Thin-Film Baroresistors Based on Sm$_{1-x}$Gd$_x$S Solid Solutions

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Received June 1, 2020; revised September 7, 2020; accepted September 14, 2020

Abstract—The effect of the Gd concentration on the temperature and pressure coefficients of the resistance of thin polycrystalline films of Sm$_{1-x}$Gd$_x$S solid solutions, where $x = 0, 0.05, 0.1, 0.2, 0.33$, and $0.5$ is studied. The films are grown by explosive evaporation in vacuum of powders of the initial compounds and sedimentation of the latter from the gas phase onto glass substrates. The dependences of the temperature $\alpha$ and pressure $\beta$ coefficients of the resistance are determined, as well as their ratios $\gamma$ on the Gd concentration $x$ in the system of SmS–GdS solid solutions, based on which the optimum compositions for fabricating thin-film piezoresistors and baroresistors are determined.

Keywords: piezoresistor and baroresistor, Sm and Gd concentrations, samarium monosulfide, resistance coefficient

DOI: 10.1134/S1063782621010103

1. INTRODUCTION

For several years, piezoresistive materials based on samarium monosulfide (SmS) have been studied and grown at the Ioffe Physical–Technical Institute. These experiments have shown that some compositions of the SMS–GdS solid solution (SS) system can be promising for fabricating electrical semiconductor sensors of mechanical values on their basis, i.e., piezoresistors and baroresistors. In [1], a strain-sensitive semiconductor material was proposed, which represents SS $\approx 0.6$ mol % Gd in Sm$_{0.994}$Gd$_{0.006}$S with a temperature coefficient of resistance (TCR) of $\alpha = 2 \times 10^{-5}$ K$^{-1}$, i.e., 200 times lower than that of pure SmS at an almost equal piezoresitivity coefficient $K = \Delta R/(R\varepsilon) = 138$, where $\Delta R/R$ is the relative increment of the material resistivity under strain $\varepsilon$. A significant disadvantage of this material is its low resistivity $\rho \approx 8.2 \times 10^{-3}$ $\Omega$ cm, precluding its applicability as a sensitive element of single-crystal high-pressure sensors.

In this paper, we present the results of studying the temperature (in the range of 20–150°C) and pressure (to 0.6 GPa at 20°C) dependences of thin polycrystalline films of the Sm$_{1-x}$Gd$_x$S SS system, performed to consider the possibility of developing highly piezoresistive and baroresistive materials for film electrical sensors of hydrostatic pressure (baroresistors) with TCRs suitable for practical applications.

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2. EXPERIMENTAL

Thin polycrystalline films of Sm$_{1-x}$Gd$_x$S SSs, where $x = 0, 0.05, 0.1, 0.2, 0.33$, and $0.5$ were grown by the explosive (discrete) evaporation of powders of the initial compounds in vacuum and sedimentation of the latter from the gas phase onto glass substrates heated to 400°C [2]. Nickel contacts for subsequent electrical measurements were also deposited in situ onto the polycrystalline films of the synthesized materials formed on the substrates. As a result of completing the technological cycle, 144 films with electrical contacts were grown on four glass substrates (supports) in a vacuum evaporator, which were used as workpieces for piezoresistors and baroresistors. The substrates removed from the setup were cut by diamond disks into individual films on supports, and copper measuring wires were soldered to the nickel contacts; piezoresistors and baroresistors fabricated in such a way were submitted for preliminary control of their resistance. Then the piezoresistor and baroresistor film material was subjected to X-ray diffraction and phase analyses. The results of the study by X-ray methods, i.e., SS lattice constants, X-ray coherent-scattering regions (CSRs), and film phase composition appeared identical to those previously obtained in [3] for the indicated SSs. The film thicknesses, as in [3], were $\approx 5$ $\mu$m.

The temperature dependences of the resistance $R$ of the film piezoresistors and baroresistors were studied in the temperature range of 20–150°C in air in a
thermostat. The samples under study were placed at the thermostat center in an alundum container filled with corundum micropowder (fractions of 3/5 μm) to create a gradient-free thermal field in it during dc electrical measurements.

Based on the dependences $R(T)$ measured for samples of various compositions, their TCR $\alpha(x) = \partial \ln R / \partial T$ were calculated for a temperature range of 20–150°C. The temperature of the samples in the container was measured using a copper—constantan thermocouple; the general temperature in the thermostat was additionally monitored by a mercury thermometer.

To study the pressure dependences of the resistance of the piezoresistors and baroresistors at $T = 300$ K, a compact high-hydrostatic-pressure (to 1.8 GPa) piston chamber (HPC) [4] was used. The samples to be studied were placed on a stand in the HPC. As the medium transferring hydrostatic pressure $P$ to the examined materials, polyethyilsiloxane PES-5 liquid was used [5]. Direct-current measurements of $R(P)$ to 0.6 GPa were performed at $T = 300$ K. The chamber pressure was measured using a high-pressure Mangnin sensor. Based on these dependences $R(P)$, PCRs $\beta = \partial R(P)/\partial P$ were calculated for films of the SSs considered in this study.

