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## Surface spectroscopy study of CdSe and CdS thin-film oxygen sensors

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### Abstract

Two principal forms of oxygen chemisorption on the surface of CdSe and CdS gas sensors have been revealed by X-ray photoelectron spectroscopy and thermal desorption mass spectrometry experiments. For the chemisorbed  $O_2^-$ , the characteristic binding energy of the O 1s electrons is found to be  $531.8 \pm 0.2$  eV and for the chemisorbed  $O^-$ ,  $531.1 \pm 0.2$  eV. The concentration of the chemisorbed oxygen increases when the surface of the investigated sensor is enriched or doped with metal atoms.

**Keywords:** Cadmium selenide, Cadmium sulphide, Oxygen sensors, Surface spectroscopy, Thin films

### 1. Introduction

It is well known that many II–VI semiconductors can be used for gas-sensing applications, e.g., detection of oxygen [1–6]. Usually the conductivity of these sensors is changed significantly when an oxidizing gas is chemisorbed on the semiconductor surface heated up to  $T=370$ – $470$  K. For example, the conductivity of CdS and CdSe sensors is reduced to  $10^{-2}$ – $10^{-3}$  of its initial value [6,7]. An electrical current flowing through the sensor during oxygen chemisorption decreases logarithmically with time and the current-saturation time changes from 30 to 300 s in the temperature range  $T=370$ – $420$  K [8]. It follows from Ref. [9] that a higher surface-donor concentration must lead to an increase of chemisorption sensitivity. Such an effect was observed experimentally in the case of CdSe sensors doped with In [10]. In fact, by doping CdSe and CdS films, the sensitivity can be increased up to 100 times [11,12].

The basic parameters determining the quality of any gas sensor are the sensitivity and selectivity. However, methods for the control of these parameters are not sufficiently developed. The investigations in this field are mostly based on the measurements of macroscopic parameters (e.g., conductivity, surface potential, etc.).

These parameters are altered during the chemisorption process and the changes can be interpreted within the framework of semiconductor band theory [1–5].

CdSe and CdS surfaces have also been investigated previously by photoemission spectroscopy (see, e.g., [13–15] and refs. therein). Nevertheless, further progress in the application of these semiconductors for gas sensing may be achieved by analysing directly the interaction between some gas (e.g., oxygen) and the semiconductor surface. In the present paper basic forms of oxygen chemisorption on the surface of CdSe and CdS thin films were studied by X-ray photoelectron spectroscopy (XPS) and thermal desorption mass spectrometry (TDS) with the aim of applying these films for oxygen detection. The basic centres of oxygen chemisorption were determined and the relationship between the nature of the chemisorption centres and the form of chemisorbed oxygen was analysed on the basis of obtained experimental results.

CdSe films with thickness  $d \approx 0.5 \mu\text{m}$  were prepared by thermal evaporation in vacuum ( $10^{-3}$  Pa) onto unheated glass, ceramics and metal substrates. The film deposition rate was  $0.1 \mu\text{m min}^{-1}$ , more details on the deposition-process conditions have been published elsewhere [4,5]. The data on the chemical composition and structure of the films have been reported in Ref. [16]. The experimental results coincided qualitatively for all the substrates [4,5,8], therefore only metal substrates

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were used subsequently. The use of metal substrates enabled us to decrease considerably the effect of sample charging in XPS experiments. CdS films were made by an electrohydrodynamic spraying of liquid [17] onto glass substrates heated up to  $T=670$  K.

## 2. Results and discussion

### 2.1. CdSe films

XPS analysis of the oxygen interaction with the CdSe film surface was carried out by using a Varian IEE-15 spectrometer. The spectrometer was operated at a pressure of  $P=1.5 \times 10^{-6}$  Pa and an Mg  $K_{\alpha}$  X-ray source (1253.6 eV) was used for the photoelectron excitation. The peculiarity of this experiment consisted in the simultaneous use of the XPS and TDS techniques. TDS mass spectra were registered by using a Balzers QMG-12 quadrupole.

The film surface was cleaned by  $Ar^+$  ion etching ( $E=50\text{--}100$  eV,  $I=3$  mA) at pressure  $P=20$  Pa. High-purity oxygen was introduced into the chamber through a leak valve. Then the standard procedures of XPS and TDS were carried out.

The mass spectrum of the residual gases in the vacuum chamber featured the usual peaks of nitrogen, oxygen, etc., including the hydrocarbons from the diffusion pump oil. The state of the sample surface had a significant influence on the amplitude of the 16 and 32 a.m.u. signals; also the peaks at 14 and 28 a.m.u. changed slightly. During the annealing of the films in vacuum ( $P=10^{-6}$  Pa) the amplitude of the 32 a.m.u. signal decreased down to zero level (see Fig. 1, curve 2) in 5 min after a sample temperature of 570 K was achieved; at the same time the amplitude of the 16 a.m.u. signal remained substantial.

