XPS, ISS and TPD study of Pd–Sn interactions on Pd–SnO systems

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Abstract

The sensitivity and selectivity of SnO based gas sensors could be improved by doping of small amount of transition metals. In this work we used X-ray photoelectron spectroscopy, ion scattering spectroscopy, and thermal desorption techniques to investigate Pd evaporated on SnO thin layer substrate, prepared by spray pyrolysis. The evolution of Pd/SnO layer morphology with increasing amount of Pd deposits was studied using the XPS inelastic background shape analysis. The observations are compared to the results obtained from natural SnO crystal and metallic Sn substrates. A strong Pd–Sn bimetallic interaction was observed, resulting in the formation of PdSn alloy of noble metal-like electronic structure. This feature also corresponds to the presence of two CO desorption states with low energy peaks at approximately 390 K. The relation of our results with the operation mechanism of gas detection are discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Semiconductor gas sensors based on tin dioxide are widely used for the detection of toxic and explosive gases in air. The general operation mechanism of gas detection by a change in surface conductivity has been widely described in the literature [1–5]. In an atmosphere of air containing inflammable gases, three reactions occur independently on the surface of SnO₂: (i) gas molecules react with the surface-adsorbed O²⁻ and release electrons; (ii) O²⁻ are desorbed by thermal vibrations O²⁻ = O³ + 2e⁻; and (iii) oxygen molecules are readsorbed in the form of O²⁻ and consume carrier electrons. Different contributions to the overall conductivity of SnO₂ have been described: the grain-size effect in the case of polycrystalline samples, which depends on the sample preparation and could be affected by a small amount of a foreign metal, influence of the texture of SnO₂ type and nature of electrical contacts and namely the presence of additives and impurities into the bulk and on the surface. The bonding of transition metal atoms (Pd, Pt, Ag) at surface or bulk sites influences considerably the sensor response. The ‘doping effect’ has been studied extensively in the past, however, numerous contradictories appeared in the literature. Two possible sensitization mechanisms have been proposed [6]: an electronic effect (direct exchange of electrons between the semiconductors and the metal additive particles) and a catalytic one (metallic clusters activate the gaseous species). In the case of Pd the electronic sensitization has been suggested in Yamazoe [3]. This type of mechanism was opposed by Kappler [7], who ruled out the existence of metallic clusters or even atoms in the metallic state at the surface, which did not provide an explanation of the sensor effects by means of spill-over effects or Fermi energy control. Oxidation of Pd at the surface has been found necessary for bulk doping by in-diffusion of evaporated Pd, because only the small Pd²⁺ species could penetrate into SnO₂ [7,8]. On the other
hand, an adequate catalyst dispersion on the surface was found to be necessary for good electrical control, but no PdO phase was evidenced [9].

Metal dispersion is decisively important for promoting gas sensitivity [10]. The sensors doped by metal evaporation showed larger sensitivity than sensors prepared by layer impregnation due to the finer metal dispersion.

Recently, the bimetallic Pd–Sn system was investigated in order to prepare novel catalysts for hydrocarbon conversion [11–16]. Their specific properties were given by the strong interaction between Pd and Sn, through the hybridization of the Pd d and Sn s states, leading to the formation of PdSn alloy of noble metal-like electronic structure with the d-band centered at 4 eV below the Fermi level [17]. The Pd–Sn catalysts have also been found to be effective for low temperature (even room temperature) CO oxidation [15,18].

In this work the Pd–Sn bimetallic interaction is considered as a possible effect which influences the Pd doping mechanism via Pd/SnO$_2$ surface morphological changing and/or Pd catalytic property alterations, especially in the case of reduced tin oxide surface ($x < 2$).

2. Experimental

Experiments have been carried out in ultra-high vacuum (UHV) chambers equipped with X-ray photoelectron spectroscopy (XPS), ion scattering (ISS) and temperature programmed desorption (TPD) facilities.

