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Effect of Oxygen Chemisorption on the Electrical Conductivity of Zinc Oxide Films Prepared by a Spray Pyrolysis Method

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Abstract

Zinc oxide films (2–3 μm thick) have been deposited on alumina substrates currently used for electronic applications by a spray pyrolysis method. Their electrical resistivity–temperature characteristics were measured in nitrogen, air and oxygen. The data are explained by surface reactions involving zinc and adsorbed oxygen atoms in different forms. The comparison with the electrical response of a similar material in the bulk form is also examined.

Mittels eines Sprüh-Pyrolyse-Verfahrens wurden auf derzeit in der elektronischen Industrie gebräuchlichen Al_2O_3-Substraten 2–3 μm dicke ZnO-Schichten erzeugt. Ihre Widerstands–Temperatur Kennlinie wurde in Stickstoff, Luft und Sauerstoff gemessen. Die experimentellen Daten können durch an der Oberfläche ablaufende Reaktionen zwischen Zink und verschiedenartig adsorbierten Sauerstoffatomen erklärt werden. Das elektrische Verhalten wurde mit dem konventioneller Teile aus Vollmaterial verglichen.

Des films d'oxyde de zinc, de 2 à 3 μm d'épaisseur, ont été déposés sur des substrats en alumine, couramment utilisés dans des applications électroniques, par une méthode de pulvérisation-pyrolyse. Leurs caractéristiques résistivité électrique-température ont été mesurées dans l'azote, l'air et l'oxygène. Les résultats sont interprétés à partir de réactions de surface mettant en jeu le zinc et les atomes d'oxygène adsorbés sous différentes formes. Enfin, une comparaison est faite entre les propriétés électriques de ces films at celles d'un matériau similaire sous forme massive.

1 Introduction

Studies on polycrystalline zinc oxide in the form of sintered disks have shown that its electrical conductivity as a function of temperature is strongly influenced by the microstructure[1] and depends on the surrounding atmosphere.[2] It is explained by chemisorption or the reaction of oxygen with the surface and corresponding electron transfer. Devices based on porous ZnO have been designed in order to exploit the material's sensitivity to reducing gas between 300 and 400°C where the amplitude of the associated resistivity changes is of one order of magnitude.[2]

In the present paper the resistivity is described as a function of temperature and atmosphere for ZnO in the form of films obtained by spray pyrolysis. The different electrochemical mechanisms are examined as a function of temperature and how the high surface/volume ratio compared to bulk ceramics may influence the electrical response is also investigated.

2 Experimental

The samples were obtained by the pyrolysis on a heated substrate of an aerosol produced by an ultrasonic system.[3] The starting solution consisted of zinc acetate dissolved in water (concentration = 0·2 mol/liter). Such a precursor has been selected because of its high vapor pressure at low temperature (i.e. 200°C). Acetic acid was added in order to avoid any zinc hydroxide precipitation. This solution was contained in a glass vessel and excited by

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a piezoelectric transducer. A geyser is formed at the liquid surface and cavitation effects produce an aerosol of controlled droplet size ($4{\cdot}3\,\mu$m). The aerosol is carried by a gas towards the pyrolysis region. The direction of the flow is perpendicular to an horizontal heated substrate ($T = 475°C$) which consists of an alumina-based material currently used for electronic applications (substrate dimensions: $2{\cdot}54 \times 2{\cdot}54\,cm^2$). The deposition time was 3 h. The film has a thickness which ranges between 2 and 3 μm and is oriented along the [002] axis. Resistance measurements were recorded with a Keithley electrometer (ref: 617 programmable) and were carried out between room temperature and 650°C. The heating ramp was 5°C/min. Prior to electrical measurements, two gold electrodes were deposited on the film by sputtering under argon. Impedance measurements have shown that these electrodes are non-blocking. Mechanical contacts were made between these electrodes and platinum wires connected to the electrometer.

