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Particle Size Control and Optical Properties of Laser-synthesized Silicon Nanopowders

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Silicon nanoparticles have been synthesized by heating reactant gases with a 500 W CO_2 laser. A technique based on scattering of He–Ne laser light by particulates in a reaction flame has been developed for probing the particle size evolution during the process, in order to scale down the particle diameter (under 10 nm). The optical and structural properties of laser-synthesized silicon nanopowders obtained in different runs are reported. © **1998 John Wiley & Sons, Ltd.**

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INTRODUCTION

Opto-electronic devices based on silicon have been a goal of the electronics industry, but, until now, the weak emission of silicon has precluded the realization of a true large-scale opto-electronic integration. To this end, there has been considerable interest in light emission from new forms of silicon. Attention has been concentrated primarily on porous silicon, but now there is also a growing body of work on nanocrystalline silicon and silicon-rich silica films, which have similar optical properties to porous silicon without the related problem of stability. These systems with the configuration of grains dispersed in a matrix can be assimilated to quantum dots where it is possible to confine the electrons. The drastic change in energy levels leads to a widening of band gaps, to an increase in oscillator strength and to the appearance of a strong luminescence band in the visible range.

In this framework, the CO_2 laser-induced pyrolysis of silane has attracted new interest as a valuable tool for producing silicon nanoparticles with morphological properties that can be controlled by reaction parameters.[1,2] This technique was first reported by Haggerty in 1981, and it has been shown that, by adjusting the reaction conditions, the chemical composition and morphological properties of powders can be controlled.[3,4] Although variations in the characteristics of the product powder have been studied extensively as a function of the process parameters, the properties of the reaction itself remained more difficult to characterize, among them the evolution in time of particle size, i.e. the particle size scaling by reaction parameters. For the silicon synthesis, we developed a technique based on scattering of He–Ne laser light by particulates in a reaction flame for probing the particle size evolution during the process, in order to obtain silicon powders with very small diameters (under 10 nm) which exhibit luminescence spectra above the band gap of bulk silicon.

In this work, we report the results obtained by this technique on the growth control of silicon crystallites by the reaction parameters, and a preliminary study on the optical properties of laser-synthesized silicon nanoparticles.

EXPERIMENTAL

The silicon powders were synthesized by heating the silane to the dissociation limit with a 500 W CO_2 laser. The reactants interacted in a laminar flow confined by a carrier beam (He,Ar) in a collision environment; for the silicon powder synthesis, silane (99.998%; Air Liquide) was used

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as the precursor because of its strong absorption at 10.6 μm which provides coupling with the laser radiation. The gaseous stream intersected the horizontal laser beam, absorbing optical energy which raised the temperature of the reaction zone, where a flame was created. The temperature of the reaction zone was determined by micro optical pyrometry corrected for emissivities. The particles nucleated and grew in the small laser-heated region, then passed rapidly out of the hot zone entrained by the carrier beam and collected downstream in a tank. Typical residence times of particles in the reaction flame were 1–10 ms, leading to high cooling rates as they left the laser beam. The cell pressure, read on a baratron capacitance manometer, was maintained constant during the reaction by means of an automatic throttle valve; powder production was continuous, with the rate determined by the gas flow rate.

The process begins when the silane decomposes into silicon particles. Using the aerosol growth law developed for the free molecular regime,[5,6] we find that the most significant parameters for the scaling of particle dimensions are the initial number of monomers and the residence time of particles in the flame: the concentration of monomers is proportional to the system pressure and depends upon reaction flame temperature, while residence time increases with increasing cell pressure and decreasing reactant flow rate.

Particle size evolution during the process is followed by measuring the extinction and scattering of a polarized He–Ne beam from the cloud of particles in the reaction flame.[7] The Lorentz–Mie theory of scattering has been applied to this case by assuming that each particle scatters separately with no optical interference among scattering. If the incident and scattered light are polarized orthogonally to the scattering plane, the scattered light at right angles measured from the detector in a solid angle $\delta\Omega$ is $W^{\perp}$ and the scatter/extinction ratio is given by Eqn [1], where I_0 and I are the incident and transmitted He–Ne laser intensity, $i^{\perp}$ the Mie scattering function and C_{ext} the extinction cross-section per particle. The scatter/extinction ratio depends on the particle size, the particle index of refraction and the wavelength of incident light. It is a multi-valued function of particle diameter, and therefore an estimation of particle size requires that the particle growth is followed from the beginning. The scattering and extinction measurements also allow the determination of the emissivity and number density of particles in the portion of the flame probed by the He–Ne laser.

