Communication

Formation of Nanometer-Size Silicon Particles in a Laser Induced Plasma in SiH_4

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Crystalline silicon particles of cubic structure are formed in the plasma which is initiated in an argon-silane mixture by a focussed 694 nm Ruby laser flash. Part of the particles can be dissolved as colloid in organic solvents. The solubilization is increased by small amounts of 1,3-propane-dithiol. The raw material has a broad size distribution. Centrifugation and filtration methods are applied to obtain samples with narrow size distribution. Small silicon particles have structured absorption spectra. The particles luminesce after etching with HF under air. The larger particles have a red luminescence (peaking at 720 nm) and the smaller particles emit a blue luminesce. The luminescence effects are explained by size quantization of the electronic energy levels in the particles.

Introduction

The method of initiating a plasma by a focussed laser beam to disintegrate thin films or suspended micron-size particle in a solvent has recently been used for the preparation of colloidal metals and carbon clusters in solution [1]. In the present communication, a plasma is produced in an argon-silane gas mixture by a focussed laser beam. With the high temperature existing in such a plasma, it was hoped that the disintegration of silane would yield crystalline particles of elementary silicon.

The preparation of small silicon particles has fascinated many research groups during the past ten years. The reports include evaporation into an inert gas atmosphere [2], laser ablation and rf-sputtering of compact silicon [3], UV or IR laser photolysis [4] and pyrolysis [5] of silane and of disilane, and a microwave discharge in SiH_4 plus H_2 or Ar [6]. A chemical synthesis based on the reduction of $SiCl_4$ by sodium at 385 °C and > 100 bar [7] and the combustion of silane [8] were also reported. Various particle sizes and structures were obtained in these experiments, and often the particles formed a dense film. They often had an amorphous outer layer containing hydrogen or oxygen atoms. Partially oxidized particles are of special interest with respect to the formation of luminescent silicon [5b, 6].

In the present investigation, especially small silicon particles are described, which are obtained by filtration/sedimentation of the material initially formed in the laser induced Si disintegration. A method for luminescence activation of colloidal Si particles is also reported.

Experimental

The irradiation vessel has already been described (Fig. 1 A in Refs. 1). The vessel is filled with argon, and 5 to 10 vol.% SiH_4 is then injected through the septum. The laser beam (ruby laser; $\lambda = 694$ nm; 0.85 J per pulse before focus) is focussed into the middle of the vessel. The light is dissipated in the gas mixture by multi-photon absorption processes. A bright spark is produced by each flash. After a few flashes, the vessel contains a gaseous sol which slowly settles on the wall as a yellow-brown powder. 5 to 10 cm^3 deaerated solvent, such as ethylene glycol, cyclohexane, tetrahydrofuran or a cyclohexane-propanol-2 mixture, is then added through the septum and the vessel is slightly shaken. A yellowish solution of suspended particles is obtained this way. The solution is stable for days in the case of ethylene glycol; in the case of the other solvents, it remains for only a few hours until a precipitate is formed. It was found that more concentrated and more stable solutions of the silicon particles could be obtained when the solvent contained $5 \cdot 10^{-4}$ M 1,3-propane-dithiol, $SH(CH_2)_3SH$. Fractions of particles of different size were obtained by treating the colloidal solution in a laboratory centrifuge (4600 rot./min) for 20 minutes and filtering through a Teflon micropore filter (Millipore SJHVL 04 NS, type HV, 0.4 µ); these operations were carried out under argon to prevent the silicon particles from coming into contact with air.

For preparation of samples for electron microscopy, a drop of the suspension was placed onto a carbon coated (ca. 50 Å) copper grid and allowed to dry; this procedure was carried out in a nitrogen filled glove box. The dried grid was then transferred into the vacuum holder (Gatan model 647) from the glove box to a Phillips CM 12 microscope, equipped with an EDAX 9800 analyzer. The silicon particles never came into contact with air during the whole procedure.

