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Formation and characterization of nanoparticle-bearing threads of silicon, germanium and tin

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Abstract. We report the formation and characterization of nanoparticles and their assemblage to form a threadlike microstructure of silicon, germanium and tin, by the process of thermal deposition in helium ambient under varied conditions of pressure. The structural characterization of the nanoparticles was done by transmission electron microscope (Philips CM12). Resistance versus temperature (R–T) measurements, on the thin films embodying nanothreads, exhibited anomalous behaviour embodying erratic changes in R–T variations. This was suggestive of variation of nanoparticle distribution with increase in temperature.

1. Introduction

Nanoparticles and assembly of nanoparticles have attracted significant attention on both experimental [1] and theoretical [2] fronts. Nanoparticles of elemental semiconductors such as silicon and germanium, especially silicon—porous silicon—have generated much interest because of their special optoelectronic properties and potential applications. Although crystalline silicon is an indirect band gap (1.1 eV) material with poor photoemission efficiency, nanoparticles of silicon can exhibit photoluminescence [3] with the wavelength depending on particle size [4]. It has been proposed that quantum confinement [5] in the nanocrystallites can increase the width of the gap so that recombination can occur in the visible range.

Several studies have been carried out to understand the morphology of the parent silicon and there are reports of column-like structures [6] with nanometric diameter ($\sim$3 nm) microcrystals of few nanometres in diameter [7] and particle-like silicon structures [8] in light emitting porous silicon. Various methods have been applied to produce the nanocrystalline silicon such as electrochemical anodization [3], plasma enhanced chemical vapour deposition [9], non-thermal microwave plasma [10–12], chemical vapour deposition on a porous substrate [13] and a spark-erosion technique [14]. There are reports of nanoparticles of semiconductors, *viz.* porous Si, SiGe [15] dot structures and others, being used to construct light emitting diodes. The application of these nanoparticles in optoelectronics requires a better insight into the microstructure of these materials and thereby better synthesis routes.

The present authors have reported [16] the formation of nanoparticles (threadlike nanometric structures, the occurrence of tubule-like and whisker formation and possible fullerenes in silicon) by evaporation of silicon in helium ambient. Later Zhang and co-workers made a similar investigation [17]. They have reported the dependence of the diameter of Si threads on the ambient pressure. The purpose of this communication is to report the validity of the procedure, reported earlier [16], to deposit thin films of Ge, Sn and SiGe, besides that of Si, embodying their thready microstructure and the temperature dependence of electrical

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resistance of these films. Suggestions have been put forward to explain the variation of the electrical resistance with temperatures and the difference from the natural trend in terms of microstructural aspects.

2. Experiment

The nanoparticles arranged to give a thready appearance for Si, Ge and Sn were found in a similar way as reported before i.e. evaporation in helium ambient [16]. The experimental set-up consisted of a heater assembly inside the vacuum system. The substrates (mica/formvar coated copper grids) were pasted with silver glue on the heater base. Electrical contacts from the substrates were taken outside the vacuum system to study the effect of the thready microstructure on the variation of electrical resistance with temperature. The films were deposited on mica and on the formvar coated copper grids at 1.34×10^{-3} mbar helium pressure and room temperature. The resistance of the as-deposited film was determined in the temperature range of 30–300 °C.

In order to accomplish one of the objectives *viz.* behaviour of electrical resistance of the films containing threads of nanoparticles, proper precautions were taken to have electrically continuous films. This was an additional constraint which could be circumvented by finding suitable deposition parameters. We found that the films deposited at 1.34×10^{-6} mbar of helium were electrically conducting but with no nanothreads and those deposited at 134, 268 and 670 mbar contained nanothreads but were not electrically conducting. After several depositions suitable parameters could be determined at which the nanothreads are formed and at the same time the electrical conductivity is also present in the film. Graphite boats were used as heating and supporting material. The evaporated material was condensed on freshly cleaved mica and on formvar coated copper grids. These substrates were supported on the heater assembly inside the vacuum chamber and were maintained at room temperature at the time of deposition. An Hg tube manometer was connected to the system to monitor the pressure of helium. The optimum pressure inside the chamber was 1.34×10^{-3} mbar of helium. The distance between the graphite boat and substrate was maintained at 15 cm.

