

Cd_xS- AND Sn_xWO_y-BASED GAS SENSORS: THE ROLE OF CHEMICAL COMPOSITION IN CO SENSING

Electronic structure of chemisorption complexes on surface of oxidic α -Sn_xWO_y- and Cd_xS-based gas sensors with different elemental composition were comparatively studied by XPS, CEMS and IR-spectroscopy combined with conductivity measurements. The surface sites of Cd and Sn with different coordination were characterized by chemisorption of CO. It was found, differing from the case in well-oxidized SnO₂, that electrical conductance of Sn_xWO_y and Cd_xS films appeared to either increase or decrease when exposed to CO depended on concentration of surface Sn and Cd ions, partial pressure of analyzed gas and operating temperature.

It is argued that surface metallic species on the investigated films are responsible for oxidizing and reducing types of chemisorption reactions. The relative location of energy levels, formed in band gap by external orbitals of chemisorbed complex to Fermi energy was considered as determining factor for the observed different chemisorption mechanisms.

1. Introduction

The molecular understanding of sensing mechanisms on prototype materials has proved to be prerequisite for the development of new sensor systems. On the other hand, the role of adsorption/desorption mechanism and that of surface sites in creation of transducing conductance signal in semiconductor gas sensors is, to some extent, in a controversial state. For instance, two different models are commonly discussed to explain the role of metallic surface species at chemisorption and catalysis in influencing electronic charge-transfer reactions: metallic surface defect may act as specific sites for chemisorption and/or dissociation of molecules to be detected or they may pin Fermi energy.

The approach applying model of external orbitals within the band scheme of semiconductor was reported by author in Ref. [1]. In this case, the interaction between separate orbitals of adsorbate and semiconductor surface should be considered taking into account the energy position of orbitals in band gap of semiconductor. Therefore, studies of observed low-temperature dual response induced by CO in conductance of α -SnWO₄- and CdS-based sensors depending on partial pressure of analyzed gas and operating temperature together with similar effects caused by SO₂ [2] can be extended by considering the interaction between the sorption subsystem

characterized by local parameters of chemisorbed complex (e. g., configuration and location of external orbitals) and the electronic subsystem, described by collective characteristics of crystal (e. g., values of band bending and bulk position of conduction-band edge relative to Fermi level).

The values of collective parameters of crystal can be calculated on the basis of modified Volkenstein model [1, 3]. Local characteristics of the sorption subsystem can be estimated using methods of quantum chemistry, dealing with limited molecular systems, and considering the interaction between corresponding molecular fragments [4]. Cluster model is particularly convenient for the understanding of interactions between chemisorbed molecules and surface sites with different degree of coordination. For instance, metal atoms on extended faces, edges, steps and corners can be easily simulated with cluster model.

Cluster approach was used to study electronic structure of SnO₂ and to simulate adsorption of oxygen and carbon monoxide on surfaces of SnO₂ and CdS. Energy levels related to metallic surface species with different coordination and different kind of oxygen vacancies were described for the basic SnO₂ and CdS clusters together with levels originating from O₂ and CO adsorbates [5].

2. Experimental

The electro-hydro-dynamical technique was used for deposition of CdS thin films from CdCl₂ and (NH₄)₂CS solution on heated (480 °C) glass substrate [3]. A variation of stoichiometric composition of CdS films was obtained by mixing the initial solutions in different proportions of Cd/S ions.

Stannous tungstate films were grown by means of refractive co-sputtering with Balzers BAS 450 magnetron sputtering system, where tin target was

in d. c. mode and tungsten target in r. f. mode, respectively. Both thermally oxidized Si(111) and glass were used as substrates for the films. The deposition sputtering was made in argon atmosphere containing 11% of oxygen. Different sputtering powers (75—150 W) were selected to the tin target and 150 W to tungsten target in order to obtain films with different Sn/W ratios.

XPS (X-ray Photoelectron Spectroscopy) was used for determination of atomic ratios at the film surfaces. EDS (Energy Dispersive Spectroscopy of X-rays) and CEMS (Conversion Electron Mossbauer Spectroscopy) were used to characterize CdS stannous tungstate and stannous tungstate films. The ratios of Cd/S ions in the bulk determined from EDS measurements were from stoichiometric to 1,96. The surfaces of Cd_xS films have been enriched by metal species. Three different film types with Cd/S surface ratios of 1,6 (I-type), 2,4 (II-type) and 3,2 (III-type) were used in the study. The values of x from 0 to 1,5 were determined by EDS measurements for Sn_xWO_3 thin films. The samples Cd_xS and Sn_xWO_3 used in the study are identified in table 1.

