

# The sensitization of semiconductor gas sensors

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## Abstract

In this paper the sulphur dioxide response on a CdS-based thin-film gas sensor, deposited by spray pyrolysis, has been studied. It is found that for 5–30 ppm of sulphur dioxide the sensitivity of the films increases considerably with the applied electric field  $E = 2 \times 10^2$  V/cm between the electrodes. Such behaviour cannot be explained in terms of a simple adsorption theory. The increase of sensitivity is pointed out to be closely connected with the relaxation processes, which destroy the electrical homogeneity of a sample. A phenomenological theory of the observed sensitization of the semiconductor film to acceptor gas, based on the creation of a negative charge region near the anode and the occurrence of adsorption–desorption processes on the charge surface, is suggested. The breakdown of electrical homogeneity is confirmed by potential probe experiments. The experiments show that the sensitivity increases by a factor of 5 to 10 in comparison with the characteristic sensitivity in the region of low electric field and Ohmic current–voltage relationship. The results obtained can be used in the manufacture of a semiconductor gas sensor.

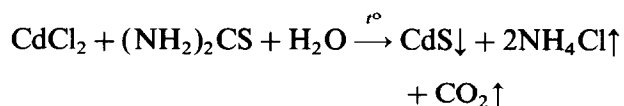
## 1. Introduction

During the adsorption of gases on the surface of a semiconductor, changes of equilibrium carrier concentration near the surface occur. For example, when adsorption of a reduction gas, i.e., donor gas, takes place on an n-type adsorbent, the electrons from the adsorbed atoms or molecules transfer to the semiconductor, thus increasing the concentration of free carriers and the conductivity of a sample. When an oxidizing, or acceptor, gas adsorbs on the surface of an n-type semiconductor, the number of carriers and the conductivity decreases. The values of these changes give information about the presence of different gases in the environment and enable their concentrations to be defined. Many semiconducting oxides, such as SnO, SnO<sub>2</sub>, ZnO, CdO, Cu<sub>2</sub>O, WO<sub>3</sub> and their mixtures, show resistance changes in the presence of ppm concentrations of many gases in air. Wide-gap metal oxides are useful, because of the high sensitivity of their conductivity to various dopants. It has been shown that the wide-gap semiconductors, like CdS, can also be used as gas detectors [1]. Although they are characterized by short times of adsorption–desorption processes and selectivity, semiconductor detectors also require a high degree of stability, which is not easy to achieve. The rapid desorption process concerns the applica-

tion of semiconducting sensors at rather high temperatures,  $T \geq 400$  °C. Such temperatures often cause the degradation of the semiconductor. That is why investigations on new structures, which are sensitive to gases at lower temperatures, are of great importance.

## 2. Experimental

In this paper the influence of sulphur dioxide on the adsorption sensitivity of CdS and CdSe thin films was investigated. Thin films of CdS were obtained by spray pyrolysis on substrates, heated to 480 °C in air, by the chemical reaction



and also by vacuum evaporation. The CdSe layers were deposited only by evaporation. All films were deposited on glass and quartz substrates. The concentrations of CdCl<sub>2</sub> and (NH<sub>2</sub>)<sub>2</sub>CS in solution were chosen in such a way that the S/Cd ratio in the spray-deposited films was equal to one. The resistivity of the films was in the range 10<sup>8</sup>–10<sup>12</sup> Ω cm. Film thicknesses were 0.3–0.5 μm, which was comparable to the Debye length in order to avoid shunting of the surface of the

sample by its volume. Evaporated indium was used for contacts. All the contacts used were found to be Ohmic and to have symmetric behaviour with respect to the voltage polarity. The adsorption sensitivity to a fixed concentration of sulphur dioxide was defined by the change of conductivity of a sample and was measured as the ratio  $\sigma/\sigma_0$ , where  $\sigma$  is the conductivity of a sample in the presence of  $\text{SO}_2$  in the test chamber, and  $\sigma_0$  is the conductivity of a sample in ambient air. The concentration range of  $\text{SO}_2$  was 5–30 ppm. During the experiments the temperature of the layer was kept constant, but it could be changed from 25 to 400 °C.

Great attention has been given to investigations of the homogeneity of the semiconducting layers. Such investigations were made by probe experiments with the help of a light probe. The light probe was formed by a slit diaphragm, which was imaged on the sample. The width of the slit image on the sample during the experiments was 0.01 mm and it could travel across the sample in steps of 0.02 mm. The current–voltage measurements and probe experiments were carried out in the experimental chamber under controlled pressures from atmospheric to  $5 \times 10^{-5}$  Torr.

