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ZnO:Ga Thin Films Produced by RF Sputtering at Room Temperature: Effect of the Power Density

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Abstract. Ga-doped polycrystalline zinc oxide (GZO) thin films have been deposited at high growth rates by rf magnetron sputtering. The dependence of electrical, optical and morphological properties on the rf power density were investigated. The lowest resistivity of 1.9×10^{-4} Ωcm was obtained for a rf power density of 9 W/cm^2 and an argon sputtering pressure of 0.15 Pa at room temperature. The films are polycrystalline with a hexagonal structure and a strong crystallographic c-axis orientation (002) perpendicular to the substrate surface. The films present an overall transmittance in the visible spectra of about 85%. The low resistivity, accomplished with a high growth rate deposited at room temperature, enables the deposition of these films onto polymeric substrates for flexible optoelectronic devices and displays.

Introduction

Transparent conducting oxides (TCO) with optical transmission more than 80 % in the visible region (550 nm) and resistivity less than 10^{-3} Ωcm have been widely used as electrodes for optoelectronic devices [1] and solar cells [2]. Most of the previous research on TCOs has been focused on indium tin oxide (ITO) and fluorine tin oxide (FTO). However, TCO films based on zinc oxide are taking a great impact because of the advantages of low cost, resource availability (about a factor of 1000 more abundant than indium), non-toxicity and high thermal/chemical stability [3]. Non-doped zinc oxide usually presents a high resistivity due to a low carrier concentration. Al, In and Ga have been reported as an effective dopant for zinc oxide based films. Most of the works related to zinc oxide use aluminium as dopant. Nevertheless, aluminium presents a very high reactivity leading to oxidation during the growth of the film, which may become a problem [4]. Galium is less reactive and more resistant to oxidation compared to aluminium. On the other hand, the covalent bond lengths of Ga-O and Zn-O are estimated to be 1.92 and 1.97 Å, respectively. The slightly smaller bond length of Ga-O than that of Zn-O is an advantage since it allows to minimize the deformation of the ZnO lattice even in the case of high gallium concentrations. These were the main reasons why gallium was chosen as dopant. Several methods have also been used like, metal organic chemical vapour deposition, evaporation, magnetron sputtering, sol gel, plasma assisted molecular beam epitaxy, among others [5]. However, most of these techniques need to use moderate temperatures, to obtain low values of resistivity. In addition to the several advantages presented by rf magnetron sputtering, it is also possible to produce highly conductive and transparent GZO without heating the substrate, since additional energy is delivered from the plasma to the growing film – a characteristic of a plasma assisted process. In this paper the electrical, structural and optical properties of GZO were analysed in detail and the effects of the rf power density on the deposition process were investigated.

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Experimental Details

The GZO films were deposited onto soda lime glass substrates by rf (13.56 MHz) magnetron sputtering using a ceramic oxide target ZnO/Ga_2O_3 (98:2 wt%) from Super Conductor Materials, Inc. with a purity of 99.99%. The sputtering was carried out under room temperature and the rf power density was varied from 5 to 9 W/cm^2. The distance between the substrate and the target was 10 cm and the argon flow rate and sputtering pressure were maintained constant at 20 sccm and 0.15 Pa, respectively, for all depositions. The film thickness (800 nm in average for all the samples) was measured using a surface profilometer (Dektak 3D from Sloan Tech.). The electrical resistivity (ρ), free carrier concentration (n) and Hall mobility (μ_H) were inferred by the four point probe method and Hall effect measurements using the van der Pauw geometry (Biorad HL5500) at a constant magnetic field of 0.5 T. X-ray diffraction measurements were performed using Cu-K_α radiation (Rigaku DMAX III-C diffractometer). The optical transmittance was measured using a UV-VIS-NIR double beam spectrophotometer (UV-3100 PC, Shimadzu) in the wavelength range from 300 nm to 2500 nm.

Results and Discussion

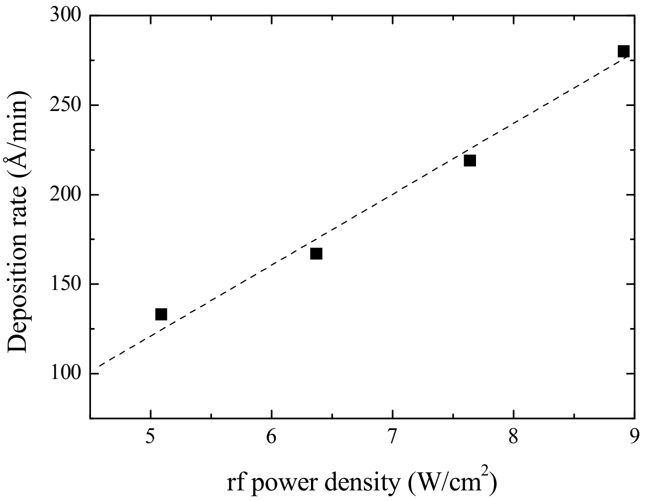

Fig. 1. Dependence of growth rate on the rf power density. The films were deposited at room temperature and with a pressure of 0.15 Pa.

