Influence of oxygen adsorption and diffusion on the overlapping of intergranular potential barriers in SnO$_2$ thick films

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Abstract

Complex impedance analysis and transient response studies in SnO$_2$ thick films show the impedance dependence on gaseous environment and temperature. Possible mechanisms responsible for the found behaviors are proposed. The influence of temperature on the oxygen diffusion into the grains annihilating oxygen vacancies was detected. In particular, we found the transition from having bulk regions unaffected by surface phenomena to the overlapping of potential barriers due to an oxidizing gas.

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1. Introduction

Semiconductor gas sensors based on tin oxide have been widely accepted for detecting and monitoring oxidizing or reducing gases [1–3]. Small tin oxide grains in contact with each other form thin or thick films, or disks as the sensing material. The sensing ability of tin oxide sensors is based on their semiconducting properties. In particular, the depletion layers at grain surfaces that have to be crossed by the current in passing from one grain to another determine the material resistance [4,5].

According to the generally accepted interpretation for electrical conduction in polycrystalline semiconductors, discrete energy levels within the band gap are responsible for the formation of Schottky barriers at grain surfaces. The n-type character of tin oxide is a consequence of oxygen vacancies that act as donors. Then, the negative charges due to chemisorbed oxygen at grain surface increase the Schottky potential energy barriers at the intergrains, having a pronounced effect on the electrical conductance. Reducing gases like CO react with oxygen species adsorbed at the intergrains, then the Schottky barriers decrease and the electrical conduction is facilitated [6].

For grains large enough, there exists a bulk region that remains unaffected by surface phenomena. Small grains, on the contrary, can be completely depleted if potential energy barriers overlap [7–9]. It is possible that the exposure to an oxidizing gas causes the overlapping of potential barriers and that due to the exposure to reducing gases a depleted grain becomes only partly depleted.

In contrast to the widespread applications of tin oxide based gas sensors and to the success in their developing, the understanding of their characteristics founded on basic mechanisms is still immature. Indeed, despite extensive research and development, there is no complete consensus regarding the basic mechanisms responsible for the sensor behavior. In fact, different models and interpretations coexist [7,9,10]. In this work, we present results of a complex impedance study in order to identify the processes taking place in tin oxide thick films. To analyze the possible conduction mechanism involved in the film a transient study during heating and cooling is also reported.

2. Experimental

Commercial high purity SnO$_2$ (Aldrich) was ground until a medium particle size of 0.4 μm (P1) was attained. A thermal treatment carried out at 1100°C for 2 h led to powders with larger particle size (P2) [11]. Then, a paste with an
organic binder (glycerol) and the powder thermally treated was prepared. The used solid/organic binder ratio was 1/2 and no dopants were added. Thick, porous film samples were made by painting onto insulating alumina substrate on which gold electrodes with an interdigit shape were deposited by sputtering. Finally, samples were thermally treated during 2h in air at 500 °C. Samples were labeled S1 (derived from powder P1) and S2 (derived from powder P2).

To image the tin oxide surfaces, a Philips 505 SEM was employed. Size particle distributions of the powders (P1 and P2) were determined by the Sedigraph technique with a Micromeritics and the mean thick of the films using a coordinates measuring machine Mitutoyo BHS06.

In this work, an impedance analyzer HP4191A in a frequency interval of 5 KHz to 13 MHz was used. The system was linked to a computer for programming the measurements and for storing and handling the data. Z’ versus Z’’ curves were measured at different temperatures changing the atmosphere of nitrogen (760 mmHg) into oxygen flux (160 mmHg). Also, temperature cycling experiments were carried out. Experimental data were fitted with a R (RC) equivalent circuit using the Zview 2.1 program for windows software. In resistance versus temperature cycling experiments, measurements were carried out while raising and then decreasing the temperature in the range 50–425 °C at a rate of ∼4 °C/min with the sample kept in oxygen (8.4 mmHg) and in vacuum (10⁻⁴ mmHg). Resistance versus time curves were determined changing the vacuum (10⁻⁴ mmHg) into an oxygen atmosphere (8.4 mmHg) and then, after having reached quasi-saturation, back to vacuum. Sensors of the same type do not present the exact same impedance values. However, we focus here on their qualitative behavior, so the same sensor was used for a complete set of measurements. We emphasize, however, that shown results are representative of the ten samples we tested and that the conclusions are of general validity.

