# Resistance and capacitance analysis of Pd-doped and undoped SnO$_2$ thick films sensors exposed to CO atmospheres

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## Abstract

It was found that resistance and capacitance of Pd-doped SnO$_2$ thick films are largely modified by CO reaction with previous adsorbed oxygen at the grain surface while in undoped SnO$_2$ thick-films adsorption and reaction processes influence the response. In our analysis, the presence of Schottky potential barriers at the grain boundaries was consistent with the observed results. An increasing of sensitivity due to the addition of Pd is found to be related to the enhanced reaction of CO with the previous oxygen adsorbed at the grains surface. Mechanisms responsible for the sensor response are discussed.
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## 1. Introduction

It is well established that gas sensors based on semiconducting oxides and manufactured by screen-printing technique offer the desirable attributes of cheapness, simplicity, and process reproducibility. However, their selectivity and stability are still the key problems to be solved theoretically and experimentally. The sensing mechanism of these gas sensors involves an electrical conductance change caused by gas adsorption at the grains surface, which is highly dependent on the surface stoichiometry [1]. Also, the sensing properties are influenced by microstructural features such as the grain size, the geometry, and the connectivity between particles and dopants [2].

The technological progresses in tin oxide gas sensors as well as the basic understanding of all semiconductor gas sensors have deepened through the elucidation of the role of Schottky barriers and adsorbed oxygen [3,4]. It is known that the n-type semiconducting behavior of tin oxide is due to oxygen vacancies that act as donors. In these materials, grain boundary barriers depend on the amount of chemisorbed oxygen, and determine the electrical conduction. Oxygen, chemisorbed from the atmosphere, forms charged species trapping electrons at the grain boundaries that modify the potential barriers. Reducing gases, like CO, remove some of the adsorbed oxygen, the potential barriers are changed (and then the overall conductivity) originating a sensor signal.

Doped SnO$_2$-based sensors have many advantages such as fast response and good reproducibility including a long-term stability, and are not much affected by ambient disturbances, at least compared with other kinds of sensors [5–8]. It has been proposed that the high sensitivity of Pd-doped SnO$_2$ is due to the support/catalyst interactions, like spillover and Fermi energy control. Spillover has been extensively studied and it has been suggested that oxygen atoms, and even CO, can "spillover" from the catalyst metal, where they become activated, onto the surface of the support. By Fermi energy control, we are referring to the case where the supported catalyst pins the Fermi energy of the semiconductor support at the Fermi energy of the catalyst [1].

In this paper we present a study of the influence of Pd on the conduction process in SnO$_2$ thick films. These films were

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previously exposed to oxygen and finally were treated in a CO atmosphere. Isothermal electrical resistance and capacitance temporal responses under a CO atmosphere are presented. An interpretation of the possible sensing mechanisms is discussed.

## 2. Experimental

Commercial high-purity $SnO_2$ (Aldrich) was ground until a medium particle size of 0.42 μm. A thermal treatment process carried out at 1100 °C for 2 h led to powders with larger particle size (0.66 μm). The dry impregnation method was used in the preparation of Pd-doped $SnO_2$ thick films, 1% of tetraamin Pd (II) nitrate (Merck, reagent grade). Subsequently, the sample was dried at 60 °C during 24 h; the final content of Pd in the doped sample was 1%. After the impregnation the powders were thermally treated at 500 °C during 2 h. Then, a paste was prepared with an organic binder (glycerol) and the powders thermally treated and impregnated. The used solid/organic binder ratio was 1/2. Thick, porous film samples were made by painting onto insulating alumina substrate with interdigit shape gold electrodes deposited by sputtering. Finally, doped and undoped samples were treated during 2 h in air at 500 °C.

Through differential thermal analysis (DTA) (Shimadzu DTA-50) and thermogravimetric analysis (TGA) (Shimadzu TGA-50), the decomposition temperature of tetraamin Pd(II) nitrate was determined. The present phases were studied using X-ray diffraction (XRD) (Philips PW1830, Co Kα, filter of Fe, at 40 kV and 30 mA). A Philips 505 SEM was employed to image the tin oxide surfaces. The mean thick of the films was measured using a coordinates measuring machine Mitutoyo BH506.

We used an HP4284A LCR analyzer (frequency range of 20 Hz–1 MHz) with the computational support needed for the data acquisition. Capacitance and resistance vs. time curves were isothermally measured at 400 °C and 40 Hz for doped and undoped samples by changing the atmosphere from vacuum ($10^{-4}$ mmHg) to 40 mmHg of CO.

## 3. Results and discussion

Through DTA and TGA techniques it was determined that the decomposition temperature of tetraamin Pd(II) nitrate occurs at 240 °C. From the XRD analysis, carried out on calcinated doped powders, only the signals corresponding to Pd and $SnO_2$ were observed.