### 3. Results and discussion

The experiments show that the CdS films sprayed on glass substrates are sensitive to microconcentrations of  $\text{SO}_2$  in ambient air. The operating temperature was 95–100 °C. The changes of conductivity during the CdS– $\text{SO}_2$  interaction are shown in Fig. 1. It was found that the adsorption sensitivity of the films depends considerably on the applied voltage. Figure 2 shows the current–voltage curves of CdS films measured in different ambients. The layers demonstrated sensitivity to  $\text{SO}_2$  only under applied voltages corresponding to the superlinear section of the  $I$ – $V$  characteristic, but not under voltages within the Ohmic region. Besides this, the distinctive feature of such films is the increasing relaxation of conductivity with applied voltage beginning from 10–15 V. The increasing relaxation of the conductivity was not observed in the films deposited on quartz substrates. The  $I$ – $V$  characteristics of these films were Ohmic in the whole range of applied voltages and there was no response of the film to sulphur dioxide. Thus the close rela-

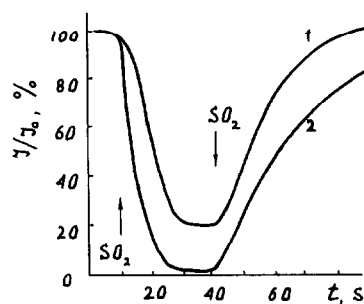


Fig. 1. Changes in current as a function of adsorption and desorption of  $\text{SO}_2$  (15 ppm) vs. time for a CdS film deposited by spray pyrolysis. Curve 1,  $d = 0.1$  cm, measured under  $V = 50$  V at 100 °C. Curve 2,  $d = 50$   $\mu\text{m}$ , measured under  $V = 50$  V at room temperature.

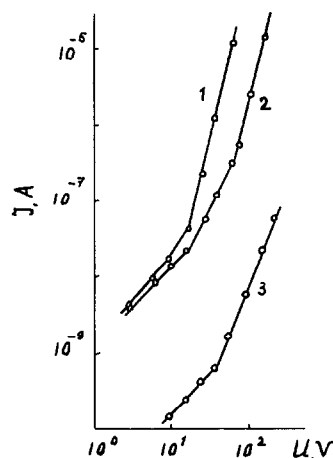


Fig. 2. Log–log plot of the steady-state current vs. voltage for CdS pyrolysed samples. Curve 1,  $d = 0.1$  cm, measured in air at 100 °C. Curve 2,  $d = 0.1$  cm, measured in  $\text{SO}_2$  (15 ppm) at 100 °C. Curve 3,  $d = 50$   $\mu\text{m}$ , measured in  $\text{SO}_2$  (15 ppm) at room temperature.

tionship of relaxation processes in sprayed CdS films and their adsorption sensitivity to sulphur dioxide were demonstrated experimentally.

The instability of the dark conductivity in semiconducting layers of II–VI compounds has been investigated in many papers. It was shown that such relaxation phenomena may arise from the migration of mobile defects in the semiconductor with the formation of electrical inhomogeneity in the interelectrode space [2, 3]. Taking into account the possibility of creating such inhomogeneity in the investigated samples after relaxation has taken place, probe experiments were carried out. The light probe with a width of 0.01 mm crossed the interelectrode space (0.1 cm) and indicated the existence of a region of high resistance formed near the anode, as shown in Fig. 3. Thus, near the anode the electric field reaches the value  $10^3$  V/cm, which is sufficient for the development of a space-

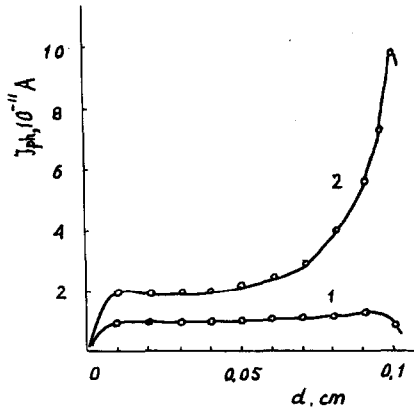


Fig. 3. The distribution of photocurrent caused by a light probe with width 0.01 mm in the interelectrode space of the CdS pyrolysed film. Curve 1, measured under  $V = 2$  V at room temperature before relaxation of conductivity occurs. Curve 2, measured under  $V = 2$  V at room temperature after relaxation of conductivity has occurred.

charge-limited current (SCLC). This injection current causes the superlinear section of the  $I-V$  curves. It is characteristic that the application of alternating voltage (with frequencies of 100 Hz–20 kHz) makes it impossible to form an isolating layer near one of the electrodes and leads to the correct linear  $I-V$  curve, because the averaged electric field within the whole interelectrode space does not exceed  $10^2$  V/cm, which is insufficient for the appearance of SCLC. The close connection between adsorption and relaxation phenomena is justified by the fact that there is no sensitivity to  $\text{SO}_2$  under an alternating voltage up to 300 V. Such behaviour cannot be explained in terms of a simple adsorption model, because there is no dependence between the adsorption sensitivity and the frequency of the applied voltage.

The experiments conducted allow us to assume that in order to achieve high sensor sensitivity to the investigated gas, the regime of SCLC is necessary. To justify this assumption, samples with 50  $\mu\text{m}$  interelectrode spacing were made on identical films of CdS and CdSe. Such an interelectrode width corresponds to the width of the isolating layer near the anode formed by the relaxation process. The curves in Fig. 2 represent the  $I-V$  curves of such samples, which are superlinear, as expected. In this case, the injected current is stable, because of the small distance between the electrodes. It is interesting that superlinear  $I-V$  curves are now also observed in the films deposited on

quartz substrates. All these samples demonstrate a high adsorption sensitivity, as shown in Fig. 1.

