83

PHYSICAL PROBLEMS OF THE RELIABILITY OF SENSORS BASED ON $A^{II}B^{VI}$ SEMICONDUCTOR COMPOUNDS*

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The development of gas-analytical technology is responsible for the search for new materials for designing chemical sensors capable of replacing traditional sensitive elements in instruments for determination of gases. The high adsorption sensitivity, the comparatively low operating temperatures, the high capacity, and the diversity of the production process make materials based on $A^{II}-B^{VI}$ compounds promising, in particular CdSe and CdS, for preparation of sensors capable of registering the change in concentration of various gases [1]. However, the use of the sensors in practice is constrained by the instability in their operating characteristics. The problem of sensor reliability is important especially because, as a result of placing the sensor and the primary signal processing system on the same substrate, it becomes possible to obtain an intelligent sensor. The goal of this work was to study the processes responsible for the changes over time of the properties of sensors based on cadmium selenide.

EXPERIMENTAL AND DISCUSSION OF RESULTS

The sensors were made using the technology for vacuum deposition of the original material on an insulating substrate [2]. In this case, a film of thickness 1 μm was formed which was equipped with planar indium ohmic contacts. The electrode gap was 2 mm. At the operating temperature, such sensors function mainly under conditions of changing current and resistance when exposed to a variation in gas concentration. We systematized the results of studies of these parameters together with data on simultaneously occurring transformations of the structure of the film sensors. In the initial state (immediately after preparation), the temperature dependences of the conductivity in the region T > 270 K obtained both for d.c. and a.c., have approximately equal activation energies (Fig. 1, curves 1 and 2). From this it follows that in the operating temperature region, the major conduction mechanism is electron transfer along the conduction band. This is confirmed by the absence of a frequency dependence of the electrical conductivity (σ) in this temperature region (Fig. 2, curve 3). One factor determining the conductivity mechanism might be the crystal structure of the material. It was shown previously [3] that in these films, two crystalline phases of cadmium selenide are present, cubic and hexagonal, with predominance of crystallites of the hexagonal modification.

During operation under sensor conditions with temperature elevation in the region T ≥ 370 K, the deviation of its operating characteristics (such as its sensitivity) from the original values is accompanied by an increase in the resistance. These relaxation changes may last hundreds of hours. We simultaneously observe recrystallization of the sensor material to the hexagonal modification [4]. It is reasonable to connect the changes in the sensor properties during use with the structural transformations; however, this does not reveal the mechanism for the deviation of the sensor characteristics (sensitivity, selectivity) from the calculated values.

In the region T > 270 K, the frequency dependence of the conductivity (Fig. 2, curve 2) is characteristic for the case of impurity band conduction [5]. Evidence for this comes from the absence of a temperature dependence for the conductivity in the region T < 270 K for an a.c. electric field (Fig. 1, curves 2-4). The impurity band can be formed by defects acting as electron traps, which are apparent in the thermally-stimulated conductivity spectra of similar samples (Fig. 3, curve 1). As a result of holding the sensor for a long time at the operating temperature, the concentration of electron trapping centers is reduced by at least a factor of ten (Fig. 3, curve 2). Consequently, the signs of impurity conduction are less pronounced (Fig. 2, curve 3). Thus during use of the sensors, simultaneously with the phase

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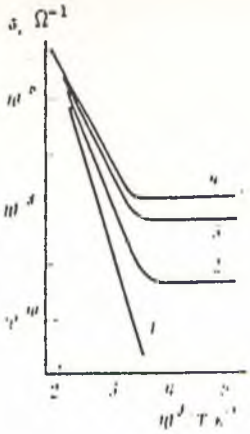

Fig. 1

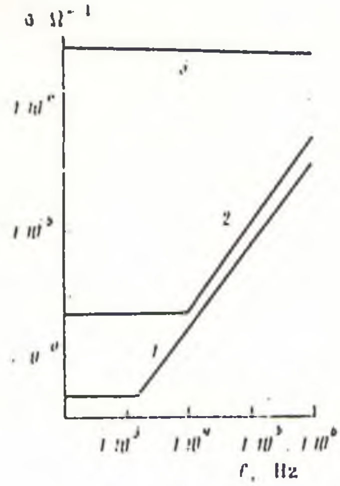

Fig. 2

Fig. 1. Temperature dependence of the dynamic conductivity of a polycrystalline layer of cadmium selenide at different frequencies for an a.c. electric field. Frequency, kHz: 1) 0; 2) 10; 3) 50; 4) 350.

Fig. 2. Dependence of the conductivity of a polycrystalline layer of cadmium selenide on the frequency of the electric field. T, K: 1) 170; 2) 300; 3) 600.

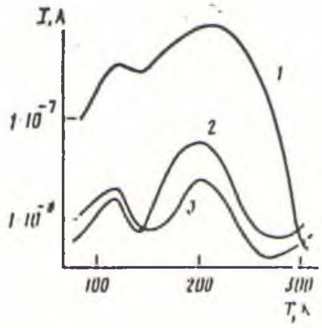

Fig. 3. Thermally-stimulated conductivity of polycrystalline layers of cadmium selenide: measured for three states of the layer. 1) Original state: 2) after vacuum thermal annealing at 500 K; 3) same for 600 K.

transformations there also occurs degradation of the impurity conduction band as a result of the decrease in the concentration of defects responsible for its existence.

In the investigated polycrystalline two-phase layers of cadmium selenide, there are two intercrystallite potential barriers: the Hall mobility of the electrons depends exponentially on the temperature with the exponent (the activation energy) equal to 0.05-0.1 eV. As a result of operation of the sensor at T = 370 K, both the electron mobility ($\mu = 1 \cdot 10^{-3}$ $m^2 \cdot V^{-1} \cdot sec^{-1}$) and the activation energy for its temperature dependence do not change substantially. This is evidence for an insignificant change in the intercrystallite potential barriers during use, which nevertheless may be one factor determining the adsorption properties of the sensor. Consequently, structural transformations and a change in the concentration of energy states in the forbidden gap are the major processes determining the mechanism for the deviation of the sensor characteristics from the operating values during their use.

85

CONCLUSIONS

Analysis of the electrophysical properties of the materials in sensors based on $A^{II}B^{VI}$ semiconductor compounds are evidence that the stability of the structure and the spectrum of the energy states in the forbidden gap exert an indirect effect on the operating parameters of the sensor, in particular the sensitivity and the selectivity. Accordingly, one way to stabilize the sensor parameters may be to form layers with a homogeneous crystalline structure.

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