For imaging, axial illumination as well as "nanoprobe mode" were used; in the latter method, the beam spot size could be reduced to 1 nm to observe the diffraction of single clusters. All images were made under conditions of minimum phase contrast to avoid artefacts [9]. The micrographs were digitized with a DATACOPY model 610F electronic digitizing camera (Data Copy Corporation, Long Beach, USA) supported with an IBM computer. The scan step size was 13 µm which was equivalent to 0.23 Å at the sample level. All the calculations in the image processing were done on a µ Vax workstation. The clusters of interest were extracted in image fields 512×512, 256×256 or 128×128 pixels depending on cluster size. To extract the periodical information content of each cluster, the image processing procedure described by Giorgio [10] was applied.

Results

The left part in Fig. 1 shows an electron micrograph of the raw material which was obtained after application of 5 laser pulses. It can be seen that particles with a broad size distribution are formed. One can readily derive from the electron diffraction pattern (right hand part of figure) that crystalline cubic silicon is present.

The absorption spectrum of colloidal solutions, after removal of the largest particles by centrifugation, is shown in Fig. 2. The particles were solubilized by a 1 : 1 mixture of

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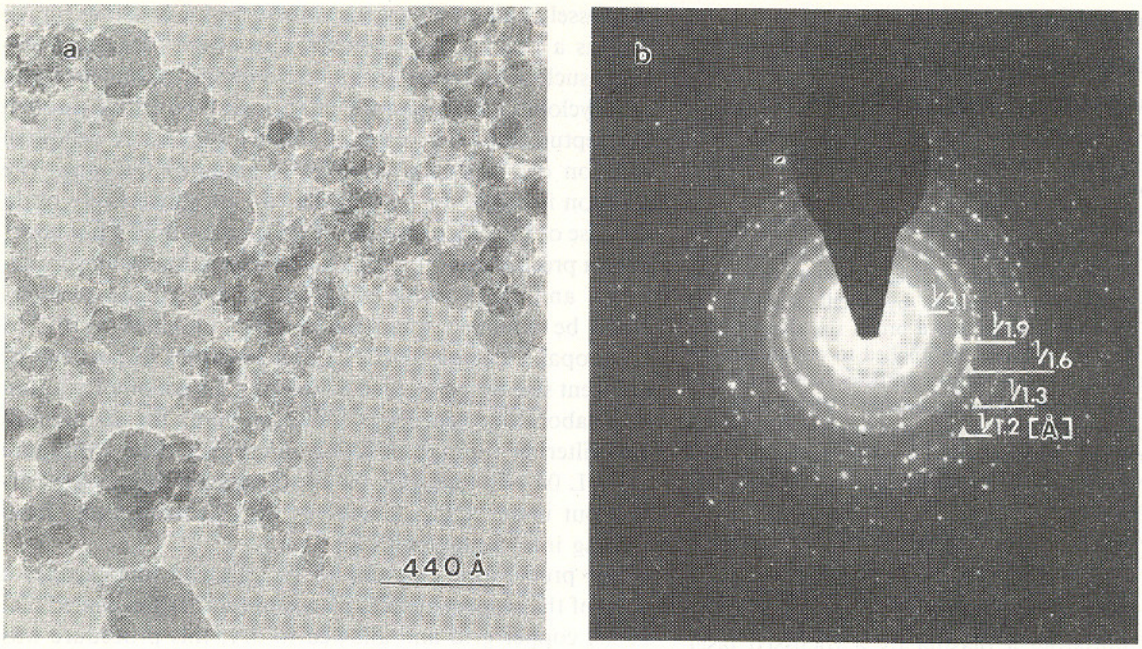

Fig. 1
Left: Electron micrograph of the raw material obtained after application of 5 laser flashes and suspending the material in cyclohexane-propanol-2 (1 : 1) mixture. Right: Electron diffraction pattern

cyclohexane and propanol-2; in the right part of the Fig. 2, the thiol stabilizer was present in the solvent mixture. In both cases, the absorption spectrum is weakly structured: note the maximum at 260 nm and the shoulder at 370 nm (arrows). The filtered solutions also show structure: a broad shoulder at 260 nm, and, in the presence of the stabilizer, shoulders at 310 and 230 nm. It should also be mentioned that the fraction of small particles (present after the filtration) is much larger in the presence of the thiol stabilizer.

