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Silicon nanowires and whiskers obtained by arc discharge

N Korpinarov 1, 3, M Marinov 2, D Dimova-Malinovska 1, H Nichev 1, M Konstantinova 1 and D Vasilev 2

1 Central Laboratory for Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
2 Institute of Physical Chemistry, Bulgarian Academy of Sciences, Acad. G. Bontchev Str., Bl. 11, 1113 Sofia, Bulgaria
E-mail: koprin@phys.bas.bg

Abstract. Crystalline nanostructures such as nanotubes and nanowires have received increasing attention due to potential applications in nanoscale electronic, optical and sensing devices. Silicon nanowires are of practical interest because of their semiconducting properties. In particular, dimension reduction to a nanometer scale gives rise to several advantages in terms of device applications, due to size and quantum confinement effects. Silicon nanowires have been synthesized by different physical and chemical methods. However, the fabrication of silicon nanowires and nanowhiskers depends on some specific properties of Si and is still a challenge. Here we report the synthesis of silicon nanowires and nanowhiskers by DC arc discharge using a graphite cathode and a graphite anode filled with a Si and C powder mixture. The reactor was operated in a pre-evacuated argon-filled chamber at a pressure of 3x10^4 Pa. The arc current was maintained at 75 A by a DC power supply. No catalysts were used. The synthesis products were grey-white in color. The material obtained was studied by SEM. The structures (nanowires and nanowhiskers) are described and discussed.

1. Introduction
The carbon nanotubes (CNT) are very promising materials for use in different fields, including nanoelectronics, catalysts, absorbers, nanosensors and actuators. The unique CNT properties and similarities between silicon and carbon encourage scientists to seek Si-based nanostructures, expecting to obtain even better properties than those of C-based nano-materials. In contrast to the sp^1, sp^2 and sp^3 hybridization of C, the low hybridization energy of Si gives it a preferential sp^3 hybridization. However, this hybridization makes tubular structures unstable and difficult to fabricate. The calculations of Seifert et al. [1] and Ponomarenko et al. [2] show that the excess strain energy of such Si nanotubes (SiNT) is reduced and the tubes become stable when they are hydrogenated on the inside and the outside. Stabilization can also be achieved by reducing the free Si bonds with a metal-like Ni [3]. Different methods for fabricating Si nanoparticles have been developed [4-10]. However, none has so far been proven to be better than the others in terms of making it possible to create uniform structures.

3 To whom any correspondence should be addressed.
2. Experimental
The fabrication of Si nanoparticles is based on our experience in the fabrication of carbon nanotubes and the similarities between Si and C. We used an arc discharge between carbon electrodes and an inverse temperature gradient between them. This method, schematically illustrated in figure 1a, was initially developed for production of CNT [11]. The cross-sectional area of the cathode was 6 mm$^2$. The anode, with a cross-sectional area of 12 x 10 mm, had two 4 mm openings, placed 1.5 mm apart (see figure 1b). Both openings were filled with a mix of Si crystals (~10 $\mu$m) and a fine carbon powder, mixed in a ratio of 90/10 wt.%. The working atmosphere was pure Ar with a pressure of 3x10$^4$ Pa. No catalyst or hydrogen for stabilization was used in the experiment. The DC arc was ignited by touching the electrodes together and then separating them.

The material grown on the anode was studied, without additional treatment, by SEM (Jeol-SEM JSM 6390).

3. Discussion
In the case of DC arc discharge between carbon electrodes, the temperature of the anode is higher than that of the cathode, due to the energy transport caused by electrons emitted from the cathode. This increases the carbon sublimation, which takes place on the anode. In the method presented here, we equalized the temperatures of the two electrodes by cooling the anode and heating the cathode. We used water-cooling and a bigger cross-section for the anode to reduce its temperature and to stop its sublimation. In contrast, a small cathode diameter increases its temperature, increasing its thermo-electron emission and affecting its very weak sublimation.

