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Influence of hydrogen plasma thermal treatment on the properties of ZnO:Al thin films prepared by dc magnetron sputtering

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ZnO:Al transparent and electrically conductive thin films were deposited on glass surfaces by d.c. pulsed magnetron sputtering from an AZOY (ZnO = 97.88 mol%, Al_2O_3 = 2 mol%, Y_2O_3 = 0.12 mol%) target. In order to study the influence of sputtering pressure on the optical and electrical properties of the as-deposited thin films, different argon flow rates were used for deposition. It is shown that a lower argon pressure leads to lower film electrical resistivity. The influence of different annealing temperatures (between 473 and 723 K) performed at different pressures (0.5, 8.0, 46.7 and 120 Pa), on the final electrical, optical and structural properties of the films, was investigated. An electrical resistivity of $\sim 1.2 \times 10^{-3}$ Ω cm and a transmittance of ~80% in the visible region for thickness of ~200 nm was achieved for samples submitted to a one hour hydrogen plasma treatment with a working pressure of 0.5 Pa at a temperature of 623 K. This treatment proved to be a very efficient in enhancing the electrical properties of these films. Concerning the thermoelectric properties, a maximum power factor of 7.27×10^{-5} W/mK^2 was obtained at 350 K for the sample deposited with the lowest sputtering pressure (0.37 Pa).

1. Introduction

Aluminum-doped zinc oxide (ZnO:Al) films have been extensively studied as transparent and conductive oxide (TCO) layers because they reconcile high optical transmittance, high band-gap (>3 eV) with low electrical resistivity. ZnO:Al is an alternative material to tin-doped indium oxide (ITO), which has been the most used to date, but has a higher cost, low stability to hydrogen plasma and it is toxic, contrary to ZnO:Al. These ITO/TCO films are used in many applications such as transparent electrodes in photovoltaic solar cells and flat panel display devices [1–3].

Many authors admit that, among common thin film deposition techniques such as sol–gel [4], pulsed laser deposition (PLD) [5], chemical vapor deposition (CVD) [2], the sputtering process is one of the best methods for preparation of ZnO:Al films because of its simplicity, reproducibility, low processing temperature, good adhesion of films to substrates and high deposition rates [2,6–10].

ZnO is a II–VI n-type semiconductor with a direct band-gap of ~3.36 eV at room temperature [11–13]. Many studies have shown that a lower electrical resistivity can be achieved by doping ZnO with group-III elements, such as aluminum or gallium [6,7]. It was shown that the optical and electrical properties of ZnO:Al thin films can be improved by using optimized deposition conditions, and these properties can be enhanced after some post-treatments techniques such as a thermal treatment in a reducing atmosphere [1,14]. Thermal treatments can promote film crystallization and the creation of oxygen vacancies that act as intrinsic electron donors, leading to an increase of the conductivity of the films [15]. The electrical conduction in undoped ZnO is governed by oxygen vacancies and Zn^{2+} interstitial atoms; on the other hand, the electrical conductivity in ZnO:Al is higher when Al^{3+} ions are present in substitutional sites of Zn^{2+} ions and when Al interstitial atoms are present, in addition to oxygen vacancies and Zn interstitials [16].

In this paper, aluminum-doped ZnO thin films were deposited by d.c. pulsed magnetron sputtering from an AZOY (ZnO = 97.88 mol%, Al_2O_3 = 2 mol%, Y_2O_3 = 0.12 mol%) target in an argon atmosphere, at a substrate temperature of ~473 K. The as-deposited films were then subjected to two different heat treatments: in vacuum and in a hydrogen plasma atmosphere. The

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influence of hydrogen plasma-assisted thermal treatment parameters, such as temperature and pressure, on the final properties of the films, was investigated.

The aim of this paper is to study the influence of deposition and annealing treatments parameters on the electrical, optical and structural properties of ZnO:Al thin films, for future application as front contact layers (electrodes) in photovoltaic solar cells.

2. Methods

2.1. Thin film deposition and thermal treatments

Aluminum-doped zinc oxide transparent thin films (no yttrium was identified by Energy-dispersive X-ray spectroscopy) were deposited in an argon (Ar) atmosphere on glass substrates (76 mm × 26 mm and 1 mm thick), using a custom-built d.c. pulsed magnetron sputtering equipment. An AZOY target with a diameter of 10 cm, fabricated by GfE Metalle & Materialien GmbH, was used. Prior to the depositions the chamber was evacuated with a turbo molecular pump to achieve a base pressure of $\sim 10^{-4}$ Pa. The substrate temperature was fixed at ~ 473 K for all the depositions.

The glass substrates were ultrasonically cleaned in Isopropyl alcohol (2-Propanol) and rinsed in an ultrasonic bath for 15 min. The purpose of glass substrate cleaning is to remove the contaminants on its surface that may arise during storage and handling, which moreover deteriorate the adhesion between substrate and film [17].