XPS experiments were performed using the OMICRON EA 125 multichannel hemispherical analyzer and a dual Al/Mg X-ray source. For the ISS measurements an incident He$^+$ ion beam with a primary energy of 2 keV was used at an incident angle of 56° with respect to the surface normal. The substrates were cleaned by Ar$^+$ ion bombardment. The substrate cleanliness, stoichiometry and amount of deposited Pd were checked by XPS.

The tin oxide substrates, with various surface structure and/or stoichiometry, were used as a support. SnO$_2$ thin polycrystalline samples with thickness of 30–70 nm were deposited by a spray pyrolysis method, using a 0.2 M SnCl$_4$–water solution (T$_{prep} = 350$°C) [19]. Films were deposited on low resistivity Si (111) substrates to minimize charging effect during XPS measurements. The more stoichiometric surfaces were prepared by cutting (without an orientation) a natural SnO$_2$ crystal (cassiterite). The substrates were heated in vacuum ($10^{-7}$ Pa, 500 K, 10 min) and cleaned by argon ion bombardment (500 eV) in order to remove the residual surface contamination.

Small Pd clusters were deposited on the samples in situ at room temperature using the micro electron beam evaporation source (MEBES) [20] which enables control of the evaporation rate by monitoring the Pd$^+$ ion current.

3. Results and discussion

The tin oxide thin film was investigated by combining XPS and ISS methods. The core-level Sn 3d spectra (not shown) did not exhibit resolved features due to individual Sn$^0$, Sn$^{2+}$, or Sn$^{4+}$ states, which were observed in the case of oxygen-deficient SnO$_2$ surfaces [21,22]. The peak maximum located at a binding energy of 487 eV corresponded to the stoichiometric SnO$_2$. The O 1s spectra also showed a narrow peak at 530.5 eV characteristic for SnO$_2$ lattice oxygen. However, the XPS quantitative analysis indicated the non-stoichiometric SnO$_x$, giving $x = 1.2$. The most probable explanation of this discrepancy was the presence of a tin-rich thin surface layer, which influenced the ‘average’ value of the Sn concentration, obtained by the quantitative analysis over the thicker surface region, given by the XPS information depth. This assumption was in agreement with the results obtained by ISS that can be seen in Fig. 1. He$^+$ ion scattering spectra (2 keV), which provided the information on the first layer composition, showed only a small residual oxygen signal, O/Sn intensity ratio being 0.06.

The valence-band (VB) XP spectra of the same sample are presented in Fig. 2. The three main peaks were confined to energies between 4 and 12 eV, that was characteristic for the SnO$_2$ electronic structure. On the other hand, a small peak usually attributed to Sn 5s states characteristic for SnO [22–24] can be seen at 3 eV.

In order to be able to determine more precisely the sample surface composition, we performed the Sn 3d
peak background analysis using Tougaard’s method [25]. This method was based on the fact that the XPS peak shape depends on the surface structure of the solid at an nanometer depth scale. By means of interactive QUASES software [26] it was possible to provide a quantitative and non-destructive in-depth analysis, allowing determination of in-depth concentration profiles. The inelastic background shape analysis showed the presence of an adlayer on the tin oxide surface that could be associated with metallic tin only because XPS did not show the presence of any other element except Sn and O. Taking for granted that the adlayer was composed of metallic Sn, and using an appropriate inelastic mean free path value, the adlayer thickness was evaluated between 3 and 5 Å (1−2 ML). The resolved feature corresponding to metallic tin was not observed on the Sn 3d core-level spectra. This fact could be explained by general effects of the peak shift to higher BE given by the low coordination number of atoms presented in an ultrathin metallic layer.

The same analysis was performed on the reference sample prepared by cutting the natural cassiterite crystal and cleaned by the same annealing and dose of Ar ions. The XPS quantitative analysis showed nearly stoichiometric SnO₂, the ISS spectra gave the O/Sn intensity ratio of 0.16 and VB spectra did not exhibit Sn²⁺ features at 3 eV. The comparison of the two samples showed that the SnO₂ film surface had an oxygen-deficient structure in regard of the reference cassiterite sample. Similar results of surface oxygen deficiency were observed by Cox [27] on heavily bombarded SnO₂(100).

