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High conductivity and transparent ZnO:Al films prepared at low temperature by DC and MF magnetron sputtering

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Abstract

Aluminum-doped zinc oxide thin films have been deposited by DC and MF magnetron sputtering from a ceramic oxide target in argon atmosphere without direct heating of the substrates. The samples were prepared at different predetermined conditions of input power or discharge voltage and the influence upon electronic, optical, and microstructural properties has been investigated. The as-deposited layers show low resistivity, such as 9×10^{-4} Ω cm minimum for DC excitation and 1.2×10^{-3} Ω cm for MF mode, with growth rates up to 130 nm/min, and resulting substrate temperatures always below 200 °C. Low resistivity of the films is combined with high transmission, 85–90% in the visible wavelength range (400–800 nm). A strong (002) texture perpendicular to the substrate has been found, with lower strain for DC than for MF sputtering.

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Keywords: Sputtering; Transparent conductive oxide (TCO); Structure

1. Introduction

Transparent conductive oxide coatings have applications in several electro-optical devices such as flat panel displays and photovoltaic solar cells. For many of these applications there is an increasing interest in reducing the coating preparation temperature in order to minimize interdiffusion processes on previously deposited materials and/or to allow the utilization of plastics for replacing the conventional glass substrates [1–3]. Aluminum-doped zinc oxide, ZnO:Al (AZO) has emerged as one of the most used transparent conducting films, becoming increasingly used in the aforementioned applications.

ZnO:Al films have been prepared by a large number of techniques including continuous direct current (DC) or pulsed mid-frequency (MF) and radio-frequency (RF) sputtering from either metallic, alloyed, or ceramic targets [4–9]. Main limitations for the sputtering processes are related with the method and target used which determine the final electrical, optical and structural properties of the AZO layers. RF sputtering yields good quality material, but with a low deposition rate caused by the small voltage that is generated at the target [4,5]. In DC and MF sputtering, the utilization of metallic or alloy targets in reactive atmosphere makes the processes difficult to control so as to guarantee stable oxide film formation at high deposition rates [6,7]. More recently, DC and/or MF sputtering of conductive ceramic targets have emerged [8,9] as a potential solution to the above listed problems, allowing to achieve high deposition rates without the need of reactive process control equipment. In order to achieve high transparent and conductive AZO films, substrate and/or post-deposition heating temperatures above 300–400 °C are usually utilized [8,9]. Such high temperatures promote material crystallization, film densification and the creation of oxygen vacancies that act as intrinsic donors [8].

In this work, DC and MF magnetron sputtering from ceramic oxide target in argon atmosphere have been developed to obtain AZO thin films without direct heating of the substrates. The process behavior upon sputtering has been followed by means of the input power, target voltage and substrate temperature. The structure, optical and electrical properties of the sputtered AZO layers have been analyzed as a function of the experimental parameters in order to achieve high transparent and conductive coatings at low temperature

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and high deposition rate, as required for photovoltaic and other electro-optical applications.

2. Experimental details

Aluminum-doped zinc oxide films have been deposited in stationary mode on 60×60 mm^2 soda lime glass substrates in a homemade high vacuum sputtering system. The substrate holder was positioned at 15 cm in front of the target, consisting of 99.995% purity ZnO:Al$_2$O$_3$ 98:2 wt.%, 177 cm^2 area. The sputtering chamber was evacuated to a base pressure of $2-3 \times 10^{-4}$ Pa. Then, controlled flux of pure argon was introduced into the chamber to act as sputter gas, giving a typical process pressure three orders of magnitude higher than the base pressure. The discharge power was varied from 200 to 1400 W, in both continuous (DC) and pulsed (MF at 100 kHz pulse frequency, 1056 ns pulse width) excitation modes. The substrates were not heated intentionally, but their temperature increased as a consequence of the energy flux during deposition, as has been measured by a K-type thermocouple.

Electrical sheet resistance of the coatings was determined from the four-point probe method, being the resistivity obtained after film thickness calculation by profilometric measurements. The crystallographic structure was analyzed by X-ray diffraction (XRD) by using the nickel-filtered Kα1 emission line of copper ($\lambda = 1.5405$ Å), in a Philips X'pert instrument. Optical measurements of the samples were done with unpolarized light at normal incidence in the wavelength range from 250 to 1500 nm, with a double beam spectrophotometer Cary 5000, taking the air as reference.

