Oxygen interaction of CdS-based gas sensors with different stoichiometric composition

V. Golovanov [a], V. Smyntyna [a], G. Mattogno [b], S. Kačiulis [b], V. Lantto [c]

[a] Faculty of Physics, Odessa State University, Pastera 42, 270100 Odessa, Ukraine
[b] Istituto di Chimica dei Materiali, CNR, CP 10, via Monterotondo, 00016 Rome, Italy
[c] Microelectronics Laboratory, University of Oulu, Linnanmaa, 90570 Oulu, Finland

Abstract

The interaction of oxygen with surfaces of CdS thin films with different stoichiometric compositions was studied by X-ray photoelectron spectroscopy (XPS) and thermal-desorption mass spectroscopy observations combined with conductivity measurements. Three different types of film with different atomic ratios of Cd/S were used in the study of oxygen chemisorption in a low-temperature range between 300 and 570 K. Spray pyrolysis was used for the deposition of the films on glass substrates; XPS and energy dispersive spectroscopy of X-rays together with atomic force microscopy and scanning electron microscopy were used for the characterization of the composition and structure of the films. It was possible to distinguish different temperature ranges for the thermal desorption of the different adsorbed oxygen species. A comparison of the data from XPS and mass-spectroscopy observations with conductance measurements allows to conclude that metallic surface atoms are responsible for different interactions of oxygen species with CdS surfaces.

Keywords: Gas sensors; Cadmium sulfide; Oxygen interaction

1. Introduction

It is well known that many of II–VI compounds semiconductors can be used for gas-sensing applications [1]. The basic characteristics of such semiconductor gas sensors are their integral parameters (e.g., conductivity, surface potential, etc.), which are changing during the chemisorption processes and can be interpreted within the range of the band scheme of the semiconductor. However, an atomistic understanding of the sensing mechanism during the adsorption–desorption processes is not clear at present. Therefore, the chemisorption of oxygen on surfaces of a prototype material such as CdS in the form of this films was studied in a low-temperature operating interval (300–570 K). Indeed, CdS films provide a suitable model system because: (i) they have well-known structure; (ii) their bulk properties are well known; (iii) they show high photo- and chemi-sensitivity, and (iv) it is possible to vary widely the elemental composition on the surface and the Fermi level position in the band gap.

The X-ray photoelectron spectroscopy (XPS) has proved to be unrivalled in giving direct information on the composition and structure of semiconductor surfaces. In order to study the oxygen interaction of CdS thin films, having different elemental compositions in the bulk and on the surface, were analysed by XPS, energy dispersive spectroscopy of X-rays (EDS) and atomic force microscopy (AFM) experiments combined with conductivity measurements.

2. Experimental

CdS thin films were deposited by an electro-hydro-dynamical spray pyrolysis of 0.01–0.06 molar solutions of $CdCl_2$ and $(NH_2)_2CS$ on a glass substrate, heated at 670–750 K in air, by the chemical reaction:

$$CdCl_2 + (NH_2)_2CS + 2H_2O \longrightarrow$$

$$CdS + 2NH_4Cl + CO_2 \quad (1)$$
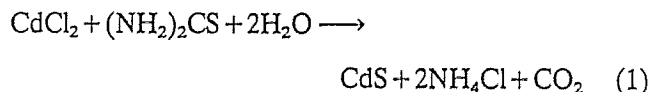
A variation in the surface composition of the films with different Cd/S ratios (from XPS measurements) of 3.2 (I-type films), 2.4 (II-type films), and 1.6 (III-type films) was obtained by mixing the initial solutions in different proportions, where the ratios of Cd/S ions

were 10:1, 1:1 and 1:10, respectively. The average grain size of the films, from AFM observations, was 100–200 nm. The atomic ratios of Cd/S in the bulk of the films, from EDS measurements, ranged from stoichiometric (III-type films) to ~2 (I-type films).

The samples were mounted in a test chamber and dry gas mixtures were allowed to flow through the chamber at a fixed flow rate. The desired temperature (300–520 K) was obtained by heating the films in an oven. Temperature-stimulated d.c.-current measurements were performed with a heating and cooling rate of 2 K/min in a dry gas mixture containing 2×10^5 ppm of oxygen in nitrogen (synthetic air).