In order to study the effect of Ar flow rate on the electrical and optical properties of the films, different flow rates in the range of 32.5–60.0 sccm were used, leading to the sputtering pressures listed in Table 1. Depositions were carried out with the following fixed parameters: cathode current density of 5.1 mA/cm^2, d.c. pulsed frequency of 100 kHz and 70% duty-cycle, bipolar pulsed bias voltage of −40 V with a frequency of 100 kHz and 70% duty-cycle, with a positive pulse of 16 V. Some samples were deposited in dynamic mode, with a substrate holder rotational speed of 12 rpm, during 30 min, whilst the remaining ones were deposited in static mode for a deposition time of 5 min.

In order to enhance the electrical and optical properties, the as-deposited ZnO:Al thin films were subjected to the following hydrogen thermal treatments:

1st step – In this step it was studied the influence of different annealing temperatures: 473, 623 and 723 K, with fixed Ar and H_2-flow rates of 20 and 50 sccm, respectively, ensuring a working pressure of 8.0 Pa, for 60 min.

2nd step – By fixing both temperature (623 K) and treatment time (60 min), it was studied the influence of different working pressures during the annealing: 0.5, 8.0, 46.7 and 120 Pa. The pressure was increased while maintaining a constant hydrogen to argon flow ratio.

Table 1
Results obtained from the Hall effect measurements and from the optical simulation program, SCOUT.

Deposition mode	p_s (Pa)	d (nm)	T (%)	n ($\times 10^{20}$ cm^{-3})	N_{Dr} ($\times 10^{20}$ cm^{-3})	E_g (eV)	ΔE_g
Static	0.37	396	79.3	2.2	3.8	3.67	0.31
	0.40	339	81.0	5.6	3.8	3.67	0.31
	0.48	282	80.8	3.1	2.7	3.60	0.24
	0.80	221	80.7	2.0	2.0	3.55	0.19
Dynamic	0.37	390	80.0	2.5	3.6	3.62	0.26
	0.40	372	79.0	2.2	3.4	3.61	0.25
	0.48	335	81.7	2.1	3.3	3.65	0.29
	0.80	288	80.5	1.6	2.4	3.61	0.25

p_s is the sputtering pressure, d is the film thickness, T is the average transmittance in the visible region, n and N_{Dr} are the carrier concentration obtained respectively from the Hall effect measurements and from the SCOUT simulation, E_g is the band-gap energy estimated from the Tauc plots, and ΔE_g (E_g − 3.36 eV) is the band-gap widening.

These thermal annealings with hydrogen were carried out in a chemical vapor deposition (CVD) chamber. The CVD chamber was evacuated to a base pressure of $\sim 10^{-4}$ Pa before the beginning of the thermal treatments; the plasma was generated by applying an RF power density of 318.3 mW/cm^2 on the sample and by flowing argon and hydrogen gases.

In order to understand the effect of vacuum annealing (in the absence of hydrogen) and compare with the effect of the hydrogen annealing, a few samples were treated in vacuum, in a resistance furnace. A base pressure of $\sim 10^{-4}$ Pa was achieved before the beginning of the thermal treatment.

2.2. Electrical characterization

Throughout this work, an in-depth study of the electrical properties of the ZnO:Al thin films is done, based on Hall effect measurements performed at room temperature and under atmospheric pressure, for the measurement of the electrical resistivity (ρ), carrier mobility (μ) and carrier concentration (n). A Hall effect measurement system – Ecopia model HMS-5000 – with d.c. four-point probe apparatus in the Van der Pauw configuration was used. The sheet resistance and the Hall voltages were obtained using a magnetic field of 0.560 T.

Carrier concentration and carrier mobility were obtained from [18]:

$$n = 8 \times 10^{-8}\frac{IB}{de|V|_s} \tag{1}$$

$$\mu = \frac{1}{endR_S} \tag{2}$$

In the above equations, I is the electric current, B is the magnetic field (in Gauss), d is the film thickness, e the elementary charge, V_S is the total Hall voltage and R_S is the sheet resistance. For a good accuracy of the results, the contacts should be sufficiently small and at the periphery of the sample. Furthermore, the thin film should be of uniform thickness and free of pinholes [18].

2.3. Optical, structural and morphological characterization

Optical transmittance and reflectance spectra were carried out on the as-deposited samples, using a Shimadzu UV-3101PC spectrophotometer (in a wavelength range of 250 and 2500 nm). The experimental curves were modeled by a commercial optical simulation program (SCOUT), and the thickness and dielectric function of all samples were calculated.

X-ray diffraction (XRD) analyses were performed to investigate the crystallographic structure of the ZnO:Al thin films, using a Bruker AXS D8 Discover diffractometer, operated in θ–2θ geometry with CuKα radiation. XRD patterns were obtained with a step size of 0.04° and an integration time of 1.5 s.

A scanning electron microscope (SEM) was used to investigate the morphology and cross-section of the ZnO:Al films deposited under different sputtering pressures.

3. Results and discussion

For the commercial application of ZnO:Al as an efficient transparent electrode, it is very important to achieve low electrical resistivity and high optical transmittance. The first step in the present research was therefore to study the influence of argon pressure