An electron micrograph of the particles in the filtered solution, which contained the thiol stabilizer, is shown in Fig. 3, left part. It can be seen that the sample contains particles of 30 Å with a narrow size distribution. The same picture was obtained from a solution in which no stabilizer was present. A high resolution micrograph for an individual particle is shown in the right part of Fig. 3. The lattice planes typical for cubic silicon can clearly be seen.

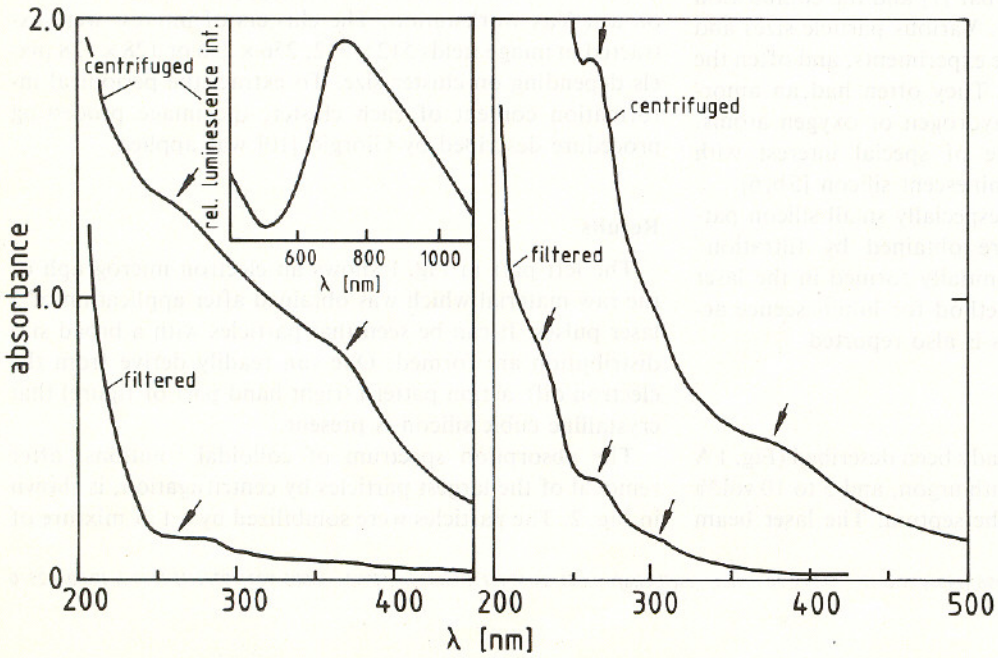

Fig. 2
Absorption spectra of centrifuged and filtered silicon particles. Right: thiol-stabilizer present in the cyclohexane-propanol-2 solvent mixture. The spectra of the solutions were taken towards blanks containing the solvent mixture (plus stabilizer). Inset: luminescence spectrum of the etched particles in solution; excitation wavelength: 360 nm

