Electrochemical formation of germanium nanostructures using low-melting-point metal particles

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Introduction

The study of germanium nanostructures, in particular nanowires, has recently attracted significant interest, due to the great potential of their application in lithium- and sodium-ion batteries, photovoltaics, optics, and thermoelectric systems. For the formation of germanium (Ge) nanowires, gas-phase deposition using metal catalysts is mainly used according to the vapor-liquid-crystal (VLC) mechanism, where the size of the metal particles determines the location and geometric parameters of the nanowire (diameter and length) [1]. However, the processes of gas-phase deposition often require the use of complex technological equipment and are carried out at sufficiently high temperatures, as well as toxic and expensive precursors.

From this point of view, the use of electrochemical deposition is a good alternative. However, the cathodic polarization of solid-state electrodes in aqueous solutions of germanium (IV) oxide ensures the formation of films with a thickness of only a few monolayers. At the same time, the use of molten metal particles such as Hg and Ga as crystallization centers makes it possible to obtain both films of sufficient thickness and Ge nanowires [2, 3]. During the electrochemical deposition of Ge, the seed metal dissolves in Ge, and the metal impurity concentration exceeds the theoretical solubility by several orders of magnitude. The presence of this metal will affect the conductivity type of Ge nanowires. The possibility of cathodic deposition of Ge using Indium (a p-type dopant for Ge) nanoparticles has been shown [4].

In this work, it has been demonstrated the features of Ge nanowires growth using Sn (isoelectronic impurities) and BiSn (Bi – n-type dopant for Ge) nanoparticles.

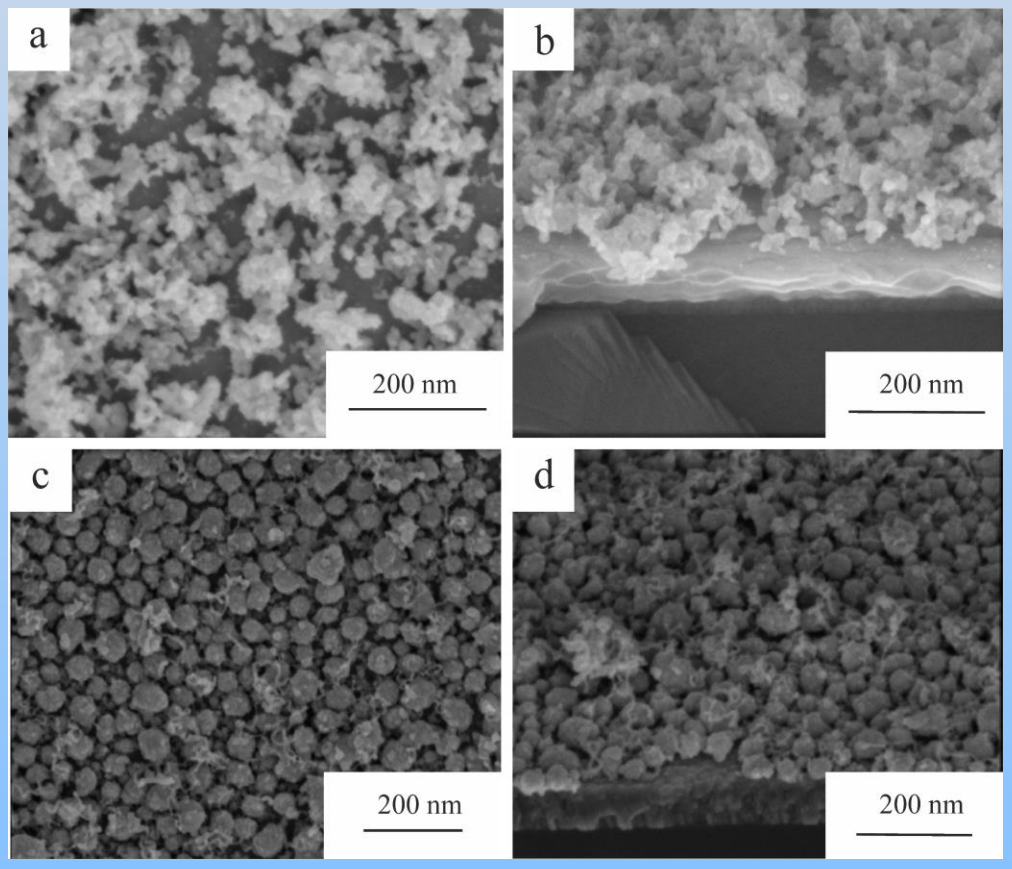

Fig. 1. *SEM images of obtained samples after Ge electrodeposition using Sn nanoparticles.*

Experiment

Arrays of spherical Sn and BiSn nanoparticles have been deposited by the vacuum-thermal evaporation at a residual pressure of 1 x10^{-5} Torr of material from a Mo evaporator, placed at 40 cm from the substrate. After depositing the metals, the samples have been annealed in a vacuum at 250°C for 10 min. The electrochemical formation of Ge nanostructures on the obtained Sn and BiSn nanoparticles has been carried out in an electrolyte solution of the following composition: 0.05 M germanium (IV) oxide GeO_2, 0.5 M potassium sulphate K_2SO_4, and 0.5 M succinic acid. The electrolysis has been carried out in the galvanostatic mode at a current density of 2 mA/cm^2. The morphology of the obtained samples has been studied using scanning electron microscopy (SEM).

