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PHYSICAL PROBLEMS OF GAS SENSORS' RELIABILITY

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Abstract.–The main physico-chemical processes which influenced the declination of gas sensors' parameters under exploitation from their operating values were investigated.

These parameters are strongly connected with the structural transformations and the changes of band gap states' concentration.

I. INTRODUCTION

The gas-analytic technique development conditions the search for new materials for chemical sensors production. They may be used in the gas analytic devices instead of traditional sensitive materials. The choice of materials is conditioned by many reasons. They are: high adsorptive sensitivity, comparatively low operating temperatures, high output, multivariant technological process. The II-VI semiconductor materials of CdS or CdSe type are those that mostly correspond to the mentioned demands and may be used for the detection of low gas concentrations changes [1].The practical use of sensors made of different materials is restrained by instability of their electrical parameters. If the problem of sensors' reliability is solved, it will become possible to create on one and the same substrate the complex "sensor + primary circuit of data processing", that is an intelligent sensor.

II. EXPERIMENTAL RESULTS AND DISCUSSION

In order to solve the formulated problem of sensors' reliability, the processes causing the CdSe sensor's, parameters changes were investigated.

The studied sensors were made by the vacuum deposition technology with CdSe as basis material like in [2]. The CdSe film with thickness of 1 ÷ 5 μm was deposited on the insulating substrate and fitted with indium ohmic contacts of planar geometry.

This type of sensors operate when the detected gas concentration's variation influences the electric resistance change. While these processes take place at a definite operating temperature which initiates the material's structure transformations, it is necessary, on our opinion, to analyse the complex problem: the electrical parameters changes conditioned by crystal transformations.At the sensor's material initial state (just after preparation) the dark current temperature dependence in the temperature region T>270 K both for direct and alternating current investigations (dc, ac) have exponential type curves with constant exponential indexes (activation energy) (Fig. 1, curve 1, 2).

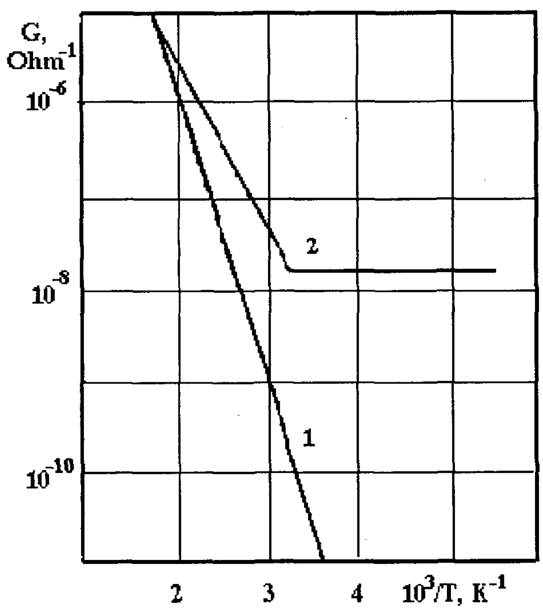

Fig. 1. A. c. conductivity temperature dependence measured for polycrystalline cadmium selenide layers (cubic + hexagonal):
1 - 0 kHz; 2 - 350 kHz.

It means that in the mentioned temperature region electrons are transported within the conduction band. This conclusion is also supported by the fact of absence of G vs f dependence in this temperature region (Fig 2, curve 3).

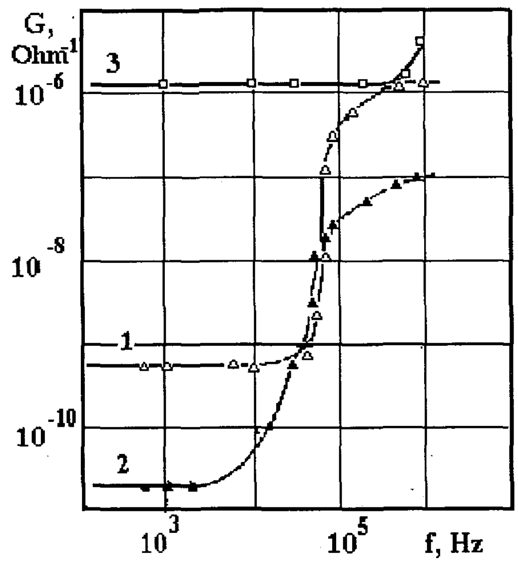

Fig. 2. The frequency dependence of conductivity, measured in hexagonal polycrystalline CdSe layers.
1 - measured at T_1= 130 K
2 - measured at T_2= 300 K
3 - measured at T_3= 600 K