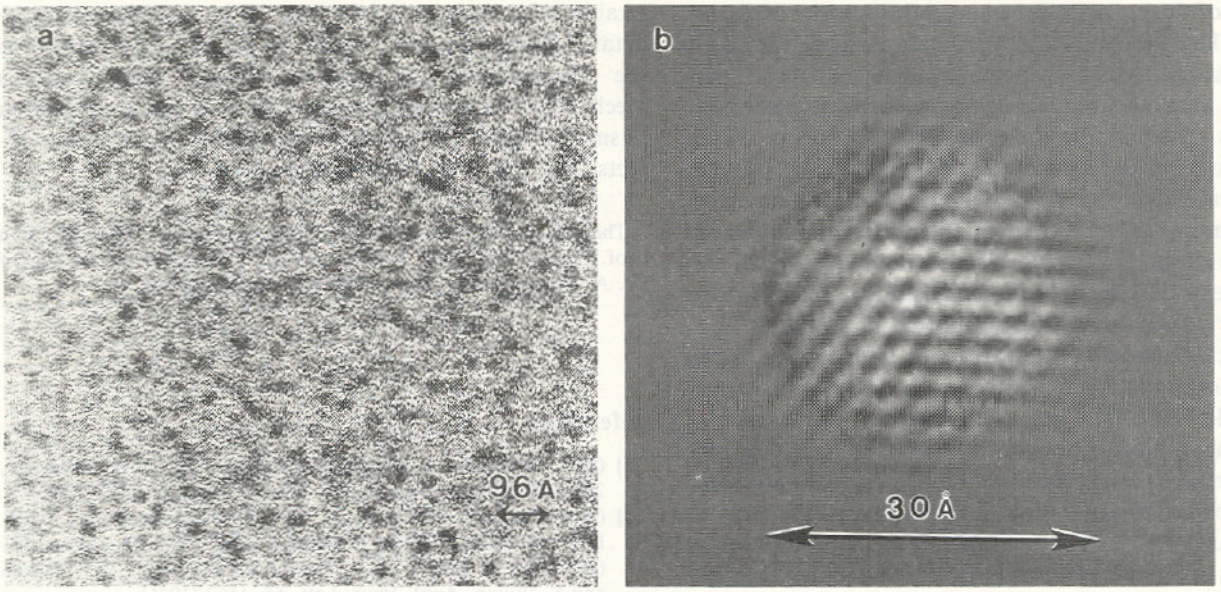

Fig. 3
Left: electron micrograph of the particles present in the filtered solution. Right: electron micrograph of a single particle at high resolution after image processing

The electron micrographs reveal a crystalline structure of the particles up to the surface. When the particles were exposed to air, a slow oxidation took place, producing an amorphous layer around the particles. Fig. 4 shows this for a larger silicon particle. The particles were stable towards oxidation when carrying the thiol stabilizer.

The mean size of the silicon particles formed was found to be greater when a larger number of laser pulses were applied. For example, when 20 pulses were used (the interval between successive pulses being 3 s), the material consisted of 60 to 80 Å particles after centrifugation without a noteworthy contribution of substantially smaller particles as in Fig. 3.

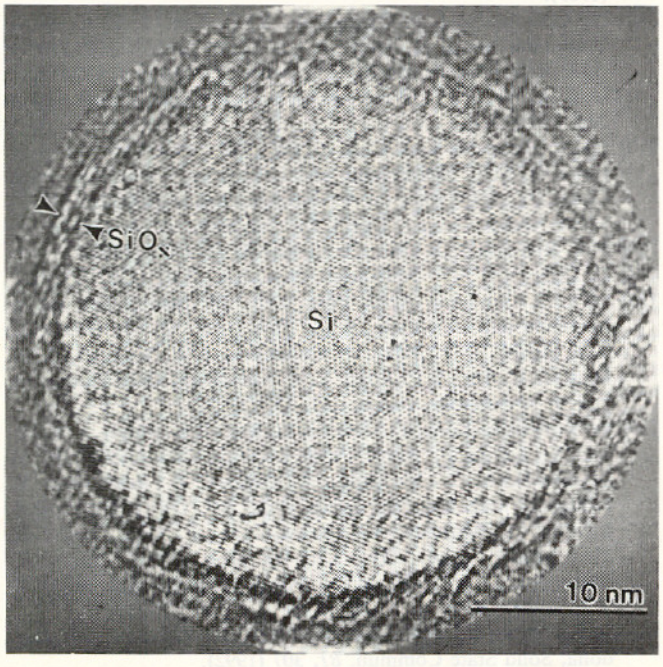

Fig. 4
Electron micrograph of a larger silicon particle after oxidation by exposure of the colloidal solution to air for 5 hours

The infrared absorption spectrum of the silicon particles was found to contain bands at 2912 and 2240 cm^{-1} which are characteristic for the Si–H bonds on the surface of crystalline silicon.

