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LETTER TO THE EDITOR

Formation and characterization of silicon nanoparticles—threads, tubules and possibly silicon fullerene-like structures

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Abstract. We report the formation of nanoparticles of silicon (thread-like nanostructures of diameter ≈2 nm and length a few microns, as if nanocrystals are linked together along curly tubules), the occurrence of a tubule-like configuration, whiskers and a new phase with large periodicity, $a = 14.25$ Å, f.c.c.. Silicon, when evaporated under helium ambience (100 Torr) and characterized through transmission electron microscopic techniques, revealed several curious characteristics as mentioned above. We have suggested the possibility of a new phase with $a = 14.25$ Å for the f.c.c. lattice, being formed by an assembly of Si_{28} clusters. The geometrically calculated lattice parameter of the f.c.c. lattice resulting from an assembly of Si_{28} clusters is in reasonable agreement with the observed lattice parameter.

In the last decade intense scientific attention has been paid to nanoparticles [1] (i.e. polycrystalline material with grain sizes in the nm range), clusters and also cluster-assembled [2] crystallographic versions. This provides unique access to addressing the question of how properties change for material forms ranging from atoms through atomic clusters/nanoparticles, to bulk. Nanoparticles sometimes display special properties different from those of the bulk (e.g. the quantum interference effect [3]) and therefore have potential for applications. In fact the discussion extends further to consider clusters (i.e. collections of atoms and cluster-assembled materials), for example Buckminster fullerene—a cluster of 60 carbon atoms and its related f.c.c. lattice with $a = 14.17$ Å. In this context silicon has offered an interesting scenario, namely that nanoparticles of silicon exhibit photoluminescence in the visible range. Although silicon is an indirect-band-gap material with poor photoemission efficiency, nanoparticles of silicon can exhibit photoluminescence with wavelengths depending on the size of the particles [4]. Lee and Peng [5] have reported blue light emission from thermally treated porous silicon obtained by anodic etching (using an HF electrolyte and Si as an anode) when excited by a He–Cd laser. Thus one can resort to nanoparticles of silicon to construct light-emitting diodes [5].

The purpose of this communication is to report a newer synthesis route for nanoparticles of silicon (a thread-like microstructure, as if nanocrystals have been linked together along curly tubules) by evaporating it in helium ambience, and their electron microscopic characterization. We also report on an electron microscopic investigation revealing the occurrence of a tubule-like configuration in silicon whiskers and a new phase corresponding to an unusually large periodicity, namely $a = 14.25$ Å for a f.c.c. lattice. Elementary

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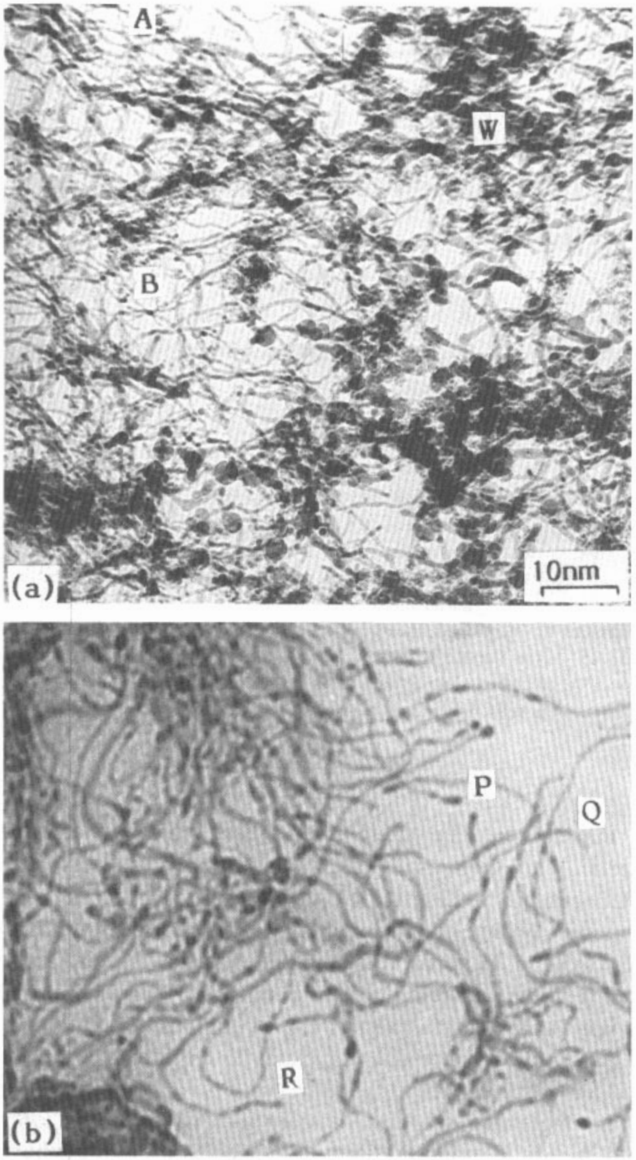