Fig. 1 shows the dependence of the growth rate (R) on the rf power density (P). It is observed a linear increase on R as the rf power density increases, due to the amount on the number of sputtered particles [6]. A maximum R (280 Å/min) was obtained for a rf power density of 9 W/cm^2.

Deposition rate efficiency (R_E) was defined as the slope of the linear deposition rate versus power density [7]:

$$R_E = R\ (\text{Å/min})/P\ (W/cm^2) \qquad (1)$$

R_E is a useful concept for optimising deposition conditions, magnet arrangements, source-substrate spacing, etc. From the slope of Fig. 1 a R_E of 35 $Åcm^2/Wmin$ was obtained. The low value obtained, is similar to that ones obtained for ceramic targets, mainly due to the lower sputtering yield for this type of materials [8, 9].The dependence of the electrical properties (ρ, n and μ_H) of the GZO films as a function of the rf power density is shown in Fig. 2. The lowest electrical resistivity was obtained for a P = 9 W/cm^2 which corresponds to a maximum of the carrier concentration (2.9×10^{21} cm^{-3}). Another remarkable point observed in these films produced at room temperature, is the lowest ρ values registered on GZO films (typically requiring high temperature), close to the theoretical physical limits [2], which are values in the range of 4×10^{-4} Ωcm. These values are only explained by a high efficiency of the gallium dopant atoms, without significant defects ascribed to the grain boundaries and so, no significant barrier effect exists limiting the carrier's transport between grains.

Fig. 3a) shows a typical XRD pattern obtained for a sample prepared with an rf power density of 9 W/cm^2. It can be clearly seen that the only peak that is present is the {002}, showing that there is a very strong preferential orientation of these crystallographic planes parallel to the substrate.

A set of programs for X-ray diffraction peak profile analysis, using different methods, has been previously implemented and tested for the study of a quenched tool steel [10]. In the present paper,

a single-line profile analysis has been performed in order to calculate the crystallite size, giving the values depicted in Fig. 3b).
Fig. 3b) also depicts the variation of the net area of the peaks normalized for the film thickness. These graphs show a continuous increase of the crystallite size as well as of the degree of crystallinity as the rf power density increased.

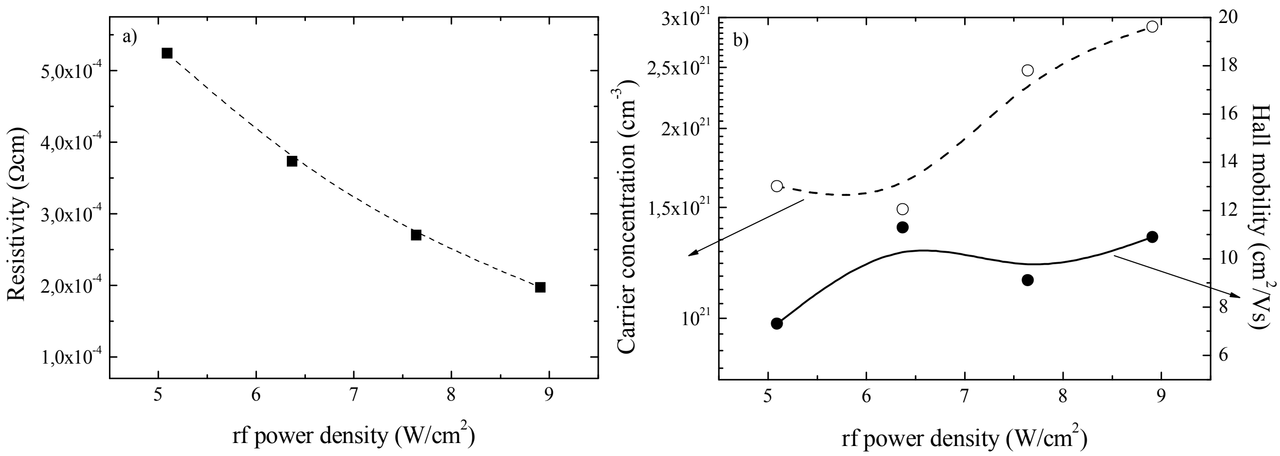

Fig. 2. Dependence of the: a) electrical resistivity; b) carrier density and Hall mobility of GZO films deposited at room temperature and with a sputtering pressure of 0.15 Pa, on the rf power density.