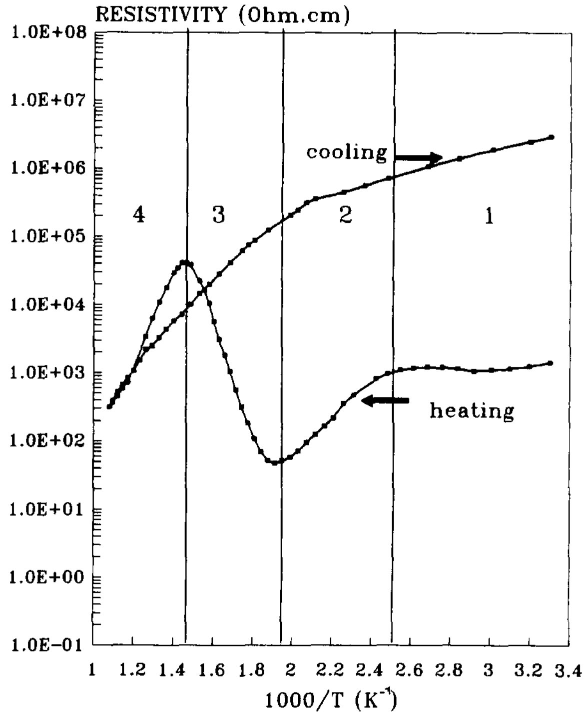

Fig. 2. Resistivity as a function of reciprocal temperature under oxygen.

3 Results

Since the resistivity (ρ) of zinc oxide as a function of temperature is usually analyzed according to

$$\log(\rho) = A + B/T$$

where A and B are constants and T is the absolute temperature, the resistivity is plotted as a function of reciprocal temperature under different atmospheres ($1/T$–ρ curves, Figs 1–4). When the resistivity is measured during heating in air or oxygen (Figs 1 and 2) it decreases gradually (zone 1) and drops to a minimum at about 250°C at the end of zone 2. It is followed by a resistivity increase for $250 < T < 410°C$ or 440°C in oxygen and air, respectively

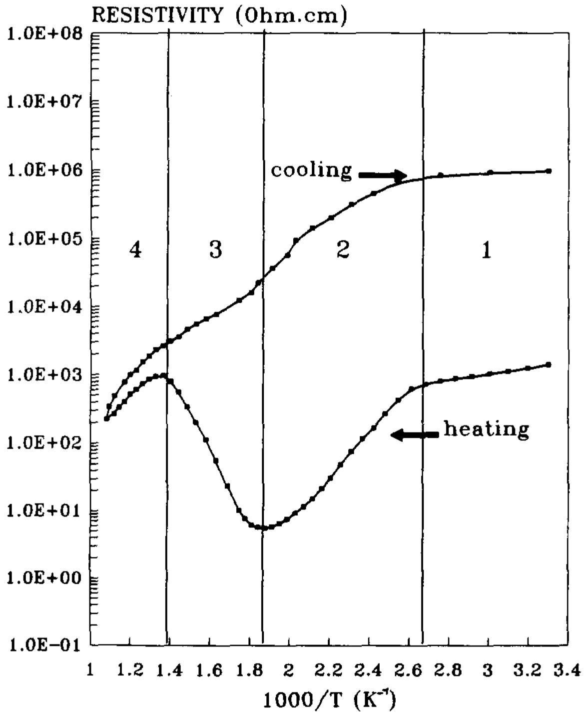

Fig. 1. Resistivity as a function of reciprocal temperature under air.