3. Results and discussion

In the following we proceed to describe the electron microscopic observations made in the deposited thin film of Si, Ge, SiGe and Sn. As reported earlier [16], deposited thin films of Si consisted of thread-like features formed by interlinked nanocrystals. The lengths of these structures were in microns or still longer. The selected area electron diffraction pattern showed the bulk periodicity (diamond-like, $a = 5.43$ Å). Figure 1(a) shows similar thready microstructures obtained in the as-deposited (67 mbar helium) thin films of Ge. Figure 1(b) is the selected area diffraction pattern, from this region, conforming to bulk germanium (diamond-like, $a = 5.65$ Å). In the case of Sn the thread formation was not very apparent. In accordance with our earlier report [16], deposition at higher pressure only resulted in decreasing the density of the threadlike structures. Later on, similar results were reported by Zhang and others [17]. Their microstructures were very similar in appearances to those obtained by anodising silicon electrodes [3]. The diameters of the threadlike structures varied in a narrow range, 15 nm being a typical value. On several instances, the arrangement of silicon nanoparticles giving rise to closed rings was also observed, as shown in figures 2(a) and (b). These films have been deposited at 402 mbar helium ambient. As mentioned above, this resulted in decreasing the density of threads. In figure 2(b) a hexagonal ring can be noticed very clearly. This observation

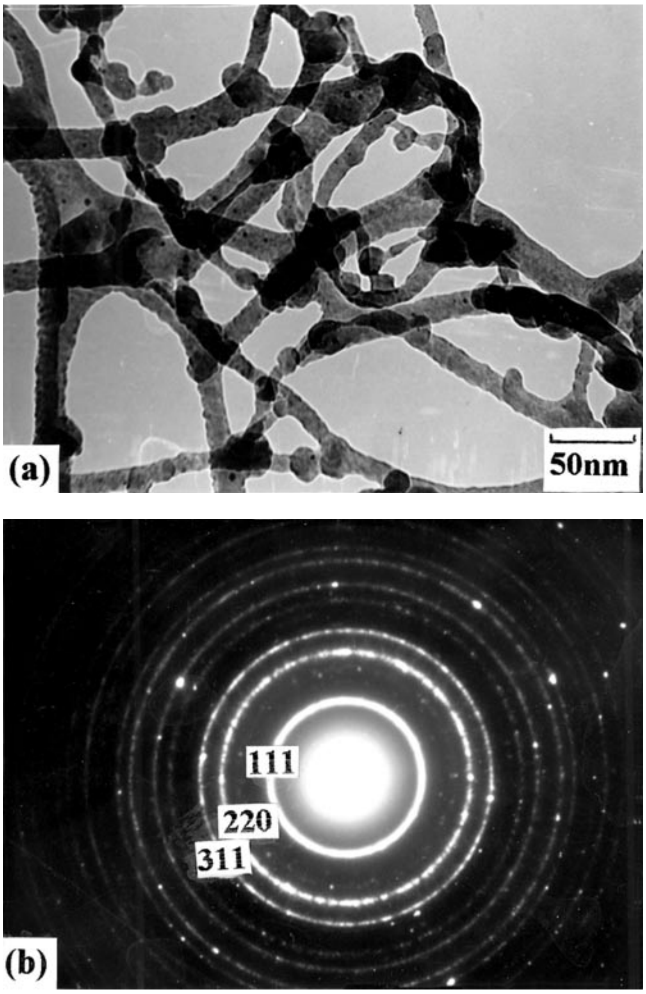


Figure 1. (a) Threadlike microstructures observed in a thin film of germanium deposited in 67 mbar helium ambient. (b) Selected area diffraction pattern from the film conforming to germanium.

is similar to the computer simulated picture reported by Schuth *et al* [2]. It may be mentioned that such closed ring structures may be of special significance from the magnetism point of view involving Raman's postulate that the flow of current around ring systems can lead to high specific susceptibility [18, 19]. In fact, radical changes in the magnetic properties may occur in low dimensional systems e.g. quasi-two-dimensional nanoparticles of palladium are ferromagnetic though bulk Pd is paramagnetic [20].