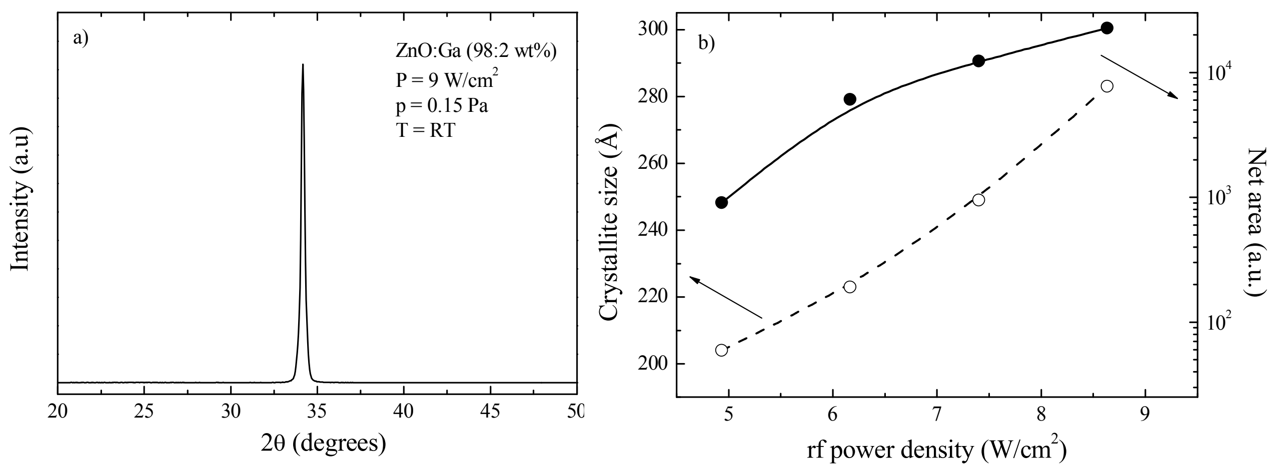

Fig. 3. a) Typical XRD pattern for a ZnO:Ga thin film produced with a power density of 9 W/cm^2; b) crystallite size versus rf power density and net area of the peaks (normalize to the thickness) versus rf power density.

Fig. 4 shows the transmission spectra in the visible and near infrared spectrum for the films deposited as a function of rf power density. The near-infrared transmittance decreases as the rf power density increases, whereas the average transmittance at the visible range is for all the films around 85%. These changes of the optical properties are consistent with the changes observed in the electrical properties, mainly the ones associated to the increase of the carrier concentration, which leads to a lower value associated to the plasma frequency [11]. It can be seen also that the band edges shift to short wavelengths as the rf power density increases. The value of the plasma frequency shifts to lower wavelengths as the rf power density increases due to the increase on the carrier concentration.

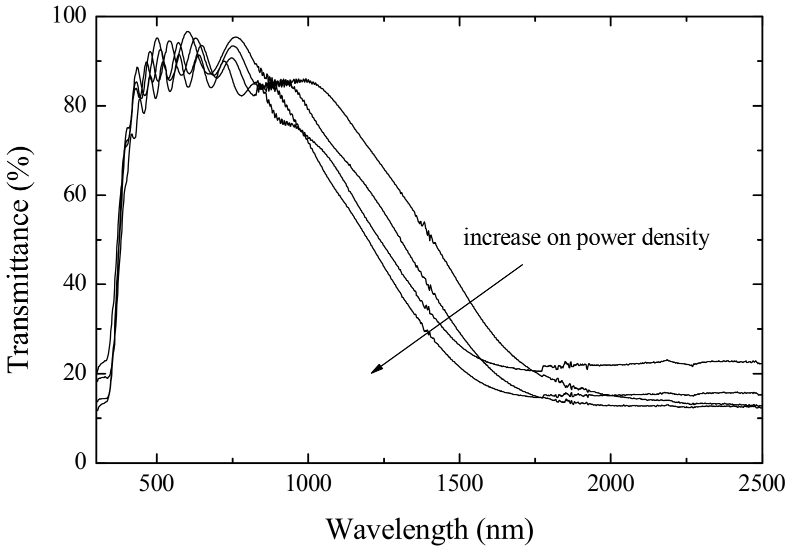

Fig. 4. Optical transmittance as a function of wavelength for GZO films deposited under different rf powers densities. The thickness of the films is 800 nm in average.

Summary
Highly conducting and transparent GZO films have been produced by rf sputtering at room temperature and at high growth rates. The films are polycrystalline with a hexagonal structure and a strong crystallographic c-axis orientation [002] perpendicular to the substrate surface and a crystallite size along this direction in the range of 20 to 30 nm.

The lowest resistivity achieved was 1.9×10^{-4} Ωcm (sheet resistance ≈ 2 Ω/sq. for a thickness ≈ 800 nm) and was obtained at an argon sputtering pressure of 0.15 Pa and an rf power density of 9 W/cm^2. The films present an overall transmittance in the visible spectra of about 85%. As far as we know, these are the highest values recorded concerning the ratio of the optical transmittance and the sheet resistance typically considered as a figure of merit of the material.

These results fulfill the minimum requirements necessary for producing transparent electrodes on flexible optoelectronic devices using inexpensive polymeric substrates.

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