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Effects of thermal treatments on the conductance of tin oxide

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Abstract

Temperature dependence of electrical conductivity during heating and cooling under different atmospheres and resistivity transients at step isothermal changes in oxygen pressure of SnO_2 sintered pellets are investigated. It is found that different thermal treatments in sample preparation give rise to diverse conductivity behaviors as a function of temperature and transient responses. These results indicate that grain sizes and widths of the depletion layers are responsible for the observed results. Also, oxygen diffusion into the tin oxide grain plays a significant role accounting for the observed conductance changes.

Keywords: Electrical conductivity; Grain boundaries; Sensors; SnO_2

1. Introduction

Semiconductor gas sensors have been extensively investigated and important devices for detecting a variety of gases have been developed. Highly porous tin oxide (SnO_x) has been shown to be suitable as the sensing element of gas sensors.[1,2] These sensors are employed in gases detection due to their simplicity, sensibility, and low cost. The sensing mechanism of SnO_2 gas sensors is essentially related to their granular nature. For this reason, control of their microstructure is important in the optimization of the sensor performance.[3]

The electrical conductivity of ceramic semiconductors can change by exposing their surface to different gases. When the SnO_2 surface is exposed to a reducing atmosphere containing a flammable gas, the gas reacts with adsorbed oxygen molecules and then electrons that have been trapped as negatively charged ions (O_2^-, O^-, and O^{-2}) are released. The contact of flammable gases with SnO_2 does not only eliminate adsorbed oxygen but can also create oxygen vacancies by the reduction of SnO_2 itself. Both processes give rise to the increase of the carrier concentration.[4–6]

It is well known that many factors affect the sensing properties of semiconductor gas sensors. It is generally accepted that gases are responsible for an electron transfer between bulk and grain surfaces and then double Schottky barriers at the grain boundaries are modified. These barriers are modulated by the type and amount of intergranular species which is thus sensed through the resistivity of the sensing element.[6] Electrical conductance is directly related to surface band bending which is modified by chemisorption that induces surface states. Also, the variation of bulk defect concentration due to atomic diffusion has been considered to affect the sensor response[7] and microstructure details have been shown to modify electrical properties of polycrystalline materials.[8,9] The details in all these mechanisms are not completely understood.

Three main gas sensing models have been proposed for polycrystalline devices: the double Schottky model, the neck model, and the ultrafine particle model.[10] Xu et al. have presented a study for the conduction grain size effects on the sensing elements. They proposed that when the grain size is far larger than the length of two depletion layers, the grain boundary controls the conductivity. On the other hand, when the grain size is comparable to the length of two depletion layers, necks control the conductivity and, when the grain size is smaller than the length of two depletion layers, the grain is responsible for the observed conductivity.[11]

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Despite the many contributions in the field, there are still many unknown details about the mechanisms of the sensor resistivity response to gas exposure. Among them, thermal treatments during sample preparation can affect the sensing process due to the possible effects on the grain sizes, grain boundaries, and necks formation. In this work, samples sintered with different thermal treatments were studied in order to analyze the effect of the grain size and the shape of intergranular barriers in the conduction process. The relevance of the mechanisms responsible for the changes in electrical conductance of gas sensors based on tin oxide is discussed.

2. Experimental details

Samples were made of commercial high purity SnO_2 (Carlo Erba). They were ground in an agate mortar and pressed at 200 Kg/cm^2 into disks of 1 cm of diameter and 0.1 cm thick. Samples were sintered in air at 1000 or 1100°C for 3 h, and then they were quenched or cooled in steps of 50°C and 20 min between 700 and 300°C. The microstructural characterization of the fractured samples was performed by Scanning Electron Microscopy (SEM) (Philips 505). Specific surface area measurements were carried out using the BET method with a Micromeritics Flowsorb II 2300. Densities of the samples were measured using the Archimedes' method. Electrical characterization was performed on silver painted samples. The resistance was first allowed to stabilize in vacuum at a given temperature in the range 190–320°C. Resistance vs. time curves were measured while changing the vacuum into oxygen flow and, after having reached quasi-saturation, changing the oxygen flow back into vacuum. In temperature cycling experiments, conductance was measured while raising and then decreasing the temperature in the range 20–283°C at a rate of ~2°C/min with the sample kept in oxygen (30 mm Hg) and in vacuum (10^{-4} Torr).

