Silicon nanowhisker formation during SiO2 evaporation by arc discharge

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Abstract. Nanoscale silicon is interesting in various areas, including electronics, photovoltaics, solar and Li-ion energetics. This work describes processes of electric arc sputtering of SiO2 in a graphite electrode in a helium medium, leading to formation of silicon nanowhiskers. A fan-shaped turbulent jet of vapors of the sprayed electrode flowing from the interelectrode space, resulting in formation of areas with different component compositions and temperatures, is considered. Interaction of SiO and Si vapors leads to the formation of the silicon nanowhisker structure.

1. Introduction

Nanoscale silicon is of interest in various fields due to its luminescence [1], electronic [2] and electrochemical properties [3]. In the field of solar energy, interest in silicon nanostructures is due to the large surface to volume ratio, which gives a huge area for the adsorption of light. The interest in silicon as applied to the production of Li-ion batteries is associated with the large theoretical capacity that silicon can provide. However, the saturation of silicon with lithium ions is accompanied by large volumetric changes, which leads to anode instability and its destruction [4]. Therefore the use of nanoscale silicon is interesting not only from the point of view of the huge active area, but also from the point of view of increasing a stability of the anode material during intercalation-deintercalation of lithium ions [3].

One-dimensional Si-derived nanostructures, such as nanowires, nanofibres, nanowhiskers, are of particular interest. Their synthesis has many variations, including chemical vapor deposition (CVD) [5], plasma-enhanced CVD (PECVD) [6], molecular beam epitaxy (MBE) [7], laser ablation (LA) [8], reactive ion etching (RIE) [9], metal-catalyzed electron etching (MCEE) [10], etc.

There are also works that describe the growth of Si-based nanofibers during arc discharge [11-13]. In [11], the authors have synthesized SiC nanofibres on the cathode using electric arc spraying of SiO2 + C mixture, while spraying of Si + C mixture has not form nanofibers. The authors attribute this phenomenon to the fact that SiC nanofibres grow from gaseous SiO on SiC nuclei. In another paper [12], the arc sputtering of the Si + SiO mixture, without adding any catalysts, has led to the production of silicon nanowires. In [13], the arc discharge has sputtered SiO in the medium of deionized water. As a result, the silicon nanofibers coated with the thin oxide layer have been synthesized. The proposed mechanism of the formation of silicon fibers is as follows: SiO molecules form condensate, which in the presence of Si is transformed into Si(1+x)O. At the same time, oxygen moves to one edge of the particle, forming a silicon structure behind it, and on the other hand, it attracts new silicon atoms and transforms them into silicon chains. Repeating this process leads to the combination of silicon particles...
and the growth of silicon fiber. Current work is connected with study of silicon nanowhisker formation during sputtering of SiO2 with a graphite cathode in helium.

2. Experimental setup
Plasma-chemical sputtering was performed using the electric arc reactor, detailed in [14]. The reactor consists of a sealed vacuum chamber with a volume of 7 liters, where a movable cylindrical graphite cathode with a diameter of 20 mm and a rigidly fixed sputtered anode are located. The anode is a cylindrical graphite rod with a diameter of 8 mm and a coaxial cylindrical cavity with a diameter of 6 mm, which is tightly filled with SiO2 powder. Helium is used as a buffer gas at a pressure of 12 Torr. The electric arc is ignited by mechanical contact of the electrodes. Next, the electrodes are separated by a distance, providing a voltage of 25V. The arc current is kept constant and is 100A. During the arc discharge burning and anode sputtering the interelectrode distance is maintained at the constant value by the moving of the cathode. As a result of the arc discharge, a nanomaterial is formed in the gas phase, which is deposited on a water-cooled screen, from which the nanomaterial is collected for further analysis.

3. Results and discussions
Transmission electron microscopy (TEM) of the synthesized material showed that the material contains graphene planes with dimensions greater than 200 nm, where SiC nanoparticles are located (Figure 1 (a)). Silicon structures in the form of nanowhiskers with the average thickness of 20 nm and the average length of 130 nm, growing from a massive SiC particle (Figure 1 (b)) are also presented in the material.