After ignition, the arc was situated between the cathode and the part of the anode that is between the openings. This was caused by the high electrical resistance of the Si/C mix. Using a radiation thermometer it was estimated that the temperature in the arc zone was over 3000 °C, decreasing to 1100 °C at the anode periphery. In the openings, where Si was placed, the temperature fell linearly from 3000 to 1600 °C. Si has a melting point of 1414 °C and a boiling point of 2900 °C at atmospheric pressure. However, the boiling point depends on the pressure and decreases to 1080 °C at 1.33 10$^{-4}$ Pa. The boiling point at our working pressure was lower than 1900 °C and was reduced additionally due to the small dimensions of the Si particles. Due to the temperature distribution in the opening, it can be expected that during the arc discharge all Si particles will melt but only those that are near the arc will evaporate. We assume that the melt crystals merged together, and the temperature in the whole opening became uniform. Furthermore, the temperature increased to over 2000 °C due to the close contact with the arc and the high Si thermal conductivity, possibly causing the Si to react with the carbon to form carbide.

It is well known that up to 2000 °C, carbon does not react with Si. Therefore, C crucibles are widely used for Si thermal evaporation. To separate the drops of molten Si in the opening and to evaporate only those Si drops that are near the arc, we used a mix of Si particles and carbon powder.
The carbon powder acts as a barrier. The effectiveness of this separation can be seen in figure 2 (left-hand side) where, after the arc was switched off, the Si drops have crystallized again, not touching each other. The big difference in the evaporation temperature of Si and C causes a noticeable excess of Si atoms in the vapor flux. The vapor flux is directed onto a small area on the anode surface, because of the close proximity of the electrodes and the high velocity and high directionality of the atoms leaving the arc zone. The surface of the anode is greater than the arc diameter (see figure 1b), which results in a temperature reduction, reaching 1100 °C on the periphery. This temperature is lower than the condensation temperature of Si. Therefore, all conditions for the deposition of material on the surface of the anode are fulfilled. The growing structures depend on the local conditions, including temperature, vapor concentration, vapor flux direction and the presence of catalysts.

We observed that the particles deposited on the edges of the openings and on protruding places have shapes similar to those shown on the right-hand side of figure 2 and in figure 3. These whiskers have lengths of up to 20 µm and diameters up to 3 µm. Their Si nature was established by EDX spectroscopy. The material necessary for their intensive growth is supplied through the vapor flux, which reaches the surface of the whisker either directly or through atom migration.

**Figure 2.** Si crystals and whiskers after the arc was switched off.  
**Figure 3.** Si whiskers near the openings.  
**Figure 4.** Si nano-wires near the region with whiskers.  
**Figure 5.** Splintered Si nano-wires.
We also observed almost uniform Si nanowires beyond the whisker region, in the direction of the periphery (see figure 4). These nanowires had diameters from 0.03 to 0.3 µm and lengths from 0.3 to 5 µm. They contained up to 10,000 times less material than the whiskers, due to the much lower supply of material in these regions. The number of the arriving Si atoms was reduced because the zone is located very close to the electrode surface; the vapor flux is low and the Si atoms are consumed almost exclusively by the bigger structures. Splitting of the growing Si crystals frequently occurred. Because of this, some of the nanowires changed their directions or branched out several times during the growth (figure 5). Approaching the outer perimeter of the anode, the number of the nano-wires decreased. Their low density allowed them to grow freely with a very high speed, which is also the case for nanotubes [12]. The nanowires became longer and thinner (figure 6) and were arranged in separated groups.

The lower temperature at the periphery of the anode did not allow the creation of perfect Si structures. Only small Si islands and agglomerates could be found there. Due to the high chemical activity of Si, some of them could partially oxidize if oxygen is available in the working atmosphere.

4. Conclusion
A DC arc discharge between closely placed electrodes and with inverse temperature, developed initially for the fabrication of CNT, was successfully used to create Si nanostructures. A SEM study of material deposited on the surface of the anode showed that the conditions realized were adequate to allow the growth of whiskers and nanowires without the use of catalysts. The whiskers were found near the anode openings and on protruding places, where the vapor flux was strong and the temperature was high enough to stimulate their rapid growth and to supply additional atoms by migration. The nanowires appeared beyond the whisker regions, in areas with a lower temperature and flux. Their number decreased in the direction of the periphery of the anode.

The mixture of small Si crystals and C powder prevented the intensive formation of SiC in the anode openings. Therefore, it can be concluded that the mix of Si and C powder placed there could be used as an adequate evaporation source for obtaining Si nanowires by the method of DC arc discharge using a graphite cathode and a graphite anode.

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