3. Results and discussions

From SEM micrographies, the average grain size of samples sintered at 1100°C was determined to be 0.17 μm while for samples sintered at 1000°C the average grain size was 0.1 μm. Also, density values increase about 10% and the specific surface area decrease about 20% with the sintering temperature.[12]

Fig. 1 shows the resistivity vs. time curves for samples obtained through different thermal treatments after changing the vacuum into oxygen flow ($t = 0$) and back into vacuum. They were sintered at 1100°C and quenched (sample A) and sintered at 1000°C and cooled in steps (sample B). Measurements were carried out at ~195°C.

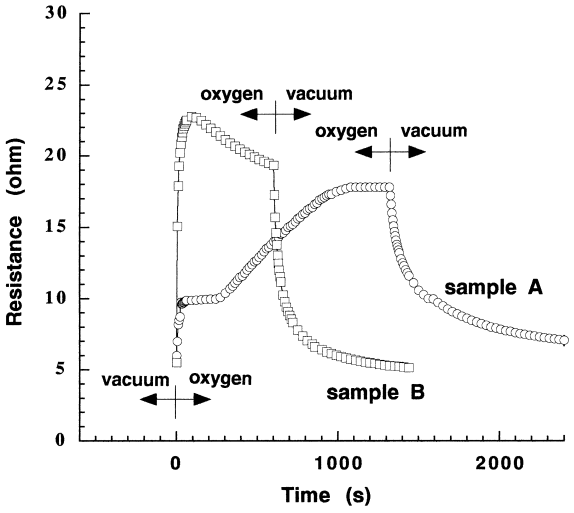

Fig. 1. Resistivity vs. time curves for a sample sintered at 1100°C and quenched (sample A) and a sample sintered at 1000°C and cooled in steps (sample B).

Sample A shows a monotonous increasing in the resistivity with time after the exposure to oxygen. Sample B also shows an increase in the resistivity with the exposing time to oxygen but after ≈1 min the resistance starts to decrease with time.

Differences in electrical response can be explained by looking into the effects of different thermal treatments: the microstructure of the polycrystalline sample and the intergrain potential barriers. Polycrystalline samples quenched from the sintering temperature present steeper Schottky barriers at the intergrains than those cooled in steps.[13] For samples cooled slowly in steps, oxygen can diffuse better into the tin oxide grains annihilating oxygen vacancies and, then, depletion layers extend into the grains farther than in quenched samples.

The rapid increase of resistivity, when the sample is exposed to oxygen, indicates that equilibrium at the surface is rapidly reached. Oxygen interaction with the surface originates an electron transfer from the bulk to the adsorbed oxygen. From this process the barrier height and the depletion layer increase, resulting in a sample with a higher resistivity. We proposed that subsequent slow changes in resistivity are due to oxygen diffusion into the grains that affects the oxygen vacancies concentration and then the Schottky barrier widths.[12]

The electrical behavior of sample B can be understood by considering grains with overlapping Schottky barriers due to the small grain size. A reduction of the donor concentration in grains where depletion layers do not overlap implies a higher resistivity since electron transport across wider barriers is more difficult. On the other hand, a reduction in the donor concentration for overlapped barriers raised the bottom of the conduction

band at the grains bulk. We propose that this effect facilitates electron transport since they cannot occupy low energy states at the grains.

In Fig. 2 conductance vs. temperature for a sample sintered at 1100°C and quenched in temperature cycling experiments are presented. Conductance was measured by raising and then decreasing the temperature under oxygen reaching different final temperatures. For temperature ramps in a range below 250°C, the conductivity change is small and recovers its value of room temperature. In Fig. 2 we show the consequences for the conductivity of carrying a cycle that reaches 250 and 283°C. For ramps with a highest temperature of 250°C or higher, as shown in Fig. 2, oxygen can be absorbed as determined from the change in the final resistance after cooling the sample. Note that the conductivity after the temperature cycle decreases.