In Fig. 1 SEM micrographies of the undoped and Pd-doped samples show the presence of agglomerates and a highly homogeneous and porous microstructure. Doped and undoped $SnO_2$ samples presented similar characteristics and differences in the grain size were not detected. The mean thick of the films was 440 μm.
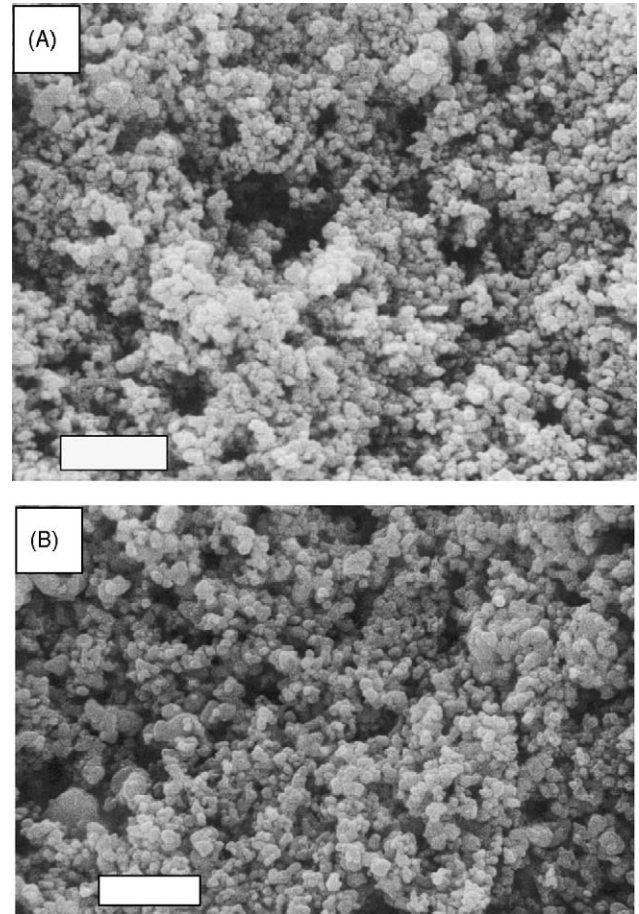


Fig. 1. SEM photomicrographs of the undoped (A) and Pd-doped (B) $SnO_2$-thick film top surface. Bar = 2 μm.

In previous work we found that thick films made of particles with size of 0.1 μm have grains with mostly overlapped potential barriers [9,10]. In this work, $SnO_2$ thick films present grain sizes higher than 0.1 μm for which barriers are almost all not overlapped.

For Schottky barriers (samples with non overlapped barriers), the capacitance is related to the electron concentration in the bulk, $n$, and the barrier height, $V_B$, as Eq. (1) [11].

$$C \propto \left( \frac{n}{V_B} \right)^{1/2} \tag{1}$$

Therefore, a diminution of the capacitance can be related to a higher barrier and/or to the reduction of the donor concentration due to the annihilation of oxygen vacancies.

In exposing the samples to CO, the experimental resistance and capacitance versus time curves will be discussed based on the following processes.

### 3.1. Process 1

It is generally accepted that carbon monoxide adsorption on a $SnO_2$ surface has a large electrostatic character

reinforced by a substantial donation of charge from CO to the Sn cation [12–14]. Thus, CO adsorption should produce an increasing in conductivity. However, in our experimental results, an initial increasing in the resistance is observed when a sample maintained in an evacuated chamber is exposed to a CO atmosphere. It is expected that, at low pressures, oxygen desorbs modifying the grain surface. Results indicate that adsorption generates acceptor states responsible for increasing the intergranular barrier height.

### 3.2. Process 2

Carbon monoxide reacts with oxygen adsorbed on the tin oxide surface according to these equations,

$$O'_{ads} + CO(g) \leftrightarrow CO_{2ads} + e' \tag{2}$$

$$CO_{2ads} \leftrightarrow CO_2(g) + S, \tag{3}$$
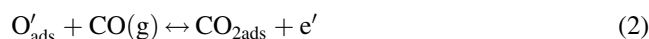
where S correspond to the sites in the surface where oxygen can be adsorbed. This reduction in the oxygen amount makes the sample conductivity and capacitance higher.

### 3.3. Process 3

Oxygen diffuses out of the grains [15]:

$$O_b \leftrightarrow O'_{ads} + V_o^+, \tag{4}$$

where $O_b$ correspond to the bulk oxygen. Once at the surface, Process 2 takes places. Thus, generated oxygen vacancies in the grains act as electron donors increasing the film capacitance and conductance. Finally, oxygen that reacted at the surface with CO desorbs as $CO_2$.

