Synthesis of Ge and Si nanoparticles by spark discharge

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Abstract. The production of airborne nanoparticles by multi gap spark discharge generators is shown to be feasible for semiconductors on the example of erosion germanium and silicon electrodes in inert atmosphere. Pure silicon and germanium crystalline nanoparticles with the mean diameter less than 15 nm combined in submicron agglomerates were obtained. Since the presence of residual oxygen in the setup partially oxidized silicon nanoparticles and core-shell germanium structures with pure Ge core and oxidized shell were also observed in the samples. This continuous nanoparticles production technique enables direct impaction of prepared nanoparticles onto a liquid or substrate for applications in the fields of electronics, biomedicine and energetics.

1. Introduction

In recent years semiconductor nanoparticles are widely studied and used in various applications in the fields of science and technology due to their unique optical and electronic properties [1,2]. For example, silicon and germanium nanoparticles can be injected into gate oxide of MOS memory devices to prevent the leakage current [3], they can be exploited as anode materials for Li-ion batteries, fluorescent bioprobes [2], functionalized Si and Ge nanoparticles deposited on wool improve photostability toward UV radiation of the fabric [4].

There are several methods for creating semiconductor nanoparticles: inorganic solution phase chemical approaches and vapor-based techniques [1, 2]. The spark discharge generation of nanoparticles permits to generate aerosol nanoparticles with a diameter of primary particles less than 10 nm from metals and oxides materials showing high chemical purity of the synthesized nanoparticles and low agglomeration properties. Due to problems with removing residual oxygen from camera setup to establish inert atmosphere it is known only one study of silicon nanoparticles generation by spark discharge [5].

The present paper discusses the investigation of nanoparticle properties produced by spark discharge method by electrical erosion of silicon and germanium electrodes in inert atmosphere.

2. Experimental

The multi gap spark discharge generator described in the paper [6] was used in the experiments with following conditions: 6 pair of single-crystal germanium (n-type) or silicon (p-type) electrodes 8 mm in diameter and 30 mm in length with resistivity of 0.005 Ohm-cm, 2 mm gap spacing, total capacitance 21 nF, frequency of the discharges was 310 Hz. Argon gas with purity of 99.9999 % from a bottle was used as a carrier gas at flow rate of 5 litres/min. The amount of residual oxygen in the discharge chamber was less than 20 ppm. The pressure of the argon gas in camera setup was held up by approximately 1.5 bar.

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The particle size distribution, morphology, crystal structure and element composition of nanoparticles were investigated using transmission electron microscope (TEM) JEOL JEM2100 with energy dispersive X-ray (EDX) spectrometer X-MAXN OXFORD Instruments. For microscopic studies, the particles were deposited directly to a TEM grid with carbon film in the setup, and transferred to a microscope in hexane to prevent extra oxidation. The real-time measurements of size and concentration of the nanoparticles in the aerosol flow were determined by an aerosol spectrometer SMPS 3936 (TSI Inc.).

3. Results and discussions
TEM analysis of nanoparticles produced by electrical erosion of germanium electrodes reveals the typical fractal-like structure of large agglomerates (Figure 1). According to aerosol spectrometer measurements the mean size of agglomerates is equal to 370 nm (Figure 2). The primary particles are spherical with quite uniform diameters, as typical for spark-generated particles. The average diameter of particles is $13 \pm 2$ nm. A typical high resolution electron microscopic (HRTEM) image of the germanium nanoparticles is shown in Figure 3. The visible lattice lines confirm the presence of crystalline material; the spacing distance is $3.22 \, \textnormal{Å}$, which is in agreement with theoretical value between the (111) Ge crystalline planes. The specific EDX line profiles of 35 nm nanoparticle show the increase in the germanium signal with the constant oxygen concentration (Figure 4). It was also observed several nanoparticles with core-shell structure, where crystalline germanium form the core of nanoparticles and germanium oxide built the amorphous shell.

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**Figure 1.** TEM image of Ge primary particles in large agglomerates.

**Figure 2.** Size distribution of number concentration of airborne Ge nanoparticles in agglomerates.
Figure 3. HRTEM image and the corresponding FFT pattern of germanium nanoparticles.

Figure 4. Representative EDX line scan with Ge Kα and O Kα signals obtained on germanium nanoparticle with the size of 35 nm.

The HRTEM images and electron diffraction patterns of obtained silicon nanoparticles show that the sample consist of agglomerates of silicon nanocrystals encapsulated within an amorphous matrix of silicon oxide (Figure 5). The size of the primary semiconductor crystalline particles is in the range of 3 to 30 nm with the mean size of 10 ± 2 nm (Figure 6). The average size of the agglomerates is about 350 nm by the aerosol spectrometer which is consistent with the TEM-data.

Figure 5. HRTEM image and the corresponding FFT pattern of silicon nanoparticles in amorphous matrix. The lattice fringes corresponding to the (111) of individual Si nanocrystals are shown by white rings.

Figure 6. Typical TEM image of silicon nanoparticles in agglomerate.

Difference in morphology structure of silicon and germanium nanoparticles can be explained in terms of energy formation of semiconductor oxides. Since the energy of formation of silicon oxide (-904 kJ/mole) is two times higher than for germanium oxide (-515 kJ/mole) germanium oxidation
reaction is slower. So we can synthesis only partially crystalline silicon nanoparticles in amorphous silicon oxide matrix.

4. Results
We have shown application of multi-spark discharge nanoparticle generator for the production of spherical semiconductor nanoparticles, including agglomerates of silicon nanocrystals encapsulated within an amorphous matrix of silicon oxide and core-shell germanium nanoparticles. The primary particle size was between 3 to 30 nm. In further experiments by controlling the residual oxygen concentration in the discharge chamber it is possible to achieve only pure semiconductor, oxides or core-shell nanoparticle structures of silicon and germanium nanoparticles.

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