

Electronic mechanism for absorptive sensitivity in semiconductor gas sensors

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Abstract

The factors determining the absorptive sensitivity of sensors based on inhomogeneous CdSe semiconductor thin films were investigated. The reproducibility of parameters of gas sensors is the open question in modern physics and technology. In connection with its crystal structure, changes in the films under the action of thermal tensions while the sensor operates were investigated. This approach gave the possibility to formulate the idea on absorptive sensitivity being influenced by electrophysical processes initiated by structural transformations in inhomogeneous systems. As in the majority of contemporary devices, in our gas sensors, the interface between crystallites of two structural modifications of CdSe plays the role of sensitivity active region. It is established that coexistence of two different crystal phases of CdSe leads to potential barrier formation at their boundary that determines the principal peculiarities of current transport in the films and their absorptive features. It is established that in the system investigated, α -CdSe- β -CdSe, the noticeable mechanical tensions of the order 10^5 - 10^6 are created because of the heat expansion coefficient differences between the separate crystallites and the substrate itself. The existence of such significant tensions causes specific structural transformations which cause, at their turn, changes in the gas sensor absorptive sensitivity. Such processes take place due to the fact that atoms-adsorbants change their space position in the crystal lattice and, hence, their energetic position in the forbidden zone of the semiconductor.

The phenomenon described below was related to the so-called effect of anomalous dark current temperature dependence (ADCTD) in polycrystalline layers of CdSe [1, 2]. As it is known [3], in not degenerated semiconductors electroconductivity increases with temperature according to exponential law:

$$G(T) = G_0 \exp\left(-\frac{E_a}{kT}\right) \quad (1)$$

Activation energy E_a , in common, does not coincide with energetic distance from the Fermi level up to the bottom of the conduction band. The increasing dependence of $G(T)$ in agreement with eqn. (1) was often registered in the polycrystalline CdSe layers. In some work [4] it was noted that the activation energy E_a (eqn. (1)) varies in different temperature intervals in CdSe. At the same, time-temperature dependence of electroconductivity in CdSe is often characterized by the decreasing part of $G(T)$, see Fig. 1.

Figure 1 has three curves (1, 2 and 3); 1 and 2 with ADCTD. The curves 1 and 2 were often registered in different semiconductors of the A^2B^6 group. But in that case, only irreversible changes in the conductivity were discussed. In other words, when the sample was heated, then $G = G(T)$ corresponded to curves 1 and 2; but when the heating was stopped and the cooling

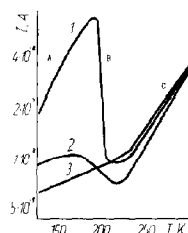


Fig. 1. Temperature dependence of dark current in polycrystalline layers of $(\alpha + \beta)$ -CdSe: (1) sample is at initial structural state (as-prepared); (2) sample is after a second cooling/heating cycle; (3) sample is after 10 following cooling/heating cycles.

commenced, the temperature dependence followed curve 3, and the part of curve with ADCTD was absent.

Irreversible changes in conductivity while heating are related to the different processes in the defect systems of the crystallites, e.g., transition of some defects from the not electrically-active state to the active one, e.g., oxygen adsorption when the acceptor level is formed.

In general, this ADCTD phenomenon including its two components: a reversible one, which is the ADCTD itself and an irreversible (Fig. 1, curve 3) was investigated with the help of a wide spectrum of physical methods: X-ray structural analysis, photoelectrical and optical methods, Hall-effect measurements, frequency depen-

dent conductivity, etc. Further, this phenomenon was also identified in the experiments of the migration of defects under the action of the electrical field. As a result of this, the sample became space inhomogeneous. Results of all mentioned experiments [5] were in good agreement with the point of view that the $G = G(T)$ dependence described in Fig. 1 consists of two components; the irreversible one, which is due to changes in the defect system, will be discussed here.