The XPS spectrum of the O 1s line measured after the TDS of molecular oxygen contained a peak at

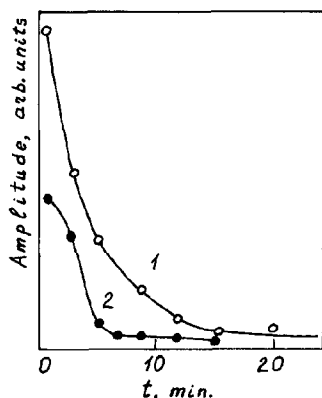


Fig. 1. Time dependence of the amplitude of atomic (1) and molecular (2) oxygen peaks in mass spectra measured during thermal outgassing of the CdSe film at  $P=10^{-6}$  Pa,  $T=570$  K.

binding energy  $E_b=531.2 \pm 0.2$  eV (see Fig. 2, curve 1). It can therefore be related to the chemisorbed oxygen atoms. This finding coincides with earlier experimental results [13,18].

After repeated exposure of the sample to oxygen, the initial amplitude of the 32 a.m.u. peak in the mass spectrum was restored and the O 1s line was shifted towards  $E_b=531.7 \pm 0.2$  eV (see curve 2 in Fig. 2), which is related to the molecular form of oxygen. This chemisorption of molecular oxygen was confirmed by the following experiment. After 15 min of thermal outgassing (Fig. 1, curve 1), when the basic chemisorbed form turned out to be  $O^-$ , the surface was etched by  $Ar^+$  ions ( $P=15$  Pa,  $I=3$  mA) and then exposed to vacuum ( $P=10^{-6}$  Pa). As a result, the peak at  $E_b=531.7$  eV, attributed to the chemisorption of molecular oxygen, was restored (curve 2 in Fig. 2).

The different films evaporated onto the unheated substrates have been prepared from an initial powder of pure CdSe (samples #4 and #9) or from a powder enriched with cadmium (sample #11). Their surface composition was modified by  $Ar^+$  ion etching and by the evaporation of cadmium or indium. The corresponding results ( $E_b$  of the oxygen line and relative atomic concentration of oxygen) are listed in Table 1.

The relative atomic concentration of oxygen was calculated by using the usual XPS quantification routine, including Wagner's energy dependence of the attenuation length (see [19] and refs. therein). On the surface of the CdSe films evaporated from the stoichiometric powder (sample #4), the basic form of chemisorption was atomic, corresponding to the O 1s line at 531.2 eV. If during the growth of such films the surface enrichment in Cd occurred due to growth-process pe-

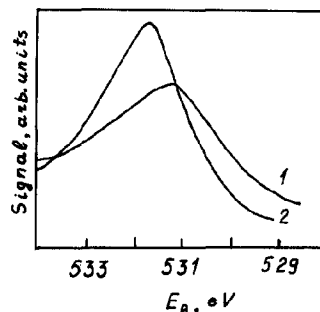


Fig. 2. XPS spectra of the O 1s line of CdSe films: 1, after 10 min of thermal outgassing at  $P=10^{-6}$  Pa,  $T=570$  K; 2, initial sample.

Table 1  
Binding energies ( $E_b$ ) and relative atomic oxygen concentrations of different CdSe samples

Sample #	4	9	11
$E_b$ (eV)	531.2	532.6	531.7
O conc. (%)	61.7	69.3	84.4

cularities (sample #9), it led to the prevalence of the weak absorption of oxygen with  $E_b = 532.6$  eV, attributed to adsorbed hydroxyl groups. The enrichment of the initial sample (#4) with cadmium (#11) caused the transition from atomic ( $E_b = 531.2$  eV) to molecular ( $E_b = 531.7$  eV) chemisorption. The previously mentioned surface enrichment with Cd also resulted in the increase of total adsorbed oxygen amount, as demonstrated above.

From these results we can deduce that the basic centres of oxygen chemisorption are the metal atoms. This assumption is confirmed by the TDS mass spectra of the films doped with metal. The sharp decrease of chemisorbed atomic oxygen concentration (see curves 1, 2 in Fig. 3) and the simultaneous increase of chemisorbed molecular oxygen (see curves 4, 5 in Fig. 3) in the films doped with cadmium indicate that the centres of molecular oxygen chemisorption are the cadmium atoms. The role of the metal atoms as centres of molecular oxygen chemisorption was finally confirmed by doping the film surface with indium, after which the amplitudes of the 32 and 16 a.m.u. signals became approximately equal (curve 6 in Fig. 3).

