

Dependence of sensitivity and reproducibility of CdS oxygen sensors

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Abstract

The electrical conductance of the CdS-based sensors increased or decreased when exposed to CO or SO₂ gases, depending on the operation temperature and stoichiometric composition of the film. A correlation between the IR spectrum and inversion of the chemisorbed complex charge state was observed. This is considered to be a favourable basis for the detection of atmospheric pollutants in ambient air, by combination of two sensor systems.

Introduction

Success in the fabrication of semiconductor gas sensors is linked to sensors based on metal oxide structures characterized by improved sensitivity, stability and quick response time. The rapid desorption processes which occur during the application of semiconducting sensors at rather high temperatures, often cause a degradation of the semiconductor. Therefore, investigations on new structures which are sensitive to gases at lower temperatures are of great importance. It has been shown that the wide-gap semiconductors, like CdS, can also be used as low-temperature gas detectors [1].

On the other hand, in real circumstances, sensors have to detect the presence of one or several chemical compounds. The actual problem is lack of selectivity and this impedes industrial utilization of such sensors.

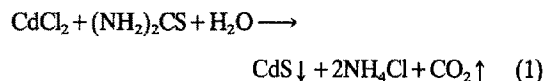
To overcome this problem, chemically selective bulk materials and surface membranes which can respond to the desired substance must be developed. Their structure must be such that specific interaction between the sensor and the molecular products to be detected, leads to a physicochemical change in the detector which can be measured by a coupled physical transducer. Direct measurement of this physical change is often not possible [2].

Improving the selectivity and sensitivity of semiconducting sensors gave rise to the development of sensor fusion in order to obtain non-negligible improvements of these fundamental parameters. Sensor arrays have been recognized to have a certain interest also in the chemical sensing frame, in conjunction with pattern recognition, that yields essential advantages for the identification and monitoring of gases in robotics [3].

This paper deals with a model that is useful for the design and evaluation of those systems based on sensors characterized by low selectivity and different sensitivities to CO and SO₂ gases. The gas sensors based upon CdS thin films have been studied in a low-temperature operating regime.

Sensor manufacture

The sensors are deposited by an electrohydrodynamical spray of 0.01-0.06 M solutions of CdCl₂ and (NH₂)₂CS on a glass substrate heated at 670-750 K in air:



Variation of the stoichiometric composition of the films with Cd/S ratios of 5/1 (type I sensors) and 1/5 (type II sensors) was achieved by mixing the initial solutions in different concentrations. The films were controlled by XPS and mass spectra analysis. The grain size of the investigated films obtained with SEM observation was about 100 nm and was comparable with the Debye length.

Evaporated indium was used for the contacts. All the contacts used were found to be ohmic and had symmetric behaviour with respect to the voltage polarity.

The resulting films are highly sensitive over the entire visible part of spectrum and show steep ampere-lux characteristics. A quite intense absorption band at 0.58 to 0.60 μm, the result of CO chemisorption, was

observed. The resistivity of the films was in the range 10^8 – 10^{12} Ω cm.

The experimental procedure consists in measuring the change in conductivity after modification of the CO and SO₂ concentration in a dry gas mixture with N₂, by exchange of gas atmosphere at constant pressure. During the experiments, the temperature of the layers was kept constant, but it could be changed from 280 to 500 K. IR measurements were performed using IKS-29 and Perkin–Elmer-577 spectrometers. The XPS experiments were carried out with a VG ESCALAB MkII spectrometer. An Al K α radiation source (1486.6 eV) was used for the photoelectron excitation in the base pressure of the analysis chamber $P=10^{-8}$ Pa. The surface of the films was cleaned by ion sputtering, using a rastered and differentially pumped Ar⁺ gun at 1.5–2.0 keV and $P=10^{-5}$ Pa.

Results and discussion

The investigation of semiconducting gas sensors is usually based on the measurement of the integral characteristics (e.g., conductivity, surface potential, etc.). These integral parameters change during the chemisorption process and can be interpreted within the theory of solids [4]. Recent research of chemisorption processes revealed a dual response induced by different gases in the conductance of the oxide and A₂B₆ films [1, 5]. It must be noted, that such a behaviour could not be explained in terms of a simple adsorption theory.