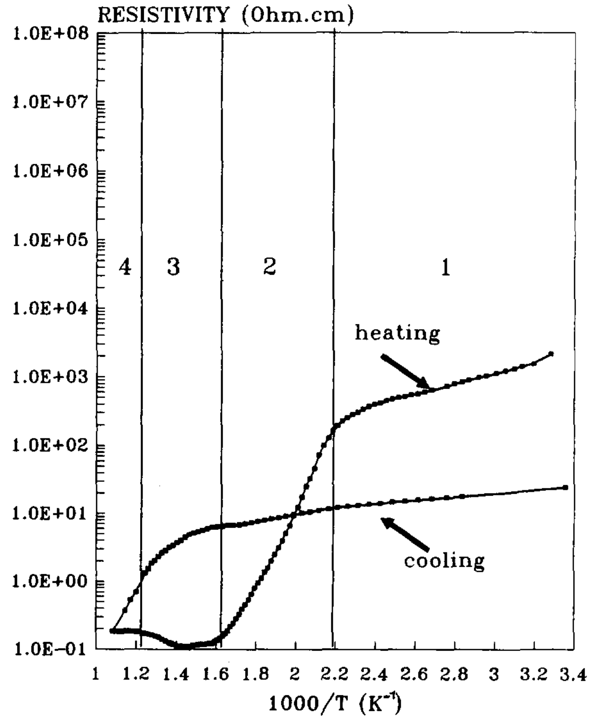

Fig. 3. Resistivity as a function of reciprocal temperature under nitrogen.

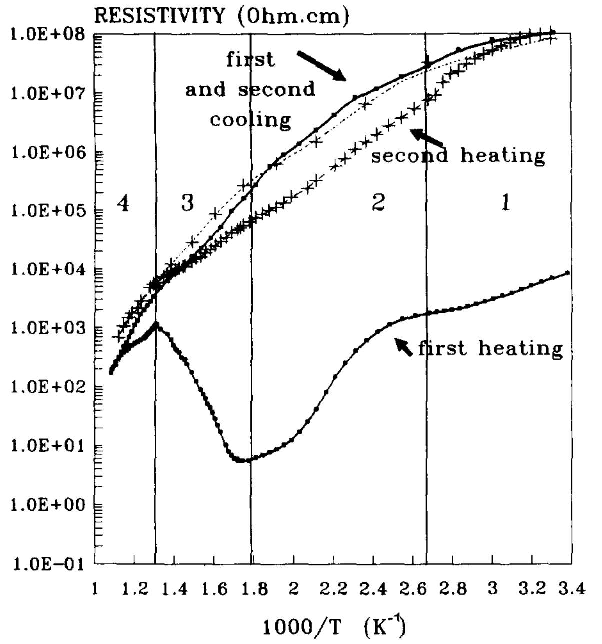

Fig. 4. Resistivity as a function of reciprocal temperature under air during two thermal cycles. ■, First run; +, second run.

(zone 3), and finally drops when T increases up to 650°C (zone 4). When the film is cooled down the resistivity increases linearly. Analogous measurements under nitrogen show identical trends in zones 1 and 2 (Fig. 3). However, in zones 3 and 4, the amplitudes of the resisitivity changes as a function of temperature are small.

When a film is reheated in air several times after a first thermal cycle, the resistivity minimum and maximum observed in the first run disappear (Fig. 4). The $1/T$–ρ measurements during these successive heating and cooling runs exhibit an identical type of behavior.

4 Discussion

It is important to know the chemical nature of the species which may participate in the electronic conduction in order to discuss the results.

ZnO is an n-type semiconductor, in which carriers are due to excess zinc at interstitial positions acting as electron donors. They are formed according to equilibrium (1):

$$ZnO \rightleftharpoons Zn_i^x + 1/2\,O_2 \qquad (1)$$

These interstitial atoms are ionized through two dissociation equilibria (2) and (3):

$$Zn_i^x \rightleftharpoons Zn_i^{\cdot} + e' \qquad (2)$$

$$Zn_i^{\cdot} \rightleftharpoons Zn_i^{\cdot\cdot} + e' \qquad (3)$$

Zn_i^x, $Zn_i^{\cdot}$, $Zn_i^{\cdot\cdot}$ are a zinc atom, a monovalent and a divalent cation at an interstitial site, respectively, and e′ a conduction electron. Previous studies have shown that equilibrium (3) affords a small fraction of the total ionization in the present temperature range.[4]

Zinc is not the only species which can take part in conduction. The effect of chemisorbed oxygen must be taken into account. According to the literature, chemisorbed oxygen is transformed with increasing temperature as follows:

$$O_{2\,ads} \rightarrow O^-_{2\,ads} \rightarrow 2O^-_{ads} \rightarrow 2O^{2-}_{ads} \qquad (4)$$

where $O^-_{2\,ads}$ and O^-_{ads} can be the two forms prevalent at room temperature. The passage between oxygen gas and one of these forms is accompanied by an electron-transfer process.