IR spectra were recorded with Perkin-Elmer-577 spectrometer interfaced with a 3600 Data Station. The pellet was mounted in an IR cell, which allowed both heating and cooling *in situ* under vacuum or controlled atmosphere.

Two-point method was used in electrical conductivity measurements and wire contacts to stannous tungstate films were made with low-temperature gold paste. The computer-controlled measuring system employing the flow-through principle was used for varying gas concentration, heater voltages of the films and for data acquisition, handling and storage. The d. c. voltage of 1 V was used in conductance measurements of the films.

3. Results

The unusual dual response in case of exposure of n-type semiconductor CdS as thin films to CO and SO_2 in low-temperature interval (300—500 K) was reported by author in Refs. [2, 6]. Here we describe the dual response caused by carbon monoxide in conductance of Cd_xS and $\alpha-Sn_xWO_3$ thin films with different elemental composition on the surface.

Figure 1 shows the conductance response G_g/G_0 above the border temperature T^* and G_0/G_g below T^* to 100 ppm of CO in dry nitrogen (oxygen and humidity concentrations are few ppm) for three different CdS film types I, II and III. G_0 is the measured conductance in nitrogen and G_g — the conductance after exposure to CO. CO behaves as a reducing gas at all temperatures with I-type film, but has the border temperatures T^* at 300 K and 320 K with the II- and III-type films, respectively. With these two film types, the behavior of CO changes from reducing to oxidizing when temperature of films decreases through T^* . The enrichment of surface by Cd (III-type films) has decreasing effect

on T^* . The increase of the sensitivity to CO with increasing surface content of Cd is also shown in fig. 1, both above and below T^* .

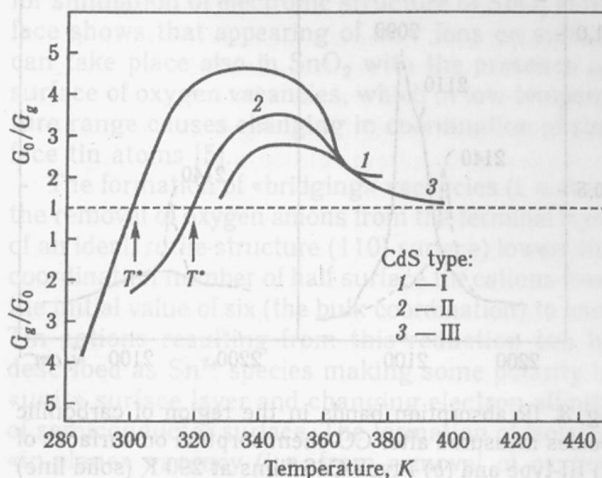


Fig. 1. Conductance response G_g/G_0 (and G_0/G_g) of I-, II- and III-type CdS films to 100 ppm CO in nitrogen at different temperatures:

T^* is the border temperature between oxidizing and reducing behaviour of CO

Figure 2 shows typical response (τ_{res}) and recovery (τ_{rec}) times (corresponding to a change of 90% of the total change) of III-type films in case of exposure to 100 ppm of CO in nitrogen at different temperatures. The temperature T^* plays important role in temperature behavior of both τ_{res} and τ_{rec} .

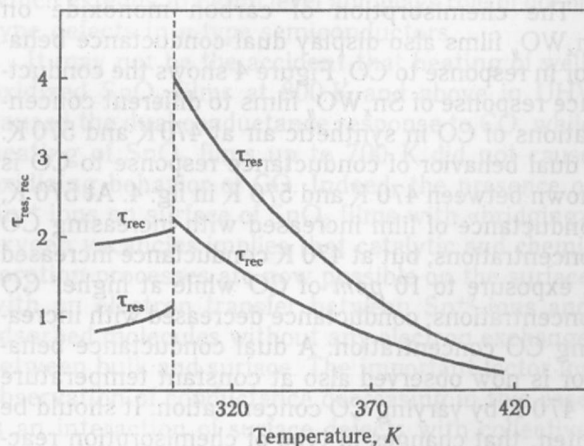


Fig. 2. Response (τ_{res}) and recovery (τ_{rec}) times of an III-type CdS film at different temperatures for 90% conductance changes after introducing and removing 100 ppm of CO in nitrogen, respectively

