

ON THE THERMOELECTRIC PROPERTIES OF ZINC OXIDE FILMS PREPARED BY D.C. MAGNETRON SPUTTERING

RUSU D.I., RUSU I.I.

University of Bacau

Abstract: The dependence on the temperature of the electrical conductivity during the heat treatment is studied. After this treatment consisting of several successive heating/cooling cycles, the structure of the ZnO films becomes stable and the dependence of the electrical conductivity on the temperature becomes reversible. Two series of ZnO films obtained in similar technological conditions are submitted to thermal treatment in vacuum and air respectively the nature of the electrical conductivity variation during the heating and cooling of the film (when the thermal treatment takes place in air) is discussed.

Keywords: electrical conductivity, thermal treatment, thin films

1. INTRODUCTION

In the last two decades, zinc oxide has been used as a basic material for the production of varistors. The interest for the study of electrical, optical and photoelectrical properties of ZnO thin films increased, in the purpose of using these films for the production of ultraacoustic and acoustic-optical devices and also passive or active transducers.

Zinc oxide has become a promising material for the manufacture of solar cells of the ZnO/CdS/CuInSe₂ type having the forbidden bandwidth large enough (3.2eV). Further more, zinc oxide is a serious candidate for the substitution of indium oxide and tin oxide in the manufacture of the conductive electrodes of the solar cells due to its high stability.

Zinc oxide is a semiconducting material which has a crystalline structure of the wurtzite type, having the constants of the crystalline unit cell $a=3.24\text{\AA}$ and $c=5.19\text{\AA}$ respectively.

2. EXPERIMENTAL PROCEDURE

For the preparations of oxides, reactive deposition in oxygen atmosphere is the most frequent used method. The oxygen is introduced in the sputtering chamber together with a work gas – in the most of cases the argon. The best results are obtained when we use a mixture of oxygen and argon in different volumetric proportions that is prepared before being introduced in the installation.

By reactive sputtering in the magnetron (the magnetic field is applied perpendicularly to the electric field of the discharge), we can obtain high-quality films, the deposition rate growing substantially. The substrate temperature can be maintained constant during the deposition, due to the low electronic bombardment of the tin.

For the preparation of the ZnO films whose structures, electrical, optical and photoelectrical properties have been studied, we used two installations, both of the magnetron type, but with different auxiliary devices, which allow the measurement of the various parameters.

3. RESULTS AND DISCUSSION

We have experimentally found that, if measured immediately after deposition, the electrical conductivity presents an irreversible dependence of the temperature. Such dependence can be explained by some changes of the film structure (granule, size, the characteristics of the contacts between them) while they were heated in the atmosphere. For the verification of this assumption, ZnO films prepared on the glass substrates have been submitted to a thermal treatment, which consisted of successive heating and cooling in the temperature range of 300-500°C.

In figure 1, we present the dependence of the electrical conductivity on the temperature during the thermal treatment for a ZnO film with a thickness of $0.35 \mu\text{m}$. The respective film has been submitted to two successive heating and cooling. We found that after the successive heating the film stabilizes (becomes homogenous) and presents a normal dependence of the electrical conductivity on the temperature.

After these heating and cooling cycles, the dependence of the electrical conductivity on the temperature becomes reversible.

The value of the electrical conductivity in the low temperature range can be influenced by the existence of some crystalline defects, weakly linked to the hexagonal network of the ZnO, as well as by other factors, such as: absorbed and adsorbed gases, oxygen or zinc atoms which in excess to the normal stoichiometric composition.

In figures 2 and 3 we present the variation curves of the electrical conductivity logarithm on the inverse of the temperature for the case of the thermal treatment in air and vacuum.

From the analysis of the $\sigma = f(10^3/T)$ dependences presented in figures 2 and 3, we found that the oxygen enrichment of the atmosphere in which the thermal treatment of the ZnO films takes place, leads to their homogenization (as a result of the decrease of the concentration of the free Zn atoms in excess, determined by the oxidation of the respective atoms). This process is accompanied by a decrease of the electrical conductivity of the films. We suppose that in the interior of the crystallites, there is a high concentration of free charge carriers and certain energy is necessary for them to perform the transition from one crystallite to another.

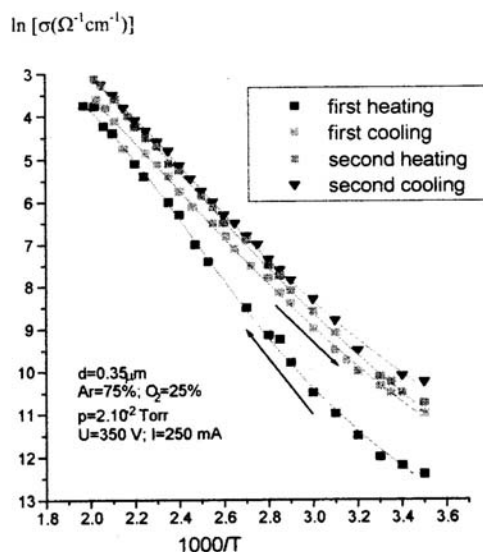


Fig.1 The influence of the thermal treatment on the electrical conductivity of thin ZnO films

Obviously, the value of the electrical conductivity will depend on the characteristics of the contacts between them.

The heat treatment produces a raise of the granule size, the film getting a more compact structure, which determines a raise of the electrical conductivity.

As we can see in figures 2 and 3, in the case in which the thermal treatment takes place in vacuum, the $\ln \sigma = f(1000/T)$ curves present a more pronounced movement compared to the case in which the treatment is carried out in air. We can state that a high influence is due to the presence of the oxygen in the case of thermal treatment in air (the changes of the structure in this case are almost reversible), while in vacuum, the oxygen is eliminated from the film.

