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On the electronic interaction between additives and semiconducting oxide gas sensors

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A model for the electronic interaction between additives and semiconducting oxide gas sensors is presented. The model is based on the depletion layer that is created due to the metal–semiconductor contact forced by the presence of a metallic additive. This depletion layer corresponds to an active grain size that is smaller than the geometrical one. Thus, the work function of the metal is connected to the change of sensor characteristics. Moreover, the dependence of the sensitivity on the amount of the deposited additive is explained on the same basis. Experimental results are presented in the case of tin oxide thin film gas sensors with Pd, Pt, and Ni in the presence of zero grade air and carbon monoxide. The experimental results are in excellent qualitative agreement with the proposed model. © 1996 American Institute of Physics. [S0003-6951(96)01331-9]

The widespread applicability of semiconducting oxides, such as SnO₂ or ZnO, as gas sensors is related both to the range of conductance variability and to the fact that it responds to both oxidizing and reducing gases. In these sensors, small amounts of noble metals, such as Pd and Pt, are often dispersed as activators or sensitizers. Among the models that have been proposed, two types of interaction between additives and semiconductors may be distinguished. The first is a chemical interaction by which additives assist the redox processes of semiconductor oxides. For example, spillover of hydrogen and possibly of CO on Pt–SnO₂ has been suggested by Bond *et al.*¹ At appropriate temperatures, reactants are first absorbed on the surface of additive particles and then migrate to the tin oxide surface to react there with adsorbed or surface oxygen species, resulting in an increase in surface conductivity. The second interaction is an electronic one in which additives interact electronically with the semiconductor as a sort of electron donor or acceptor. For example, changes in the work function of the additive due to the presence of a gas will cause a change in the Schottky barrier between the metal and the oxide and, thus, a change in conductivity.

The above two types, which may be distinguished by x-ray photoemission spectroscopy surface analyses,^{2,3} can provide applicable models for Pt, Pd, and Ag doped tin oxide gas sensors. But the results are only in qualitative agreement with the experimental ones. For example, these models cannot answer questions like why Ag doped tin oxide is more sensitive than the Pd doped one or how the sensitivity depends on the amount of the additive.

Deposition of SnO_x films was performed with a Leybold Z-400 planar magnetron sputtering system, which was dc operated in a controlled, high purity Ar–O₂ mixture. Two different discharge modes may be obtained, the metallic mode and the reactive mode, where the target is, respectively, free from or covered with reaction products. The compound formation reactions are desirable in the metallic mode for high rate depositions, and for a more precise control of

the O₂/Sn ratio of the deposited film. This necessitates the use of a plasma emission monitor (PEM) system, which allows us to select and maintain the degree of target oxidation,⁴ using the tin emission line intensity at 450 nm for the control loop of the reactive gas mass flow controller.

Films were fabricated at a relatively high total gas pressure of approximately 1.0×10^{-2} mbar. The substrate holder was at a distance of 7 cm from the 10 cm in. diam target. The total power into the target was 115 W with a total current of 0.36 A, thus, achieving a deposition rate of approximately 100 nm/min. The argon flow was adjusted manually at 20 ml/min, while the oxygen intake was controlled by the aforementioned PEM control unit, so that the intensity of the tin emission line remained constant.

By varying deposition temperature and pressure, we can control film structure. Density and crystallite size increase with temperature. It was found⁵ that at a deposition temperature of 460 °C, we have a low density film (43% single crystal) with a medium crystallite size (11 nm) and a high specific area (50 m²/g). This structure is suitable for high sensitivity, but the mechanical properties of the film depend on the density in an opposite sense to the sensitivity. For even higher deposition temperatures (560 °C) the microstructure is even more dense (85% single crystal) with a larger crystallite size (30 nm) and a lower specific area (15 m²/g). A scanning electron micrograph of such a sample shows a fine modular microstructure with spherical grains. Moreover, we know that total pressure during deposition affects film structure.⁵ Films are compact for total pressures less than 5×10^{-2} mbar, become columnar for pressures up to 0.8 mbar, and become spongy for pressures higher than 0.8 mbar.

The deposition of our films was carried out on Al₂O₃ substrates with dimensions 12×26 mm and heated at 300 °C, a temperature that ensures that the film consists mainly of [110] crystallites.⁶

The additive (Pt, Pd, Ni) was deposited using an Edwards Auto 306 electron beam evaporator. Information concerning the structure of the ultrathin film of metal catalysts was obtained indirectly by activation energy for conductance

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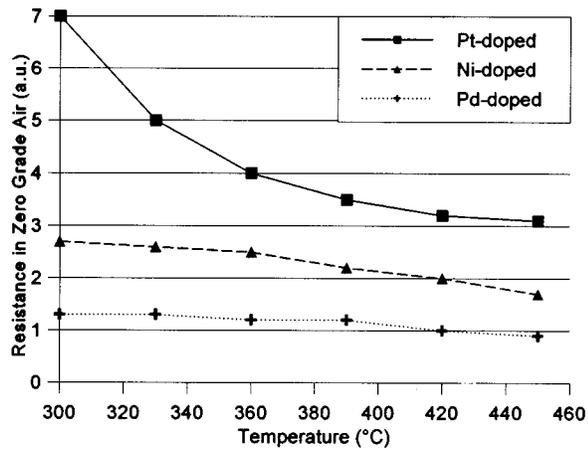


FIG. 1. Resistance from 300 to 450 °C in zero grade air for three films, one doped with Pt, one with Pd, and one with Ni.

measurements.⁷ It was found that the film of metal catalysts consists of discontinuous islands with an average dimension of a few nanometers (3–8 nm) and an average separation between particles in the same order of magnitude. Such results ensure adequate catalyst dispersion onto tin oxide grains, while a conductive noble metal layer with ohmic behavior is not formed.