IR spectroscopy has been used in order to study possible changes in chemisorption of CO on CdS surfaces above and below temperature T^* . Typical results in absorption region of carbonic species, 2000...2300 cm^{-1} are shown in fig. 3 for I-type and III-type films. An exposure of III-type films to 100 ppm of CO in nitrogen at 290 K led to the immediate appearance of broad and intense absorption peak in region 2085...2115 cm^{-1} . The peak consisted

of two components at 2090 cm^{-1} and 2110 cm^{-1} . At the same time, the decrease was observed in con-

ductivity of films. The border temperature T^* is around 500 K . $\alpha\text{-SnWO}_4$ was found from SEM and

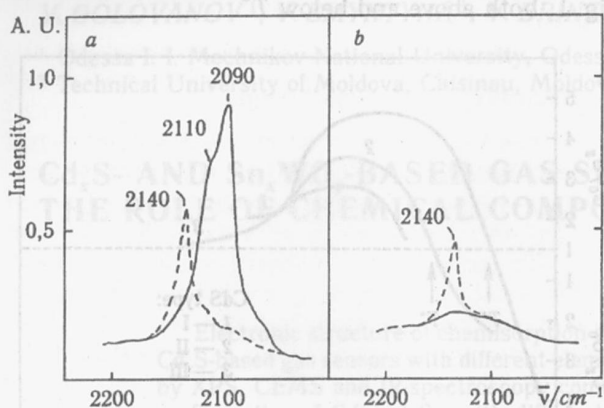


Fig. 3. IR absorption bands in the region of carbonilic species measured after CO chemisorption on surfaces of (a) III-type and (b) I-type CdS films at 290 K (solid line) and 340 K (dashed line)

ductivity of films. After removing of CO from the atmosphere, the band at 2110 cm^{-1} disappeared first, while the band at 2090 cm^{-1} decreased gradually and vanished after 15 min. A shift of adsorption peak up to 2140 cm^{-1} was found after increasing film temperature above T^* to 340 K . At the same time, inversion of CO behavior from oxidizing to reducing has been observed. IR spectra measured from I-type films, did show only a less intense peak at 2140 cm^{-1} (fig. 3, b) and was accompanied by reducing behavior of CO.

The chemisorption of carbon monoxide on Sn_xWO_y films also display dual conductance behavior in response to CO. Figure 4 shows the conductance response of Sn_xWO_y films to different concentrations of CO in synthetic air at 470 K and 570 K . A dual behavior of conductance response to CO is shown between 470 K and 570 K in fig. 4. At 570 K , conductance of film increased with increasing CO concentrations, but at 470 K conductance increased at exposure to 10 ppm of CO while at higher CO concentrations, conductance decreased with increasing CO concentration. A dual conductance behavior is now observed also at constant temperature of 470 K by varying CO concentration. It should be noted, that changes in type of chemisorption reaction from oxidizing to reducing was observed also on III-type of CdS thin films, when CO concentration has been increased from 5 to 100 ppm . As it is shown in fig. 4, both response and recovery times have large differences between 470 K and 570 K .

It was found that dual conductance response to CO did not depend only on temperature and CO concentration, but also on tin content in $\alpha\text{-Sn}_x\text{WO}_y$ films. This is shown in fig. 5 where conductance ratios between synthetic air (G_0) and 250 ppm of CO in synthetic air (G_g) are plotted for different films in table 1, having different tin concentration in temperature range between 420 K and 670 K . Only III-type films show dual conductance behavior with

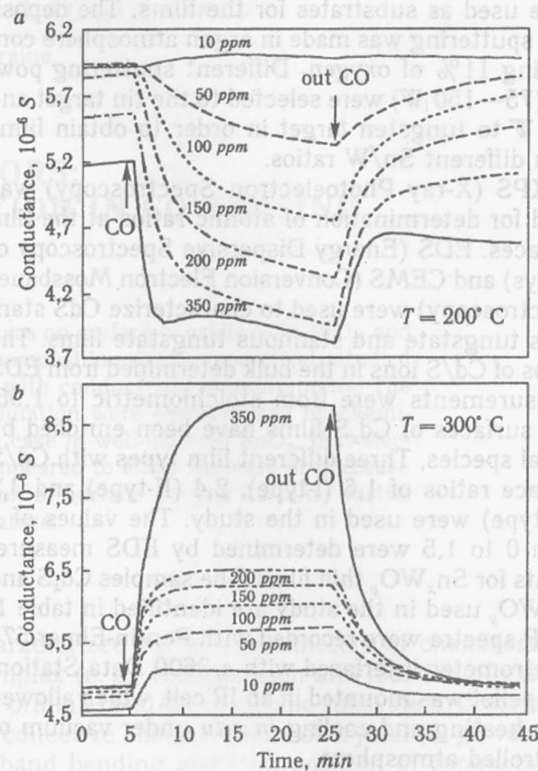


Fig. 4. Conductance response of III-type $\alpha\text{-Sn}_x\text{WO}_y$ film to different concentrations of CO in dry synthetic air (a) at 470 K and (b) — 570 K

AFM images to be the matrix phase in these films. The strong increase of the conductance ratio G_g/G_0 of pure WO_3 film (I-type film) at 320 K is shown in fig. 5.

