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Effects of previous treatments on the electrical response of SnO_2-thick films exposed to a CO atmosphere

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Abstract

The influence of CO on the electrical conductivity on SnO_2 thick films is studied. Possible sensing mechanisms are discerned by measuring the conductivity as a function of temperature during heating and cooling, and the transient responses to step changes in CO pressure at constant temperature. Studies of samples with prior treatments confirm the proposed mechanisms responsible for the observed film responses. The film conductivity is affected by CO adsorption and by reaction with previously adsorbed oxygen. Also, the oxygen vacancy concentration in the grains can be altered and, as a consequence, the sample resistivity.

Keywords: Tin oxide; Electrical properties; Sensors; SnO_2

1. Introduction

Tin oxide thin film sensors have been widely studied due to their high sensitivity, fast response to gases, and low power consumption [1]. The pioneer works were reported in 1962 by Seiyama et al. [2] and Taguchi [3]; however, their selectivity, stability, and reliability are still key problems to be solved theoretically and experimentally. The sensing mechanism involves an electrical conductance change caused by gas adsorption on the semiconductor surface, which is highly dependent on the surface stoichiometry [4,5]. Also, the sensing properties are influenced by the microstructural characteristics, such as the grain size, the geometry, and the connectivity between particles [6]. 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 sensor resistance.

Oxygen chemisorbed from the atmosphere forms charged species at the grain boundaries modifying the potential barriers. Reducing gases, like CO, remove some of the adsorbed oxygen, thus the potential barriers are changed and then the overall conductivity is modified resulting in a sensor signal [7–10]. Resistance versus time curves are generally carried out in a system with continuous gas injection. Lu et al. studied the time response of ZnO thin films in an alcoholic atmosphere using gas injection into a flowing system and into a closed container [11]. They attributed the conductance diminution to the oxygen concentration reduction due to reaction, which increases with temperature.

In this paper a study of the influence of CO on the conduction process in SnO_2 thick films using a closed container is presented. With this experimental set-up, it is possible to identify the effects of CO reaction with adsorbed oxygen and due to the modification of the oxygen vacancies concentration on the sample resistance. Electrical conductance as a function of temperature during heating and cooling of thick films and transients at step changes in CO pressure at constant temperature are presented. Also, the resistance versus time curves of samples with previous treatments are analyzed. Finally, to get confidence on our results, capacitance transient response in SnO_2 thick films are studied.

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2. Experimental

Commercial high-purity SnO_2 (Aldrich) was ground until a medium particle size of 0.42 μm (Sedigraph Technique) and a specific area of 5.5 m^2/g (BET area, Flow Sorb F2300, Micrometrics) were reached (labelled powders P1). A thermal treatment performed at 1100 °C for 2 h led to powders with a particle size of 0.66 μm and an specific area of 2.5 m^2/g (BET area) (labelled powders P2). Then, a paste was prepared with an organic binder (glycerol) and the powders P1 or P2. The used solid/organic binder ratio was 1/2, and no dopants were added. Thick porous film samples were made by painting onto an insulating alumina substrate on which Au electrodes with an interdigit shape had been deposited by sputtering. Finally, samples were thermally treated for 2 h in air at 500 °C that is the normal treatment that samples receive during their preparation. Samples were labelled S1 (small particle size) and S2 (large particle size). The mean thickness of the films was 100 μm determined using a coordinates measuring machine Mitutoyo BH506.

A Philips 505 SEM and a commercial scanning tunnelling microscopy (STM) Nanoscope II were employed to image the tin oxide surfaces. All experiments with the STM were conducted in the dark with the microscope placed on a vibration-isolated optical table. Samples were secured with a small metallic clip connected to the microscope ground. A platinum–iridium tip with a sample-tip voltage of 8 V and a current of 0.5 nA was used to acquire the STM images. We were successful in imaging the sample under a nitrogen atmosphere.

An impedance analyzer HP4284A in a frequency interval of 20 Hz to 1 MHz was used. Capacitance versus time curves were measured at 410 °C after a sudden change of the atmosphere from vacuum (10^{-4} mmHg) to CO (40 mmHg).