The particles did not luminesce. However, a red luminescence with a blue tinge was initiated by etching the particles with hydrogen fluoride and exposing them to air: 1 volume of hydrofluoric acid (36%) was added to 2 volumes of the cyclohexane-propanol-2 solution of the centrifuged particles and the mixture shaken for a few seconds. Two phases appeared. The supernatant solution of the particles (containing mainly cyclohexane as solvent) was separated, the solvent evaporated under air, and the particles were resuspended in the cyclohexane-propanol-2 mixture after two hours. The luminescence spectrum of this solution, which peaks at 730 nm (1.7 eV photon energy), is shown in the inset of Fig. 2. When the filtered solution was treated with HF as described, a flue luminescence was observed.

Discussion

The disintegration of silane under the present conditions is not attributed to direct photolysis, as SiH_4 does not absorb at the wavelength of the Ruby laser; we attribute it to pyrolysis in the plasma which is created by the intense laser flashes. When silane is pyrolysed at temperatures below 700 °C, amorphous particles are formed [5b]. The fact that we obtain crystalline material is taken as evidence for the temperature in the plasma being higher than 700°. The

mean size of the particles depends on the number of flashes applied. This is attributed to the small particles formed in the first flashes, which participate in the coalescence processes that take place in the plasma produced by the following flashes. The particles are crystalline throughout, as the lattice planes can be seen up to the surface. The infrared data indicate that the surface bonds are terminated by hydrogen atoms. The centrifugation and filtration methods enable one to obtain samples of rather monodisperse Si particles; it seems that the particles shown in Fig. 3, left, are the smallest crystalline Si particles reported up to-date.

The particles undergo a slow reaction with oxygen, forming an amorphous layer at the surface (Fig. 4). They are more stable when they are solubilized in the presence of 1,3-propane-dithiol. Thiols are known to strongly adsorb on gold surfaces [11]. It seems that the Si particles produced in the pyrolysis of silane bind the thiol in a similar way as do gold particles, the result being that the solubility of the Si particles in organic solvents is increased and that they less readily agglomerate than in the absence of the stabilizer. Thus, in the presence of the thiol, one obtains a larger yield of the very small particles when the solution of the raw material is centrifuged and filtered.

The absorption spectra in Fig. 2 are more strongly structured than the spectra of larger particles reported by other authors [5b]. The 370 nm shoulder is attributed to a high direct optical transition. At the present time, we cannot make a final attribution of the maxima which appear at shorter wavelengths. They could be attributed to Mie resonances due to the surface polarization of the particles. The anormal dispersion, or, in other words, the real part of the dielectric constant, is possibly dependent on the size of the particles, producing a blue-shift with decreasing particle size. The presence of several maxima in the spectrum of the small particles (260 and 310 nm) is possibly due to a splitting of the Mie resonance in agglomerated small particles. On the other hand, they could also stem from size quantization of the very small particles present in the filtered samples. Such effects have thoroughly been investigated for II – VI and II – V semiconductor particles [12]. It may also be mentioned that the red luminescence of the colloidal suspension can be quenched by added thiol; thus, quenching experiments with Si particles become possible in solution as it is usually the case for luminescing dyes and II – VI semiconductor particles [12].

The strong red luminescence (peaking at 720 nm in Fig. 2) is attributed to the larger etched particles in the centrifuged sample, and the blue luminescence (below 500 nm in Fig. 2) is attributed to the smaller particles. The silicon nucleus in the latter particles after etching and exposure to air is probably very small. This strong blue-shift of the luminescence band as well as the fact that the red luminescence occurs at photon energies greater than the band gap energy of bulk silicon would best be understood in terms of size quantization [13, 14] as in the case of the II – VI and II – V semiconductor particles [12]. As in those cases, surface states with energies within the band gap of the quantized Si particles might be involved. Further investigations are necessary to establish the mechanism of Si particle luminescence in more detail; this luminescence has to be seen in close context to the luminescence of porous silicon, where various mechanisms have been proposed, such as size quantization in small areas of the porous material [15], surface state effects [16], and the effect of siloxanes [17].

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