Before discussing the results it should be noted that the resistivity value at room temperature can change within a batch of samples prepared in the same experimental conditions. In fact, the resistivity is a function of parameters such as ambient moisture, carbon dioxide or oxygen content, etc. Moreover it was noticed that the films are sensitive to light from room temperature up to 200°C. However, the photo-effect is less pronounced for $T > 100$°C and is no longer detectable at 200°C. As a result the resistivity measured at room temperature is not specifically dependent on the material. This remark also applies to literature data where the room-temperature resistivities can be quite different depending on the authors.[1,2] Nevertheless, from 100°C upwards, the influence of these parameters is negligible and the measured resistivity becomes truly dependent on the material.

Starting from zone 2, the $1/T$–ρ data can be partly explained considering the following equilibria proposed in the literature:[5]

$$O^-_{ads} \leftrightarrows 1/2\,O_2 + e' \qquad (5)$$

$$O^-_{ads} + Zn_i^x \leftrightarrows (ZnO)_{surface} + e' \qquad (6)$$

$$Zn_i^x \leftrightarrows Zn_i^{\cdot} + e' \qquad (7)$$

These reactions move to the right as the temperature is raised. Reaction (5) predominates at low temperature and has been used in the literature for temperature ranges which correspond to zone 2 in the present case (Figs 1 to 3). It is characterized by oxygen desorption as the temperature goes up and also by an electron release which is responsible for a conductivity increase. It is noticed that the desorption of oxygen occurs more extensively in nitrogen (Fig. 3), where the oxygen partial pressure is low, than in air (Fig. 1) or oxygen (Fig. 2). The resistivity values reached in the three cases are respectively equal to 0·1, 5 and 50 Ω.cm under nitrogen, air and oxygen. It is thus assumed that most of the adsorbed oxygen is likely to be released under nitrogen atmosphere and the O^-_{ads} concentration drops towards zero. In some cases, a slight resistivity increase is noticeable at the beginning of zone 2, as shown in Figs 2 and 4 for oxygen or air atmospheres. Barry *et al.*[6] noticed that a small fraction of adsorbed oxygen can sometimes change its charge and therefore participate to a slight resistivity increase.

At higher temperatures (zone 3), reaction (6) predominates. O^-_{ads} and Zn^x_i are consumed. In order to maintain the equilibrium, reactions (5) and (7) move to the left.[5] The net result is a decay in the number of free electrons and an increase in the resistance. It is particularly marked when the measurements are made in air or in oxygen. The resistivity rise is almost identical in both cases and reaches 2·4–2·9 orders of magnitude. It is improved compared to similar measurements made on bulk materials where the resistivity change is of one order of magnitude.[1,2] Since the present films have a very high specific area, the number of zinc atoms sitting in interstitial positions on the film surface is probably greater than for the same material in the sintered form, which may explain the greater magnitudes of the resistivity changes. Adding the fact that these films are very thin, it is assumed that most of Zn^x_i is used up in zone 3. Two arguments can support this last statement:

(1) Similar orders of magnitude for measurements under air or oxygen indicate that the resistance increase in zone 3 depends on the Zn^x_i concentration, which should be the same in both cases, since the films have been prepared in identical experimental conditions. The resistance rises occur until the reservoir of zinc atoms in interstitial positions is empty.

(2) The reversibility of the $1/T$–ρ curves during successive heating and cooling runs (Fig. 4) and in particular the disappearance of the resistivity minimum and maximum during the second and third heatings (Fig. 4) shows that reaction (6) no longer takes place because of the lack of Zn^x_i.

In the specific case of $1/T$–ρ data under nitrogen atmosphere, the values are almost constant in the first half of zone 3 ($350 < T < 420$°C). It is not surprising if an almost complete consumption of O^-_{ads} species at the end of zone 2 is postulated, as stated earlier.