As can be seen, the experiments show unambiguously the importance of the SCLC regime for the stimulation of adsorption sensitivity. However, the injection of carriers from the contact must not exert a direct influence on their capture by the adsorbed molecules.

The experimental data can be explained as follows. The direct result of the injection current flow in the sample is an increase of free majority-carrier concentration in the semiconductor. This effect has been investigated most intensively. But it must be noted that the increase of free-carrier concentration is related to its transfer from the metallic contact. This causes the material to be charged. The charge of injection carriers may be quite large. Such an injection charge can be evaluated in two ways. The slope of the  $I-V$  curve at the given voltage  $V'$  is determined by the differential conductivity of the sample,  $G_{\text{dif}}$ . In the superlinear section of the  $I-V$  characteristic this conductivity is a function of the applied voltage and can be defined from the experimental curves in Fig. 2 by

$$G_{\text{dif}} = \left. \frac{\Delta I}{\Delta V} \right|_{V'} \quad (1)$$

$\Delta I$  and  $\Delta V$  are the changes of current and voltage, referred to the working point  $V'$ .

On the other hand,  $G_{\text{dif}}$  is also given by

$$G_{\text{dif}} = \sigma \frac{Lh}{d} = en\mu_n \frac{Lh}{d} \quad (2)$$

Here  $\sigma$  is the conductivity of the material,  $e$  is the electronic charge,  $n$  is the concentration of electrons,  $h$  is the thickness of the semiconducting film,  $L$  is the electrode width,  $d$  is the interelectrode space and  $\mu_n$  is the electron mobility.

If the carrier mobility of the material is known, the excess carrier concentration  $n_{\text{inj}}$ , injected into the sample, can be determined. Thus, the density of excess charge is given by

$$\rho_{\text{inj}} = en_{\text{inj}} = \left. \frac{\Delta I}{\Delta V} \right|_{V'} \frac{d}{\mu_n Lh} \quad (3)$$

where  $\mu_n = 0.5 \text{ cm}^2/\text{V s}$ . For curve number 3 in Fig. 2 and a voltage  $V = 10^2$  V, such a calculation gives the value  $0.3 \text{ C/m}^3$ . However, the real density of injected charge may be larger, because of a partial capture of charge by the electron trapping states. This charge does not participate in the

current flow. The total density of injected charge can be defined by the method suggested in ref. 4 using the formula for a plate capacitor. According to this formula, the electrodes represent the plates of the capacitor and the semiconductor represents the dielectric:

$$\rho_{\text{inj}} = \frac{\epsilon\epsilon_0 V}{d^2} \quad (4)$$

where  $\epsilon$  is the permittivity and  $\epsilon_0$  is the permittivity of free space. For the same point  $V'$  of the experimental  $I-V$  curve, eqn. (4) gives the value  $3.5 \text{ C/m}^3$ , which is expected to exceed the value obtained by taking into account only mobile carriers.

Therefore, the indirect result of the injection current in a thin film is the storage of considerable negative charge. The influence of uncompensated charge on its adsorption sensitivity is known and described elsewhere [5]. According to ref. 5, the stimulation or reduction of the adsorption sensitivity depends on the type of semiconductor and on the sign of the additional uncompensated charge that was brought into the semiconductor, and also whether the gas is a donor or acceptor. In our case, both CdS and CdSe are n-type semiconductors, the injection charge is negative and  $\text{SO}_2$  is an acceptor gas. It follows [5] that in such a case, stimulation of the adsorption sensitivity must take place, as has been shown experimentally. The degree of adsorption sensitivity is conditioned by the electric field near the charged surface. In our case of main carrier injection from the electrode, the electric field above the surface of the semiconductor, for the value of uncompensated charge stated above, is  $10^3 \text{ V/cm}$ . This electric field is sufficient to give a considerable increase of adsorption sensitivity.

It is necessary to explain one more experimental fact. As shown above, the increasing relaxation of the current and superlinear current-voltage curve was observed only for films deposited on glass substrates and not for quartz substrates. The glass, being a multicomponent material, can serve as a dopant source for the CdS film. It is noted [6] that

one of the basic components of glass is Na, which has rather a high mobility in cadmium sulphide. However, quartz substrates provide film stability and, therefore, an isolating layer is not created near the anode. So, injection and adsorption sensitivity can be observed for samples with a small interelectrode space.

#### 4. Conclusions

The experiments conducted illustrate the phenomenon of sensitization in CdS and CdSe semiconductor thin films to an adsorbing acceptor gas,  $\text{SO}_2$ . The application of rather a large voltage to the semiconductor causes a relaxation process, which forms a narrow region of increased resistance near the anode. The concentration of electric field in this region causes the SCLC regime in the sample. As the result of electron injection, the CdS film acquires a large negative charge, which stimulates the adsorption sensitivity to acceptor gases. The conditions for stimulation may be created artificially by a small space between the electrodes, which is necessary for the realization of SCLC.

The results obtained can be useful in the manufacture of semiconductor gas sensors.

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