Electron microscopic studies of the helium ambient deposited silicon films also showed the presence of tubule-like structures. Figure 3(b) corresponds to the diffraction pattern from the silicon tubule-like structures. Such elliptical diffraction patterns have been observed in the tubule-like structures in carbon [21], though the nature of spots on the diffraction patterns and the spacing between the rings were quite different. These have been explained on the basis of a proposed model for the cylindrical reciprocal space for a sample containing carbon nanotubes, described elsewhere [21]. The observation of the elliptical diffraction pattern in Si samples renders credibility to the fact that these are nanotubes of silicon.

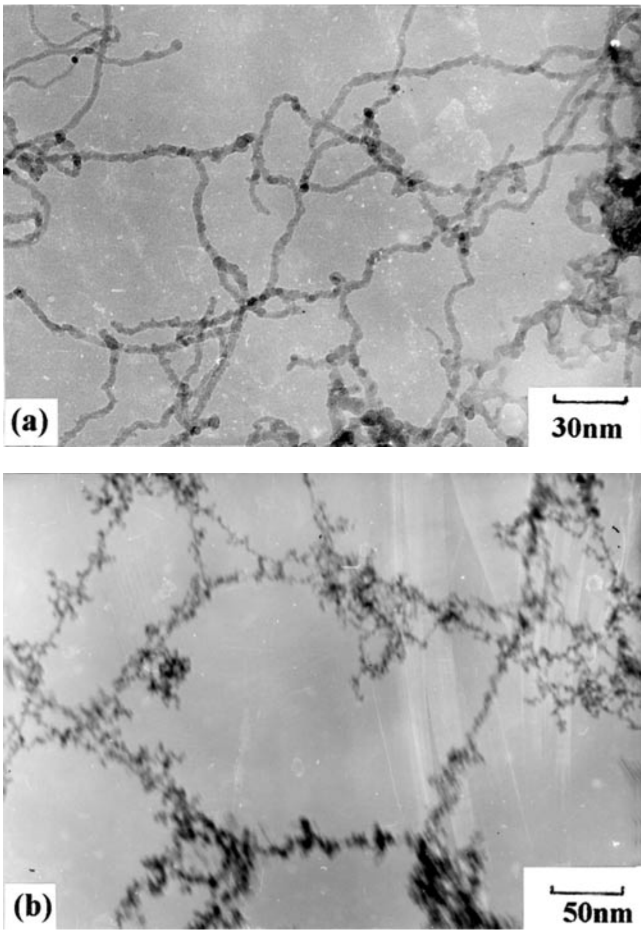


Figure 2. (a) and (b) show the arrangement of the nanoparticles to form closed rings in the helium ambient (402 mbar) deposited silicon films. (b) shows a hexagonal ring formed by the nanothreads of silicon.

The annealing of thin films of silicon during the resistance versus temperature measurement resulted in agglomeration of the threadlike structure (figure 4(a)). On the other hand, *in situ* electron beam annealing of the as-deposited film caused the threads to melt and form perfectly spherical agglomerates like those shown in figure 4(b).

Similar experiments were done on SiGe alloy, synthesized by melting silicon and germanium (80% Si and 20% Ge) in an r.f. induction furnace. The thin films of SiGe were deposited on formvar coated copper grids which were then investigated in the transmission electron microscope. Figure 5 shows the transmission electron micrograph of the deposited film. This consists of nanothreads with the tips exhibiting more contrast in comparison to the rest of the nanothreads. This seems to be a distinguishing feature for a two-element system *vis à vis* a one-element system. We conjecture that the particle of one element may be pinning the growth of thread of the other element. The typical size of the thread is 15 nm for the thinner threads and 50 nm for the thicker threads.

