Polycrystalline intrinsic zinc oxide to be used in transparent electronic devices

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Abstract

In this paper we present results of intrinsic/non-doped zinc oxide deposited at room temperature by radio frequency magnetron sputtering able to be used as a semiconductor material on electronic devices, like for example ozone gas sensors, ultra-violet detectors and thin film transistors. These films present a resistivity as high as $2.5 \times 10^8 \ \Omega \ \text{cm}$ with an optical transmittance of 90%. Concerning the structural properties, these films are polycrystalline presenting a uniform and very smooth surface.

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1. Introduction

ZnO thin films are nowadays attracting considerable attention for their possible use as an active semiconductor material in transparent electronic devices. ZnO is a very interesting material, due to its high transmittance in the visible region and to its high chemical, thermal and mechanical stability. It is a semiconductor material with a hexagonal structure [1]. The great advantage of using ZnO thin films in transparent electronic devices lies in the fact that it is possible to grow at room temperature high quality and transparent polycrystalline zinc oxide films [2].

Several techniques have also been used to grow non-doped ZnO thin films, like metal organic chemical vapor deposition, evaporation, magnetron sputtering, sol gel, plasma assisted molecular beam epitaxy, among others [3–7]. However, most of these techniques need to use high temperatures in order to obtain high quality polycrystalline material.

ZnO is a wide band gap material (3.2 eV), it is transparent in the visible and therefore also less light sensitive than other materials [8]. Films from ZnO can also be used for gas sensing because of high sensitivity to many gases. The conductivity of ZnO can change over orders of magnitude after exposure to UV light and subsequent oxidation [9]. Also, transparent oxide semiconductor based transistors have recently been proposed to be used as active channel intrinsic zinc oxide [10–13].

In this work, we report results concerning the optimization of the deposition conditions of non-doped zinc oxide films, produced at room temperature, to be used as a gas sensor.

2. Experimental details

The ZnO films were deposited onto soda-lime glass substrates by radio frequency (13.56 MHz) magnetron sputtering, using a ceramic oxide target ZnO from Super Conductor Materials, Inc. with a purity of 99.99%. The sputtering was carried out under room temperature, with a partial pressure of oxygen that was varied from $1.2 \times 10^{-3}$ Pa to $8.0 \times 10^{-3}$ Pa, and a total deposition pressure (argon...
and oxygen) of 0.15 Pa. The distance between the substrate and the target was 10 cm and the rf power was varied between 2.5 W/cm² and 9.0 W/cm².

The film thickness was measured using a surface profilometer (Dektak 3D from Sloan Tech.). The electrical resistivity was measured using thermally evaporated aluminium electrodes in a coplanar configuration, in a cryostat system, CS8900. The optical transmittance was measured using a double beam spectrophotometer (UV-3100 PC, Shimadzu) in the wavelength range from 300 nm to 2500 nm. The structural properties of the films were determined using X-ray diffraction measurements with Cu-Kα radiation (Rigaku DMAX III-C series). The surface morphologies were analyzed using a Field Emission Scanning Electron Microscope (FE-SEM, S-1400 Hitachi).

3. Results and discussion

3.1. Growth rate

Fig. 1a, b show the dependence of the growth rate \( R \) on the rf power \( P \), and the oxygen partial pressure, respectively. We observe a linear increase of \( R \) with \( P \) according to \( R = -43.8 + 27.5 P \). This is due to the increase of the sputtered particles, by the increase of the energy delivered by the ions at the sputtering target [14]. A maximum of 180 Å/min was obtained for the rf power \( P = 9.0 \) W/cm². We define the deposition rate efficiency \( R_E \) as the slope of the linear deposition rate, versus power density [15]

\[
R_E = \frac{dR}{dP}
\]  

From the slope of Fig. 1a, an \( R_E = 27.5 \) Å cm²/W min was obtained. The low value obtained is similar to those obtained for ceramic targets, mainly due to the lower sputtering yield for this type of materials [16,17]. In Fig. 1b we observe a decrease on the growth rate with the increase of oxygen flow. An energy screen effect promoted by oxygen, which makes the surface environment of the target less conductive, explains this behavior. A maximum of 95 Å/min was obtained for an oxygen partial pressure of 2.5 × 10⁻² Pa.

3.2. Electrical properties

The dependence of electrical resistivity of the ZnO films as a function of the rf power, without the use of oxygen, and as a function of the oxygen partial pressure, for \( P = 5.1 \) W/cm², is shown in Fig. 2a, b. As the rf power \( P \) increases, the resistivity \( \rho \) decreases. For an rf power of \( P = 5.1 \) W/cm² we
obtain films with a resistivity $\rho=0.27 \ \Omega \ \text{cm}$, a value much different from those obtained for higher rf power. We have observed a strong variation in the resistivity by increasing the oxygen partial pressure from $1.8 \times 10^{-3}$ Pa to $2.2 \times 10^{-3}$ Pa. The resistivity $\rho$ did not change much, for higher values of oxygen partial pressure.