The unusual conductance response of some SnO_2 thick films to CO after fast cooling process is de-

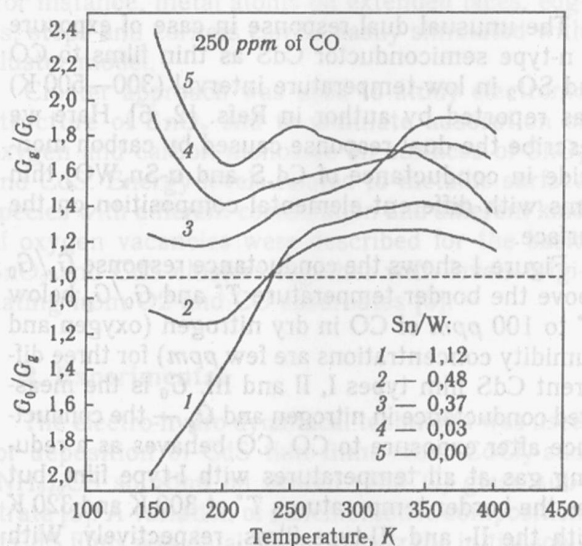


Fig. 5. Conductance response G_g/G_0 (and G_0/G_g) of different Sn_xWO_y films in table 1 ($x = \text{Sn}/\text{W}$ ratio) to 250 ppm of CO in synthetic air at different temperatures

scribed in Ref. [7]. The situation with those SnO_2 films resembles the present situation where the unusual dual conductance behavior appears only by films with high cation concentrations and high conductivity at temperatures below T^* . It should be noted, that study of SnO_2 films prepared by usual thick-film technology, shows that CO behaves as reducing gas increasing the conductance of n -type semiconductor on the well-oxidized (1 Torr of O_2 at 700 K for 10 min) SnO_2 films, but only heating at 800 K and above in UHV causes the dual conductance response to CO in low-temperature range (300–500 K).

4. Discussion

The oxidizing behavior of CO, in connection with dual response, is very difficult to explain. Its appearance in both oxidic $\alpha\text{-Sn}_x\text{WO}_y$ and CdS films may rule out changes in the amount of donors as the origin for the behavior. Different electrode materials used for CdS (indium) and $\alpha\text{-Sn}_x\text{WO}_y$ (gold) films may also rule out electrodes as the origin for the behavior. Then, the origin should be at the film surfaces. The abrupt changes in response and recovery times (fig. 2) and in CO chemisorption (fig. 3) at border temperature T^* also support this reasoning.

It is well known, that carbon monoxide in carbonilic form coordinates onto metal sites via carbon atom [8]. This fact along with appearance of oxidizing behavior of CO only on Cd_xS and Sn_xWO_y films with high cation concentrations permits to conclude that metallic atoms at surface of investigated films play an important role in CO chemisorption.

The possibility for oxidizing behavior is that CO behaves as surface acceptor trapping electrons on surface of semiconductor. The red shift in carbonyl stretching band in fig. 3, *a*, when the CO behavior changes from reducing to oxidizing below T^* , is in agreement with that interpretation. The transfer of an electron from surface site to antibonding $2\pi^*$ orbital of CO leads to significant weakening of C—O bond and is attributed to the typical band in 2085...2115 cm^{-1} region.

The important consequence of the approach considering interaction between collective and local subsystems is the dependence of local energy levels, originating from adsorbates, on configuration and location of external orbitals of surface defects. Indeed, charge transfer reactions between adsorbates and semiconductor surface may cause the changes in collective electronic subsystem of semiconductor. On the other hand, changes in local subsystem i. e. in polar surface layers of ionic semiconductors and corresponding changes in electron affinity of semiconductor may reflect in injection rates of electrons from adsorbed species. For that reason, characterization of the surface sites, their coordination and charge state are of great importance for atomistic understanding of sensing mechanisms.