The films fabricated were annealed for about one week at 400 °C in order to make their response stable. Figure 1 shows the resistance of the films in the presence of zero grade air [(ZGA), dry, purified mixture of 80% N₂ and 20% O₂] as a function of temperature, while Fig. 2 shows the sensitivity of the same films at 2000 ppm CO diluted in ZGA, for all three kinds of additives. Figure 3 shows the maximum sensitivity as a function of additive density in the case of CO for the three aforementioned additives. The *x* axis in Fig. 3 is the deposition time of the additive.

In the case of porous or thin film tin oxide based gas sensors, the large changes in conductivity in the presence of some gases cannot be explained only by the exchange of electrons between the crystal and the adsorbants. Thus, one has to consider the changes in the potential barriers at grain boundaries. This happens because the adsorbant can be rep-

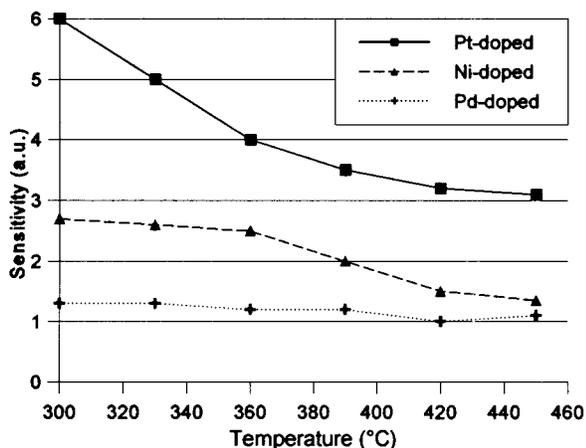


FIG. 2. Sensitivity in CO from 300 to 450 °C for three films, one doped with Pt, one with Pd, and one with Ni.

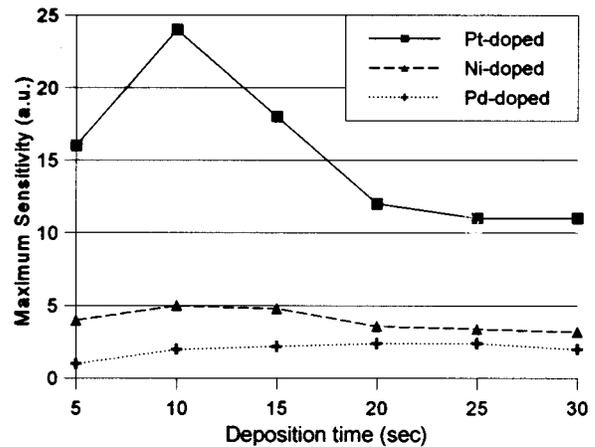


FIG. 3. Maximums of sensitivity in CO for Pt, Pd, and Ni doped films as a function of additive deposition time.

resented by a surface density of states that are of acceptor or donor type. The acceptor- or donorlike behavior depends on the kind of the adsorbant. Then, the crystal is depleted or accumulated. The degree of this depletion or accumulation depends directly on the grain size. This can be modeled by assuming that the induced surface state density is constant. In the case of oxygen, for example, this is true and is known as the Weisz limit.⁸ Then, the number of surface states is proportional to r^2 , where r is the radius of the assumed spherical grain. The number of electrons inside the grain is proportional to r^3 . Thus, stronger depletion or accumulation will occur in a smaller grain than in a larger one.

On the other hand, the contact of the metallic additive with the semiconducting oxide creates a barrier that is fully characterized by the electron affinity of the semiconductor, the work function of the metal and the density of surface states of the semiconductor that are located inside the energy band gap.^{9,10} Thus, in equilibrium and without the presence of an active gas, if the metal work function is great enough (greater than the sum of the electron affinity and the energy difference between the Fermi level and the conduction band of the semiconductor), a depletion layer will be developed in the semiconductor. The depletion layer thickness is modeled assuming a cylindrical grain with radius a , that is covered with a metallic additive in an angular aperture θ (in cylindrical coordinates from $\varphi = -\theta/2$ to $\varphi = \theta/2$). Then, using the abrupt approximation,¹¹ the depletion layer is developed across the radius in distance W and across the surface in the same distance or equivalently in an angular aperture W/a . Then the depleted area is

