Surface & Coatings Technology 347 (2018) 245–251

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Effect of substrate temperature on the deposition of Al-doped ZnO thin films using high power impulse magnetron sputtering

Martin Mickan[a,b], Ulf Helmersson[b], David Horwat[a,*]

[a] Université de Lorraine, Institut Jean Lamour, UMR7198, Nancy F-54011, France
[b] Plasma & Coatings Physics Division, IFM–Material Physics, Linköping University, Linköping SE-581 83, Sweden

ARTICLE INFO

Keywords:
ZnO
Transparent conducting oxide
HiPIMS
Temperature
Electrical properties
Thin films

ABSTRACT

Al-doped ZnO thin films were deposited using reactive high power impulse magnetron sputtering at substrate temperatures between room temperature and 600 °C. Two sample series with different oxygen partial pressures were studied. The films with the lowest resistivity of $3 \times 10^{-4}\,\Omega\,cm$ were deposited at the highest substrate temperature of 600 °C. The improvement of the electrical properties could be related to an improvement of the mobility due to the improved crystallinity. This improved crystallinity also increased the stability of the films towards ambient moisture. On the other hand, the detrimental influence of negative oxygen bombardment could be avoided, as the HiPIMS process can take place in the metal or transition mode even at relatively high oxygen partial pressures.

1. Introduction

Transparent conductive oxides (TCOs) are important materials for wide ranges of applications in optoelectronics and energy conversion, that can be used for example as transparent electrodes in solar cells [1] or flat panel displays [2]. A common TCO is ZnO, that is usually doped with group III elements such as Al, in order to achieve low resistivity. However, the solubility limit of Al in ZnO is quite low at around 0.3 at % [3]. To reach high active dopant concentrations in Al-doped ZnO (AZO) films, the films need to be grown using a non-equilibrium method such as physical vapor deposition (PVD) [4]. A commonly used technique for the deposition of AZO films is direct current (DC) or radio frequency (RF) magnetron sputtering as it can be easily scaled up to large deposition areas [5].

As the properties of the growing films are governed by both kinetics and thermodynamics, the substrate temperature is an important parameter in the deposition of AZO films. There have been several studies about the influence of the substrate temperature in magnetron sputter deposition of AZO films in the case of DC and RF magnetron sputtering. He et al. [6] studied DC sputtering of AZO films at deposition temperatures up to 480 °C. They observed an increase in both mobility and charge carrier concentration with increasing substrate temperature. Similarly, Park et al. [7] observed an improvement of the electrical properties with the substrate temperature in their study of RF magnetron sputtering of AZO films at substrate temperatures up to the 500 °C. On the other hand, Vinnichenko et al. [8] observed a degradation of the electrical properties above an optimum temperature of 200 °C. They explain this by the formation of an insulating metastable phase at higher temperatures. Bikowski and Ellmer [9] find an optimum temperature of 300 °C in the case of RF magnetron sputtering of AZO films.

An upcoming technique is high power impulse magnetron sputtering (HiPIMS). HiPIMS uses short pulses of high current density [10]. Recently, it has been shown that highly conductive and transparent AZO films can be deposited without substrate heating using HiPIMS [11]. However, there are only few studies that investigate the influence of the substrate temperature in the case of HiPIMS deposition of AZO films. Ruske et al. [12] used substrate temperatures of up to 200 °C and improved the resistivity of the AZO films by an order of magnitude as compared to deposition at room temperature.

There seems to be no clear conclusion about which temperature is the optimum temperature for the deposition of AZO thin films. The optimum temperature might depend on the deposition technique, as well as the deposition parameters. In this work, AZO films are deposited by reactive HiPIMS at substrate temperatures between room temperature and 600 °C using two different O_2/Ar ratios. Their electrical, optical and structural properties are investigated. Another common effect in AZO films is the degradation of the electrical properties in a humid environment [13]. It has been shown that a heat treatment of deposited AZO films at 650 °C in vacuum can make the films stable towards humid environments [14]. Therefore, the aging behaviour of the films in ambient moisture is also studied.

* Corresponding author.
E-mail address: david.horwat@univ-lorraine.fr (D. Horwat).

https://doi.org/10.1016/j.surfcoat.2018.04.089
Received 15 October 2017; Received in revised form 12 April 2018; Accepted 30 April 2018
Available online 05 May 2018
0257-8972/

Table 1
Experimental conditions for the two sample series.

	Ar flow rate (sccm)	O_2 flow rate (sccm)	O_2/Ar ratio (%)
Series 1	47	17	36.2
Series 2	59	24	40.7

2. Experimental

AZO films were deposited onto Si and fused silica substrates mounted on a rotatable substrate holder using reactive HiPIMS of a 50 mm Zn/Al target with 2 at% of Al. The substrate temperature was controlled with a resistive heater for two different sample series. In series 1, the temperature of the substrate was varied between room temperature and 500 °C and in series 2 the temperature was varied between room temperature and 600 °C. The substrate temperature without intentional heating is expected not to exceed 45 °C [11]. The oxygen and argon flow rates have been slightly changed between the two series as indicated in Table 1 in order to assess the robustness of the process. The total pressure in the chamber was controlled by a throttle valve to be 1 Pa in all cases. The HiPIMS unit (Melec Spik 2000A) was charged by an Advanced Energy Pinnacle Plus DC power supply. The DC supply was set to a constant voltage of 560 V and the HiPIMS unit delivered pulses of a length of 100 µs with a frequency of 1000 Hz. This leads to an average power of around 120 W and a peak current of around 2.6 A. The distance between the target and the substrate was 11 cm and the deposition time was 10 min.