3. RESULTS AND DISCUSSION

During the study, Sm$_{1-x}$Gd$_x$S thin films of the above compositions were synthesized, and their standard certification was performed.

For these films, the dependences of the TCR and PCR on the content $x$ of the Gd component doping SmS were constructed. The data obtained are shown Fig. 1.

We begin an analysis of the results obtained with consideration of the dependence of the TCR on the Gd content $x$ in the Sm$_{1-x}$Gd$_x$S SS. Of note is the fact that the room-temperature TCR $\alpha(x)$ rather rapidly decreases in magnitude with increasing $x$; however, it remains negative (which is characteristic of non-degenerate and low-degenerate semiconductors) even when passing through the phase interface (C): semiconductor (I) and intermediate valence (IVS) states of Sm cations (II). This nontrivial fact of the conservation of negative TCRs can be explained under the assumption of the possible transfer of one of the 4f-electrons of the Sm cation to the excitonlike (localized) 5d-level due to a phase transformation actuated by an increase in the Gd-cation concentration $x$ in SSs: above 15 mol % in the bulk samples and 12% in the films [3]. Electrons occupying localized 5d states are injected to the conduction band by heat, thus providing the activation mechanism of electromigration. As the Gd concentration $x$ increases in the system of SmS–GdS SSs, one can observe, first, a decrease in the lattice parameter, which is especially sharp in the region $x \leq 12$% in the films and $\leq 15$% in the bulk samples, i.e., so-called “chemical collapse”; second, the free electron concentration increases, since each Gd cation delivers 1 e$^-$ to the conduction band. As a result of the joint action of the described processes, an electron fraction leaves the localized 5d states of Sm cations to the conduction band, additionally increasing its degree of occupation, thus raising the chemical potential in the material. Upon reaching a certain free electron density, metal conductivity observed in the Sm$_{0.5}$Gd$_{0.5}$S compound at $T = 300$ K is established in the SmS–GdS SS system.

The behavior of the dependence of the PCS on the Gd concentration $x$ in Sm$_{1-x}$Gd$_x$S is similar to that for the TCR $\alpha(x)$ with a small difference that the function $\beta(x)$ does not enter the region of positive values for all studied Sm$_{1-x}$Gd$_x$S compositions. This fact is explained by a change in the structure of the electronic spectrum of the objects under study upon exposure to uniform compression. In this case, the depth of localized 5d states of Sm ions decreases, which promotes retention of the activation mechanism of electromigration in the SSs.

The dependences of the temperature and pressure coefficients of resistance on the Gd concentration $x$ in the Sm$_{1-x}$Gd$_x$S system, obtained in this study, make it possible to determine compositions optimal for fabricating sensitive elements of thin-film piezoresistors and baroresistors. To solve the problem of searching for such compositions for each studied films of Sm$_{1-x}$Gd$_x$S SSs, the parameter $\gamma = \alpha/\beta$ was calculated and the curve $\gamma(x)$ was constructed (see Fig. 2). Of note is the nonmonotonic behavior of the depen-

Fig. 1. Dependence of the TCR and PCR of Sm$_{1-x}$Gd$_x$S SS thin films on the dopant-component content $x$: Gd:I is the semiconductor phase region of SmS–GdS SSs under normal conditions; II is the intermediate valence state (IVS) phase region of Sm cations in SmS–GdS SSs under normal conditions; C is the phase interface.

One can gain insight into the problem of Sm IVS ions in SmS and SSs on its basis with Gd in [6].
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Solid-solution films from region II of phase states exhibit a low sensitivity to pressure (see Fig. 1) and simultaneously low TCRs.

Along with that, they do not undergo phase transformations under uniform compression, hence, can be of interest as materials for developing high-pressure baroressistors (more than say exceeding 0.65-GPa pressure of the phase transition in SmS [6]).

It follows from Fig. 2 that the composition Sm$_{1-x}$Gd$_x$S with $x \approx 0.4$ has a TCR of $\alpha = 0$ and, due to this circumstance, seems promising to develop a temperature-independent baroresistor on its basis.

4. CONCLUSIONS

Based on the results obtained, the range of compositions close to Sm$_{0.9}$Gd$_{0.1}$S was determined, which features high PCRs at a rather weak temperature effect on their resistivity. The applicability of thin polycrystalline Sm$_{0.9}$Gd$_{0.1}$S films as the sensitive element of piezoresistors and baroresistors was indicated.

It was shown that the Sm$_{0.6}$Gd$_{0.4}$S composition should have a close-to-zero TCR, hence, it can be used as a sensitive element in high-pressure film sensors.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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Translated by A. Kazantsev