Analysis of slopes $G = G(T)$ dependences shows that parallel with the existence of CdSe single crystal activation energies, -0.6 eV, the registered energy level was 1.2 eV. Such a great activation energy, which is more than $E_{g/2} = 1.8$ eV for CdSe single crystal, according to our opinion, is connected with stimulation of lattice processes. This is in agreement with the fact that in this same temperature region of investigation (140–300 K) crystal structure transition was registered. The object investigated is CdSe of two crystal modifications, cubic and hexagonal, that exist at one and the same time. This may explain the fact that when the object is being cooled, only the activation energy (0.6 eV) is registered. This value is considered to be caused by the processes in the electron system.

From Fig. 1, curves 1 to 3, it is seen that resistance in the layer increases starts at the first thermocycle up to the last. This increase in resistance is related to the rise in the acceptor's concentration. Hence, electrons may occupy the acceptor levels. Figure 1 demonstrates the results taken at the film at the initiative structural state (as prepared). If this film will be annealed at two temperatures, 450 and 600 K, we may obtain the results shown in Fig. 2. These temperatures are not arbitrarily used. They correspond to two main structural processes which may be stimulated by these heatings. If the as-prepared sample contains two structural phases α and β , the annealing will lead to a crystal-phase transition followed by formation of only the hexagonal phase of CdSe.

According to the results obtained it was evident that the structure investigated has potential barriers, at least

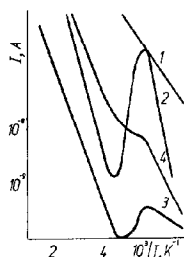


Fig. 2. Dark current temperature dependence of polycrystalline layers of CdSe: (1) initial structural state (as-prepared $\alpha + \beta$ CdSe); (2) structural state after annealing at 450 K; (3) and (4) structural state after two annealings each carried out at 600 K.

of two types. Firstly, potential barriers between two different crystal phases (α and β), and, secondly, between the grain and intergrain space. The results of the thermostimulated conductivity made it evident that in the temperature region investigated two processes take place in the defect subsystem. They are (i) formation of defects which act as acceptors when the sample is lightened, and (ii) acceptors may migrate into the bulk of crystallite from the intergrain boundary. This important conclusion was supported by several independent experiments analysing time intervals necessary for the ADCTD curve, decreasing different speeds of heating and cooling and the resulting hysteresis. All these time intervals were compared with the time necessary for diffusion processes.

Increasing of the defectness of layers investigated at heating and cooling thermocycles is taking place because of the action of forces of mechanical tensions. These tensions may arise because of convergence of α - and β -CdSe lattice parameters, different grains and their boundary parameters [6].

This reason may well explain the processes of migration of defects from intergrain boundary into the grain itself, it takes place at low temperatures, when the stimulating role of heat may be neglected.

Elastic tensions may cause the migration of defects because the action of elastic forces of deformation is the source of energy which is necessary for such migration. When elastic tension forces take place, the prior direction of the motion appears in the crystal system, and therefore defect, having one and the same possibility, may cover more distance than in the case of the arbitrary diffusion process, when such force is absent and all the directions are equally possible. As mentioned earlier, the defect migration may cause the decrease in conductivity as seen in Fig. 1. We have already shown that in the intergrain boundary-acceptor type centres play the most important role, because donor electrons may be captured by them. Availability of such acceptors in the intergrain boundary, and the possibility to change their concentration was shown in the earlier mentioned investigations of photoelectrical phenomena. They are (i) temperature and IR-quenching of photoconductivity, and (ii) photoluminescence. It was shown that such centres are r -type: $E_v + 0.24$ eV.