Two doses of Pd were deposited consequently on the SnO₂ film surface using the calibrated molecular flux of Pd atoms. The first deposit corresponded to 1 ML of Pd. The core-level XPS Pd 3d signal exhibited the shifted value of 336.5 eV, in respect of bulk value 335.5 eV. The shift agreed with the general trend of BE variations. BE was higher for the dispersed phase due to the reduction of screening effects and final-state energy variation [12,28].

The ISS spectra of the Pd/SnO₂ sample (Fig. 1), did not show any Pd deposition-induced changes, giving the same Sn intensity without any Sn peak broadening or shift due to the convolution with close lying ISS peaks of Pd. On the other hand, the cassiterite reference sample, measured at the same conditions, exhibited the Pd−Sn signal mixture [29]. Therefore we can conclude that Pd atoms deposited on Sn-rich surface diffused into the sub-surface layer, that can be well understood by comparing their surface free energy values (Pd, 2.1 J/m²; Sn, 0.71 J/m²) [30,31]. Pd formed a Pd−Sn alloy phase, confirming the strong Sn–Pd alloying tendency that was observed in the literature [11,14,21].

The Pd 3d peak background analysis confirmed the buried layer structure of Pd in the region between 6 and 9 Å under the surface. The formation of this layer is schematized in Fig. 3a,b.

The subsequent deposition of 3 ML of Pd on SnO₂ thin films showed interesting results. The corresponding difference VB spectra, obtained by subtracting the SnO₂ background, are presented in Fig. 4, together with the spectra obtained by depositing the same amount of Pd on pure polycrystalline thick films of Sn and on the reference cassiterite. The spectra exhibited two Pd 4d band peaks at 4 eV (a) and 2 eV (b), respectively. The peak (a), shifted by 2 eV to higher BE relative to the Pd 4d peak (b), typical for metallic Pd was given by the d-centroid shift effect caused by the transition-metal/s,p-metal bimetallic interaction, induced by a strong hybridization of the Pd-d and Sn-s,p
We observed a similar effect recently in the case of Pd/Al interaction [32].

The ISS results (Fig. 1) showed that the first surface layer was composed of Pd, Sn and O atoms. The Pd/Sn concentration ratio was 0.74 while the oxygen/metal atomic concentration O/(Sn + Pd) increased surprisingly to 0.14. The Pd 3d peak background analysis [25] showed the formation of a non-continuous Pd layer with average island height of 15 Å and relative surface coverage of 0.5. Assuming a hemispherical shape of Pd clusters, the layer was formed by approximately 40 Å large particles.

We can conclude that at higher deposited amounts the Pd atoms form Pd clusters, due to the high Pd atomic cohesion, which were encapsulated by a Sn/Pd alloy overlayer reducing the high Pd free surface energy. This hypothesis was in full agreement with the observation of the Pd–Sn surface alloying and Pd/PdSn interaction in the case of the Pd–Sn model catalysts [11,12,14]. The relatively mobile Sn metallic atoms diffused towards the Pd particle surface disclosing the buried O sites, being driven by the tendency to minimize the system surface energy (see Fig. 3c). If we consider that the ISS oxygen signal was provided by 50% of the substrate surface, not covered by Pd, the relative oxygen concentration increased five times, corresponding to the relative ISS oxygen intensity enhancement 0.06–0.14.

The observed effect of the surface Sn atom extraction can be used for the tentative explanation of two currently observed properties of Pd doped tin oxide sensors: (i) Pd-doped thin films have a higher resistivity than undoped ones [33]; and (ii) increase of the sensor sensitivity, due to the increase of the number of active surface oxygen sites.

