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Article *in* Sensors and Actuators B Chemical · January 1995

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Sensors and Actuators B 24–25 (1995) 628–630

SENSORS AND ACTUATORS B CHEMICAL

Influence of chemical composition on sensitivity and signal reproducibility of CdS sensors of oxygen

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Abstract

It is well known that due to the high sensitivity of CdS to oxygen chemisorption, thin films of this semiconductor can be used as oxygen sensors. In this work CdS sensors are produced by an electrohydrodynamic spray of liquid onto glass substrates heated up to the equilibrium temperature of the deposition process. Three types of CdS film with different ratios of initial solvent components have been investigated: Cd:S = (a) 10, (b) 1.0 and (c) 0.1. It is established from XPS quantification that the Cd:S ratio is increased in the film produced from an initial solution with higher Cd:S ratio. Simultaneously the total amount of oxygen on the sensor surface is increased. The obtained experimental data demonstrate that an elevation of oxygen concentration is caused by chemisorption, i.e., the chemisorption sensitivity is increased in the case of higher Cd:S ratios.

Keywords: Cadmium sulphide; Oxygen sensors

1. Experimental

The new method of electrohydrodynamic spraying of liquids (EHDSL) [1–3] has been used for the preparation of CdS thin films with a thickness $d = 1$–30 nm. An aerosol of working liquid was produced in a special generator and the monodisperse unipolar charged particles were deposited onto a hot glass substrate.

Specially prepared dry oxygen was used and chemisorbed on the CdS surface in the preparation chamber at atmospheric pressure, $T = 300$ K for 0.25–5 h and at $T = 500$–600 K for 0.25–2 h. Before the chemisorption process the film surface was cleaned by thermal annealing in UHV at $T = 550$–600 K for 0.3–4 h or by Ar^+ ion sputtering for 5 min.

XPS measurements were carried out in a VG ESCALAB Mk II spectrometer using Al Kα radiation as the excitation source ($h\nu = 1486.6$ eV). The spectrometer's hemispherical analyser was operated in constant-energy mode at 20 eV. All the spectra were recorded at a pressure lower than 10^{-8} Pa. The accuracy of the measured E_b was ± 0.2 eV. The spectra were recorded and processed using a Digital Micro-PDP computer system and VG S5250 software.

The relative atomic concentrations of chemical elements were calculated from the peak areas by using an XPS quantification routine, including Wagner's energy dependence of the photoelectron attenuation length [6].

A differentially pumped ion gun was employed for the Ar^+ sputtering. A primary Ar^+ beam of 2 keV energy and 1 μA ion current was applied to the sample for surface cleaning and depth profiling. In both cases the beam was rastered over the sample area of 4 mm × 4 mm.

2. Results and discussion

A typical spectrum of the O 1s line is shown together with peak-fitting results in Fig. 1. Two components of the O 1s line obtained by the peak fitting are situated at $E_b = 533.0$ and 531.8 eV. The relative concentration of molecular oxygen species with $E_b = 531.8$ eV [4] exceeds the concentration of the other species over twice (see Fig. 2(a), (b)). The ratio of the total oxygen concentration to cadmium can easily be 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

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SSDI 0925-4005(94)01434-J

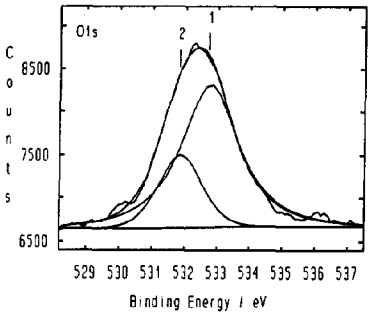

Fig. 1. XPS spectrum of O 1s line of untreated (initial) CdS films. Curves 1 and 2 are obtained by a peak-fitting routine and are the O 1s peaks of two oxygen species.

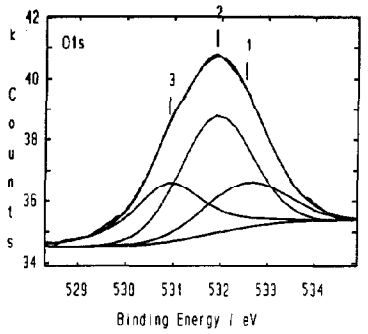

Fig. 3. XPS spectrum of O 1s line measured after 2 h of oxygen chemisorption on CdS film at $T=470$ K. Curves 1–3 obtained by a fitting routine are O 1s peaks of three oxygen species.