It is possible to conclude from CEMS results that, differing from the case in SnO_2 , tin is the divalent form Sn^{2+} in $\alpha\text{-Sn}_x\text{WO}_y$ films. Cluster approach used for simulation of electronic structure of SnO_2 (110) face shows that appearing of Sn^{2+} ions on surface can take place also in SnO_2 with the presence on surface of oxygen vacancies, which in low-temperature range causes changing in coordination of surface tin atoms [5].

The formation of «bridging» vacancies (i. e. from the removal of oxygen anions from the terminal layer of an ideal, rutile-structure (110) surface) lowers the coordination number of half surface tin cations from the initial value of six (the bulk coordination) to four. Tin cations resulting from this reduction can be described as Sn^{2+} species making some polarity to «unit» surface layer and changing electron affinity of semiconductor surface. The formation of isolated «in-plane» vacancy (i. e. from removal of oxygen anion from what is normally the second, tin-containing, atomic plane of ideal (110) surface) lowers coordination number of one adjacent surface tin cation from four to three, while the other two nearest neighbours go from fivefold to fourfold coordination.

It was shown in ref. [9] that defect electronic states which appeared low in band gap for annealing temperatures less than 800 K in UHV arised from «bridging» oxygen vacancies. Heating at 800 K or above causes the formation of «in-plane» oxygen vacancy. The «in-plane» oxygen vacancy is characterized by occupied states higher in band gap which extends to Fermi level and plays role of donor-type defects in n -type semiconductors.

It may not be the accident that heating of well-oxidized SnO_2 films at 800 K and above in UHV caused the dual conductance response to CO, while heating of SnO_2 films up to 700 K did not cause oxidizing behavior of CO. Indeed, the presence of Sn^{2+} ions on surface of SnO_2 films with «bridging» oxygen vacancies implies that catalytic and chemisorption processes are now possible on the surface with an electron transfer between Sn^{2+} ions and adsorbed molecules without any electron exchange between bulk and surface. The important factor for observation of conductance decreasing in this case is an interaction of surface defects with collective subsystem of crystal, e. g., location of external orbitals of such surface defects near Fermi level, as it takes place with formation of «in-plane» oxygen vacancies.

The temperature-stimulated conductance measurements on freshly deposited CdS III-type films in pure nitrogen exhibit Arrhenius slope of 0.05 eV, related to cadmium interstitial species [3]. $\alpha\text{-Sn}_x\text{WO}_y$ III-type films also feature by Arrhenius slope of 0.05...0.07 eV, corresponding to donor-type defects related to Sn^{2+} ions [6]. Therefore, on investigated films CdS and $\alpha\text{-Sn}_x\text{WO}_y$, Cd^+ and Sn^{2+} surface species play dual role of centers determining dark conductivity behavior and basic sites for chemisorption. This fact provides a good opportunity for studies

of interaction between local and collective subsystems in semiconductor surface-active structures.

The increase of operating temperature above 320 K for CdS films and above 450 K for α - Sn_xWO_y films caused the considerable reduction of electron presence in external orbitals of metallic species and, hence, the shift of Fermi level towards the middle of band gap promoting the changes in type of chemisorption reaction from oxidizing to reducing.

The atoms with the lowest coordination on surface are the most reactive towards the interaction with gas phase. On such «active centers», reactions take place with appreciably reduced activation energies. These atoms or groups of atoms normally represent a modest fraction of total number of exposed ones and are thought to be located on edges, steps, corners or other defects of microcrystals or microparticles. The III-type CdS and Sn_xWO_y films, enriched by Cd and Sn species, may have the high number of those presented on such edges, steps, corners and other surface defects, where coordination number can be exceptionally low. Conversely, at surface of I-type film Cd and Sn atoms are basically with higher coordination at crystal faces. For that reason, different features in IR spectra, measured from CdS films with different surface composition, may be considered in terms of interaction of adsorbates with surface Cd atoms having different coordination.

The peaks fitting results for the IR spectrum show presence of two types of chemisorbed complexes on the surface of I-type CdS films. One absorbing at 2090 cm^{-1} , is assigned to Cd(0)CO complex stabilized on interstitials reduced cadmium species with low coordination number (Cd_i). The other, absorbing at 2110 cm^{-1} , is attributed to Cd(I)CO acceptor-type complex chemisorbed above surface cadmium ions with higher coordination in crystal. The last ones featured by reduced density of valence electrons on external orbitals resulting of donation into semiconductor conduction system and chemisorption take place with trapping of conduction electron from the collective subsystem of the crystal. The spectra peak at 2140 cm^{-1} has been attributed to the donor-type Cd(I)CO chemisorbed complexes, which are characteristic of less reduced areas, where electron availability is poor, while the acceptor-type Cd(I)CO complexes related to spectra peak at 2110 cm^{-1} characteristic of more reduced areas, where electron availability was large. This assumption corresponded to the results of IR, VIS, UV study of CO chemisorption reported in ref. [8].

