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Effect of thermal annealing on the composition of Ge-Co nanostructure obtained by electrochemical deposition

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Abstract: Cobalt-based catalysts are one of the possible candidates for catalysts that accelerate the decomposition of water to produce energy. In this work, the one-dimension Ge-Co nanostructures have been prepared by electrochemical deposition in a three-electrode cell. The samples have been annealed in atmosphere at various temperature (300 °C, 450 °C, 600 °C). Effect of thermal annealing on the composition of Ge-Co nanostructure has been studied. The morphology of the obtained Ge-Co nanostructures has been investigated using scanning electron microscopy The method of X-ray diffraction analysis has been used to investigate composition changes of Ge-Co. Diffractograms show the presence of Co_2GeO_4 catalyst at an annealing temperature of 600 °C. The sample with this annealing temperature shows the best properties as oxygen evolution catalyst.

Keywords: Ge-Co nanostructures, oxygen evolution catalyst, Ge nanowires, electrochemical deposition

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Влияние термического отжига на фазовый состав наноструктуры Ge-Co, полученной методом электрохимического осаждения

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Аннотация. В работе получены наноструктуры Ge-Co с помощью электрохимического осаждения. Исследовано влияние температурного отжига (300 °C, 450 °C, 600 °C) на фазовый состав этой структуры методом рентгеновского дифракционного анализа. Выявлено присутствие катализатора Co_2GeO_4 при температуре отжига в 600 °C. Образец при таком отжиге также показал наилучшие каталитические свойства.

Ключевые слова: наноструктуры Ge-Co, катализатор, нанонити Ge, электрохимическое осаждение

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Introduction

At present, due to the development of the global energy industry, there is a need to use clean and cheap fuel, including to reduce carbon dioxide emissions.

One of the ways to obtain ecological fuel is the electrolysis of water to produce hydrogen [1]. However, this process has a disadvantage, which is the slow reaction rate on conventional electrodes. To eliminate it, it is necessary to investigate various substances that accelerate electrochemical reactions, which are called catalysts. In this case, catalysts are needed for two processes on two electrodes: the hydrogen evolution reaction and the oxygen evolution reaction (OER). Oxygen evolution reaction (OER) is a limiting reaction in the process of generating molecular oxygen through chemical reaction, such as electrolysis of water into oxygen and hydrogen, and electrocatalytic oxygen evolution from oxides and oxoacids [2].

One of the promising areas of research on effective and stable oxygen evolution catalysts (OECs) are cobalt-based catalysts because of its OER activity and thermal stability [3]. There are many known methods for the synthesis of a cobalt-based catalysts, such as a method of selective reduction-oxidation from metal nitrates for getting cobalt catalyst doping Ag [4] or synthesis by chemical reduction followed by a process of thermal oxidation, which allows to obtain a compound of cobalt with rare-earth materials: ruthenium and iridium in powder form [5]. There are also such methods for obtaining cobalt-based catalysts as the sol-gel method [6] and vacuum-diffusion method [7] and electrochemical deposition [8]. The electrochemical deposition method is characterized by the absence of a high vacuum system, its speed and the ability to vary the parameters of the process to obtain various materials.

In this work, we report about formation OEC based on the one-dimension nanostructure Ge-Co by electrochemical deposition and investigate effect of thermal annealing on the composition of this structure.

Materials and Methods

In the syntesis of Ge-Co nanostucture the 50 μm-thickness titanium foil (batch VT 1–00) has been used as a substrate. These titanium samples have been previously cleaned in a mixture of H_2O_2:NH_4OH:H_2O (1:1:4) at 80 °C for 15 min, and then they have been washed in hot and cold deionized water for 5 min and dried. Then the samples surface has been activated in a mixture of HF:HNO_3:H_2O (1:2:6), washed in deionized water and dried again.