The results of Fig. 2 are consistent with those of sample A (of the same thermal treatment) in Fig. 1. Considerations on the effects of oxygen indiffusion of the vacancy concentration make it possible to rationalize why conductivity decreases. Indeed, oxygen indiffusion reduces the vacancy concentration and then double Schottky barrier become wider and then the conductivity decreases. The opposite effect is observed when the cycle is performed under vacuum (not shown): oxygen is outdiffused and the original conductivity is recovered. Temperature facilitates thermionic and tunneling currents through the intergrain barriers. This effect competes with oxygen adsorption that raises barrier heights and then decreases conductivity. The thermic effect clearly dominates in the upper range of our studies.

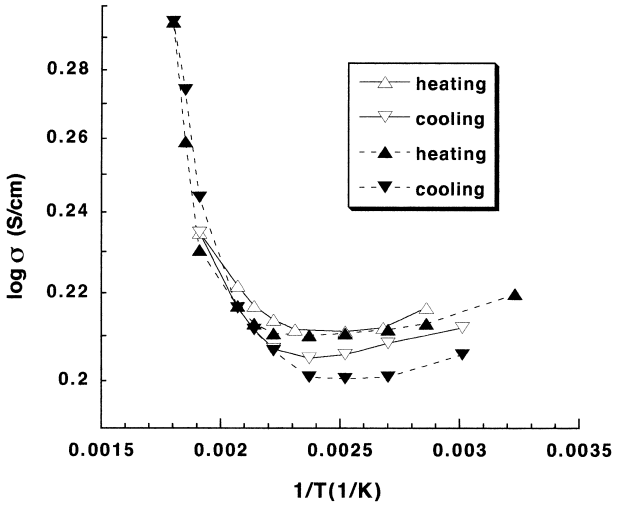

Fig. 2. Electrical conductivity of a sample sintered at 1100°C and quenched measured during heating and cooling under oxygen (30 mm Hg) as a function of reciprocal temperature. Open symbols correspond to a cycle with a maximum temperature of 250°C and closed symbols to a subsequent cycle with a maximum temperature of 283°C.

Yoon et al. also observed hysteresis after a temperature cycle.[14] They attributed the final resistivity difference to the adsorption and desorption of water vapor. In our experiments this mechanism is not present because samples are heated up to 350°C under vacuum and kept under vacuum before the temperature cycles are carried out. Their samples, having large grains, show a weak temperature dependence for $T < 200$°C. This is similar to our results of Fig. 2 indicating that the same conduction mechanism governs conductivity in both systems.

In Fig. 3 conductance vs. temperature for a sample sintered at 1100°C and cooled in steps in temperature cycling experiments is presented. As in the case of Fig. 2, for temperature ramps in a range below 250°C, the conductivity change is small and, after cooling, recovers its value of room temperature. Conversely, the effect of heating and cooling under oxygen with ramps that reach a temperature of 250°C or higher produces in these samples a final effect of increasing the sample conductivity. A subsequent cycle under vacuum has almost no effect (not shown). Also, note that the conductivity is much sensitive to changes in temperature. These results indicate that a different conduction mechanism, than that for the sample of Fig. 2, dominates in this case. We propose that depletion widths are now large enough to produce the overlapping of the intergranular barriers. Apparently, in the temperature cycle under vacuum, competing mechanisms — oxygen indiffusion vs. desorption — keep the conductivity almost unchanged.