The nanoparticles of a material are known to exhibit properties quite different from the parent bulk materials, e.g. they have low melting and boiling points, enhanced diffusion

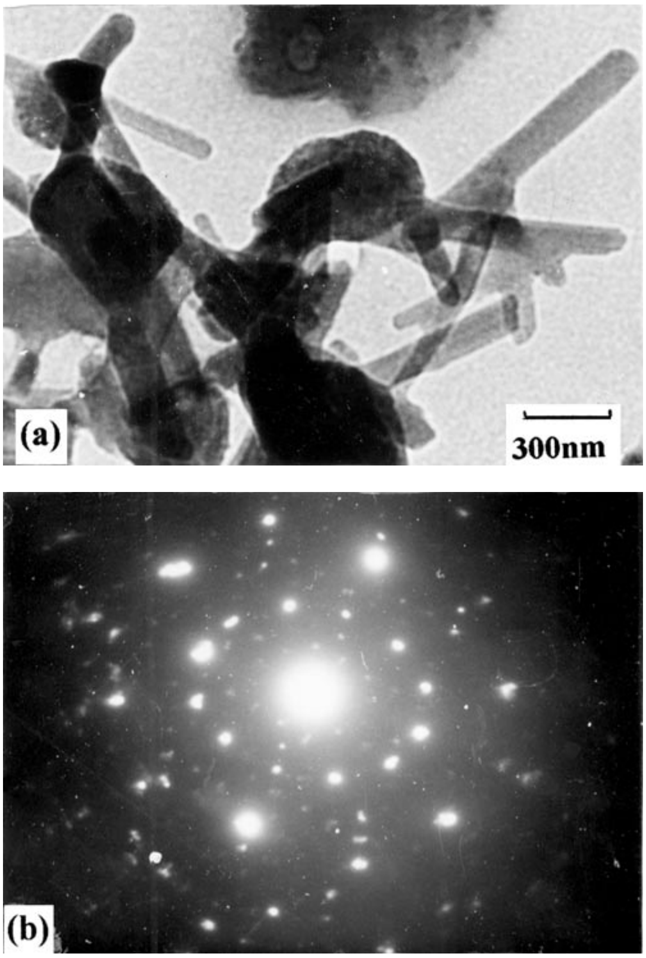


Figure 3. (a) Micrograph of tubule-like structures in silicon and (b) elliptical diffraction pattern from the same. See text for description.

coefficients etc [22]. This prompted us to investigate the electrical properties, in particular the electrical resistance of the nanoparticles of Si (Ge and Sn) and study its variation with temperature. The microstructure of the as-deposited films show reasonably large, open spaces available. This will eventually mean that the resistivity calculated by incorporating the cross sectional area of the films is much larger than the actual resistivity. In view of the fact that it is rather difficult to have a reasonable estimate for the vacant space available, we shall discuss the film in terms of resistance and not its resistivity.

In the case of the deposited films of Si, unlike the expected behaviour of the semiconductor, the resistance was found to increase with temperature (figure 6(a), C–D). On cooling the film the resistance did not reverse, instead in conformity with the usual trend of semiconductors it increased with the lowering of the temperature (figure 6(a), E–F). The film so treated was again heated up to 300 °C but the annealed film did not show the anomalous behaviour mentioned above. A possible explanation for the increase in resistance against the general trend in semiconductors may be a microstructural effect. For example breaking of contacts between the threads and loss in electrical conductivity due to agglomeration can increase the