After that an array of spherical indium nanoparticles has been deposited by vacuum-thermal evaporation at the residual pressure of 1×10^{-5} Torr of material weighed portion of 35 mg from a Mo evaporator, placed at 40 cm from the substrate. After depositing the metals, the samples have been annealed in vacuum at 150 °C for 10 min.

Ge-Co structures have been formed on the substrates by electrochemical deposition in a three-electrode cell. A platinum plate has been used as an counter electrode, and a standard silver chloride electrode has been used as a reference one.

The solution contained 0.05 M of germanium (IV) oxide GeO_2, 0.5 M of potassium sulfate Na_2SO_4 and 0.1 M of tartaric acid with the addition of 0.05 g $CoCl_2$. The solution pH has been brought to 6.5 by adding NH_4OH. The solution temperature has been controlled using a LAUDA Alpha thermostat (LAUDA, Germany).

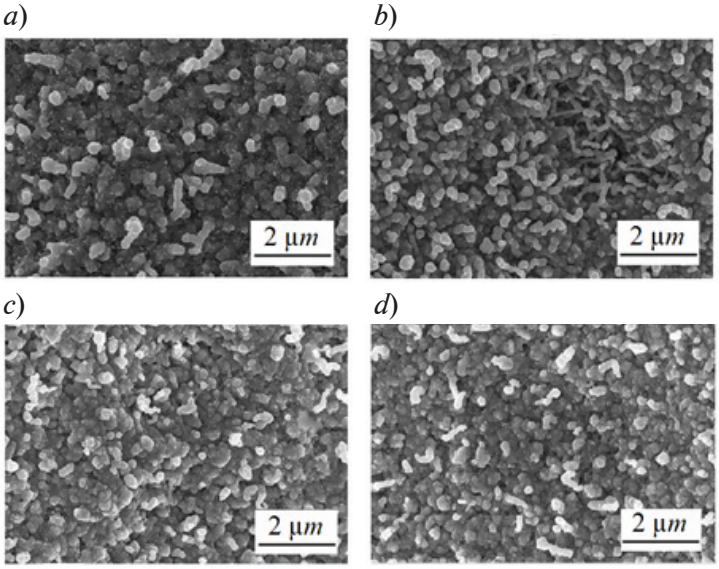

Fig. 1. SEM images of Ge-Co nanowires: sample without annealing (*a*), annealing 300 °C (*b*), annealing 450 °C (*c*), annealing 600 °C (*d*)

Deposition has been performed at constant voltage of −1.3 V for 1 min at the solution temperature of 85 °C. The voltage has been set using Autolab PGSTAT302N potentiostat/galvanostat (Metrohm, Netherlands).

After deposition, the samples have been annealed in atmosphere at various temperature (300 °C, 450 °C, 600 °C).

The method of X-ray diffraction analysis (XRD) has been used to deteminate the crystalline phases (germanium, cobalt, their oxides, etc.) after the formation of the Ge-Co compound and to investigate the effect of annealing at different temperatures on the composition of Ge-Co.

X-ray diffraction patterns (diffractograms) of synthesized samples have been obtained using the RADIAN DR-02 device with a copper X-ray tube and a nickel filter.

CV measurements have been performed by sweeping the potential from a value of 0.1 to 1.2 V (vs Ag/AgCl) using Autolab PGSTAT302N and a three-electrode system.

Results and Discussion

The images of the morphology of the Ge-Co structures both with annealing and without it obtained by scanning electron microscopy are shown in Fig.1.

According to the SEM images, a structural transformation of nanowires is observed in the annealing process. In the image of the sample without annealing (Fig. 1,*a*), some nanowires formations with a thickness of 250 nm can be seen, but the nanowires structures are not predominant. At 300 °C more nanowires appear, the thickness of which varies from 150 to 200 nm (Fig. 1,*b*). Annealing at 450 °C and 600 °C has a similar effect on the morphology of Ge-Co nanowires (Fig. 1, *c*, *d*). Nanowires become less visible, the thickness of nanowires decreases to about 100 nm. However after annealing at 600 °C it can be noticed more nanowires than that after annealing at 400 °C.