Fig. 4 shows a plot of conductance vs. temperature for a sample sintered at 1000°C and cooled in steps. At room temperature, the conductivity is lower than for samples sintered at higher temperatures because of the smaller size of its grains (implying a larger number of

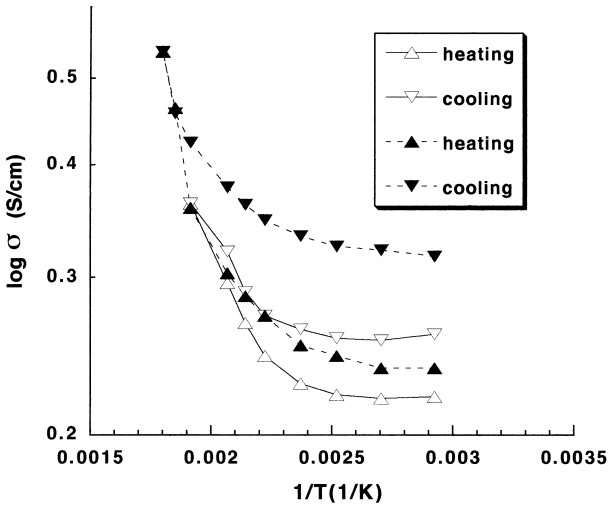

Fig. 3. Electrical conductivity of a sample sintered at 1100°C and cooled in steps during heating and cooling as in Fig. 2.

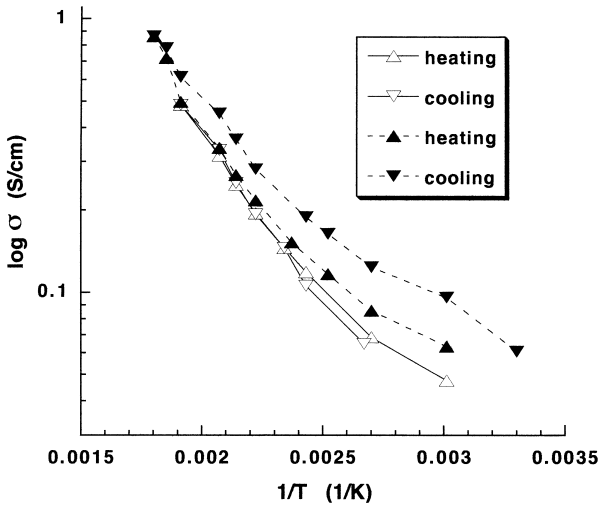

Fig. 4. Electrical conductivity of a sample sintered at 1000°C and cooled in steps measured during heating and cooling as in Fig. 2.

intergrain barriers). However, as temperature raises, the conductivity increases to greater values than for samples with larger grains. Also, note that the conductivity can be fitted with a straight line indicating that its behavior could be represented with an activated process. We propose that, in this case, most of the grains present a barrier overlapping that is responsible for the observed change in conductivity temperature dependence. As for samples of Fig. 3, oxygen indiffusion is responsible for increasing the sample conductivity. The subsequent temperature cycle under vacuum also increases the sample conductivity (not shown) as expected from a dominant effect of oxygen desorption and the reduction of the barrier heights.

4. Conclusions

Our findings can be explained as a consequence of Schottky-like barriers at the intergranular contacts. We needed to include two effects due to the presence of oxygen: the barrier heights and barrier widths modulations due to the oxygen adsorption and diffusion into the tin oxide grain. These mechanisms produce changes in the resistivity as a function of time that depend on the sensing element microstructure. In particular, for samples sintered at 1100°C and quenched from the sintering temperature (grain size 0.17 μm), the oxygen diffusion into the grain produces an increase of the resistivity because of the increase of the barrier widths. Conversely, for samples sintered at 1000°C and cooled in steps (grain size 0.1 μm), after a sudden increase in the resistivity as expected after an increase of the barrier heights, the resistivity decreases. We attribute this unexpected behavior to the barrier overlapping involving a different conduction mechanism.

The above conclusions are supported by the temperature cycling experiments performed on samples of different preparations. We found that sample preparation has a crucial role on the electrical properties observed. The sintering temperature and the cooling protocol determine the grain sizes and the intergranular electrical barriers. Results presented in this work emphasize the interplay between microstructure and electrical properties. In particular, once the contact to oxygen is made, the conductivity is reduced because of the increase of barriers height. However, while for grains large enough the oxygen indiffusion decreases the conductivity (as seen in Fig. 2), an oxygen indiffusion increases the conductivity in samples with narrower grains or wider barriers (as seen in Figs. 3 and 4). Also, porous samples, those sintered at lower temperature, present a higher sensitivity since intergrains are easier reached by oxygen.

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