However , it is known that the films contain two crystalline phases - cubic and hexagonal [3], which are not stable at the elevated temperatures. Hence, it seems to be important to compare the peculiarities of the structure changes with the corresponding to them electrophysical features of the sensor's basic material in the investigated temperature range.

If the sensors operate at T > 370 K it causes the structural transformations of the material followed by the current transport changes (e.g. I vs T; I vs ω; etc.). Naturally their working parameters (sensitivity, selectivity) gradually decline from the initial values. These macroscopic changes may last for hundred hours. Simultaneously with the described processes the recrystallisation of the sensor material takes place which is appeared to be the formation of CdSe hexagonal structure [4]. It seems to be natural to try to establish the correlation between the sensor's parameters changes and the corresponding to them crystalline structure's variations in the material.

Further investigations were provided at a.c. In the temperature region T > 270 K conductivity vs frequency dependence may be given by Fig. 2, curve 2. It is shown [5] that such types of G vs f dependence may be explained as the impurity band conductivity. This point of view is supported by the absence of G vs T dependence at a.c. measurements (Fig 1, curve 2) in the same temperature region. The impurity band may often be formed by the defects, which may act as electrons' traps. The latter are detected by the experiments with the thermally stimulated currents (Fig. 3, curve 1).

When the sensors are treated at the operating temperatures for a long time, the decrease of trap concentration by a factor of more then 10 (Fig. 3, curve 2) is registered. All these limited data show that heat treatment, while exploitation, leads to the structure's transformations and impurity band failure, caused by the defect concentration decrease.

At the same time authors take into consideration that the films have a lot of potential barriers at the two crystalline phases boundaries, but nevertheless there are enough of experimental verifications for the above mentioned point of view.

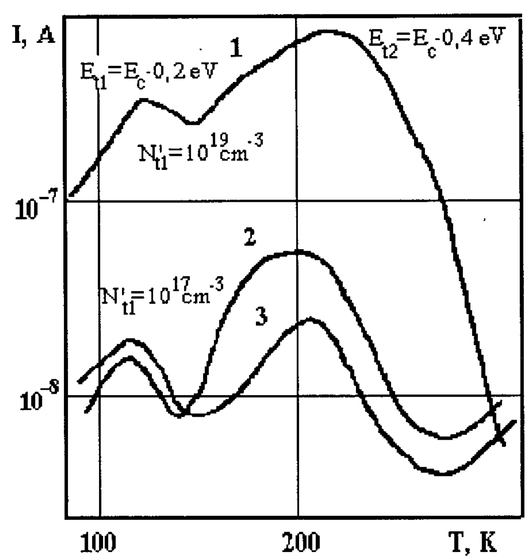

Fig. 3. Spectra of thermostimulated conductivity in polycrystalline CdSe layers:
1 - sample was measured at the initial state (as prepared);
2 - sample was measured after annealing at 450 K;
3 - sample was measured after annealing at 600 K.

Thus, it is concluded that the potential barrier influence on the stability of the sensor's parameters is less than the phase transformations contribution, which causes the defects concentration changes.

The proposed ideas development may become the basis for the technological procedure of the controllable forming of materials with stable properties.

III. CONCLUSION

The authors presented the CdSe layers investigation fulfilled by various experimental methods: thermostimulated conductivity analyses, alternating current conductivity measured at different electric field frequencies together with the structural transformations research. The results obtained were compared with the main operating characteristics of the sensors.

It was established that the principal sensors' electrical parameters deviations correlated with the degradational transformations in electrons' spectrum in the impurity zone of the material and structural changes.

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