We suppose that the origin of the forces of elastic tension may cause the formation of the intergrain boundary (IGB) charge. Some ideas on the distribution of such a charge between IGB and the grain itself will be given as well as the electric field distribution in the space. Let us consider that on the surface of IGB and the grain itself there are acceptor-type centres of Q_s^- surface charge density, concentration of acceptor centres in the bulk of crystallite, N_a , and donors, N_d . Some of

these donor electrons are captured by the acceptor centres (in darkness) of the bulk of the grain, the rest of them are in a free state. In n-type semiconductor, as we have for CdSe, an inequality has place $N_d - N_a > 0$. Condition of electrical neutrality for the bulk of the grain is $N_d^+ = N_a^- + n$. When free electrons from the bulk of grain are captured by acceptor-type centres in the IGB, then the electric field E_0 is formed:

$$E_0 = \frac{Q_s}{2\epsilon\epsilon_0} \quad (2)$$

Under the action of this field electrons will drift from IGB to the bulk of the grain. The bulk density of not compensated positive charge near IGB will be equal to n . Then the electric field variation with the coordinate may be defined from

$$\epsilon\epsilon_0 \frac{dE}{dx} = en \quad (3)$$

We are taking into consideration only an example when the electric field is perpendicular to the IGB surface, and the surface itself has a coordinate equal to 0. Solvation of this equation for half-space $x \geq 0$ is:

$$E(x) = \frac{enx}{\epsilon\epsilon_0} - A \quad (4)$$

Using E_0 from eqn. (2) and solving to x we shall find:

$$x = \frac{Q_s}{2ne} \quad (5)$$

where x is a linear dimension of the space charge region in the bulk of the crystallite.

For typical figures of $Q_s/e = 10^{11} \text{ cm}^{-2}$ and $n \sim 10^{16} - 10^{17} \text{ cm}^{-3}$, we shall obtain $X \sim 10^{-5} - 10^{-6} \text{ cm}$, that is much more less than L (linear dimension of the crystallite). Evaluation of the value of space charge region corresponds to the data obtained from dynamic conductivity experiments. Hence, the main electric tension falls in the IGB region and, therefore, injection of electrons into IGB may be realized. So, for our case, an equality must be fulfilled $Q_s \ll enL$, or $l \ll L$ (Fig. 3).

Having defined $E(x)$, we may find the value of potential barrier, from the expression for potential distribution, $\varphi(x)$:

$$E(x) = - \frac{d\varphi}{dx} \quad (6)$$

Taking into consideration $E(x)$ from eqn. (4) and integrating x in the limits from 0 to L we shall obtain that the potential barrier height E_{drift} is:

$$E_{\text{dr}} = e[\varphi(x) - \varphi(L)] = \frac{Q_s^2}{8\epsilon\epsilon_0 n} \quad (7)$$

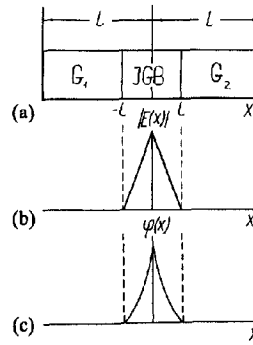


Fig. 3. (a) Principle scheme of the system, consisting of two grains and their intergrain boundary; (b) absolute value of electrical field tension changes, caused by negatively charged acceptors in the IGB space; (c) electrical potential changes in the intergrain boundary space.

Now we may evaluate the value of the barrier height according to eqn. (7), supposing $Q_s/e = 2 \times 10^{11} \text{ cm}^{-2}$, $n = 10^{16} \text{ cm}^{-3}$, $\epsilon_0 = 8.87 \times 10^{-14} \text{ F/cm}$, $\epsilon_{\text{CdSe}} = 10$, then $E_{\text{dr}} = 0.09 \text{ eV}$, that correctly coincide with independent experiments of dynamic conductivity in a wide range of electric field frequencies.

These results also support our supposition concerning the acceptor-type centres variability. In order to vary the potential barrier height with 0.05 eV, it is necessary to vary charge Q_s on these centres in IGB for 20%, hence, the possible interval of E_{dr} values may be covered by slight changes of Q_s . Alteration of acceptor-type centres concentration takes place because of the plastic deformations in the system crystallite-IGB space. In our semiconductor, the most possible acceptor-type centre may be V_{Cd} . This defect may have double negative charge. V_{Cd} was determined by us in recombination processes and voltage-current investigations. The processes described are determined as a structural sensitive phenomenon.

References

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