SYNTHESIS OF MICRODIAMONDS AND GERMANIUM NANOTUBES IN THE ARGON-GERMANIUM ARC

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Abstract. The paper describes a technique for the synthesis of microdiamonds, germanium nanoballs and nanotubes in an argon-germanium arc. The evaporation of germanium atoms was carried out from the surface of a graphite rod, which served as the anode of the arc discharge. The synthesis of microdiamonds was observed on graphite substrates near the anode; germanium nanotubes and germanium nanoballs were also found nearby. It has been established that germanium promotes the synthesis of nano and microdiamonds. Synthesized diamonds have a classic structure with rectangle faces and four hexagons adjacent to the edges of this rectangle. The sizes of microdiamonds reach tens of microns. The diameters of germanium nanotubes are of the order of 50-100 nm, and the length is of the order of 10 μm.

1. Introduction

Germanium is a semiconductor element with a fairly low bandgap and therefore has great application potential. Germanium has a high electronic conductivity and has a large absorption coefficient throughout the visible spectrum. This property has great prospects for the manufacture of photodetectors and solar batteries. In addition, germanium is also attractive for the synthesis of semiconductor nanoparticles, as well as a catalyst for the synthesis of nanodiamonds [1–3]. Nanodiamonds usually include carbon nanostructures ranging in size from 1 to 10 nanometers, the atoms in which are arranged in the same way as in diamond. Externally, nanodiamonds look like a light gray powder, consisting of agglomerates ranging in size from one to hundreds of micrometers. Nanodiamonds today are mainly obtained from natural diamonds by physical methods, by synthesis at ultrahigh pressures and temperatures, by chemical deposition of carbon-containing vapor at high temperatures and pressures, by detonation synthesis, and by irradiating a carbon-containing material with electron beams and argon ions.

In recent years, various approaches to the synthesis of nanostructured Ge have been highlighted, such as laser ablation, chemical reduction, and hydrothermal process. In [1-3], germanium served as a catalyst in the plasma-chemical synthesis of nanodiamonds. In [4], carbon nanostructures were synthesized from liquid hydrocarbons in a recessed arc. The results of plasma-chemical synthesis of carbon nanostructures from hydrocarbons are given in [5–6]. In [7–9], methods for increasing the stability of electric discharges in the processes of synthesis of various nanostructures were studied. In
In this work, we continued studying the process of synthesis of germanium nanoballs and nanotubes, as well as nano and microdiamonds in electric arc plasma.

2. Materials and methods

The experiment was carried out in a vacuum chamber with water-cooled walls. After evacuation, the chamber was filled with argon to a pressure of 500 Torr. Graphite rods 14 mm in diameter were used as electrodes. The distance between the electrodes could be controlled during the experiment. The graphite cathode was sharpened to precisely localize the current spot on the anode. A hole 5 mm in diameter and 6 mm deep was drilled on the anode. Germanium was crumbled into this hole. The experiment was carried out at a voltage of about 24 V and a current of 50 A. The experiment was carried out according to the following scenario. By rotating the regulator, the graphite cathode was lowered until it came into contact with the anode. After the appearance of the arc, its length was set to about 3 mm. In the first few tens of seconds, evaporation of carbon atoms occurred, and the surface of the graphite anode became hot, while germanium evaporated insignificantly. Subsequently, the evaporation of germanium increased and its intense boiling began. Vapors of germanium and carbon atoms were deposited on the surface of a graphite substrate, on the surface of the cathode, on the surface of the anode, and on the walls of the vacuum chamber. The experiment lasted for 2 minutes. These deposits have been carefully studied with optical and scanning electron microscopes. The evaporation of germanium and the growth of germanium deposits were observed through a special darkened viewing window.

3. Results and discussion

Figures 1-4 show images of the samples synthesized during the experiment. In Figure 1, at a magnification of 5000 times, we see germanium nanotubes, germanium nanoballs and nanodiamonds. Germanium nanotubes and nanoballs are conductors and are therefore black and grey in color, while dielectric nanodiamonds are white. Germanium nanotubes have a length of about 2-4 microns and a diameter of about 50 nm. The main difference between these nanotubes and those previously synthesized is the fact that they grew, as it were, on nanodiamonds. The sizes of nanodiamonds in this picture are about 800-900 nm and they represent a kind of "handle" for these nanotubes. Thus, the presence of such holders, "fasteners" will allow the use of such nanotubes in many applications where it is necessary to deal with individual nanotubes. These nanotubes have high mechanical strength. The germanium nanobeads in this image range in size from 1 µm to 100 nm.

On fig. 2 at the same magnification are germanium nanoballs and nanodiamonds. The sizes of nanoballs here reach up to 4 µm in diameter. The bulk of the nanoballs have dimensions of the order of 100–200 nm. Some nanoballs are connected to each other by nanotubes like dumbbells. The fact that these nanotubes did not break is a testament to their exceptional strength.

On fig. 3 and fig. 4 shows synthesized microscopic diamonds. On Fig. 3 diamonds have a regular geometric shape: 4 faces of four regular hexagons adjoin one face in the form of a square. Such a set of faces forms the upper cap of the crystal. The middle belt consists of four hexagons alternating with four squares. Thus, the middle belt consists of eight faces. On the lower side, the crystal ends with the same cap as the upper cap. There are 18 faces in a diamond crystal, 6 of which are squares and 12 are hexagons. The dimensions of all diamonds shown in the figure are strictly the same. Their cross section is about 1.5 µm. Diamonds are surrounded by other nanostructures. Apparently, carbon, since a deficit of these formations formed near the nanodiamonds.
Figure 1. Nanodiamonds, germanium nanotubes and nanoballs. 5000 times magnification

Figure 2. Germanium nanoballs and nanotubes
Figure 3. Microdiamonds and nanodiamonds.

Figure 4. Nanodiamonds of different geometry from the same sample.

Figure 4 shows nanodiamonds of a different geometry. Their vertex squares are much smaller than in the previous figure and average about 0.7 µm. The side hexagons also have irregular shapes. These and other diamonds play with their facets in the light.
4. Conclusion

Thus, germanium nanotubes and microscopic diamonds were synthesized in an argon-germanium arc. Diamonds have 18 facets, 6 of which are squares and 12 are hexagons. The dimensions of all diamonds shown in the figure are strictly the same. Their cross section is about 1.5 µm. Germanium nanotubes have a length of about 2-4 microns and a diameter of about 50 nm. These nanotubes grew, as it were, on nanodiamonds. The sizes of nanodiamonds in this picture are about 800-900 nm and they are like "handles" for these nanotubes. Thus, the presence of such holders, "fasteners" will allow the use of such nanotubes in many applications where it is necessary to deal with individual nanotubes. Low-temperature plasma can be used for the synthesis of various nanostructures and is well suited for the modification of various surfaces. This is shown in many works [10-13].

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