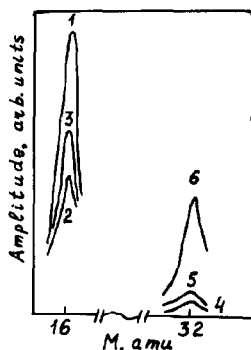


Fig. 3. TDS mass spectra of atomic (1–3) and molecular (4–6) oxygen in CdSe: 1,4, initial undoped surface; 2,5, surface enriched with Cd; 3,6, surface enriched with In.

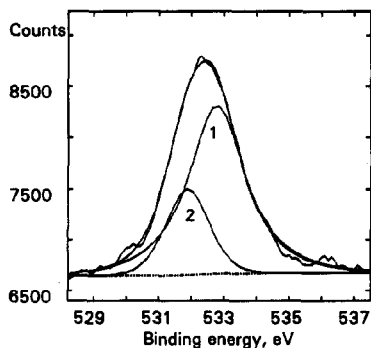


Fig. 4. XPS spectrum of O 1s line of untreated (initial) CdS film. Curves 1 and 2 are the peaks of the two oxygen species obtained by a peak-fitting routine.

## 2.2. CdS films

The samples of CdS were prepared for the measurements by using the same procedures as in the case of CdSe films. Two types of CdS films (a-type and b-type) produced by electrohydrodynamic spraying of liquid were investigated in the present work; the ratios of initial components were Cd:S=10:1 for a-type and Cd:S=1:10 for b-type.

XPS measurements, oxygen chemisorption and sample annealing were carried out in a VG ESCALAB MkII spectrometer. An Al  $K_{\alpha}$  radiation source (1486.6 eV) was used for the photoelectron excitation at the base pressure of the analysis chamber ( $P=10^{-8}$  Pa). The films were cleaned by ion sputtering, using a rastered and differentially pumped  $Ar^{+}$  gun operating at  $E=1.5\text{--}2.0$  keV and  $P=10^{-5}$  Pa.

A typical spectrum of the O 1s line is shown in Fig. 4 together with peak fitting. Two components of the O 1s line, obtained by the peak fitting, are situated at  $E_b = 533.0$  eV (adsorbed water and/or hydroxyl groups) and 531.8 eV. The relative concentration of molecular oxygen species with  $E_b = 531.8$  eV is more than twice the concentration of the other species (see Fig. 5(a,b)). The ratio of the total oxygen concentration to cadmium can be easily reduced to the value 0.66–0.75 by sample annealing in ultrahigh vacuum (2 h at  $T=570$  K) or ion sputtering. Both of these treatments resulted in the prevalence of the oxygen species with higher binding energy (Fig. 5(a,b)). Analysed O 1s spectra demonstrated that the general decrease of the oxygen concentration on the surface is caused by a decrease of the species with lower  $E_b$ , while the concentration of the second species is not changed significantly.

The increase of the sulphur concentration in the initial solution (b-type of film) reduces the total concentration of chemisorbed oxygen (Fig. 5(a)–(c)). In this case the highest ratio of oxygen concentration to cadmium does not exceed the value 0.3–0.35 (see Fig. 5).

Both types of films treated with oxygen at atmospheric pressure for 2 h produced qualitatively modified O 1s spectra (Fig. 6). In addition to the two oxygen species described above, a third peak at  $E_b = 531.0$  eV was separated by using a peak-fitting routine (curve 3 in Fig. 6). This peak can be attributed to chemisorbed atomic oxygen species [20]. Sample annealing in ultrahigh vacuum (2 h at  $T=570$  K) or surface cleaning by ion sputtering resulted in a considerable decrease of the chemisorbed oxygen concentration, mainly due to the decrease of chemisorbed species with  $E_b = 531.0$  and 531.8 eV (Fig. 5(b,c)).