In order to investigate the CO interaction with the Pd/SnO$_2$ system, we performed the TPD of CO on the SnO$_2$ film surface with different amounts of deposited Pd. In Fig. 5 the set of CO TPD curves, obtained at 10 L (1 L = 10$^{-6}$ torr s) CO exposure, is presented. The total amount of Pd increased from 1 to 8 ML. It can be seen that the TPD spectra were composed of two desorption features: the low temperature peak with maximum at 390 K and the high temperature one at 440 K. It indicated two CO desorption states, which corresponded to a weaker and stronger CO–metal bond. The desorption activation energies $E_D$, determined for these two desorption peaks, were 103 and 116 kJ/mol, respectively.

The common feature of the shift of the center of the Pd d-band toward higher binding energies, due to the formation of a bimetallic bond, is a weakening of the Pd 4d–CO 2$\pi^*$ bonding interactions [17]. It was shown that the d-band centroid shift away from the 2$\pi^*$ CO orbitals was in direct correlation to the decrease of CO desorption temperature [34]. Hence we assumed that the first peak corresponded to the alloy adsorption states, and the second one to the metallic Pd states. This assumption was supported by the fact that the considerable differences between heats of CO adsorption on Pd–Sn/SiO$_2$ and Pd/SiO$_2$ catalysts (120 and 132 kJ/mol) was found by Hill et al. [13]. Lee et al. [11] found that CO chemisorption at 300 K was strongly reduced on Pd$_3$Sn, due to lack of pure Pd ‘three-fold’ sites. On the Pd$_3$Sn phase the CO binding energy was reduced by 22 kJ/mol, relative to the clean Pd(111) surface, by decreasing the CO desorption temperature from 470 to 370 K. Thus, our TPD data were in agreement with the observation of the Pd–Sn surface alloying and Pd/PdSn interaction in the case of the Pd–Sn model catalysts [11,12,14].

The relative mobility of Sn metallic atoms diffused towards the Pd particle surface disclosing the buried O sites, being driven by the tendency to minimize the system surface energy (see Fig. 3c). If we consider that the ISS oxygen signal was provided by 50% of the substrate surface, not covered by Pd, the relative oxygen concentration increased five times, corresponding to the relative ISS oxygen intensity enhancement 0.06–0.14.
agreement with the presented hypothesis of the formation of the Pd–Sn surface alloy during the Pd deposition on the SnO_2 substrate. The low temperature ‘alloy’ peak appeared at first, followed by the high temperature peak evolution as the number of metallic-like Pd adsorption sites increased.

The weak CO bond on Pd–Sn bimetallic catalysts should cause a higher CO surface diffusion, and thereby a lower temperature of CO catalytic oxidation. The activation energy for CO oxidation at the Pd(100) surface was found to be 22–27 kcal/mol within the temperature range 443–673 K, while under the same conditions the activation energy at the c(2 × 2)-Sn/Pd(100) surface was 12 kcal/mol [15]. Similarly, due to the bimetallic effect, the Pd/SnO_2 catalyst was found to be quite effective for CO oxidation even at room temperature [18]. Thus it seems likely that the formation of a surface Sn–Pd alloy can contribute to the generally observed, but not well understood, effect of sensors’ high sensitivity at low temperature due to the addition of Pd [33].

4. Conclusion

The XPS/ISS combined study of Pd growth on SnO_2 thin film with oxygen-deficient surface shows the formation of a tin-rich adlayer having metallic character. A small amount of deposited Pd, equivalent to 1 ML, diffuses into the sub-surface region, forming the buried, atomically dispersed Pd layer. Higher quantities of several ML of Pd leads to the formation of three-dimensional Pd particles, which have mixed metallic and Pd–Sn bimetallic character. Surface Sn atoms are bonded to Pd atoms due to the strong intermixing, typical for transition-/s,p-metal interaction. The rearrangement of the surface tin layer leads to the appearance of the oxygen sites at the surface.

CO desorption experiments show the weak CO bonds at low deposited Pd quantity, and enhancement of the CO–metal bond strength with increasing concentration of Pd adsorption sites. This is typical behavior of CO adsorption on Pd/s,p alloys that confirms the presence of the Pd–Sn phase on the Pd island surface. The weakening of the CO bond strength for the bimetallic phase could be one of origin of the lowering of tin oxide sensors’ working temperature by doping them with palladium.

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