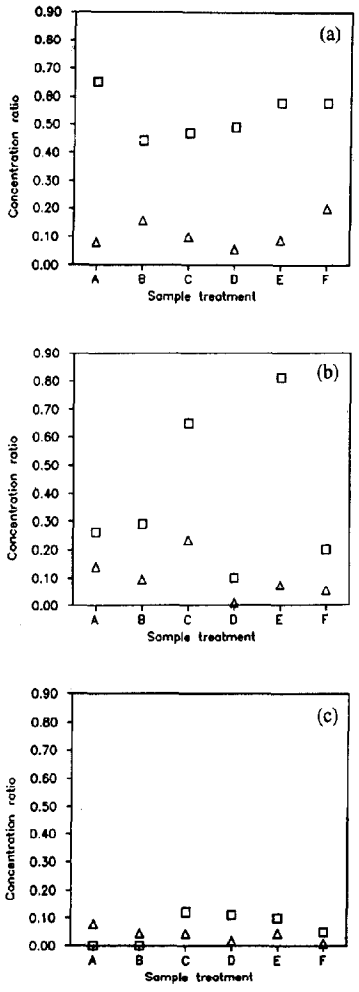

Fig. 2. The atomic concentration ratio $C_{oxygen}/C_{cadmium}$ of the different oxygen species in CdS films, calculated by XPS peak fitting: (a) species with $E_b=533.0$ eV; (b) E_b531.8 eV; (c) $E_b=531.1$ eV. Squares, CdS film of a-type; triangles, b-type. Sample treatments: A, initial (untreated); B, after Ar^+ sputtering; C, after 2 h in oxygen atmosphere at $T=470$ K; D, after second 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.

species with higher E_b (Fig. 2(a), (b)). Analysed O 1s spectra demonstrated that a general decrease of oxygen concentration on the surface is caused by the decrease of the species with lower E_b, while the concentration of the second species is not changed significantly.

The increase of sulphur concentration in the initial solution (b-type) has reduced the total concentration of the chemisorbed oxygen (Fig. 2). In this case the maximum ratio of oxygen concentration to cadmium did not exceed the value 0.3–0.35 (Fig. 2). Both types of films treated with oxygen at atmospheric pressure for 2 h produced qualitatively modified O 1s spectra, presented in Fig. 3. 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. 3). This peak can be attributed to chemisorbed atomic oxygen species [7]. Sample annealing in ultrahigh vacuum (2 h at $T=570$ K) or surface cleaning by ion sputtering results in a considerable decrease of chemisorbed oxygen concentration, mainly due to the decrease of chemisorbed species with lower E_b (531.0 and 531.8 eV), as demonstrated in Fig. 2 (b), (c).

The obtained experimental results demonstrated that the concentration of 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 [5]. Therefore, II–VI semiconductor films with metal-enriched surfaces are particularly recommended for high-sensitivity oxygen detectors.

References

[1] N. Golovan and V. Smyntyna, The sensitisation of semiconductor gas sensor, *Sensors and Actuators B, 6* (1992) 289.

[2] V.V. Golovanov, V.A. Smyntyna, S. Kaciulis, G. Mattogno and S. Viticoli, Dependence of sensitivity and reproducibility of CdS oxygen gas sensors, *Sensors and Actuators B, 18–19* (1994) 460.

[3] V.A. Smyntyna, A.E. Turetskij and G.G. Chemeresyuk, Anomalous temperature dependence of electrical conductivity of CdS films, *Russ. J. Phys. Chem., 59* (1985) 70.

[4] G. Mattogno, S. Viticoli, S. Kaciulis, V.A. Smyntyna and V.V. Golovanov, XPS study of oxygen chemisorption on CdS thin film surface, *Vuoto, 23* (1994) 86.

[5] V.S. Grinevich and V.A. Smyntyna, Physical problems of the reliability of sensors based on A2B6 semiconductor compounds, *Zh. Analit. Chimii, 45* (1990) 1665.

[6] M.P. Seah in D. Briggs and M.P. Seah (eds.), *Practical Surface Analysis,* Vol. 1, Wiley, Chicester, 1990, Ch. 5, pp. 202–212.

[7] V.S. Grinevitch and V.A. Smyntyna, Electronic mechanism for adsorptive sensitivity in semiconductor gas sensors, *Sensors and Actuators B, 18–19* (1994) 426.