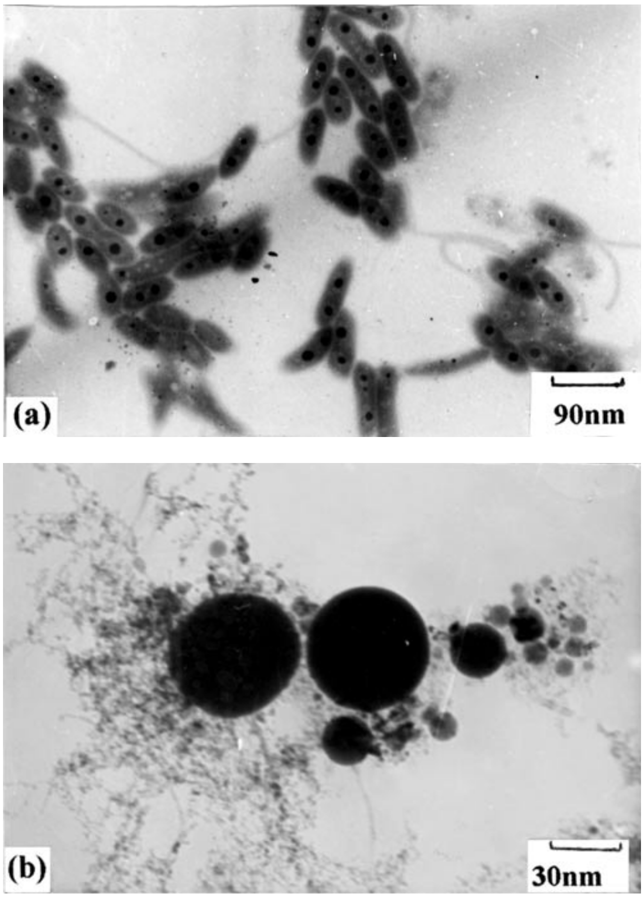


Figure 4. (a) Ellipsoidal agglomerates formed from threadlike silicon due to annealing (in the vacuum system) at 300 °C. (b) Spherical agglomerates of silicon formed by *in situ* electron beam annealing in the electron microscope of the film embodying nanothreads.

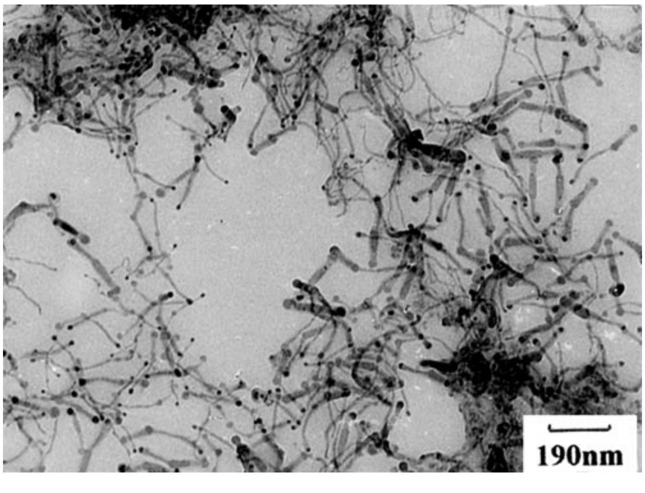
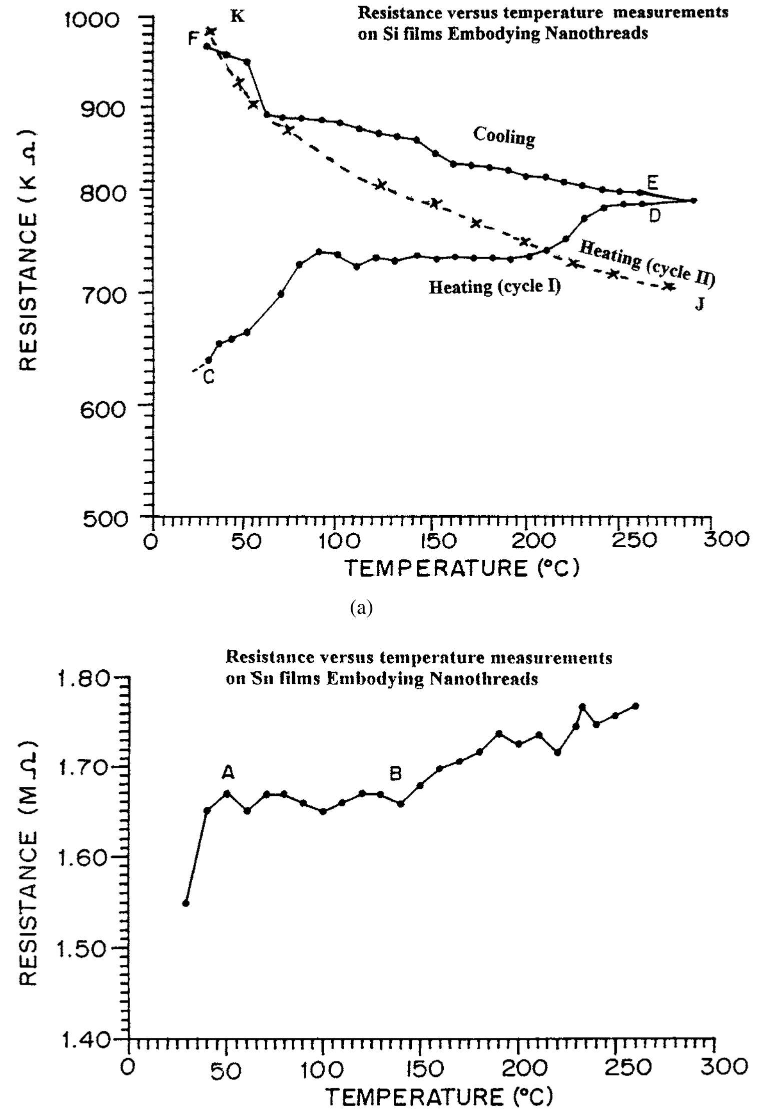