Figure 1. (a) An electron micrograph depicting the presence of thread-like silicon. The crossing of threads (A, B etc) and the coagulating of threads (W) resulting from the electron beam can be seen. (b) An electron micrograph depicting threads and isolated tips P, Q and R specifically.

suggestions have been put forward to explain the occurrence of the large-periodicity f.c.c. phase in terms of the reported Si_{28} cluster [6, 7] considered as a motif.

Taking clues from isostructural carbon variant (fullerenes and tubules) synthesis, the nanoparticles of silicon were achieved by evaporating silicon in a helium atmosphere. Suitable parameters were determined by evaporating silicon under varied conditions ranging from 10^{-6} Torr to 500 Torr of helium ambience. Evaporation of the silicon powder was accomplished by thermal and/or flash techniques. Tantalum boats were used as heating and supporting material. The evaporated silicon powder was condensed on formvar-coated copper grids maintained either at room temperature or cooled by liquid nitrogen. The cooling was accomplished by placing aluminium sheets carrying formvar-coated copper grids in good contact with the inner surface (inside the vacuum system) of a double-walled dome which was cooled by pouring liquid nitrogen from outside. A Hg-tube manometer was connected to the system to monitor the pressure of helium. The distance between the tantalum boat and the substrate was 15 cm. In these experiments we tried to control the size of the silicon particles by evaporating silicon in different ambients. At higher pressures of helium, it can logically be conceived that collision between silicon and silicon atoms, and hence their coalescence to generate particles (crystalline and/or amorphous), will be affected. Consequently it is expected that with higher pressures of helium, smaller particles of silicon will result. In continuation it can also be understood that if the substrate is maintained at lower temperatures, rapid quenching of the vapour phase will be accomplished when the latter is made to condense onto the cooled substrate. This will tend to generate amorphous material.

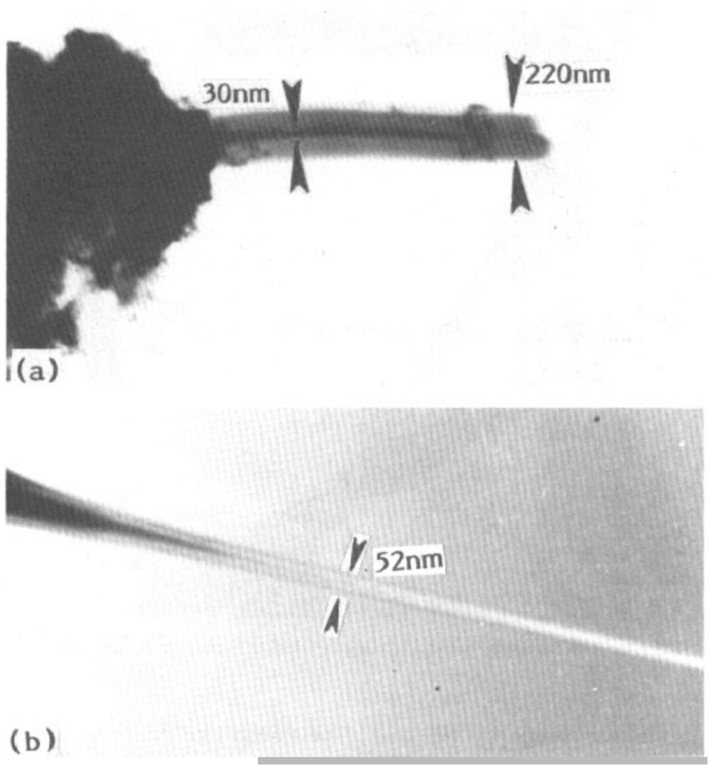

Figure 2. Micrographs (a) and (b) depict formation of tubules in silicon.