The charge-transfer reactions involving surface sites with high coordination may proceed with capture of conductance electrons from collective electronic subsystem, as it takes place, for instance, for chemisorption of acceptor-type Cd(I)CO complexes. On the other hand, interaction between chemisorbed molecules and surface sites with low degree of coordination has the high probability for charge — transfer reactions to occur only in local subsystem at semiconductor surface (i. e. chemisorption of Cd(0)CO complexes). Indeed, the differences bet-

ween τ_{rec} ($\sim 3\text{ min.}$) for conductivity changes (fig. 2) and time requested for disappearance of the peak at 2090 cm^{-1} , corresponding to Cd(0)CO complexes ($\sim 15\text{ min.}$) after evacuation of CO show that decreasing of conductance caused mainly by Cd(I)CO complexes, related to the peak at 2110 cm^{-1} , involving capture of conductance electron, while Cd(0)CO complexes does not influence essentially on the changes in conductance.

The change of stoichiometric composition towards the decrease of metal component (I-type films) leads to the essential decrease of concentration of reduced Cd_i defects with low coordination number and promotes chemisorption of CO on bare surface cations. For this reason, the band at $2085\text{--}2115\text{ cm}^{-1}$ has vanished together with acceptor-type of chemisorption reaction. The decrease of total concentration of surface metallic species may lead to decrease of sensitivity also in donor-type region and the intensity of the peak at 2140 cm^{-1} , which has been observed experimentally (figs. 1, 3).

It is well known, that CO preferentially attacks low-coordinated surface ions. Therefore, the inversion of charge state of chemisorbed complex together with shift in an IR spectra caused by increasing of CO partial pressure may be connected with the sequential interaction of CO molecules with the highly coordinated cation adsorption sites, when Cd_i defects became completely occupied. Oxidizing behavior of CO is in fact predominant at the lowest coverage.

Donor-type M(I)CO complexes are generally characterized by low stability, owing to the nature of the ion — carbon interaction, essentially in the highly charged ions, and to the electron donor properties of CO molecule. Conversely, acceptor-type M(I)CO and M(0)CO complexes are characterized by the higher stability, owing to the ability of low valence ions and metal atoms to form p -bond with CO molecule. For that reason, the change of type of chemisorption reaction should cause inversion of the ratio between τ_{res} and τ_{rec} , that corresponded to observed experimental results (fig. 2).

In the same way as the ions and/or the atoms with different coordination numbers show different reactivity towards simple molecules, they can show also different response to excitation. As discussed in Ref. [10], radiative decay pathways are more efficient for low-coordinated ions than for those with high-coordination. The ions with high coordination have the larger number of bonds to crystal and they couple more strongly with phonon and electron transitions of lattice, providing high probability for non radiative decay and charge — transfer reaction.

Indeed, the behavior of IR spectra peaks at 2090 cm^{-1} and 2110 cm^{-1} after evacuation of gas atmosphere shows that at the earlier stages of treatment only sites with larger coordination number became free from surface contaminants (carbonyl groups). Absorption at 2090 cm^{-1} assigned to the Cd(0)CO complexes was still observed. At the final step of treatment (after 15 min) the ab-

sorption due to CO molecules adsorbed above low coordinated surface sites was also decreased to zero level. The situation with CO chemisorption resembles the situation where CdS films with different elemental composition were characterized by oxygen chemisorption [11]. In that case, the increase of stability of molecular oxygen, chemisorbed at low coordinated cadmium atoms led to «frozen-in» states of adsorbates at surface.

5. Conclusions

From combined measurements of XPS, CEMS, IR spectroscopy and conductance changes, we deduce that surface metallic species are the basic centers for carbon monoxide chemisorption on CdS films. Interaction with low coordinated Cd atoms features by increased stability of chemisorbed complexes. Reduction of coordination number in the case of CO chemisorption, leads to inversion in type of chemisorption reaction from reducing to oxidizing. Sn^{2+} ions in Sn_xWO_y films are responsible for dual response in the case of exposure of Sn_xWO_y films to CO.

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