Some samples of CdS were studied by IR spectroscopy [6]. However, for further progress in the application of these semiconductors for gas sensing investigations of the interaction between the tested gas and the semiconductor surface must be made. At present, in order to link collective electronic parameters of the bulk and local characteristics of the chemisorbed complex, the CO chemisorption on CdS films surface has been studied by the IR spectroscopy combined with measuring the electrical properties of the samples.

Electrical measurements

Figure 1 illustrates the dependences of the sensitivity of sensors with the Cd/S ratio equal to that of the dry gas mixtures, N₂/2 \times 10⁵ ppm O₂ (curve 1) and N₂/10 ppm SO₂ (curve 2), as a function of the temperature. The sensitivity (β) of the sensors was calculated as the ratio of conductivity values in adsorbed (σ) and desorbed (σ_0) states of the sensor, $\beta = \sigma/\sigma_0$. Curve 1 indicates considerable sensitivity to oxygen over the entire temperature interval, with maximum at 440 K, due to the change in the chemisorption reaction of SO₂ on the CdS film surface. For curve 2, the temperature of the sample was increased to 570 K.

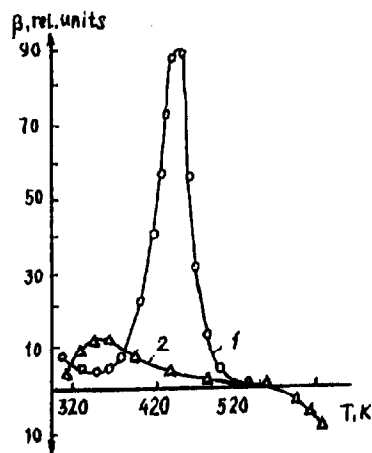


Fig. 1. Sensitivity of CdS-based sensors with Cd/S ratio equal to that of the dry gas mixtures N₂/2 \times 10⁵ ppm O₂ (curve 1) and N₂/10² ppm SO₂ (curve 2), vs. temperature.

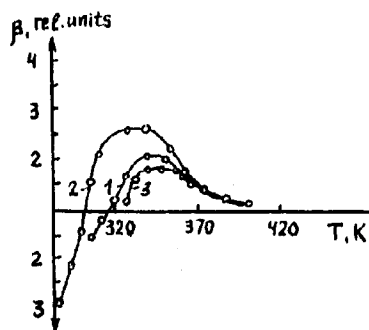


Fig. 2. Sensitivity of CdS-based sensors with Cd/S ratio equal to one (curve 1), 5/1 (curve 2) and 1/5 (curve 3) to dry gas mixture N₂/100 ppm CO vs. temperature.

Figure 2 shows the temperature-stimulated behaviour of β of sensors with a Cd/S ratio equal to one (curve 1) type I and type II sensor (curves 2 and 3). For the sensors with a Cd/S ratio equal to one, the CO causes a decrease in the conductivity in the temperature range of 280 to 320 K. Operating temperatures > 320 K cause a changing in the type of CO chemisorption from oxidizing to reducing, with maximum sensitivity at 350 K.

There was an influence of the stoichiometric composition on the character of the chemisorption processes, which is closely connected with a change in the basic type of surface adsorption centres. Enriching of the surface by metallic intrinsic species (type I sensors) caused a shift of curve $\beta(T)$ to the low-temperature interval (curve 2). The temperature of inversion of this type of reaction was found at ~ 300 K. At the same time, an increase in sensitivity over the entire temperature interval was observed. Changing of stoichiometric composition towards the prevalence of sulfur

(type II sensors) led to the disappearance of the oxidizing type of CO chemisorption and to a decrease in donor-type influence on σ in the temperature range of 320 to 370 K.