Consequently, reaction (6) cannot take place at least at the beginning of zone 3. The slight resistivity increase from 0·1 to 0·2 Ω.cm when $420 < T < 540$°C may be due to the release of the few O^-_{ads} ions left on the ZnO surface and probably tightly bonded to it. Greater temperatures are required for their desorption. In this case, the occurrence of reaction (6) is accompanied by the motion of reactions (5) and (7) towards the left. At the end of this stage, the film surface is probably cleaned of O^-_{ads} and Zn^x_i may still remain on the surface.

In zone 4 where T goes up to 650°C, the resistivity drops about 1 and 2 orders of magnitude in air and oxygen, respectively, and remains constant under nitrogen. The resistivity behavior clearly depends on the atmosphere. The Chandra *et al.*[5] interpretation, saying that in this temperature range the bulk takes part in conduction, is ruled out, as otherwise the resistivity values would not depend on the atmosphere. As O^{2-}_{ads} can exist in this temperature range, the present authors suggest that the electronic conduction is associated with a change of the adsorbed oxygen form. The passage between O^-_{ads} and O^{2-}_{ads} implies (1) a modification of all the previous electrochemical reactions, (2) the creation of new equilibria between O^{2-}_{ads} and the other species and (3) a change in the number of adsorption sites. The net result may be a resistivity drop, as shown in Figs 1 and 2. In the case of the nitrogen atmosphere, since it has been postulated that no O^-_{ads} is left, the proposed conversion $O^-_{ads} \rightarrow O^{2-}_{ads}$ does not happen. No new electrochemical reaction takes place and the resistivity remains unchanged.

Lastly, in all cases, the resistivity increases when the films are cooled down from 650°C. When the cooling is carried out in air or oxygen (Figs 1 and 2) it may be assumed that oxygen is readsorbed on the surface, either in the form of O^{2-}_{ads} or O^-_{ads} depending upon the temperature. In the case of O^{2-} being readsorbed ($T > 440$ and 410°C, Figs 1 and 2) the electrochemical equilibria which moved in one direction and led to a resistivity decrease during heating (zone 4) are displaced in the other direction when the temperature goes down. The direct consequence is a resistivity increase. Lastly, as soon as O^- is readsorbed for $T < 440$ and 410°C (Figs 1 and 2), reaction (5) moves towards the left and the electron concentration goes down. In the case of nitrogen atmosphere, the resistivity rises as the temperature goes down (Fig. 3). Such a resistivity increase, which has not been observed so far on zinc oxide in the bulk form under a reduced atmosphere,[1,5] may be justified as follows. The zinc surface has been cleaned of O^-_{ads} during heating. Moreover

Zn_i^x still remains on the surface. Therefore the film is highly reactive to oxygen gas. Even if its partial pressure is low, oxygen will readsorb on the film surface. Reaction (5) will move to the left in order to generate some O_{ads}^- which will combine with Zn_i^x (reaction (6)) which remained after heating in zone 3. Consequently reaction (7) will move to the left in order to maintain the equilibrium. The entire process leads to a decrease in the number of free electrons. It will probably stop when the temperature range is no longer suitable for reaction (6) to occur, i.e. T around 400–350°C. Indeed a change in the slope of the $1/T$–ρ curves is noticed below this temperature range. The chemical process may just be readsorption of oxygen which proceeds to a lesser extent than in air or oxygen atmosphere due to the low oxygen partial pressure.

5 Conclusion

The electrical resistivity as a function of temperature for zinc oxide films prepared by a spray pyrolysis method depends on the atmosphere. Between 350 and about 500°C, the resistivity–temperature characteristic remains unchanged under nitrogen and shows extremes in air or oxygen for $250 < T \lesssim$ 400–450°C. In these two atmospheres, the magnitude of the resistivity change in that temperature range is about 2·7 orders of magnitude greater than for the same material in the bulk form. The next stage is to exploit this greater sensitivity in designing sensors to monitor leakage of town gas.

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