The electrical properties of the films were measured using a HMS 5000 Hall effect measurement setup in the van der Pauw geometry [15]. Transmittance measurements were performed using a Cary 5000 UV-Vis-NIR spectrophotometer. The thickness of the films was measured using cross-sectional back-scattered electron images in a Philips XL30 scanning electron microscope (SEM) with an acceleration voltage of 15 kV. Additional images were taken with a LEO 1550 Gemini SEM with an acceleration voltage of 5 kV. A rough estimation of the Al concentration in the films was obtained by energy dispersive spectrometry (EDS) in the LEO 1550 Gemini SEM on selected samples. In order to reduce the influence of the substrate on the EDS measurement, the samples were tilted by 30 ° and an acceleration voltage of 3 kV was used. Crystallographic information was obtained using $\theta/2\theta$ X-ray diffraction (XRD). Two different diffractometers with Cu anodes were used. An AXS Bruker D8 Advance with an automatic sample loading system was used to scan a large 2θ range from 10 to 120 °. Scans in the range of 30 to 40 ° were performed using a PANalytical X'pert diffractometer. This allowed a fine-calibration of the alignment of the sample tilt to be able to compare the peak intensities between different samples. In this case, the contribution of the Cu Kα_2 component was removed numerically using the method by Rachinger [16]. From the line profile of the (002) peak of ZnO, the microstrain and the size of the coherent scattering domains could be determined using the method by de Keijser et al. [17].

3. Results

Magnetron sputtered AZO films often show a lateral variation of the properties along the substrate surface [18]. It has been shown that this variation decreases in the case of HiPIMS-deposited films [11]. There is also a lateral variation of the properties for the films in this experiment, however this lateral variation is much smaller than the variation of the properties with the temperature. The lateral variation is therefore only shown in the errorbars in the figures. The small lateral variation can be related both to the effects of the HiPIMS process, as well as the large distance between the target and the substrates.

Fig. 1 shows the deposition rate as a function of the substrate temperature. There is an 170% (100%) increase in deposition rate between room temperature and 500 °C for series 1(series 2). The deposition rate decreases again at a temperature of 600 °C. The increase in deposition rate at high temperature is stronger for sample series 1. This result could have several possible reasons, such as the change in the gas density due to the temperature. A change in gas density could have an effect on both the target condition as well as the film growth.

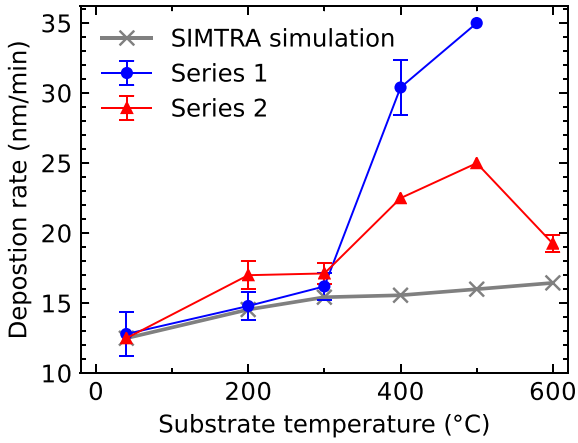

Fig. 1. Deposition rate of the AZO films as a function of temperature and the simulated normalized deposition rate using SIMTRA.

Under the assumption that the gas temperature is in equilibrium with the substrate temperature, the gas density decreases by 60% between room temperature and 500 °C, as the pressure is kept constant at 1 Pa. A decrease in the gas density causes an increase in the mean free path of the sputtered atoms, which could explain the increase in the deposition rate. In order to estimate the magnitude of this effect, the deposition rate was simulated using the software SIMTRA [19] and normalized to the measured deposition rate at room temperature (12.5 nm/min). This simulated deposition rate is also shown in Fig. 1. The simulations show only an increase of about 28% in the deposition rate between room temperature and 500 °C, which is much lower than the experimentally observed increase. Hence, the change in the mean free path with temperature is not the main origin for the increase in deposition rate.

Another possible explanation could be the decrease in the reactive gas density, that would move the process further into the metal mode and therefore increase the deposition rate. The increase in deposition rate being more pronounced in series 1, i.e. at lower oxygen partial pressure, supports this interpretation. A shift in the reactive sputter process towards the metal mode should affect the shape of the discharge current waveforms [20]. However, the discharge current waveforms, shown in Fig. 2 for series 2, do not show any significant changes with the temperature. For all the samples, the current reaches a peak value of about 2.7 A after about 35 µs and decreases afterwards due to the rarefaction effect [21]. The current waveforms for series 1 (shown in Fig. S1 in the Supplementary material) look similar. There is no significant difference in the shape of the current waveforms and the peak current is relatively constant, suggesting that the effect of the substrate temperature on the target conditions should be small.

The resistivity of the films has been measured using the Hall effect setup. The results are shown in Fig. 3a as a function of substrate temperature. The resistivity decreases with increasing substrate temperature for both series from a value of around $9 \times 10^{-3}\,\Omega\,\mathrm{cm}$ at room temperature to around $3 \times 10^{-4}\,\Omega\,\mathrm{cm}$ at 600 °C. The evolution of the resistivity is very similar for both series despite the different deposition parameters. This shows that the HiPIMS process indeed allows to obtain AZO films with good properties over a relatively large range of parameters.

The mobility and charge carrier concentration of the films have also been measured using the Hall effect setup, and are shown in Fig. 3b and