3.3. Optical properties

Fig. 3a, b present the optical transmittance $T$ in the wavelength range from $\lambda=300$ to $\lambda=2500$ nm, using air as reference, for the non-doped zinc oxide films deposited as a function of (a) rf power, deposited without oxygen and as a function of (b) oxygen partial pressure, deposited with an rf power $P=5.1 \ \text{W/cm}^2$. The average transmittance $T$ in the visible part of the spectra ($\lambda=400$ to 700 nm) was $T=90\%$ for all the samples analyzed, except for the sample deposited with an rf power $P=9.0 \ \text{W/cm}^2$ which presents an average of $T=80\%$ transmittance. We also observe that all the samples present the same transmittance in the near infrared region.

3.4. Structural and morphological properties

To study the structural and morphological properties we chose two samples deposited at room temperature, with an rf power $P=5.1 \ \text{W/cm}^2$. One of the samples was deposited without oxygen and the other was deposited with an oxygen partial pressure of $1.3 \times 10^{-3}$ Pa. These samples have about 1 $\mu$m thickness and we obtained a resistivity $\rho=1.2 \times 10^{9} \ \Omega \ \text{cm}$, for the sample deposited with oxygen, and $\rho=2.0 \times 10^{7} \ \Omega \ \text{cm}$, for the sample deposited without oxygen (we had obtained a resistivity $\rho=1.5$ to $2.0 \times 10^{8} \ \Omega \ \text{cm}$ for the thinner samples with 0.1 $\mu$m). Concerning the electrical properties for the ZnO films produced in the presence of oxygen (reactive sputtering), no difference is obtained meaning that the incorporation of oxygen is equal to the volume of the film. The same could not be said for the thinner and thicker ZnO films produced without the presence of oxygen. This different behavior could be attributed to a thickness effect. For the thicker sample a progressive deficiency of oxygen will take place during the growth, giving rise to an increase of the oxygen vacancies and consequently an increase on the carrier’s concentration (one oxygen vacancy contributes to two conduction electrons), leading to a lower value of the electrical resistivity.

Fig. 4a, b show the X-ray diffraction patterns of the films, deposited (a) without oxygen and (b) with an oxygen partial pressure of $1.3 \times 10^{-3}$ Pa. We can compare the X-ray diffraction patterns of the film with 1 $\mu$m thickness with the film with 0.1 $\mu$m. Other peaks were detected with the increase of the thickness.
deposited with an oxygen partial pressure of 1.3 \times 10^{-3} \text{ Pa}. For the samples deposited without the presence of oxygen a maximum of $\rho \approx 10^8 \ \Omega \ \text{cm}$ was obtained for ZnO films produced without the presence of oxygen a maximum of $\rho \approx 10^3 \ \Omega \ \text{cm}$ was obtained for $P$ between 6 and 8 W/cm$^2$. All the films are polycrystalline exhibiting the hexagonal wurtzite type presenting also a strong orientation along the $c$-axis. The average transmittance for all the films is 90% in the visible part of the spectra.

Fig. 5a, b show SEM photographs (surface and cross section) of ZnO films with 1 $\mu$m thickness, deposited at room temperature, with an rf power of 5.1 W/cm$^2$. Both films present a strong compactness, nevertheless the ZnO film deposited in the presence of oxygen (Fig. 5a) presents a strong compactness, nevertheless the ZnO grown in the presence of oxygen. This result is in line with the electrical properties observed for the case of the ZnO grown in the presence of oxygen. This was normally observed in thin films and is special for the same film.

4. Conclusions

In this paper we presented preliminary results concerning the electrical, optical, structural and morphological properties exhibited by intrinsic ZnO thin films, produced by rf magnetron sputtering at room temperature, as a function of the rf power and oxygen partial pressure. It is observed that there was a decrease on resistivity with the increase of rf power and with the decrease of oxygen partial pressure. A maximum of $\rho \approx 10^8 \ \Omega \ \text{cm}$ was obtained for ZnO films produced at a $P \approx 5.1 \text{ W/cm}^2$ and oxygen partial pressures higher than $2.5 \times 10^{-3} \ \text{Pa}$. For the ZnO films produced without the presence of oxygen a maximum of $\rho \approx 10^3 \ \Omega \ \text{cm}$ was obtained for $P$ between 6 and 8 W/cm$^2$. All the films are polycrystalline exhibiting the hexagonal wurtzite type presenting also a strong orientation along the $c$-axis. The average transmittance for all the films is 90% in the visible part of the spectra.

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