The results of X-ray diffraction after annealing germanium nanostructures with cobalt Ge-Co at various temperature are shown in Fig. 2. The sample without annealing has peaks of two phases: crystalline germanium and titanium substrate.

At annealing temperatures of 300 °C and 450 °C, there is an increase in the intensity of germanium peaks, especially the first peak (27.3°) [9]. With an increase in the annealing temperature, a slight shift of the germanium peaks to the right to the reference values is also noticeable.

However, at an annealing temperature of 600 °C, the diffractogram shows a presence of germanium-cobalt compounds in the nanostructure, particularly cobalt germanate Co_2GeO_4 at $2\theta = 30-40°$ [4], which has not been observed at lower annealing temperatures. A well-marked phase of titanium oxide and a certain amount of the compound Ti_5Ge_3 are also visible.

The first peak of germanium becomes indistinguishable due to the presence of titanium oxide, which leads to the overlap of two peaks and its sharp increase.

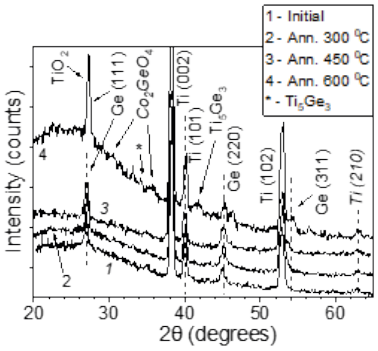

Fig. 2. X-ray diffractograms of Ge-Co samples after annealing at different temperatures

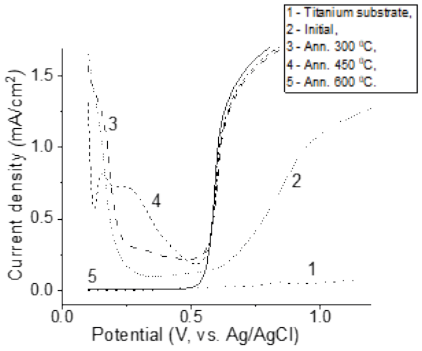

Fig. 3. CV curve of initial/annealing Ge-Co samples and titanium substrate

Additionally obtained Ge-Co samples after annealing and without it have been also tested for the OER activity in a solution of 1 M NaOH. Graphics of current density-voltage curve (CV curve) based on the results of the sample study are shown in Fig. 3. This figure also shows the CV curve of a pure titanium substrate obtained for comparison.

According to the graph of the titanium substrate, it can be seen that the current density almost does not change in the voltage range, which means that there are practically no electrochemical processes.

The current density for Ge-Co samples (except for the sample after annealing at 600°C) at a potential of 0.2 V to 0.5 V indicates reactions caused with the oxidation of germanium and cobalt. At a potential of 0.5 V, the current density increases due to the beginning of oxygen release. For a sample without annealing, the current density increases more slowly compared to annealing samples, which indicates its lower OER activity.

At the same time, with an annealing at 600 °C, reactions caused only with the release of oxygen are observed on the sample (the current density begins to increase only at a potential of 0.5 V) due to the presence of a cobalt germanate. It can be concluded that the annealing temperature at 600 °C is the most optimal temperature for the formation of an oxygen evolution catalyst based on Ge-Co nanostructure.

Conclusion

In the present work nanostructures Ge-Co have been prepared by electrodeposition from the aqueous solution. The effect of thermal annealing on the composition of Ge-Co has been investigated. According to the results of X-ray diffraction, with an increase in the annealing temperature, the crystal phase of germanium decreases and germanium compounds with cobalt are formed. On an annealing temperature at 600 °C, a compound cobalt germanate Co_2GeO_4 is found that could be a good oxygen evolution catalyst.

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