The XPS analysis was carried out in a VG ESCALAB MK II spectrometer, at $p \leqslant 5 \times 10^{-8}$ Pa. A differentially pumped Ar^+ gun was used to clean the sample surfaces at 2–3 keV ion energy. A standard Al $K\alpha$ X-ray source ($h\nu = 1486.6$ eV) was used for XPS measurements. The binding energy (E_b) scale was calibrated by measuring Au $4f_{7/2}$ and C(1s) reference peaks. A least-square routine was used in the peak fitting for the analysis of the O(1s) core levels. The accuracy of the measured E_b values was ± 0.2 eV. A digital Micro-PDP computer system and the VG S5250 software were used for recording and processing of the spectra. Oxygen, at atmospheric pressure, was chemisorbed on the CdS surfaces in the preparation chamber for 0.25–5 h at 300 K and 0.25–2 h at 500 K. Thermal annealing in UHV at around 550 K for 0.3–4 h was also used for the cleaning of the film surfaces. In addition to the XPS measurements, the mass spectroscopy (the Baltzers QMG-12 quadrupole spectrometer) was used for the analysis of thermal-desorption species.

3. Results and discussion

Results from temperature-stimulated current measurements (at a voltage of 1 V) of a II-type film as a function of inverse temperature are shown in Fig. 1.
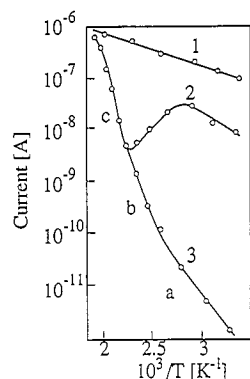

Fig. 1. Current (conductance) of a II-type CdS film as a function of inverse temperature, measured (1) in pure N_2 and in dry synthetic air (after exposure at 300 K) during (2) heating and (3) cooling with a rate of 2 K/min.

Curve (1) represents the current response of a freshly deposited film in pure nitrogen. An exposure of the film to oxygen at 300 K for 2 h led to a decrease in the current and to a sigmoid behaviour of dark conductivity during heating of the film (curve (2)). The cooling back to 300 K caused a considerable decrease in the current (curve (3)), and the form of the curve (3) was reproducible during the heating and cooling cycles in synthetic air. The Arrhenius' slopes corresponding to the activation energy of conductance are 0.2 eV for curve (1) and 0.6, 0.9 and 1.3 eV for the three parts (a), (b) and (c) of curve (3), respectively. The initial low-resistive state of the film was possible to restore by annealing at 500 K in pure nitrogen. Thus, a reversible chemisorption of oxygen species was observed. The part (a) of curve (3) was also reproducible during a heating–cooling cycle between 300 and 360 K in nitrogen, while the heating in nitrogen above 360 K led to a hysteresis in the conductance behaviour, originating from desorption processes.

Fig. 2 shows the sensitivity of I-, II- and III-type CdS films to oxygen in nitrogen as a function of the temperature. The sensitivity (β) was calculated as the ratio of conductances measured in nitrogen and in dry synthetic air. The curves show a considerable sensitivity to oxygen over the entire temperature range with a maximum at around 440 K. A decrease of the cadmium amount at the surface (III-type films) led to an increase in β in the temperature range of 300–400 K.

The mass spectrum of residual gases in the vacuum chamber contained standard peaks of nitrogen, oxygen, etc., and also peaks of hydrocarbons from the diffusion pump oil. The state of the CdS-film surfaces had also a significant influence on the amplitude of the 16 and 32 a.m.u. signals. The peaks at 14 and 28 a.m.u. did also change slightly with the surface changes. During annealing of the high-resistive films in vacuum ($p = 10^{-6}$ Pa), the amplitude of the 32 a.m.u. signal decreased to zero after annealing of 5 min at 440 K, but the amplitude of the 16 a.m.u. signal was still substantial. An increase of the annealing temperature up to 500 K led to an essential decrease in the peak amplitude
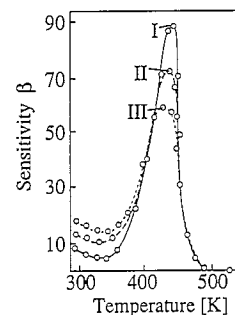

Fig. 2. Sensitivity (β) of I-, II-, and III-type CdS films to oxygen (2×10^5 ppm) in nitrogen (conductance ratios between nitrogen and synthetic air) as a function of temperature.

of the 16 a.m.u. signal. After a repeated exposure of films to oxygen atmosphere, the initial amplitude of the 32 a.m.u. signal in the mass spectrum was restored.

Mass-spectroscopy observations from CdS thin films during thermal desorption of oxygen in Ref. [2] show two temperature ranges for oxygen desorption: (i) a low-temperature range (300–400 K) with an activation energy of 0.9 eV, and (ii) a high-temperature range (400–500 K) with an activation energy of 1.3 eV, related to O_2^- and O^- oxygen species, respectively. The Arrhenius' slopes in Fig. 1 give similar activation energies for conductance at about the same temperature ranges, while the part (a) in curve (3) may be connected with the thermal activation of electrons from some crystal defects. Observed changes with temperature in the 16 and 32 a.m.u. signals in the mass spectrum may be related to different temperature ranges for the thermal desorption of atomic and molecular oxygen.