Implications of spectral features

The XPS spectrum measurements, after the chemisorption of gas mixture $N_2/2 \times 10^8$ ppm O_2 on a hot sample, show the presence of two components of O (1s) line, situated at $E_b = 531.7 \pm 0.2$ eV and $E_b = 531.1 \pm 0.2$ eV. 15 min of thermal outgassing at 320 K and etching of the surface by Ar^+ ions ($P = 15$ Pa, $I = 3$ mA) caused a shift of the peak at $E_b = 531.7$ eV, while the value of the second one did not change significantly. The parallel usage of XPS and mass spectra of the thermal desorption in the case of CdS samples demonstrated that the O (1s) peak at $E_b = 531.1$ eV corresponds to the chemisorbed atomic oxygen and $E_b = 531.7$ eV to the chemisorbed molecular oxygen. In all the investigated cases the increase in the concentration of cadmium on the sample surface led to an increase of the concentration of the chemisorbed oxygen. This suggests that the metal atoms are the basis centres of the chemisorption of oxygen on the investigated films.

The strongest IR spectral features, discussed here, were obtained during the exposure of sensors to the dry gas mixture $N_2/100$ ppm CO. CO contact with type I sensors at 290 K produced peak development in the 2090–2110 cm^{-1} region. At the same time, a decrease in the conductance of the sensor was observed. Increasing the operating temperature above 320 K caused a shift of the spectral features to 2140 cm^{-1} , and was accompanied by an inversion of the type of CO chemisorption from oxidizing to reducing. The type II sensors featured a lower intense peak at 2140 cm^{-1} only and accordingly an increase of the conductance during exposure to the CO mixture. Inversion of the charge state of the chemisorbed complex from negative to positive was observed also on type I sensors, when the partial pressure of CO was increased from 5 to 100 ppm.

The obtained experimental data can be explained in terms of model involving correlation between local characteristics of chemisorbed complex (i.e., configuration and location of border orbitals) and collective electronic parameters of the grain (i.e., value of surface band bending the Fermi level position in the band gap). The oxidizing type of reaction on type I sensor is supposed to be connected with CO chemisorption on reduced interstitial superstoichiometric metallic species (Cd_i). The transfer of an extra electron to the antibonding orbital ($2\pi^*$) of a CO unidentate stretch leads to significant weakening of the C–O bond and is attributed to the typical band in 2090–2110 cm^{-1} region

[6]. Increasing the operating temperature above 320 K caused a considerable reduction of the presence of electrons on the border orbitals of metallic species and, hence, a shift of Fermi level towards the middle of the band gap. Thus, electron transfer from bonding orbitals of CO stretch to the corresponding by configuration vacant orbitals of bare surface cations becomes energetically more preferable. The resulting donor-type chemisorption has been attributed to the spectral feature at 2140 cm^{-1} .

In the case of a change in the stoichiometric composition towards the prevalence of sulfur (type II sensors), the essential decrease of reduced Cd_i defects led to the disappearance of the oxidizing reactions and corresponding CO stretch spectral feature at 2090–2110 cm^{-1} , and promoted chemisorption of CO on surface bare cations with a high degree of coordination in the crystalline lattice.

The inversion of the charge state of the chemisorbed complex with an increase of CO partial pressure can also be explained in the framework of the suggested model and may be connected with sequential interaction of CO molecules with cation adsorption sites, when Cd_i defects became completely occupied.

Conclusions

The constructed CdS-based thin-film sensors showed high sensitivity to SO_2 , CO and O_2 at low temperatures, without catalysis on the surface that usual complicates the identification of substances.

The inversion of the type of chemisorption reaction was observed at different operating parameters and stoichiometric compositions of the films. XPS and IR studies of the gas sensors combined with measurements of the electrical properties allowed the basic adsorption sites to be determined and suggested a model of CO interaction with bare surface metallic intrinsic species with different degrees of coordination in the crystalline lattice.

Since, the inversion of the response signal at different partial pressures of oxygen was not observed, this is considered to be a favourable basis for the specific detecting of typical atmospheric pollutants (CO, SO_2) in ambient air, using the information available from signals combination of sensors array prepared or operated at different regimes. The obtained signals were transformed into the feature space to give concentration-independent but substance-specific features.

Recent research revealed a dual response induced by different gases in the conductances of the resistive sensors [1, 5], therefore future development fields are an extension of the model application to a wider range of components.

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