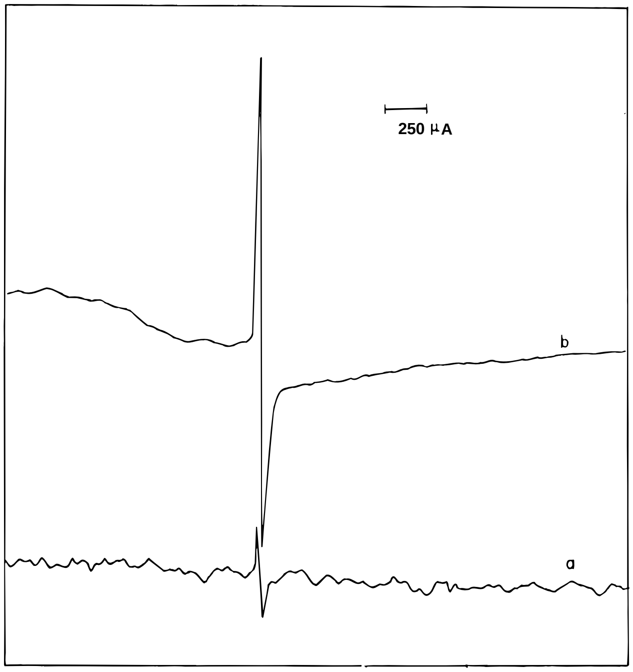

Figure 4. Room-temperature electron spin resonance spectrum of the sample in powder form: (a) acetone/$SiCl_4$; (b) β-ionone/$SiCl_4$.

In comparison, the gel obtained from acetone/$SiCl_4$ reaction shows (Figure 3a) two reversible peaks with $E_{1/2}$ values at −0.1 and +1.52 V under the same electrochemical conditions.

Electron Spin Resonance Spectra. A strong paramagnetic nature of the gel is indicated by the room-temperature ESR spectrum of the resulting polymeric product as shown in Figure 4a. More specifically, it shows a narrow bandwidth with a g value of 2.0138. It is interesting to compare this spectrum with that obtained for porous silicon, which shows a narrow peak width with a g value of 2.0052[22] and that for a silyl radical ion which gives a g value of 2.0032. The difference may be arising from the matrix-induced effects as the flexible polysiloxane matrix is entirely different from that of microcrystalline porous silicon. The narrow signal obtained in the present case is due to the dangling bonds[23] in the silicon clusters and one reason for retaining the dangling bonds is the flexibility of the siloxane matrix in which they are embedded.

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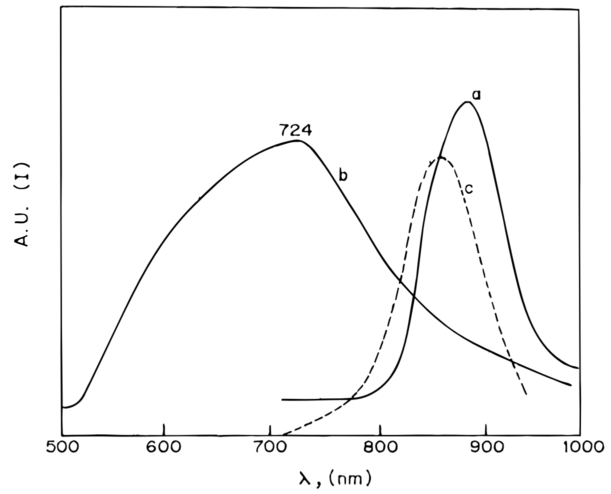

Figure 5. Room-temperature photoluminescence spectrum of the sample recorded using an argon ion laser (488 nm) as an excitation source: (a) acetone/$SiCl_4$; (b) β-ionone/$SiCl_4$; (c) porous silicon.

These dangling bonds are created by breaking weak Si−Si bonds in the cluster, or alternatively it can be formed by carrier trapping in the preexisting charged defects. The presence of nanoclusters of Si with polymeric coating is proposed on the basis of the above features and also due to similarities of ESR obtained for amorphous and microcrystalline Si although same type of ESR could be proposed by radical sites such as Si−Si•(−Si)−O or Si−Si•(−O)−O during the chemical reaction.

The gel obtained from the reaction between acetone and $SiCl_4$ also shows the similar ESR spectrum (Figure 4b), however with less intensity.

Photoluminescence Spectra. Photoluminescence spectrum of the gel recorded using an argon ion laser (488 nm) excitation source is shown in Figure 5a. The spectrum is very broad with a maximum at 724 nm (1.71 eV) and a peak width of about 0.3 eV. In comparison, colloidal Si indicates a maximum of 600 nm while amorphous silicon emits in the range 700−800 nm. It is interesting to note that the emission spectra is quantitatively matched with that reported for porous silicon (Figure 5b) and related quantum particles, where emission especially occurs from quantum sites in the crystalline interior as well as from the energetically low-lying states on the crystalline surface. The emission spectrum is shifted to higher wavelengths compared to that of plasma-deposited Si particles and colloidal silicon. The emission source in this system is the excited electron−hole pairs in the localized states associated with sp^2 carbon molecular orbitals of individual π-bonding units. The large inherent π-conjugation present in β-ionone molecule facilitates the above mechanism. The luminescent quantum yield is also high compared to porous silicon and related quantum particles.