The values obtained for the binding energies of the O(1s) electrons $E_b = 531.0 \pm 0.2$, 531.8 ± 0.2 and 532.8 ± 0.2 eV from the fitting of XPS spectra, measured from CdS films, show reversible changes during the adsorption–desorption cycles. Fig. 3 shows the XPS spectrum of the O(1s) line measured from a freshly deposited I-type film after exposure in oxygen atmosphere at 300 K together with a peak fitting. Two components of the O(1s) line at $E_b = 531.8$ and 532.8 eV were found from the peak fitting procedure. An annealing of the freshly deposited film for 2 h in oxygen atmosphere at 470 K decreased the peaks at $E_b = 531.8$ and 532.8 eV, while, at the same time, a peak at $E_b = 531.0$ eV increased substantially as is shown in Fig. 4.

The O(1s) peak at $E_b = 531.8$ eV was assigned to the molecular form of oxygen chemisorption in Refs. [3,4]. The peak at $E_b = 531.0$ eV may be related to atomic oxygen. This is in agreement with the experimental results in Ref. [5]. The peak at 532.8 eV may originate from adsorbed water [6]. Fig. 5 shows the

Fig. 4. XPS spectrum of the O(1s) line measured from a freshly deposited I-type CdS film after exposure of 2 h to oxygen at 470 K together with a peak fitting of three different oxygen species.
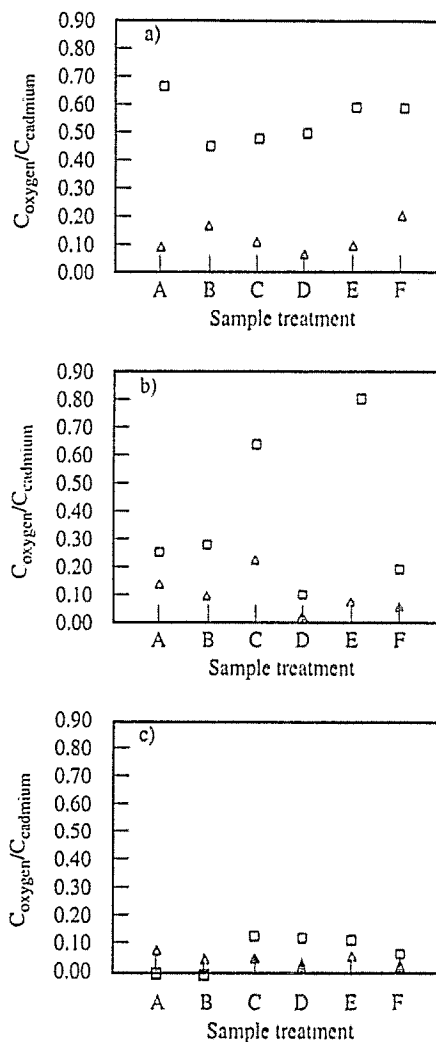
Fig. 5. Atomic concentration ratios $c_{oxygen}/c_{cadmium}$ for three different oxygen species with (a) $E_b = 532.8$ eV; (b) $E_b = 531.8$ eV, and (c) $E_b = 531.0$ eV, obtained from XPS peak fitting results for (□) I-type and (△) III-type CdS films after different treatments: (A) freshly deposited films; (B) after Ar$^+$ ion sputtering; (C) after exposure for 2 h in oxygen at 470 K; (D) after second Ar$^+$ ion sputtering; (E) after exposure for 2 h in oxygen at 300 K; (F) after annealing for 2 h at 570 K in UHV.
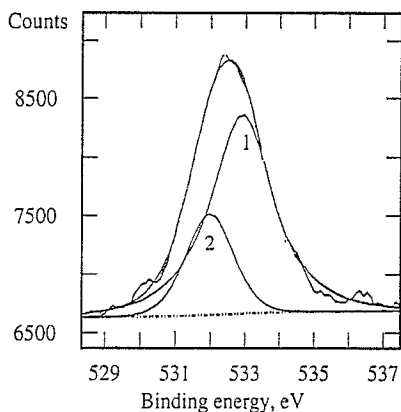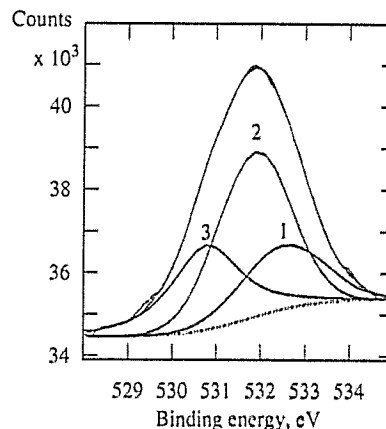