Resistance versus time curves were measured after a sudden change of the vacuum (10^{-4} mmHg) into a carbon monoxide atmosphere (30 or 45 mmHg) and, having reached quasi-saturation, changing the carbon monoxide atmosphere back into vacuum (10^{-4} mmHg). In temperature cycling experiments, resistance was measured while raising and then decreasing the temperature from room temperature up to 400 °C at a rate of ∼2 °C/min with the sample kept in the carbon monoxide atmosphere (45 mmHg).

3. Results

From SEM images for sample S1 reported in a previous work, agglomerates between 100 and 250 nm were determined. However, with STM we observed that the agglomerates were composed by particles of 50 nm [4]. The mean thick of the film, determined by the profilometer, was 100 μm. For samples labelled S2, the average particle size was determined to be between 250 and 420 nm.

Fig. 1 shows the electrical conductance versus 1/temperature curves of the sample (S1) when the temperature is increased and decreased in a CO atmosphere. This experiment was carried out on a fresh sample without any special treatment. The sample was kept in vacuum for 2 h and then a CO atmosphere was introduced into the chamber. After the first temperature cycle, with maximum temperature of 150 °C, the conductance is unchanged. In next cycles, with higher maximum temperatures, a shoulder in the conductance curves and a decreasing in the final conductance were observed.

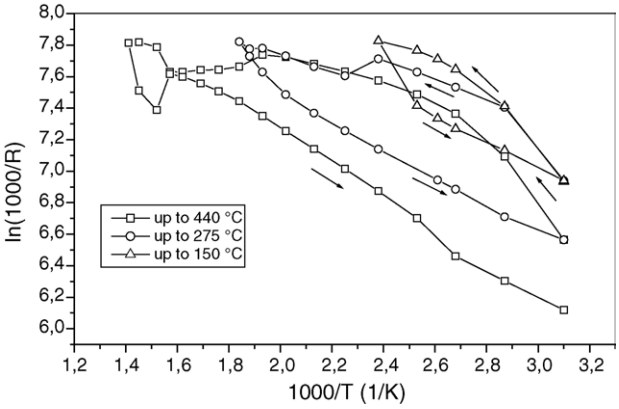

Fig. 1. Conductance vs. 1/temperature curves of a sample (S1) without previous treatments in CO when the temperature is increased and decreased in a CO atmosphere (45 mmHg).

In Fig. 2 a similar cycling set to that of Fig. 1 is reported. In this case, for complete annihilation of adsorbed oxygen, the sample (S1) was previously treated with CO at 400 °C for 4 days. As in Fig. 1, for temperature cycles in which temperatures are lower than 200 °C, the final conductance remains similar to the initial conductance. Conversely, at higher temperatures the final conductance increased.

In Fig. 3(a) a resistance versus time curve of a sample (S1) without previous treatment in CO, when the atmosphere is changed from vacuum to CO at 390 °C, is plotted. The resistance increases with time but after 75 s a diminution is

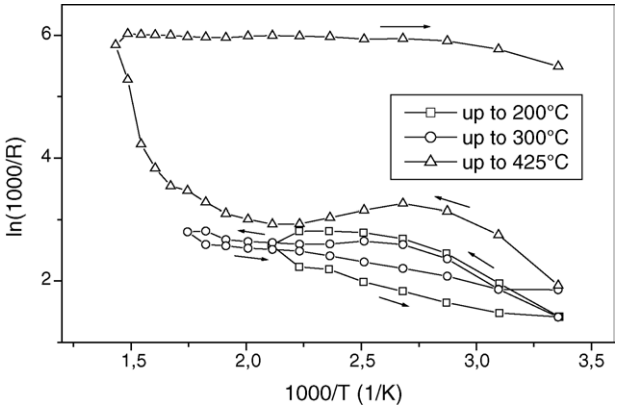

Fig. 2. Electrical conductance vs. 1/temperature curves of a sample (S1) with a previous treatment in CO when the temperature is increased and decreased in a CO atmosphere (45 mmHg).