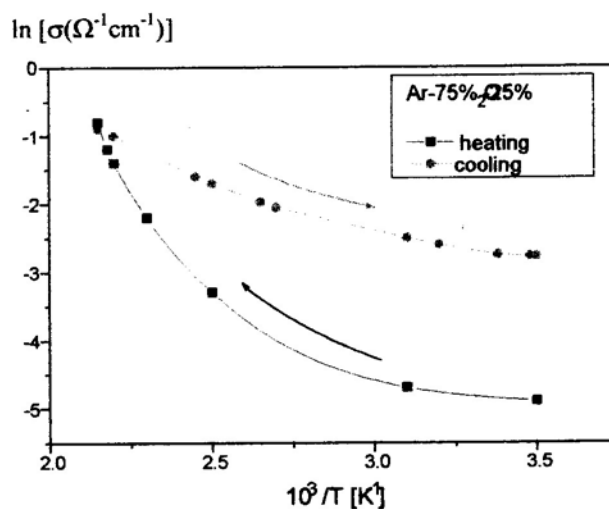


Fig.2 The $\ln \sigma = f(1000/T)$ variation for ZnO in vacuum

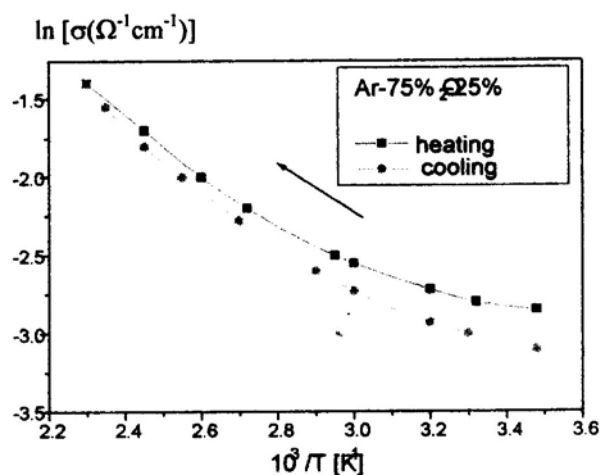


Fig.3 The $\ln \sigma = f(1000/T)$ variation for ZnO in air

At room temperature (293K), the electrical conductivity of the ZnO films prepared in 75% argon and 25% oxygen atmosphere reaches the value $\sigma = 4 \cdot 10^{-2} \Omega^{-1} \text{cm}^{-1}$. At the evacuation of the atmosphere from the measurement chamber, its electrical conductivity decreases to $\sigma = 10^{-5} \Omega^{-1} \text{cm}^{-1}$ and practically doesn't change if

we introduce inert gas (argon) in the chamber. As a result, we can presume that at room temperature, the electrical conductivity is composed of two components σ_1 - surface conductivity and σ_2 - conductivity conditioned by free electrons.

The oxygen atoms which are captured at the surface and which form weak links with the free zinc atoms in the film, are responsible for the electrical conductivity through the surface states. Since the $\ln \sigma = f(1000/T)$ graph is approximated by a continuous dependence which changes its slope from 0,5 to 10, in the 293K – 400K temperature range it is natural to consider that the oxygen atoms captured at the ZnO film surface form a continuous band of surface states localized in the 0,04 – 0,8 eV range from the minimum of the conduction band. As a result, following the thermal treatment applied to ZnO thin films in vacuum, we find that the oxygen atoms at the surface evacuate, leading to a decrease of the surface states completed with electrons. Accordingly, the electrical conductivity of the film will rise with the temperature.

At cooling, the $\ln \sigma = f(1/T)$ dependence will describe another curve when decreasing, this behavior being conditioned by the caption of the free charge carriers on the states that are localized in the volume or by their reblending with the holes in the conduction band.

The thermal treatment of the ZnO films in normal atmosphere has a weak influence on the concentration of the surface states formed by the oxygen atoms, which is confirmed by a much smaller increase of the electric conductivity at heating in the temperature interval of 293-400K, as opposed to the case of vacuum treatment. Since, at cooling, the curve which characterizes the $\ln \sigma = f(10^3/T)$ dependence moves towards higher electrical conductivities compared with the heating cycle, we can consider that in the process of slow heating of the film, the oxygen atoms will penetrate in the interior of the film, forming chemical couplings with the Zn atoms in free state. Consequently, the concentration of the atoms decreases.

4. CONCLUSIONS

We have studied the dependence on the temperature of the electrical conductivity during the thermal treatment. If the ZnO films are submitted to successive heating and cooling, they stabilize and present a normal dependence of the electrical conductivity on the temperature.

In order to study the influence of the concentration of structural defects on the electrical conductivity of ZnO films, we have submitted the two series ZnO films obtained in similar technological conditions to thermal treatment in vacuum and air. From the analysis of the $\ln \sigma = f(10^3/T)$ dependences, we have established that when the thermal treatment takes place in air, the variation of the electrical conductivity during the heating and cooling of the film is almost reversible. The oxygen enrichment of the atmosphere in which the thermal treatment of the ZnO films takes place, leads to their homogenization, as a result of the decrease of the concentration of Zn atoms in excess determined by the oxidation of the respective atoms. This process is accompanied by the decrease of the electrical conductivity of the films.

Inside the granules, there is a considerable concentration of the free charge carriers and certain energy is necessary for them to accomplish the transition from one granule to another. However, if the thermal treatment carriers out in vacuum, the $\ln \sigma = f(10^3/T)$ curve presents an increased movement during the cooling towards the higher electrical conductivity, as opposed to the case of thermal treatment in air. Responsible for the electrical conductivity through the surface states can be the oxygen atoms captured at the film surface, which form weak links with the free zinc atoms in the film.

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