Influence of thermal treatment on the morphology and composition of Ge Nanowires

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Abstract. In this work we studied influence of thermal treatment on the morphology and composition of Ge nanowires (GeNW) obtained by electrochemical deposition using In nanoparticles. The obtained results showed that thermal treatment can be used for control the composition of GeNW, what is important for technologies, where the presence of In may negatively affect the operation of the device.

1. Introduction

Nowadays much attention is paid to the formation of GeNW, which find application in lithium-ion batteries, field-effect transistors and optoelectronic devices. Work [1] describes synthesis of it using various methods. A lot of work is devoted to chemical vapor deposition (CVD), but this method requires high temperatures, which are the driving factor of the chemical reaction for the precursor and the deposition of nanostructures.

A group led by Maldonado [2] proposed to use metal liquid nanoparticles for the electrochemical deposition of Ge by mechanism electrochemical liquid-liquid-solid (ec-LLS). The nanoparticles are low-melting metals (liquid at the synthesis temperature) with low solubility of germanium, deposited on a substrate. The advantages of this method are low-temperature procedure, low-cost and non-toxic sources of Ge. But it has a specificity of dissolving metal in Ge during the growth of the nanowires (about 5-8 at. %), what could be critical for some applications. Injection was observed for different metals: for In-Bi eutectic about 5-7 at. % of In and 3-4 at. % for Bi [3]; for Ga – 8-8.5 at. % [4]. Additionally, according to [4], metal atom content exceeded equilibrium solubility by several orders of magnitude, but occurs uniformly and without formation precipitation or clusters. Similar trapping of impurities was observed also for chemical vapor deposition nanowire growth for Ge by Ga [5] and Si by Al [6]. In works [5] and [6] an excess of the equilibrium concentration of the metal atoms was also observed. The injection of impurities occurs in accordance with the process called solute trapping, which was considered by the group [7].

The inclusion of metal atoms during the growth of nanostructures can significantly change its basic properties, as electrical and optical. The incorporation of impurities (with a valency other than IV for Si or Ge) in high concentrations during the growth process can lead to p- or n-type doping. Maldonado’s group in [4] reduced Ga catalyst atoms concentration by thermal treatment in GeNW from 8 at. % to 4 at. % by thermal annealing at 250 °C for 30 min. In addition, our previous results [8] showed that...
nanowires obtained by the ec-LLS method with In nanoparticles have low thermal conductivity and may be heated to high temperatures and expose to irreversible changes after excess heating. Accordingly, it is important to control the In concentration into GeNW. So, in this work we investigated influence of thermal treatment on the morphology and composition of GeNW.

2. Experiments

We created nanostructures by cathodic electrochemical reduction GeO$_2$ solution on metal nanoparticles. As a substrate we used 50 μm thick Ti foil. As metal we used In, as it is an accessible material with low melting temperature and solubility of Ge – 156°C and 0,073 at.%. Nanoparticles were applied by vacuum thermal evaporation 18,4 mg In at a residual pressure of the atmosphere below 3∙10$^{-5}$ mm Hg, after which the samples were annealed at 150°C for 10 min at the same pressure to improve morphology.

Electrochemical deposition of GeNW samples was performed in chronopotentiometry mode at current density 0,2 mA/cm$^2$ at 20°C using Autolab PGSTAT 302, temperature was controlled by TermexVT12 Heating bath circulator.

The thermal treatment of samples was done in a vacuum at 300°C and 600°C for 30 min. The samples were annealing in a vacuum oven at a residual pressure of the atmosphere below 3∙10$^{-5}$ mm Hg, temperature was controlled using a type K thermocouple.

The study of elemental analysis of samples before and after thermal treatment was made by using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) with energy-dispersive microanalysis.

3. Results

The transmission electron microscopy (TEM) image of In nanoparticles and size distribution of it is shown in the figure 1.

![ TEM-image of In nanoparticles; b) diameter distribution histogram of In nanoparticles ]

As a result, the nanoparticles diameter of about 30 nm was predominant. Accordingly, the predominant diameter of the nanowires will be similar.

Figure 2 shows the U (t) curve recorded during the growth of GeNW.
Figure 2. Potential-time curve measured during the growth of GeNW at current density 0.2 mA/cm².

The growth of structures is carried out by the following mechanism: Ge (IV) ions are reduced on the surface of low-melting metal nanoparticles to Ge⁰, followed by dissolution in catalyst; after saturation of the catalyst particles Ge crystallizes at the metal-substrate interface. Hydrogen evolution completed the growth process and limited the possibility of Ge reduction on In nanoparticles – the moment when the potential begins to increase significantly at the end of the curve.

The structures as-prepared and after treatment were examined using Scanning Electron Microscope (SEM) (figure 3).

Table 1 Average diameter of GeNW

| thermal treatment       | as-prepared | 300°C, 30 min | 600°C, 30 min |
|-------------------------|-------------|---------------|---------------|
| current density 0.2 mA/cm² | 30 nm   | 32 nm         | 32 nm         |

The study of elemental analysis of single GeNW before and after thermal treatment presented at table 2. The results of elemental analysis showed certain effect of thermal treatment on GeNW. The morphology of GeNW does not change after treatment (figure 3 and table 1), but concentration of In has decreased. Furthermore, concentration of O was increased due to oxidation, which is noticeable at 600°C.
Table 2. Elemental composition of GeNW

| thermal treatment | Ge, at. % | In, at. % | O, at. % |
|-------------------|----------|----------|----------|
| as-prepared       | 96       | 4        | 0        |
| 300°C, 30 min     | 95       | 4        | 1        |
| 600°C, 30 min     | 96       | 0        | 4        |

After heating in a vacuum at 600°C, the concentration of In in GeNW was less than 1 at.%. It can be explained by evaporation of In, but of 300°C such result was not achieved. Probably at 300°C the diffusion of In to the surface is insufficient, so at 600°C it is enough for In evaporation.

4. Conclusion
The data of elemental analysis of samples confirms the possibility to control the composition of GeNW by following thermal treatment, what is important for technologies, where the presence of In may negatively affect the operation of the device.

In future articles, we are going to investigate intercalation in a metal-ion battery using GeNW as an anode. Indium content may affect on battery performance and its capacity. It is also necessary to describe the In diffusion process in more details in order to more accurately understanding the process.

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