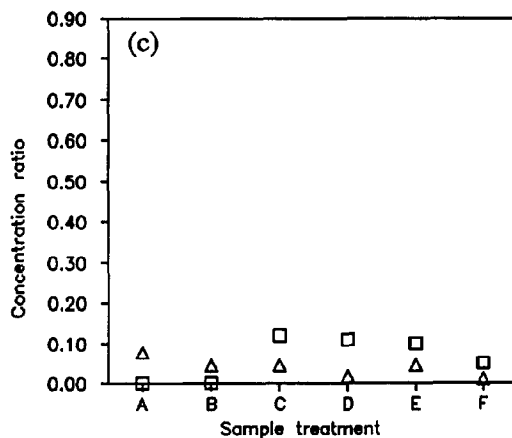
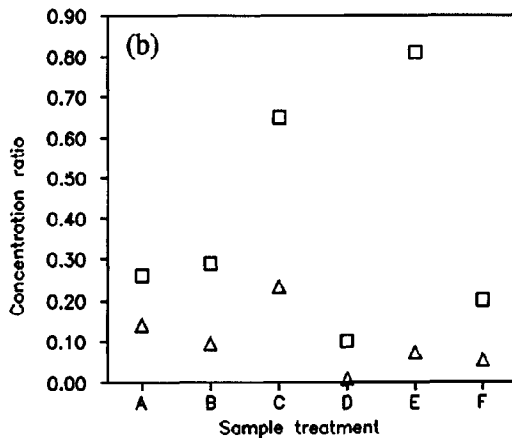
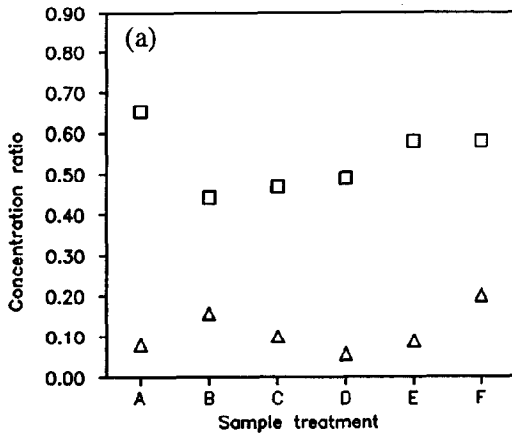


Fig. 5. Atomic concentration ratios  $C_{\text{oxygen}}/C_{\text{cadmium}}$  of the different oxygen species in differently treated CdS films, calculated by XPS peak fitting: (a) species with  $E_b = 533.0$  eV; (b)  $E_b = 531.8$  eV; (c)  $E_b = 531.1$  eV. Squares, CdS film of a-type; triangles, b-type. Sample treatments: A, initial (untreated); B, after  $\text{Ar}^+$  ion sputtering; C, after 2 h in oxygen atmosphere at  $T = 470$  K; D, after second  $\text{Ar}^+$  ion sputtering; E, after 2 h in oxygen atmosphere at  $T = 300$  K; F, after 2 h of ultrahigh-vacuum annealing at  $T = 570$  K.

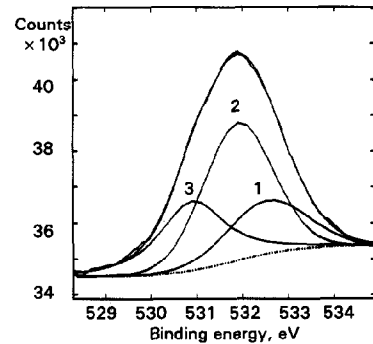


Fig. 6. XPS spectrum of O 1s line measured after 2 h of oxygen chemisorption on CdS film at  $T = 470$  K. Curves 1–3 are the peaks of the three oxygen species obtained by peak fitting.

### 3. Conclusions

Two species of oxygen with  $E_b = 531.8 \pm 0.2$  eV and  $531.1 \pm 0.2$  eV were chemisorbed on the surface of the investigated CdSe and CdS films.

The parallel use of XPS and TDS in the case of CdSe samples demonstrated that the O 1s peak at  $E_b = 531.1$  eV corresponds to chemisorbed atomic oxygen and that at  $E_b = 531.8$  eV to chemisorbed molecular oxygen. The same oxygen species have been found on CdS films of both investigated types, grown from different initial solutions.

The experimental results obtained demonstrated that the concentration of the chemisorbed molecular oxygen is higher in the case of elevated cadmium concentration on the film surface. This fact permits us to conclude that metal atoms are the basic centres of chemisorption of molecular oxygen on the investigated films, as predicted elsewhere [4,5]. Therefore, II–VI semiconductor films with metal-enriched surfaces are particularly recommended for high-sensitivity oxygen detectors.

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## Biographies

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*Giulia Mattogno* was born in 1934 in Palestrina near Rome and graduated in chemistry at the University of Rome in 1960. She was involved in the synthesis and spectroscopy of coordination compounds. Since 1970 she has been working in the field of the surface analysis (XPS, AES, depth profiling) of coordination compounds, magnetic compounds, chalcogenide compounds, semiconductors, etc. At the present time she is interested in the surface analysis of A<sup>3</sup>B<sup>5</sup> and A<sup>2</sup>B<sup>6</sup> semiconductor thin films and composite materials. She is an author of more than 120 scientific papers.

*Sesto Viticoli* was born in 1947 in Barbarano near Rome. He graduated in chemistry at the University of Rome in 1971. After working for three years in the field of synthesis and spectroscopy of coordination compounds, he joined the National Research Council (CNR) of Italy in 1975. Since then he has been engaged

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