In Fig. 2, the resistance as a function of time for an undoped $SnO_2$ is shown. This curve can be understood as follows (note that the sample was previously treated in oxygen and then has a low amount of oxygen vacancies). The initial increasing of the resistance with the CO exposition is associated to an increasing in the barrier height (Process 1). Then, the resistance diminution with time
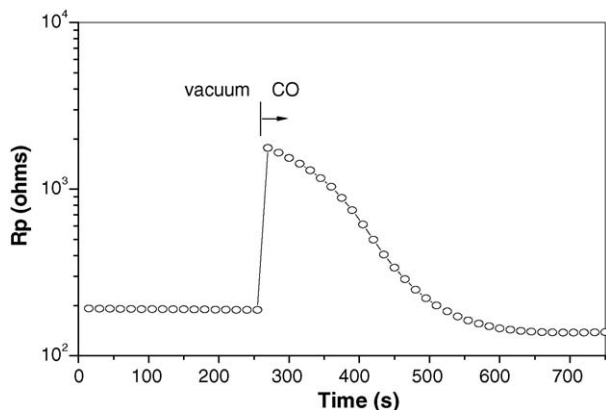


Fig. 2. Time response of resistance for undoped $SnO_2$ sample when the atmosphere is changed from vacuum ($10^{-4}$ mmHg) to CO (40 mmHg) at 400 °C.
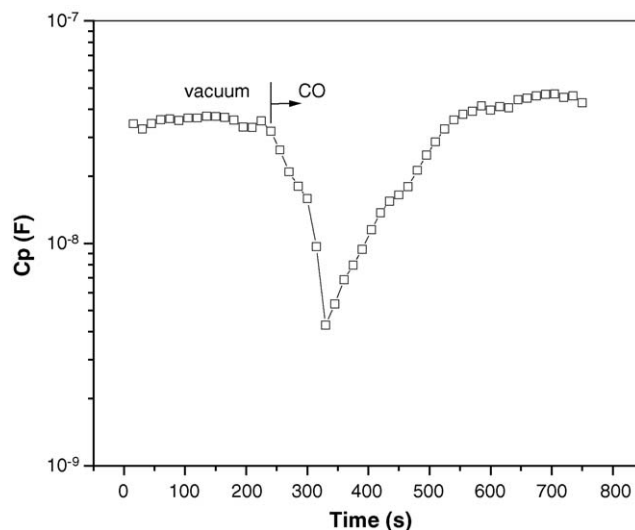


Fig. 3. Time response of the capacitance for an undoped sample when the atmosphere is changed from vacuum ($10^{-4}$ mmHg) to CO (40 mmHg) at 400 °C.

can be related to the reaction of CO with oxygen adsorbed on the grain surface since this reaction leads to a decrease of the barrier height (Process 2). Finally, the resistance presents an asymptotic value indicating that the system reached steady state.

To gain confidence in our interpretation, we also studied the capacitance as a function of time, Fig. 3. The initial decrease of the capacitance with the CO exposition is associated with an increase in height and width of the barriers (Process 1). Thus, the depletion regions of intergrain barriers become wider and constitute a larger part of the grains. Later, the increasing of the capacitance with time is related to the reaction of CO with oxygen adsorbed at the grains surface. This reaction produces a diminution of the barrier height and of the depletion width and then an increase of the capacitance is observed (Process 2). In this case, if the superficial oxygen is consumed and oxygen diffusion out of the grains becomes a relevant process (Process 3), the depletion width of the barriers becomes smaller while the barriers heights are not altered. This process would also contribute to increase the capacitance.

In Figs. 4 and 5 a similar temporal set to that of Figs. 2 and 3, but for Pd-doped $SnO_2$ films, are reported. As for undoped $SnO_2$ thick film case, the sample was previously treated with oxygen at 400 °C. During this exposition, due to the presence of Pd, a great amount of oxygen is adsorbed on the surface of the films. As in the case of undoped gas sensors, the processes that take place are those named Processes 1 and 2. However, the temporal response of the resistance for the Pd-doped sample, presented in Fig. 4, did not show the features observed in Fig. 2. Due to the Pd presence, the superficial oxygen is consumed so rapidly that Process 1 remained unnoticed. The large decrease of the resistance indicates an enhanced effect on the barrier height and the depletion width due to oxygen consumption.
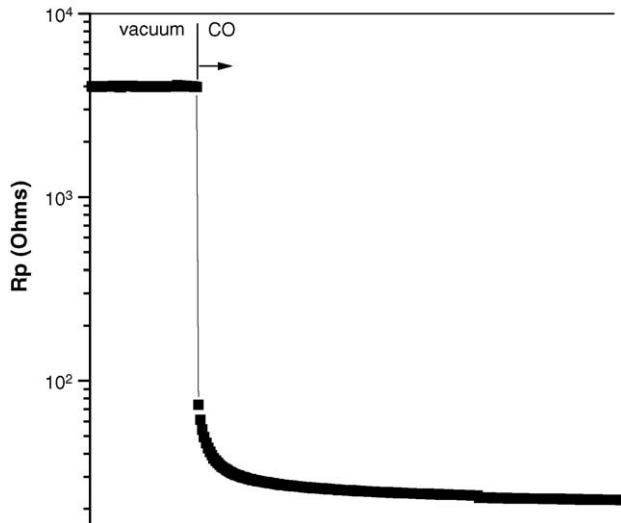
Fig. 4. Time response of the resistance for Pd-doped $SnO_2$ thick film sample when the atmosphere is changed from vacuum ($10^{-4}$ mmHg) to CO (40 mmHg) at 400 °C.