$$S = 2 \int_0^{\theta/2 + W/a} d\varphi \int_{a-W}^a x dx. \quad (1)$$

The free electrons inside the grain are then

$$n = n_0(\pi a^2 - S), \quad (2)$$

where n_0 is the free electron concentration. Considering then an equivalent grain with radius a' with the same electron concentration we have

$$a' = \sqrt{\frac{\pi a^2 - S}{\pi}}, \quad (3)$$

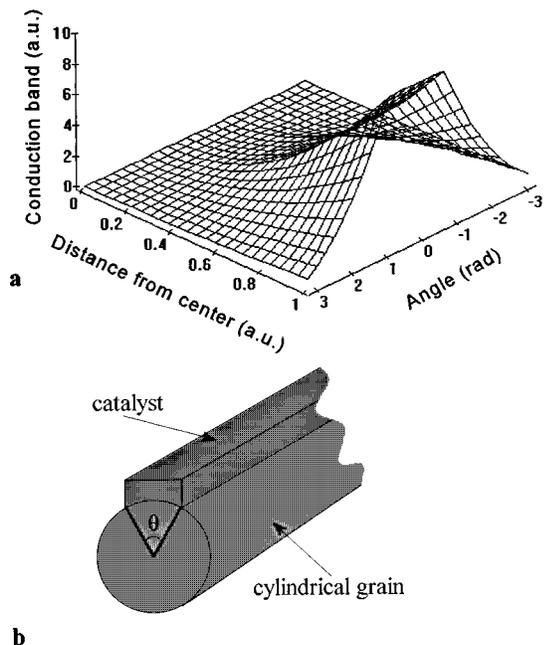


FIG. 4. (a) Conduction band of a cylindrical grain with unity radius and with a metallic cluster at its surface from $\varphi = -\pi/4$ to $\varphi = \pi/4$ and (b) model geometry.

and calculating S from Eq. (1) we get

$$a' = a \sqrt{1 - \frac{(\theta/a + 2W)(W - W^2/2a)}{\pi}}. \quad (4)$$

The depletion width W is

$$W = \sqrt{\frac{2\epsilon_s}{q^2 n_0} \left(\varphi_m - X - (E_c - E_f) - \frac{\delta}{\epsilon_i} q^2 D_s y_0 \right)}, \quad (5)$$

where φ_m is the metal work function, X is the electron affinity of the semiconductor, $(E_c - E_f)$ is the difference between the conduction band and the Fermi level of the semiconductor, δ is the thickness of the interfacial layer between the metal and the semiconductor, D_s is the density of surface states per unit area and eV, y_0 is the level below which the surface states are occupied for charge neutrality, and ϵ_i is the dielectric constant of the interfacial layer. Equation (5) was derived from the assumption that the bending of the semiconductor is proportional to the square of the depletion length.¹¹ The calculated potential in the semiconductor is shown in Fig. 4, for a grain with unity radius and for an angular aperture $\pi/2$ assuming that there is no contribution from surface states (see below).

It is equivalent, then, to assume that the active grain size is smaller than the geometrical one. Then, the conductivity of the sensor is decreased with increasing additive work function and, consequently, the sensitivity that is expressed as the change of conductivity over the initial one, is larger. This happens for two reasons; the first is that the initial conductivity decreases and the second is that the small grains are more sensitive to surface-state density changes as was mentioned above. Moreover, the greater the metal work function, the stronger the depletion depth in the semiconductor and, thus, the smaller the active grain size. This is confirmed by the experimental results as we can see in Figs. 1, 2, and 3.

The sensitivity of sensors doped with Pt with a work function of about 5.75 eV is larger than the sensitivity of sensors doped with Ni with a work function of about 5.25 eV, and this is greater than the sensitivity of sensors doped with Pd with a work function of about 5.15 eV, as is shown in Figs. 2 and 3. The same is true for the resistivity of the sensors as is shown in Fig. 1. For the work function of various metals one can see Ref. 12. The correlation between the electrically active grain size and the metal work function suggests that the role of interface states is relatively unimportant, perhaps because interface state densities are similar for the different metals.

One very important consequence is that by increasing the surface that the additive covers, the depletion layer in the semiconductor will be increased and, thus, the active grain size will be decreased. For this reason one could expect that the sensitivity will increase if the density of the additive is increased within limits. But one must consider here an additional conductivity mechanism that is due to the transition of electrons between the metallic areas. This mechanism is increased with increasing additive density and tends to decrease the sensitivity. This is confirmed by the experimental results as shown in Fig. 3, where only the maximum values of sensitivity are displayed. It is obvious from Fig. 3 that the above model is applicable for small additive concentration, where tunneling between the metallic particles can be neglected.

In conclusion, the electronic interaction between metallic additives and semiconducting oxide based gas sensors has been found to be critical in order to explain the dependence of sensitivity on various additives and at different temperatures. The dependence of the sensitivity on additive work function is explained, considering the depletion layer induced in a semiconductor by the metallic contacts. These layers decrease the electron availability of semiconducting grains, making their active size smaller than the geometrical. Correlation of the sensitivity with the grain size, allowed for the explanation of the experimental results at the presence of carbon monoxide, methane, and ethanol with Pd, Ni, and Pt doped in tin oxide gas sensors.¹³

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