$$\frac{W^{\perp}}{W_0 \delta\Omega \ln\left(\frac{I_0}{I}\right)} = \frac{\lambda^2 \cdot i^{\perp}(\sigma = 90^{\circ})}{4\pi^2 C_{\text{ext}}} = \text{scatter extinction ratio} \quad [1]$$

The surface area of laser-synthesized silicon particles has been measured by the BET method, the morphological properties have been investigated by TEM (JEOL 200 CX) and the particle size distribution has been determined by small-angle neutron (SANS) scattering. SANS measurements were carried out using the PAXY instrument installed at Laboratoire Léon Brillouin (CEA–CNRS). The experimental conditions (sample-to-detector distance, 3 m; neutron wavelength, 0.6 nm) were selected in order to obtain information on size distribution over a significant size range. The samples used for these measurements were pressed pellets approximately 1 mm thick with 1 cm^2 surface area.

RESULTS AND DISCUSSION

Particle growth

Preliminary scatter/extinction and temperature measurements have been performed on laser-heated silicon powder synthesis reactions under a range of process conditions. The particle radius as a function of position in the reaction zone is presented in Fig. 1. All measurements indicate that the particles are often nucleated before the reactant gas stream has reached the laser beam. In any case, it is clear that as the particles travel through the centre of the laser beam there is a steep growth rate that can be slowed down by decreasing the reactor pressure, by diluting the silane with inert gas and by using He instead of Ar as carrier. In this latter case a significant growth is observed after the laser beam.

The final particle sizes obtained by this technique have been compared with the values obtained by other techniques. For the laser-synthesized silicon particles, the average pore diameters were always equal to the particle diameters measured from TEM images, indicating that the particles have no porosity accessible to the surfaces. These values are lower than those obtained by scattering/extinction measurements, but in close agreement. This finding can be related to the multiple scattering from particles, resulting in a larger scattering/extinction ratio and larger particle size.

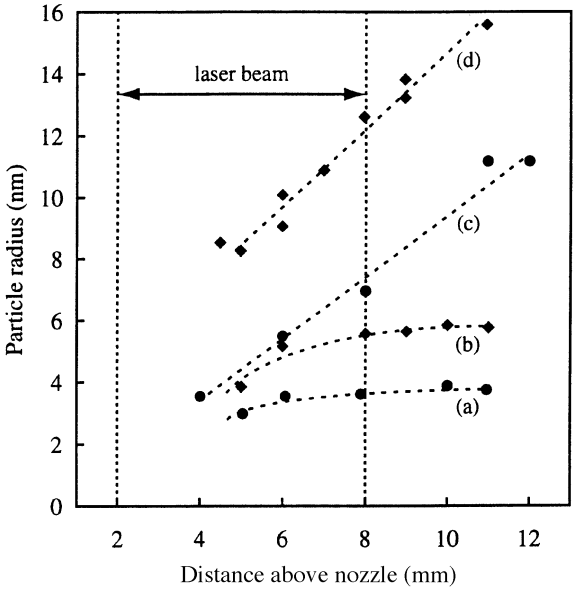

Figure 1 Particle radius evolution along the reaction flame for different experimental conditions: (a) He carrier, high silane dilution, $P = 300$ Torr; (b) He carrier, low silane dilution, $P = 300$ Torr; (c) He carrier, no silane dilution, $P = 300$ Torr; (d) Ar carrier, no silane dilution, $P = 300$ Torr.

By using the experience gained by this technique, we varied reactor pressure and silane dilution percentages, obtaining silicon particles with average diameter in the range 5–170 nm (see Fig. 2).

Photoluminescence spectra

The photoluminescence spectrometry was performed at room temperature on cold-pressed pellets and recorded on a PTI spectrofluorimeter with extended red response to about 850 nm. The wavelength sensitivity of the measuring system was calibrated with a standard tungsten lamp.

In general the photoluminescence spectra of nano-silicon showed two bands: one around 1.7 eV and a second at 1.9 eV. The relative strengths and positions of the bands varied between samples and can be correlated with particle size.

