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

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Introduction

One of the ways to obtain ecological fuel is the electrolysis of water to produce hydrogen. But it is necessary to investigate various substances that accelerate electrochemical reactions because of slow reaction rate on conventional electrodes.

One of the promising areas of research on effective and stable oxygen evolution catalysts (OECs) are cobalt-based catalysts because of its oxygen evolution reaction (OER) activity and thermal stability.

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.

Experiment

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 GeO_2, 0.5 M of Na_2SO_4 and 0.1 M of tartaric acid with the addition of 0.05 g $CoCl_2$.

Deposition has been performed at constant voltage -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 at various temperature (300 °C, 450 °C, 600 °C).

Results and discussions

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. 1a), 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.

The results of X-ray diffraction after annealing germanium nanostructures with cobalt Ge-Co at various te mperature 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°).

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 30-40°, which has not been observed at lower annealing temperatures.

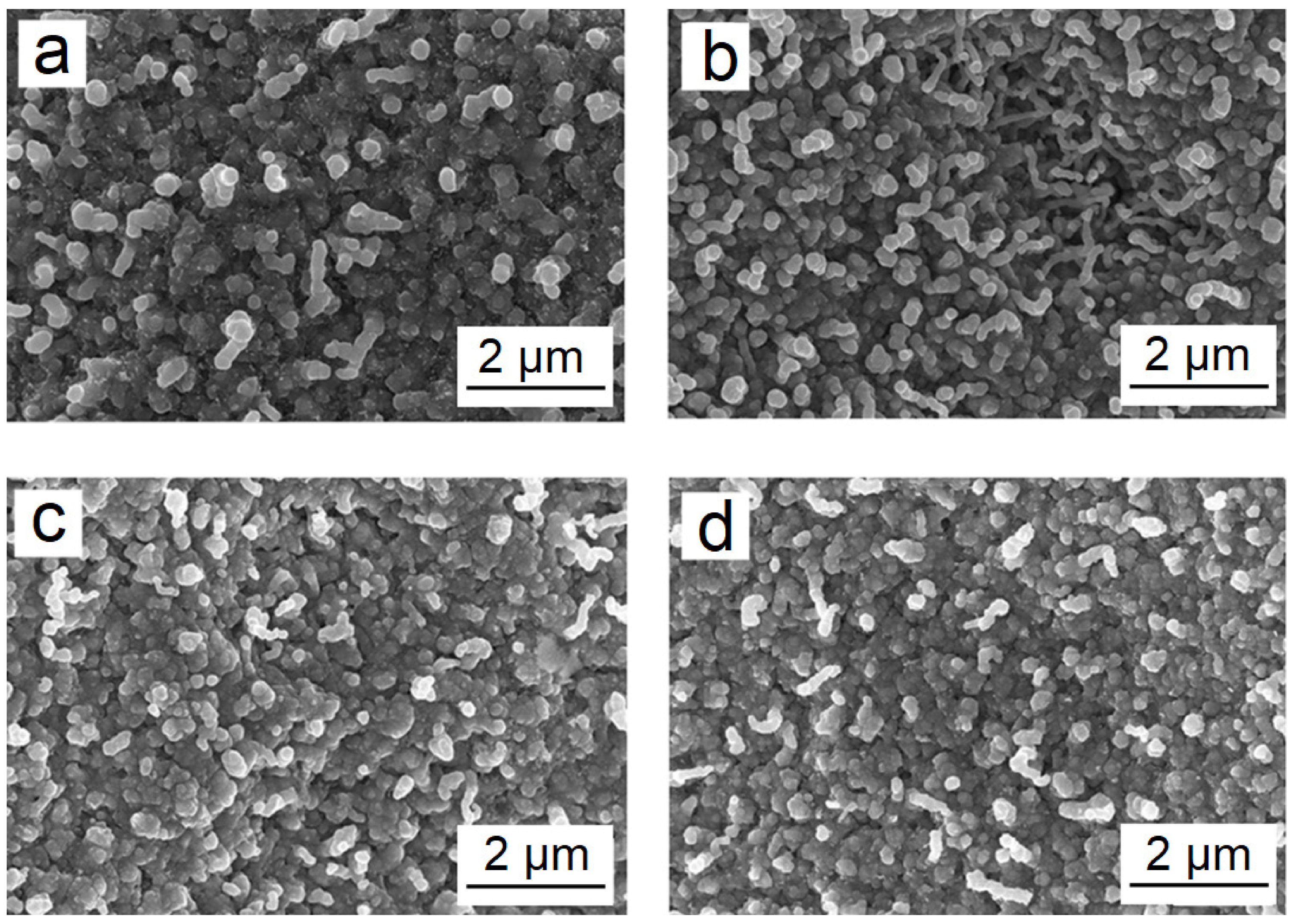

Fig. 1. SEM images of Ge-Co nanowires: a - sample without annealing, b – annealing 300 °C, c – annealing 450 °C, d – annealing 600 °C.

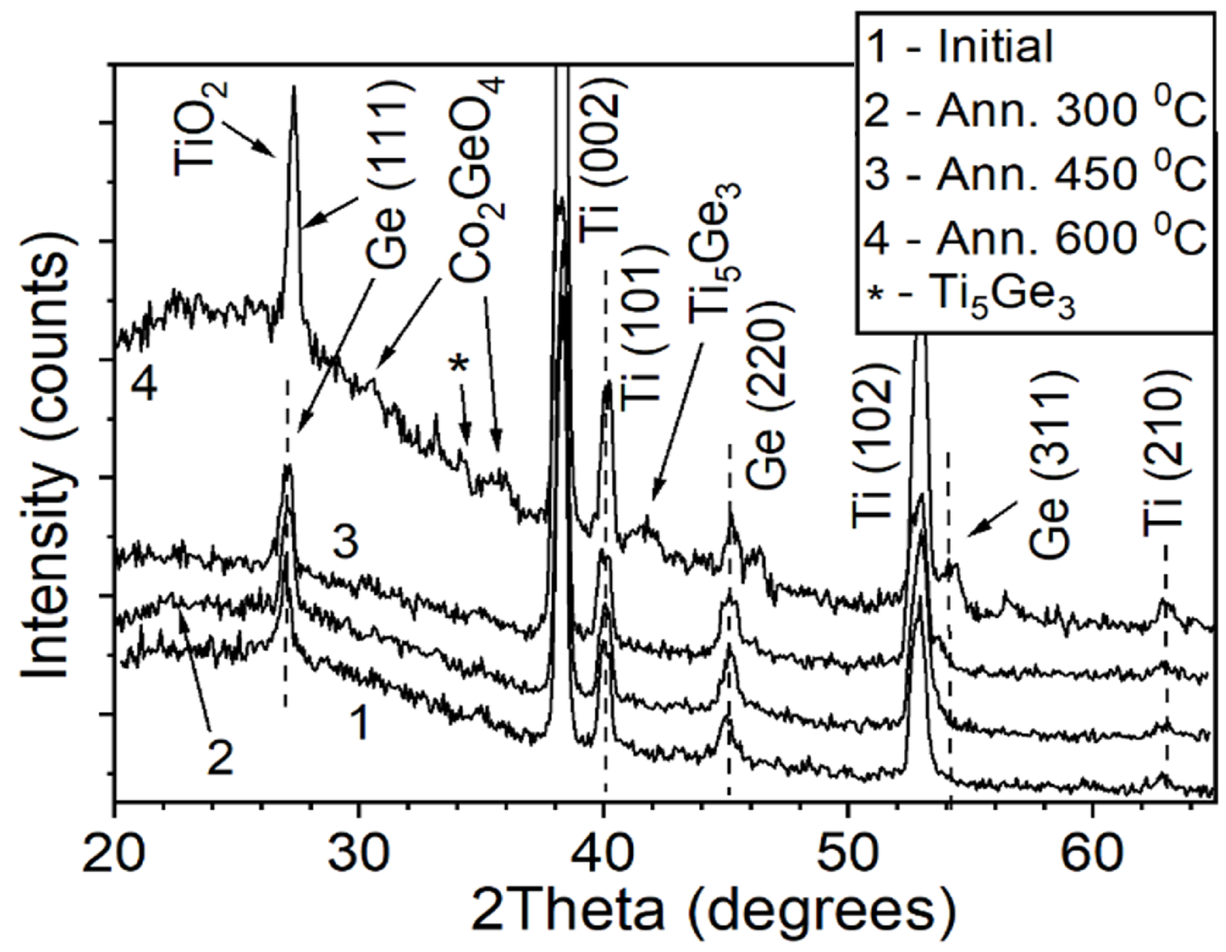

Fig. 2. X-ray diffractograms of Ge-Co samples after annealing at different temperatures.