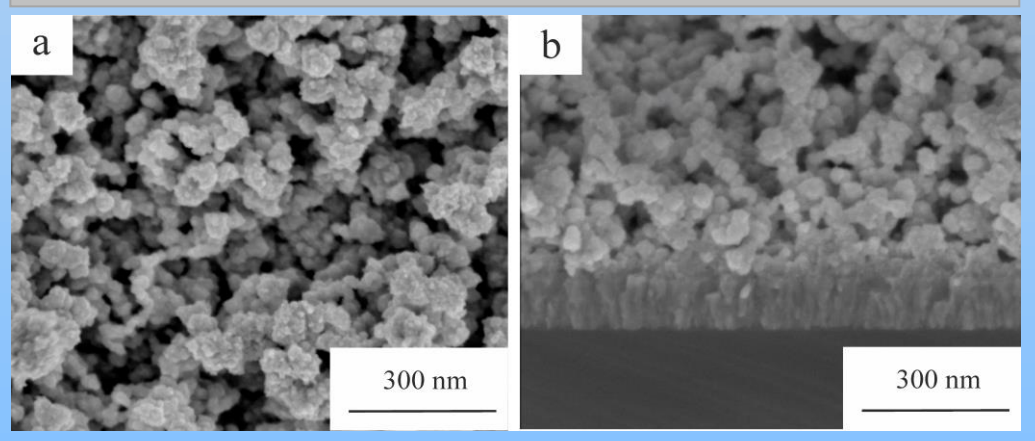

Fig. 2. *SEM images of obtained sample after Ge electrodeposition using Bi-Sn nanoparticles.*

Results

Figure 1 shows the SEM image of the resulting Ge structure with Sn nanoparticles. As can be seen, the formed samples are filamentous structures with a diameter of ~10 nm (Figure 1 a, b). With an increase in the average size of tin nanoparticles to 40 nm, the morphology of the sample has been changed (Figure 1 c, d). In some places of the surface of Sn nanoparticles, nanowire crystals are forming with a diameter of less than 10 nm. This fact may indicate that the process temperature of 90°C is insufficient for the complete melting of Sn nanoparticles and, as a consequence, for the intensive growth of nanocrystals. Apparently, small liquid droplets up to 10 nm in size are formed on the surface of a large Sn nanoparticle, which ensures the growth of such nanocrystals, as shown in Figure 1 c, d.

In its turn, the use of two-component tin nanoparticles with bismuth makes it possible to obtain Ge nanocrystals with a larger diameter (Fig. 2).

It should be noted that in the case of using two-component Bi-Sn nanoparticles, the nanocrystals have a rough surface in comparison with nanocrystals obtained using In nanoparticles. The results of the study by the Raman spectroscopy have been showed that the filamentous nanostructures are crystalline Ge (Figure 3). This follows from the detected spectral band at 300 cm^{-1}, which is characteristic of crystalline Ge [5].

Thus, Ge nanowires have been obtained by the electrochemical method using Sn and Bi-Sn nanoparticles. The results obtained will expand the range of metal nanoparticles used and control the electrophysical properties of Ge nanowires.

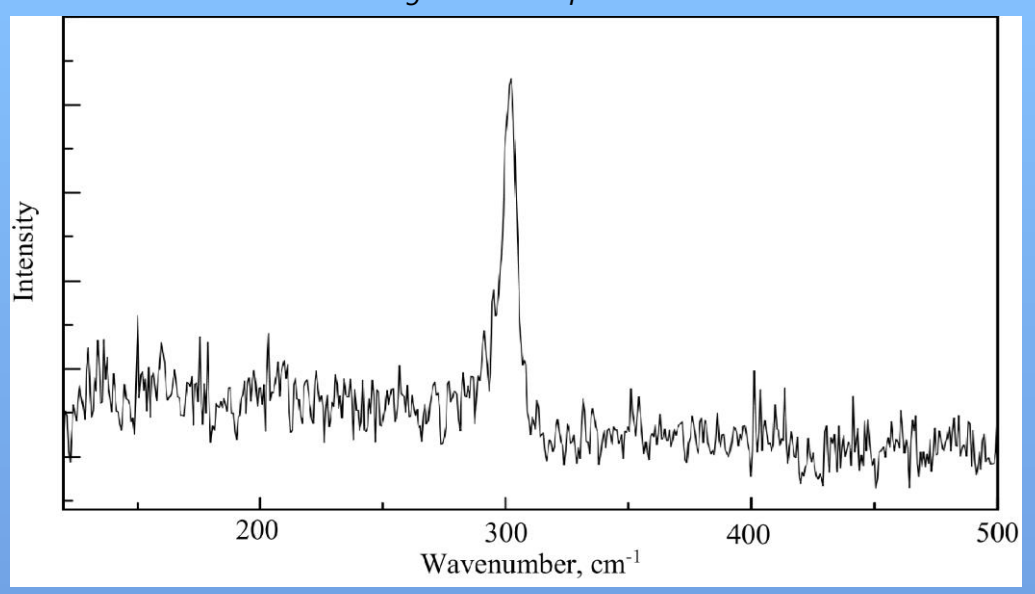

Fig. 3. *Raman spectra of sample.*

References

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