3. Results and discussions

Table 1 shows data from particle size distributions corresponding to powders P1 and P2. We considered that $D_{80}$, $D_{50}$, and $D_{20}$ are the corresponding diameters of 80, 50, and 20% vol., respectively, and $W = (D_{80} - D_{20})/D_{50}$ is a measure of the distribution width of particle size. From Table 1, it is apparent that the increasing in the particle sizes is significant after the powder calcination at 1100 °C. Also, powder P2 has a wider particle size distribution. These findings are in accord with results reported in the literature [9].

![Fig. 1. SEM photomicrographs of the SnO$_2$ thick film top surface: (A) Sample S1, (B) Sample S2. Bar = 2 μm.](image)

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$D_{20}$ (μm)</th>
<th>$D_{50}$ (μm)</th>
<th>$D_{80}$ (μm)</th>
<th>$W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>0.15</td>
<td>0.42</td>
<td>0.88</td>
<td>1.74</td>
</tr>
<tr>
<td>P2</td>
<td>0.26</td>
<td>0.68</td>
<td>3.3</td>
<td>4.47</td>
</tr>
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</table>

In Fig. 1, a SEM micrograph of the samples S1 and S2 are shown where an homogeneous microstructure with a highly porous microstructure is observed. From this figure, we determined that the particle size for S1 ranged between 50 and 150 nm and for S2 ranged between 250 and 420 nm. The mean thick of the films was 100 μm for S1 and 440 μm for S2.

Impedance curves for samples with small grains, S1, derived from powder P1 could not be obtained. By solving the Poisson’s equation under the “depletion approximation,” or resorting to the Gauss theorem, the maximum grain boundary barrier height for a spherical grain is given by

$$V_B = \frac{qN_0R^2}{6\varepsilon}$$  \hspace{1cm} (1)

where $R$ is the radius of the grain and $N_0$ is the donor density. Based on reported experiments, Schottky barrier heights are around 1 eV and the donor density is in the order
of $10^{24} \text{m}^{-3}$ [12,13]. With these values, the critical grain size (diameter) for which the grains are completely depleted is $\sim 110 \text{nm}$. It is expected then that grains in sample S1 present an overlapping of the depletion regions with grains completely depleted. Consistently with these calculations, we found that capacitances are very small and the complex impedance analysis becomes impracticable for sample S1 with the simple model regularly applied. In what follows we will focus exclusively on sample S2.

The electrical behavior of the tin oxide films was analyzed using impedance plots in which the impedance $Z$ is shown in a complex plane with the reactance, imaginary part of $Z$, plotted against the resistance, real part of $Z$ [14]. Results were fitted with a simple $R \ (RC)$ electrical model. Fig. 2 shows the equivalent circuit generally used to describe the impedance of polycrystalline semiconductors. The capacitance $C$ and the resistance $R_2$ are associated with the inter-grains and $R_1$ with the bulk.

The impedance of a resistance $R_2$ in parallel with a capacitance $C$ is given by

$$Z_2 = \frac{R_2 + j\omega C}{R_2 + j\omega C}$$

that can be expressed as

$$Z_2 = \frac{R_1 - j\omega R_2 C}{1 + j\omega R_2 C}$$

From this equation, the real part, $Z_2'$ and the imaginary part, $Z_2''$ can be easily extracted and they are connected as

$$Z_2'^2 + Z_2''^2 = R_2 Z_2'^2$$

Eq. (4) can be written as

$$\left(\frac{Z_2}{Z_2'}\right)^2 + \frac{Z_2''^2}{Z_2'^2} = \left(\frac{R_1}{Z_2'}\right)^2$$

This is a circumference of radius $R_2/2$ centered at $R_2/2$. The addition of a series resistance $R_1$ only shifts the resulting circle. Thus, $R_1$ and $R_2$ are derived from the low- and high-frequency resistance, respectively, and the capacity can be found from the maximum value of the reactance.

Results for a sample under a nitrogen atmosphere are presented in Fig. 3. Circumferences become smaller as a function of temperature. This indicates that $R_2$ is a monotonically decreasing function of temperature, effect that is expected since current transport mechanisms are all facilitated with temperature. In Fig. 4, the boundary resistance is plotted as a function of temperature (empty circles, from A to B). Assuming an Arrhenius relation the effective activation energy could be determined to be $E_1 = 0.53 \text{eV}$. Conversely, the boundary capacitance is not very affected by temperature in this range. These results are consistent with previously reported results in polycrystalline semiconductors [14]. We found that after cooling down, the value of the initial resistance was not recovered (point C in Fig. 4). This is an indication that the sample lost some oxygen while heated in an inert atmosphere.