In the following we describe the electron microscopic observations made on the silicon particles obtained by evaporating silicon under different conditions, as mentioned before. Silicon, when evaporated by flash evaporation in vacuum (10^{-6} Torr of He), gave rise to a continuous amorphous film. Evaporation of silicon in helium ambience (100 Torr) resulted in isolated particles on formvar-coated grids. The electron microstructure revealed the presence of thread-like features, as if nanocrystals were linked together along curly tubules, somewhat similar to those described for porous silicon by Nakajima *et al* [6], resulting

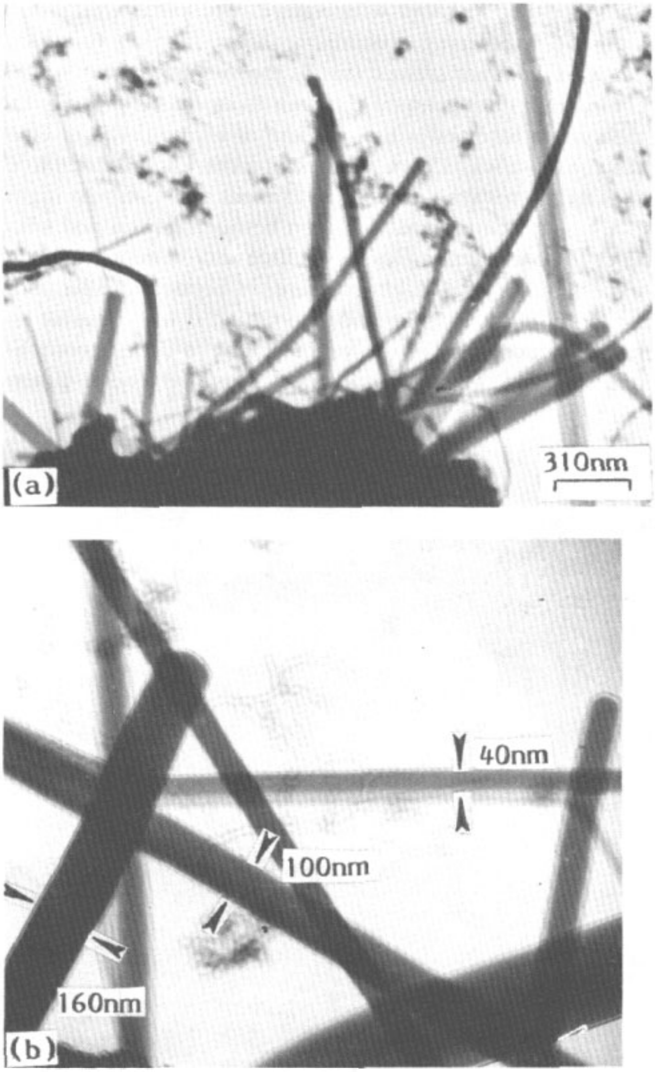

Figure 3. Micrographs (a) and (b) depict whisker formation in silicon.

from anodic etching of silicon by HF acid. The thread-like microstructures corresponded to varied diameters in a narrow range. The typical value of the diameter of the thread-like silicon corresponded to 2 nm. Quite often threads of silicon cross at a point (see figure 1(a), A, B etc). Indeed, isolated tips (marked P, Q and R in figure 1(b)) can also be seen. The threads were not confined to a plane and consequently it was impossible to adjust them all eucentrically at the same time. These microstructural properties very closely resembled those reported by Nakajima *et al* [6] for porous silicon obtained by anodizing silicon electrode. Since the latter exhibit electroluminescence, we believe that the nanoparticles formed in the present experiments will exhibit the same phenomenon. Studies in this area are in progress and results will be reported soon. In fact under certain conditions, within a narrow range of the above-mentioned deposition parameters, the colour of the slides where the silicon vapour condensed varied from colourless through yellow to blue. The thread-like silicon responded to the electron beam by coagulating (W in figure 1(a)). Figure 1(b) gives a magnified depiction of nanometric silicon threads made up of nanometric particles. The lengths of the silicon threads as observed were in microns or still longer. The effect of helium pressure was investigated by repeating the above experiments corresponding to He pressure of 200 and 500 Torr and characterizing the particles. The results were found to be more or less similar, with a small difference in density of silicon threads. This is presumably because of the reduced collision frequency and hence coalescence of silicon atoms under higher pressures of helium.