Perhaps the most interesting possibility is the approximate size calculation based on quantum confinement. If we assume that the PL emission is due to quantum size effects, the particle size can be calculated from the formula[22]

$$\Delta E = h^2/4\mu^* L^2$$

where, ΔE is the shift in PL maximum (in eV) compared to the bulk silicon (1.1 eV), L is the length of the quantum particle in angstroms, and μ^* is the reduced effective mass. Assuming electron effective mass, $\mu^*_e = 0.98 m_e$, similar to the bulk silicon[24] we get ΔE as $227.7/L^2$. The size of the quantum particle calculated using this formula for the present system is around 20 Å, which supports the proposed mechanism of the light emission through quantum confinement.

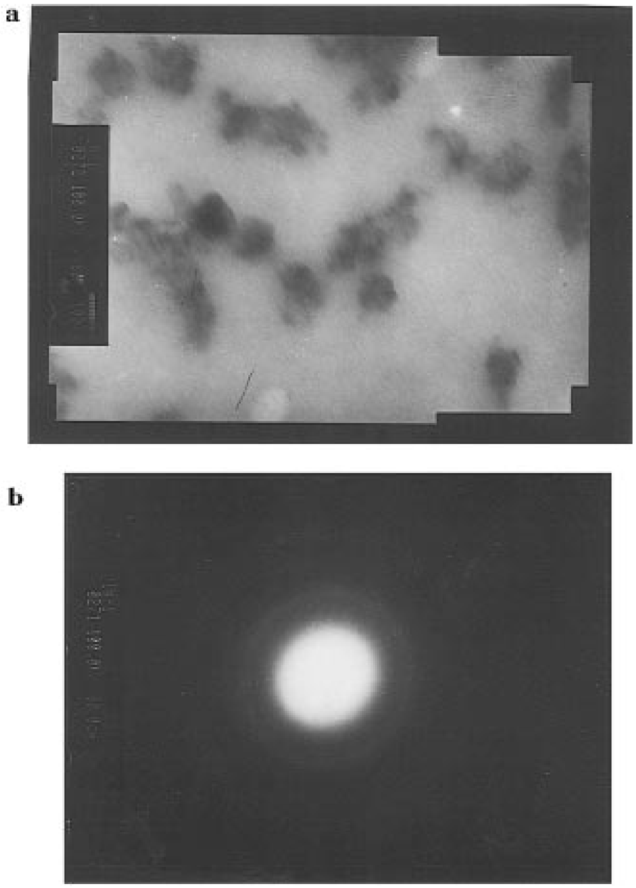

Figure 6. (a) Transmission electron micrograph of the gel obtained by the reaction between β-ionone and $SiCl_4$. (b) Electron diffraction pattern of a cluster shown in Figure 6a (scale is 100 nm).

Transmission Electron Microscopy. Figure 6 shows a representative bright-field TEM image (a) and its selected area diffraction pattern (b) where fine structure of near spherical overlapping Si particles can be clearly seen in an amorphous background. The particles are irregularly shaped and range in size from 50 to 60 nm. The TEM images are comparable to that of porous silicon,[1] which shows an irregular matrix structure and narrow silicon columns protruding beyond the matrix edge. The different sizes and shapes of the clusters will lead to bandgap variations from particle to particle causing localization of the electronic structure. Presumably the smaller particles have more contribution in the luminescence observed due to quantum confinement effects. The selected area electron diffraction patterns of the cluster is indicated in Figure 6b, which shows the amorphous nature.

Chemical Reaction. During the course of the reaction, the color of the reaction mixture was developed from pale yellow to orange red to dark brown, finally

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leading to a black oily solid. On washing with petroleum ether a dry black solid and soluble products were obtained. The petroleum ether fraction was found to be a cyclized form of β-ionone which is obtained only in small yields. Cyclization of β-ionone is known to occur in the presence of other Lewis acids.

The siloxane polymer is formed by the abstraction of hydrogen from the CH_3 group and the subsequent hydrolysis and condensation. The reaction system is very complicated and different routes can occur, although it is not clear how the Si–Si bonds are formed by the above Si–C bond cleavage. However, physicochemical characterization of the material supports the above mechanism and possibly the radical involvement as the amount of Si clusters formed is only 8% excess of that normally found in polysiloxanes as inferred from elemental analysis. This is further confirmed by the IR spectrum which shows that the gel is a functionalized siloxane polymer along with additional features for Si–Si. The UV spectrum reveals the presence of extended σ- and π-conjugation, and this together with TEM and selected area electron diffraction confirms the presence of silicon nanoclusters in the siloxane system. The CV data agree well with the known features of anion radical formation during reduction and the irreversible reduction is believed to cause Si–Si bond formation via a reductive silylation of conjugated ketones. The final confirmation arises from the ESR spectrum which shows the presence of Si–Si dangling bonds in the system and also due to the PL spectrum, which indicates the similarities of the optical properties with that of porous silicon and other Si-q particles.

Conclusions

A novel route for the synthesis of the Si-q particles embedded in polysiloxane matrix is described using the reductive silylation of the conjugated ketones such as β-ionone. The IR spectrum reveals that the polymer is a functionalized siloxane polymer, while TEM analysis suggests the presence of Si nanoparticles in the system. The ESR spectrum indicates the dangling bonds of Si clusters in the system and finally CV analysis helps to understand the electrochemical properties of the intermediates during the course of the reaction.

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