3. Results and discussion

Both DC and MF magnetron sputtering have been performed at various controlled powers. The voltage reached at a constant input power is dependent on the plasma excitation mode, such as is illustrated in the Figs. 1 and 2 by the time evolution of the discharge voltages for DC and MF sputtering. These experimental data show that for a same discharge power the voltage decreases by a factor about 0.8 when the excitation frequency is increased from zero (DC) to 100 kHz (MF). The ionization through electrons in the plasma body oscillating by the MF excitation is more effective compared to the ionization by secondary electrons from the cathode in the DC mode, and therefore much lower discharge voltages are generated at the same discharge power. In order to characterize the interaction between plasma and substrate, the increase of the substrate temperature resulting from the heat transfer during the deposition process was measured. The substrate temperature was found dependent on the discharge power and the sputtering time, as showed in Fig. 3, without significant variations between DC and MF excitation modes. In a magnetron sputtering system, the substrate heating due to particle bombardment is reduced by the confinement of the secondary electrons and the plasma in front of the target, being the thermal power only slightly dependent on the plasma excitation mode [10]. For the experimental parameters and configuration used in the present work, the substrate temperature is below 200 °C for 1400 W, below 150 °C for 800 W and below 100 °C for 400 W power.

The growth rate and the resistivity of the AZO layers have been measured as a function of the discharge power (DC and MF) for 30 min constant deposition time, and are represented in the Fig. 4. The rate is proportional to the discharge power, as expected in the energy range where the sputtering yield depends linearly on the acceleration voltage in the cathode fall [4]. For DC excitation, the rate starts to increase from about

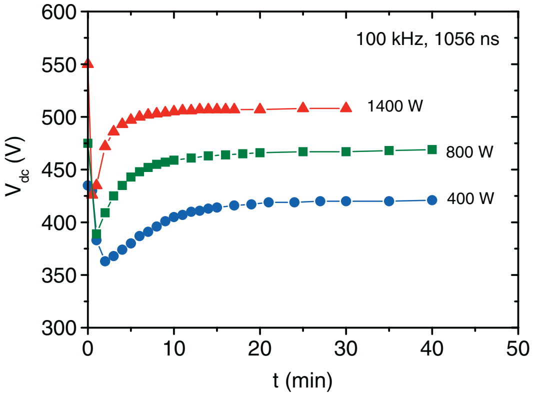

Fig. 2. Time evolution of the discharge voltage for various pulsed sputtering powers.

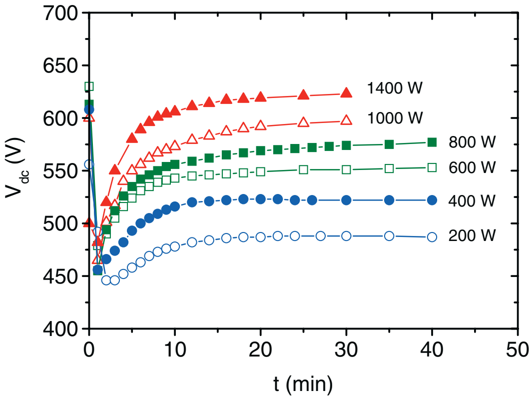

Fig. 1. Time evolution of the discharge voltage for various continuous sputtering powers.

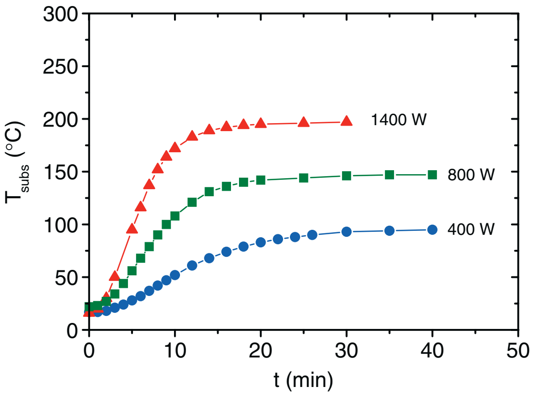

Fig. 3. Time evolution of the substrate temperature for various continuous sputtering powers.