Electron microscopic studies of the above samples prepared at 100 Torr He pressure also showed the presence of silicon nanotubes (figures 2(a) and 2(b)) and silicon whiskers (figure 3(a) and 3(b)). Their diameters vary in the wide range of 10–100 nm. The observation of the occurrence of tubules in silicon seems to be the first of its kind although this has been reported by many scientists for carbon [8]. The fact that silicon (having predominantly sp^3 bonding) differs from graphitic carbon (having sp^2 bonding), and still exhibits tubule formation similar to that of carbon, provides a platform for new thoughts and discussion. We are trying to comprehend the occurrence of the tubule-like structures in silicon and reports will be forthcoming.

The electron diffraction pattern (figure 4) from the regions shown in figures 1(a) and 1(b) exhibited the characteristic polycrystalline diffraction rings, indexable by analogy with silicon. Silicon possesses a diamond structure and it can be clearly seen that the indices of the powder diffraction rings do conform to the diamond extinction condition, namely $h + k + l = \pm 4n$ for even combinations of h, k and l.

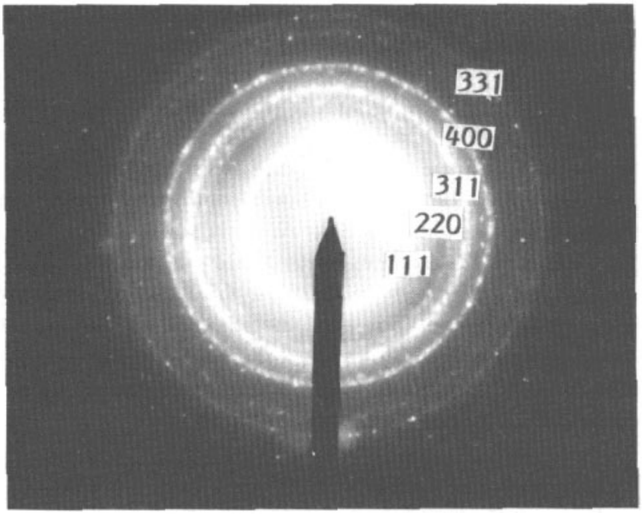

Figure 4. The electron diffraction pattern from the region shown in figures 1(a) and (b) and corresponding to silicon. Indexing of several rings is depicted.

Nanoparticles of any material are in general very sensitive to heat treatment; they have a lower melting point in comparison to the bulk and also sinter faster due to an enhanced

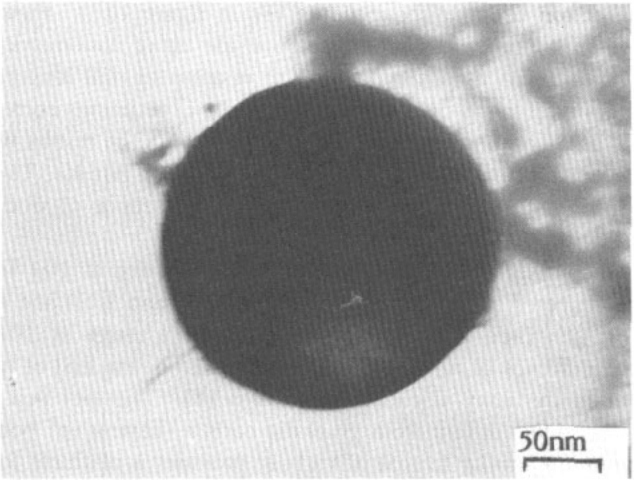

Figure 5. The spherical ball-like configuration formed by electron beam annealing (with removed condenser aperture) of thread-like silicon.

diffusion coefficient. Figure 5 shows an example where the thread-like silicon nanoparticles coalesce upon electron beam annealing to form a spherical ball-like configuration.

During the survey of the samples through electron microscopy, we have encountered observations corresponding to periodicities much higher than those expected from the known bulk structure of the silicon diamond-like cube with $a = 5.4$ Å. Figures 6(a), 6(b) and 6(c) taken together provide evidence for the occurrence of a f.c.c. lattice with $a = 14.25$ Å. The EDXA of the samples exhibiting these features revealed the presence of silicon as shown in figure 6(d). In order to comprehend the occurrence of the high-period structure we resorted to the idea of cluster-assembled crystalline structures [2]. In the following we describe the possibility of a f.c.c. lattice resulting from the assembly of Si_{28} clusters which are considered as among the stable clusters of silicon [7]. The size of Si_{28} can be estimated by noting the report that it is fullerene-like [7]. Using the fact that the radius of the fullerene structure varies as (number of atoms)$^{1/2}$ and as bond length, purely on geometrical grounds the estimated diameter of a Si_{28} cluster is 8.06 Å. This value is in reasonable agreement with the diameter of 7.62 Å of Si_{28} spheres (with cluster-to-cluster bond length = 2.35 Å) corresponding to a f.c.c. lattice with $a = 14.25$ Å. The two diameters vary by 5.45%. Spectroscopic analysis (mass spectroscopy and others) of the sample must be employed to ascertain the existence of Si_{28} clusters to verify the above proposition, which we plan to pursue in the near future.