Figure 5. The transmission electron micrograph depicting nanothreads in the as-deposited SiGe film in 134 mbar helium ambient. Note the tips of the nanothreads.



(a)

(b)

Figure 6. (a) The resistance versus temperature (*R*–*T*) plot for heating and cooling of a thin film of silicon, embodying nanothreads, deposited at 1.34×10^{-3} mbar helium. (b) The resistance versus temperature plot for a thin film of tin (deposited at 1.34×10^{-3} mbar helium pressure) while heating.

resistance and making of contacts would decrease the resistance. During the heating process the threadlike structure presumably make or break contacts with each other and the more dominant phenomenon determines the average resistance of the films. The basis of this assumption is that, while performing the TEM investigations, the make and break of contacts between the nanothreads was observed quite often. During the *R*–*T* measurement the film was annealed up to 300 °C for half an hour which caused the formation of agglomerates of the kind shown in figure 4(a). While cooling from 300 to 30 °C we observed the usual trend (figure 6(a), E–F) in the variation of the resistance. This is because the heating has stabilized the structure of the film and, therefore, it is only the intrinsic effect of the sample which is revealed in the observation.

In the case of Ge erratic changes in R–T measurements were observed. This can be made intelligible in terms of the random make and break of the electrical contacts in the threadlike structures. *In situ* annealing during the electron microscopy has also provided the evidence that the thready nanoparticles are agitating, and making and breaking contacts with each other, while being heated up. The variation of resistance with temperature in a film containing nanothreads of tin is shown in figure 6(b). Deviation from the natural trend namely the approximately constant resistance region in the range A–B with some erratic changes are suggested to be germane for the same reasons as mentioned above for silicon.

In view of the above description, the following can be concluded.

(a) The method of thermal evaporation in helium ambient is applicable for deformation of silicon, germanium and tin nanothreads.
(b) The microstructural features appears similar in all the three cases.
(c) The electrical resistance in the as-synthesized film may dominantly be affected by microstructural effects in the first cycle of heating.

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