As before, we studied the capacitance temporal evolution for the Pd-doped sample (Fig. 5). From Eq. (1), a diminution of the capacitance should be detected. However, Process 1 is not perceived. The only variation observed in the capacitance temporal response is a fast increase immediately after the gas sensor is exposed to the CO atmosphere. This is associated to a decrease in height and width of the barriers due to the rapid catalyzed reaction of CO with previous adsorbed oxygen on the grain surface (Process 2).

Steady state values of resistance and capacitance show a much larger sensitivity for the Pd-doped sample. Indeed, the resistance sensitivity is more than 200 times larger. This is consequence of two effects: the initially larger amount of adsorbed oxygen and the enhanced reaction of CO with oxygen due to the presence of Pd.
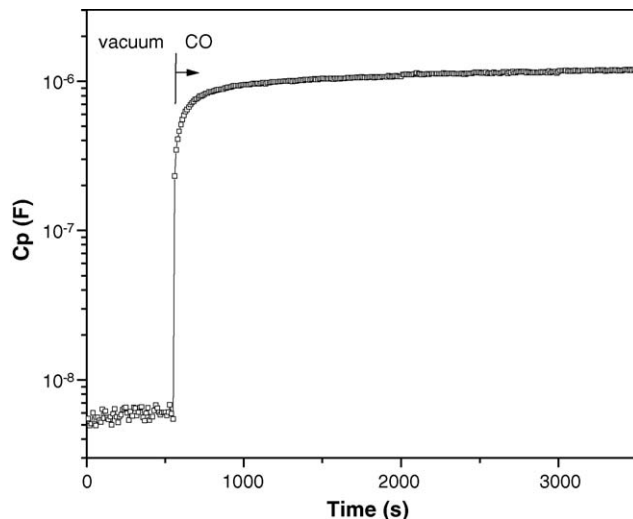


Fig. 5. Temporal capacitance response of Pd-doped $SnO_2$ thick film sample when the atmosphere is changed from vacuum ($10^{-4}$ mmHg) to CO (40 mmHg) at 400 °C.
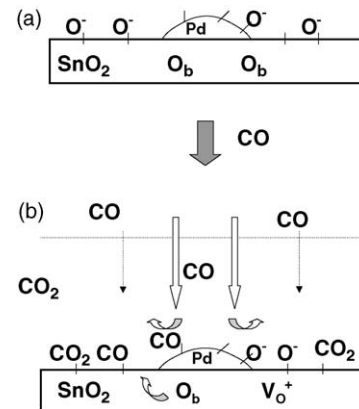


Fig. 6. Pd-$SnO_2$ thick film model for the adsorption and reaction. In (a), the previous oxygen adsorption is observed. In (b), carbon monoxide reacts with the oxygen adsorbed at the grains surface [5].

Finally, in Fig. 6 a Pd-$SnO_2$ thick film model for the adsorption and reaction is introduced. Due to the presence of Pd a great amount of oxygen is adsorbed at the grains surfaces (a). After exposition, CO occupied the empty sites of the surface (Process 1). Finally, CO and oxygen react to form $CO_2$ that desorbs (b) (Process 2) [5].

## 4. Conclusions

From the experimental results it is possible to conclude the following.

1. The CO exposure of undoped tin oxide thick films provokes an increasing of the potential barriers height. After that, the reaction of CO with previous adsorbed oxygen at the grains surface produces a diminution of the barrier height and of the depletion width and then an increase of the capacitance and a decrease of the resistance are observed.
2. The process of CO adsorption on the grain surface for doped tin oxide thick films is not detected through capacitance and resistance measurements. The resistance and capacitance responses indicate a rapid decrease in height and width of the barriers due to the reaction of CO with previous adsorbed oxygen on the grain surface.
3. The presence of Pd increases the thick films sensitivity and catalyzes the reaction of CO with previous adsorbed oxygen.

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