Fig. 3. XPS spectrum of the O(1s) line measured from a freshly deposited I-type CdS film after exposure to oxygen at 300 K together with a peak fitting of two different oxygen species.

amount of different oxygen species, corresponding to the peaks at 531.0, 531.8 and 532.8 eV, for both the I-type and the III-type films after different treatments. The amounts are given as atomic concentration ratios $c_{oxygen}/c_{cadmium}$ for different oxygen species, obtained from the O(1s) line fitting. It is shown in Fig. 5 that the surface composition of the films had a strong influence on the chemisorption of oxygen. Relative atomic concentrations at the film surfaces were obtained using a usual XPS quantification routine. In spite of the essential differences in the concentrations of Cd and S ions in the initial solutions (from 10:1 to 1:10), the surfaces of the films had always a prevalence of the metal component with atomic ratios of Cd/S from 3.2 (I-type films) to 1.6 (III-type films).

For the freshly deposited I-type films in Fig. 5 (treatment A), the XPS ratio of the total oxygen amount to cadmium was around 0.9, but only around 0.25 in the case of the III-type films. The amount of oxygen in Fig. 5(a), corresponding to $E_b = 532.8$ eV, is insensitive to different treatments, but the amount of the species in Fig. 5(b) with $E_b = 531.8$ eV is very sensitive to the film treatment, especially in the case of the I-type films. Both the Ar^+ ion sputtering and annealing in UHV are shown to decrease the amount of the species at $E_b = 531.0$ eV and, especially, those at $E_b = 531.8$ eV.

The coordination and charge state of different surface sites are of great importance for chemisorption and catalysis. The enrichment of the films with cadmium (I-type film in Fig. 5) increased the amount of chemisorbed oxygen. This fact permits to conclude that cadmium atoms at the surface are the basic centres for the chemisorption of oxygen on the surface of the investigated films.

The atoms with lowest coordination on the surface are the most reactive towards the interaction with gas phase. On such 'active centres', reactions take place with appreciably reduced activation energies. These atoms or groups of atoms normally represent a modest fraction of the total number of the exposed ones and are thought to be located on the edges, steps, corners or other defects of the microcrystals or microparticles. The I-type films, enriched by cadmium atoms, are characterized by a high number of nearest-neighbour pairs present on such edges, steps, corners and other surface defects, where the coordination number can be exceptionally low. Conversely, at the surface of III-type films cadmium atoms are basically with higher coordination at the crystal faces. For that reason, different features in XPS spectra, measured from films with different surface compositions, may be considered in terms of the interaction of adsorbates with surface cadmium atoms having different coordination.

The position of O_2^- species on the $(10\bar{1}0)$ surface of ZnO (the same wurtzite crystal structure as the CdS films) was calculated in Ref. [7] by minimizing the potential energy from attractive Coulomb interactions between surface metal atoms and the centres of the negative charge in the O_2^- molecule. The most favourable position for O_2^- was found to be above two adjacent zinc atoms. On the other hand, the maximum XPS ratio of total oxygen amount to that of cadmium on the I-type films was found to be about 0.9, which nearly corresponds to an interaction where an oxygen molecule interacts with each pair of surface cadmium atoms. The results in Fig. 5(b) show that a decrease of the surface concentration of cadmium by a factor of two led to a decrease in the concentration of the oxygen with $E_b = 531.8$ eV (molecular oxygen) by a factor of 10 or more after exposure to oxygen at 300 K (treatment E).

4. Conclusions

The different results from XPS, thermal-desorption mass spectroscopy and conductivity measurements support the interpretation, that a dissociation of the molecular oxygen ion takes place with increasing temperature on CdS thin-film surfaces as suggested in Ref. [8]. The appearance of a new peak at $E_b = 531.0$ eV from the O(1s) peak fitting of XPS spectra at higher temperatures (470 K in Fig. 4) may be related to the atomic oxygen ion. The strong hysteresis in conductivity values in Fig. 1 between the heating and cooling runs below 450 K may be also related to the dissociation of molecular oxygen ions. The Arrhenius' slopes in Fig. 1 give about the same activation energies for the film conductance, 0.9 eV in the temperature range of 300–400 K and 1.3 eV in the range of 400–500 K, that were also observed from mass spectroscopy observations for molecular and atomic oxygen species in the same temperature ranges, respectively. It was also found, from XPS results, a strong increase in the amount of different oxygen species with increasing Cd/S ratios on the film surfaces, which means that cadmium surface species are the basic centres for oxygen chemisorption on CdS film surfaces.

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