For samples with an average diameter of 10 nm the ratio between the low- and high-energy band intensities is around 5:1 (see Fig. 3), whereas for 7 nm and 5 nm samples this ratio is 2:1 (Fig. 4); in this case a 'bump' around 2.2 eV appears. The luminescence can be observed by the naked eye. No luminescence is detected by our equipment in this range from samples with a diameter greater than

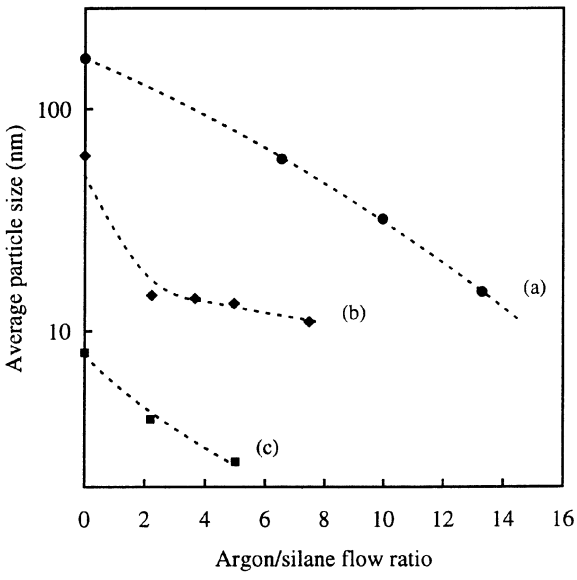

Figure 2 Particle size scaling by reactor pressure and silane dilution: (a) $P = 400$ Torr; (b) $P = 250$ Torr; (c) $P = 200$ Torr.

20 nm (samples obtained without dilution of silane in inert gas and pressure higher than 200 Torr). These findings indicate that a reduction of particle size increases the intensity of the luminescence

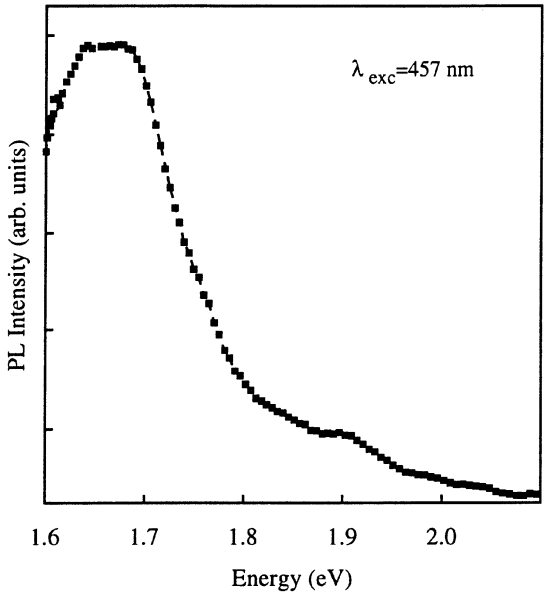

Figure 3 Photoluminescence spectra from silicon powders obtained at 200 Torr without silane dilution in inert gas (equivalent BET diameter, 10 nm).

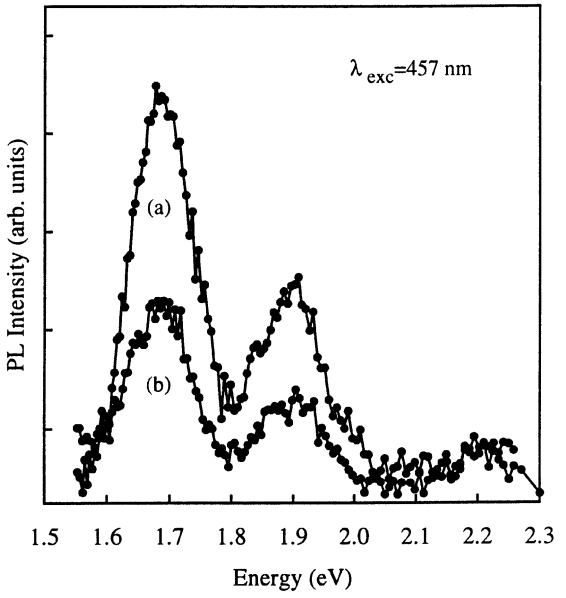

Figure 4 Room-temperature photoluminescence spectra from silicon powders obtained in different runs with (a) low dilution of silane in argon (40%), and (b) high dilution of silane in He (20%). The equivalent BET diameters are 7 nm and 5 nm, respectively.

band at higher energy, in agreement with the hypothesis of a quantum confinement effect. In this context the f.w.h.m. of about 0.2 eV indicates the presence of different sizes of nanocrystals (see the next paragraph).