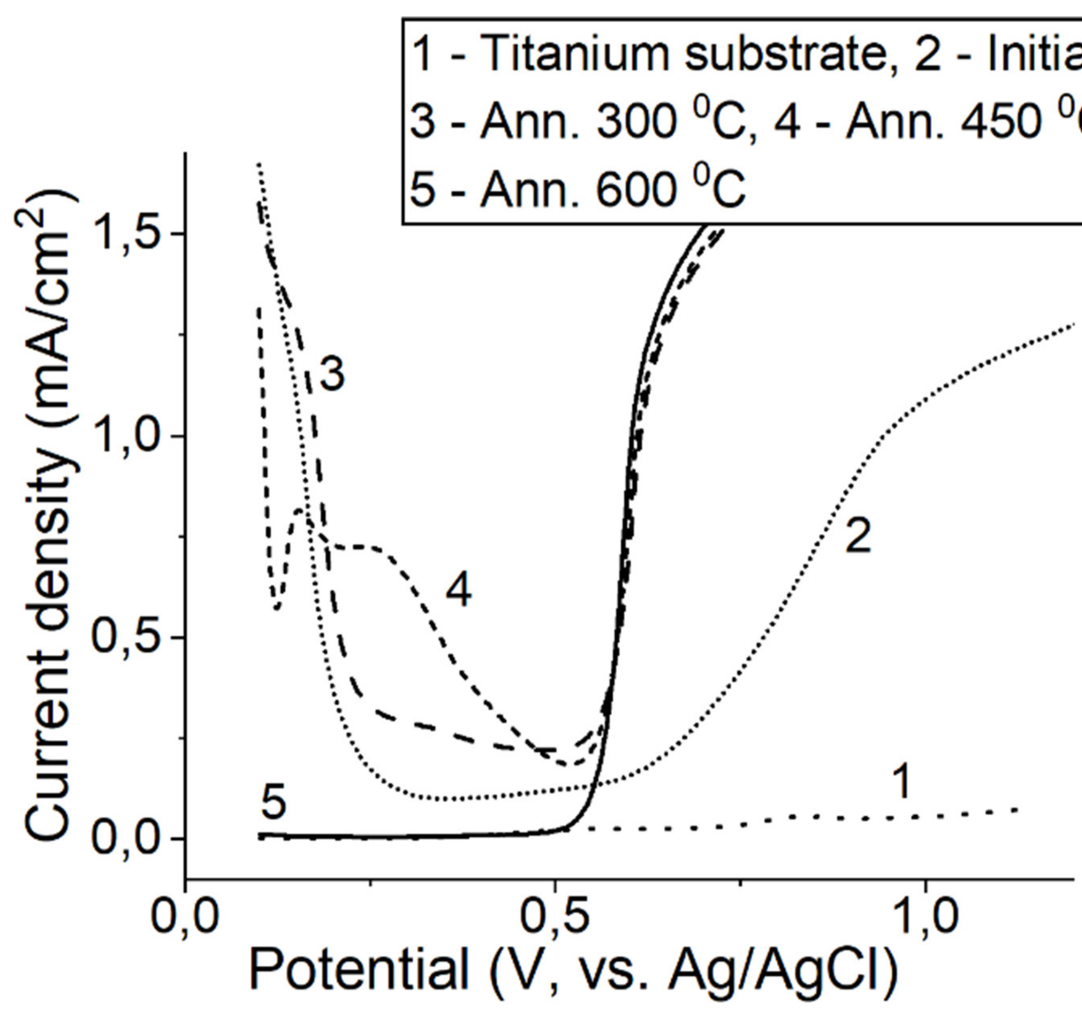

Fig. 3. CV curve of initial/annealing Ge-Co samples and titanium substrate.

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 the same time, with an annealing at 600 °C, reactions caused only with the release of oxygen are observed on the sample 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.

Conclusions

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 and CV curve on an annealing temperature at 600 °C, a compound cobalt germanate Co_2GeO_4 is found that could be a good oxygen evolution catalyst.