In Fig. 5, impedance plots under oxygen are presented. As the sample is heated up to $265 \degree \text{C}$, the impedance circles become smaller as observed in the experiment under...
bulk capacitance is related to the electron concentration in the its previous values after the cycle. In a Schottky barrier the capacity does not change much but it does not recover peratures under an oxygen atmosphere of 160 mmHg

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Capacitance (pF)</th>
<th>R₂ (kΩ)</th>
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<tbody>
<tr>
<td>160</td>
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<tr>
<td>240</td>
<td>121</td>
<td>3363</td>
</tr>
</tbody>
</table>

The diminution of the final capacity then can be related to a higher barrier, to the reduction of the donor concentration due to the annihilation of oxygen vacancies after the oxygen diffusion into the grains, or to both phenomena. The ratio between the initial and final capacities was found to be $C_{\text{initial}}/C_{\text{final}} = 1.144$ that implies, through Eq. (6)

$$\frac{n_1 V_B}{n_2 V_B} = 1.31$$

Several authors [15,16] have proposed that thermionic conduction is the dominant conduction process in SnO₂ thick films. However, tunneling through the barriers must be included for the barrier widths reported [17]. A reduction in the donor concentration, as determined from the experiments, naturally implies significant changes in the sample resistance as observed. To determine the sample resistance, the total current density is calculated here as the sum of a thermionic current and a tunneling current through a reverse-biased Schottky diode. It is found that for the values of barrier height and donor density, the tunneling current is dominant. If the change in capacitance were entirely due to a change in the barrier height, the resulting associated resistance would be much smaller than the one measured. Conversely, if the change in capacitance were entirely due to a change in the donor concentration, the resulting associated resistance would be much larger than the one measured. Assuming reasonable values for $V_B$ (0.8 eV) and $n$ (10¹⁸ cm⁻³) we found that the barrier height must increase about 0.16 eV and simultaneously the donor concentration must decrease about 10%. These findings are consistent with oxygen adsorption and diffusion into the grains.

To corroborate the above considerations we measured the conductance behavior in successive cycles of increasing maximum temperature and the transient response of the film resistance under a change in their atmosphere for several temperatures.

In Fig. 6, we analyze the conductance behavior in successive cycles of increasing maximum temperature. As observed, after every temperature cycle the film conductivity is lower than that prior to the cycle. As temperature increases, oxygen can diffuse into the film and also into the grains. Then, the observed response can be related to the oxygen adsorption at the grains surface, that increases the barrier height, and to the oxygen diffusion into the grains of SnO₂, that annihilates oxygen vacancies and then widens depletion regions. Both processes lead to a higher resistance but the diffusion at intergrains is much faster than the diffusion into the grains [18]. The hysteresis in the patterns of Fig. 6 has been observed before [19,20]. This effect has been attributed to the reaction kinetics of the interacting gases at the tin oxide surface. In our case, the hysteresis indicates that the heating and cooling rates are too fast for the system to reach steady state so the amount of oxygen at the grains is higher during the cooling down leading to a lower conductivity. At the end of each cycle there is an amount of oxygen that once diffused into the grains...
remains there and then the conductance is lower than the starting one.

In Fig. 7, we present the response of the SnO$_2$ film after the exposure to an oxygen atmosphere (8.4 mmHg). At low temperatures we observed a rapid increasing of the resistance and then a slow stabilization. We found that at high temperatures ($T > 360{\degree}C$), after a rapid increasing, the resistance shows a diminution for large enough exposing times. This is clearly observed in the response corresponding to $T = 405{\degree}C$. To explain these results we have to consider that due to the first contact with oxygen, as the diffusion of oxygen into the film takes place, new surface states at grains are responsible for increasing the barrier heights and, as a consequence, the film resistance. Then, the oxygen diffusion into the grains can occur, a much slower process than its surface adsorption. This process annihilates oxygen vacancies modifying the donor concentration. At low temperatures, the diffusion into the grains is slow compared to the time frame of our experiments. On the contrary, at high enough temperatures the diffusion into the grains is important and depletion regions increase enough so they can overlap. After this takes place, the film resistance diminishes.

4. Conclusions

From the experimental results it is possible to conclude the following:
1. A simple $R(1/C)$ equivalent circuit permits to explain the impedance plots.
2. The oxygen diffusion into the grains annihilates oxygen vacancies and modify the donor concentration leading to wider intergrain potential barriers and a lower electrical conductance.
3. Tunneling conduction correctly accounts for the observed results.
4. The overlapping of potential barriers due to an oxidizing gas was detected.

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