The dependence of the photoluminescence energy on particle size is well known and many calculations has been made which quantify the relationship between particle diameter and band gap energy.[8–10] From these data it is suggested that a band gap around 1.7 eV corresponds to particle dimensions ranging from 3 to 5 nm, whereas a band gap of 1.9–2.2 eV corresponds to particle sizes in the range 2.5–3.5 nm. However, the size dependence of the photoluminescence peak energy is very small compared with the theoretical calculations; in particular there is a large difference between photoluminescence peak energy and theoretical band gap energy in small nanocrystals.[11–14] Following these authors, we can attribute the peak at higher energy to population of particles with a diameter under 2 nm.

To gain a deeper insight in to this question we made a preliminary investigation of the particle size distribution of particles which exhibit a double peak emission.

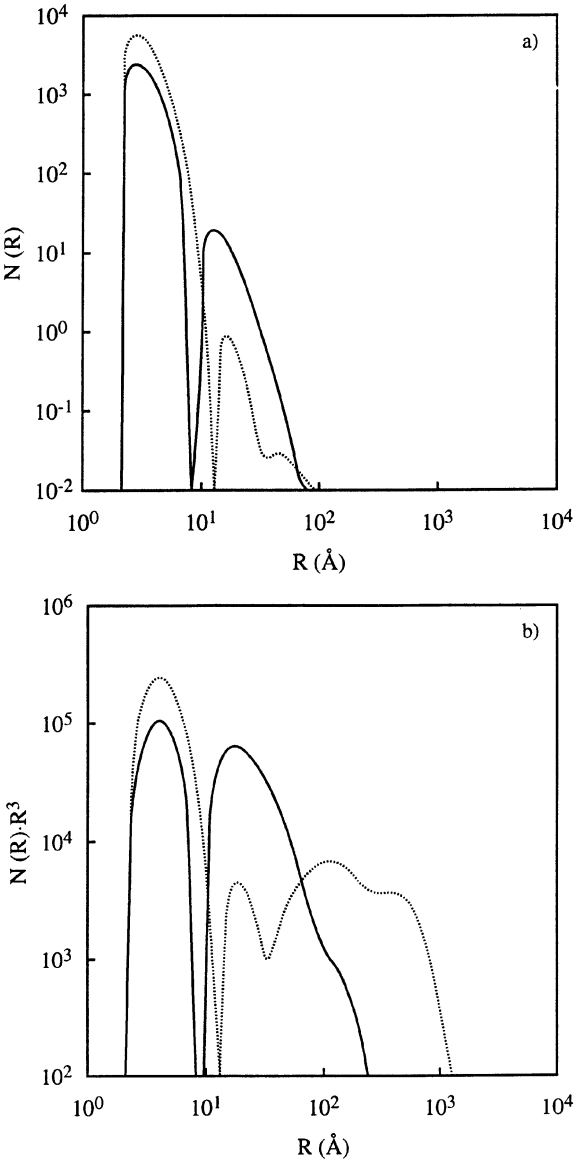

Figure 5 Size (a) and volume (b) distribution functions obtained from samples synthesized with a high silane dilution (continuous line) and with a low silane dilution (dotted line).

Particle size distribution

Information on particle size distribution of samples with lower particle sizes was obtained by means of small-angle neutron scattering (SANS) measurements; general information on this technique is available elsewhere.[15]

The size distribution functions were obtained by transforming the SANS data by the method previously reported[16] which gives a logarithmic representation of $N(R)$, the number of particles per unit volume of size between R and $R+d$, which is particularly useful to identify the presence of particles with sizes differing in orders of magnitude (polydispersed systems); this occurs quite frequently in practical cases. The results are reported in Figs 5(a) and 5(b), which refer respectively to $N(R)$ and $D(R)=N(R)R^3$ (volume distribution function), obtained by assuming spherical form factor for the samples. In both cases a dense population of very fine particles ($R \leq 1$ nm) is accompanied by a secondary population, particularly evident in Fig 5(b). As for the small particles, they are present in a larger amount and in larger size in the sample obtained with a low silane dilution.

From these data, we should attribute the peak at higher energy to the population of very fine particles, but we need a similar characterization of other samples and particles with more uniform size for a precise attribution.

CONCLUSIONS

In this work we have shown that by CO_2 laser-induced pyrolysis of silane it is possible to produce silicon particles with dimensions that can be scaled by reaction parameters over a wide range. The laser-synthesized silicon nanoparticles with smaller diameters (under 10 nm) exhibit photoluminescence spectra above the band gap of bulk silicon. A drastic size reduction is needed for the observation of visible light emission at room temperature (particles in the range 1–2 nm), in broad agreement with the results reported in the literature. The difference between the photoluminescence peak energy and the calculated band gap imply that the carrier or excitons relax from the higher-energy absorption state to the lower-energy emission state. This point deserves further investigation.

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