In view of the above-mentioned results and discussion we conclude the following.

(i) The crystalline nanoparticles of silicon can be obtained by evaporating silicon in a helium atmosphere (dry process) and condensing the silicon vapour either at room temperature or when cooled by liquid nitrogen. The silicon adopts thread-like microstructures.

(ii) Silicon tubules and whiskers can be formed.

(iii) Silicon can adopt a high-period structure with a f.c.c. lattice corresponding to $a = 14.25$ Å. The occurrence of such a structure can possibly be understood in terms of a cluster-based crystallographic variant involving Si_{28} clusters.

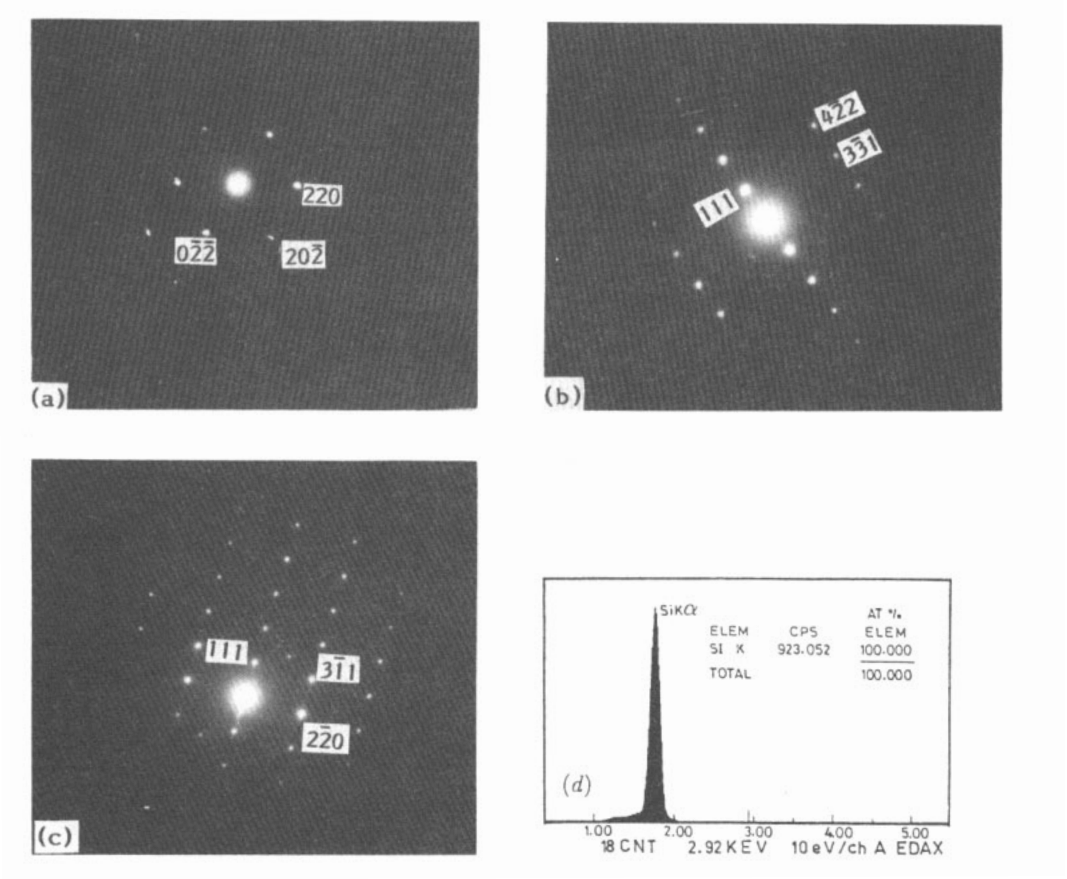

Figure 6. Electron diffraction patterns (a), (b) and (c) exhibit different reciprocal-lattice sections corresponding to a f.c.c. lattice with $a = 14.25$ Å, whereas (d) shows the EDXA of the sample exhibiting the large f.c.c. cell with $a = 14.25$ Å. A strong peak from Si can be seen.

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