Figure 1. TEM images of the synthesized material.

The electric arc discharge leads to the heating of the electrodes and evaporation of the material, whose vapors fly out from the interelectrode gap and form a fan-shaped non-isothermal turbulent jet. The structure of this jet by component composition can be divided into several areas (Figure 2). The first area is dominated by the products of dispersion of the graphite rod, the third area is dominated by the products of dispersion of SiO2, contained in the electrode cavity; in the second area the components from the first and third areas are mixed. To understand the temperature distribution, neglecting the thermal contribution of chemical reactions, it follows from the condition of jet enthalpy preservation that the temperature at the central section of the jet decreases in inverse proportion to the distance from the discharge axis. At the same time, as the gas mixture of the electrode sputtering products cools down, the processes of chemical reactions, condensation and crystallization occur, leading to formation of nanostructures. The ongoing processes are directed towards the establishment of an equilibrium composition of the gas-plasma mixture, which is described by the law of mass action, condition of mass conservation and mixture quasi-neutrality. The equilibrium state of the mixture corresponds to the
condition of minimum Gibbs energy. Based on these conditions, the equilibrium compositions of gas-plasma mixtures in the range of 1000–5000 K, with pure carbon content, with pure SiO2 content, and with mixture of C (82 mol%) and SiO2 (18 mol%) were calculated using CEA NASA software, which approximately corresponds to the compositions in the 1, 3, 2 areas of the fan-shaped jet. The calculations were carried out with the condition of the pressure of the buffer gas of 12 Torr. As it can be seen from Figure 3(a), at this pressure, substantial evaporation of carbon begins at about 3400K, with C2 dimers and C3 trimers being formed together with atomic carbon. The content of other components is negligible. The degree of ionization at 5000K is about 10-4. In the areas containing the products of sputtering of the SiO2 material, such gas components as Si, O, SiO, O2, SiO2 condense into liquid SiO2, crystallizing at 1986 K (Figure 3(b)), at temperatures below about 2400 K. It should be noted that in the range of 2400-4000K the SiO vapor predominates. The degree of ionization in this mixture at 5000K is of the order of 10-2. In the second region of the jet, where the components from regions 1 and 3 are mixed, carbon oxidation and silicon carbidization occur (Figure 3(c)). At the same time, at temperatures above ~ 1400 K, oxygen oxidizes carbon to form a CO molecule, which is stable up to 5000 K, which allows silicon to present in an unbound atomic form at temperatures above ~ 2300 K, but molecular compounds such as SiC2 and Si2C are also observed. At this pressure, at temperatures below ~ 2300 K, silicon condenses to form solid carbide SiC.

These calculations allow us to suggest the mechanisms for the processes leading to formation of the structure of the synthesized materials. In the first region, pure carbon vapor condenses, which, as is well known, leads to formation of carbon soot globules [15]. In the second region, heterogeneous condensation of carbon-silicon vapor occurs, which, as established, leads to formation of graphene nuclei, which grow in the presence of silicon vapor to form graphene planes [14]. Mixing regions 2 and 3 leads to simultaneous presence of SiO and Si molecules, which, according to [11–13], can lead to the formation of silicon nanowires.

**Figure 2.** Scheme of the turbulent jet.
Figure 3. Equilibrium plasma compositions of pure carbon (a), pure SiO2 (b), mixture of carbon and SiO2 (c)
Conclusion
Electric arc sputtering of SiO$_2$ together with a graphite electrode leads to the formation of a heterogeneous turbulent fan-shaped jet flowing from the interelectrode gap. The jet consists of several characteristic regions with different concentration and temperature conditions. Condensation of vapors formed due to arc sputtering of the electrode material, depending on the local conditions, leads to the formation of such structures as graphene with SiC nanoparticles and silicon nanowhiskers. The silicon nanowhiskers grow in the areas where the composite electrode spray vapors of rich in SiO and Si components are mixed. The interaction of SiO and Si leads to the formation of non-stoichiometric Si(1+x)O oxide, which results in the release of Si upon condensation, and the polar SiO molecule attracts new Si atoms from vapor.

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