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Room temperature deposition of homogeneous, highly transparent and conductive Al-doped ZnO films by reactive high power impulse magnetron sputtering

Martin Mickan [a,b], Ulf Helmersson [b], Hervé Rinnert [a], Jaafar Ghanbaja [a], Dominique Muller [c], 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, SE-581 83 Linköping, Sweden
[c] Laboratoire ICube, Université de Strasbourg, CNRS UMR 7357, 67037 Strasbourg Cedex 2, France

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ABSTRACT

Aluminum doped zinc oxide (AZO) films have been deposited using reactive high power impulse magnetron sputtering (HiPIMS) and reactive direct current (DC) magnetron sputtering from an alloyed target without thermal assistance. These films have been compared in terms of their optical, electrical and structural properties. While both DC and HiPIMS deposited films show comparable transmittance, their electrical properties are significantly improved by the HiPIMS process. The HiPIMS deposited films show a low resistivity down to the order of $10^{-4}\,\Omega$ cm with a good homogeneity across the substrate, making them potential candidates for electrodes in solar cells. The density of electrons reached up to 11×10^{20} cm^{-3}, making ionized impurities the main scattering defects. This improvement of the film properties can be related to the specific plasma/target interactions in a HiPIMS discharge. This allows the process to take place in the transition mode and to deposit highly conductive, transparent AZO films on large surfaces at low temperature. While the overall oxygen content is above that of stoichiometric ZnO, higher localization of oxygen is found at the interfaces between crystalline domains with substoichiometric composition.

1. Introduction

Thin films of aluminum doped zinc oxide (AZO) are highly interesting as transparent electrodes in applications such as photovoltaics [1] and flat panel displays [2]. For these applications a low resistivity of the AZO films in the order of $10^{-4}\,\Omega$ cm is required. An increasingly important parameter in the fabrication of solar cells is the deposition temperature. For copper indium gallium selenide (CIGS) solar cells a substrate temperature of less than 200 °C is preferred in order to preserve the performance of the absorber layer [3]. Another interest is to deposit such materials on flexible polymer substrates in order to meet the demand of flexible solar cells. For such substrates, low temperature fabrication methods are also needed and synthesis routes avoiding thermal assistance would be ideal in order to simplify the fabrication process. The same applies to the development of flexible electronics. A common technique to deposit AZO films is reactive direct current (DC) magnetron sputtering because of its scalability [4]. But at low deposition temperatures it is difficult to achieve the required properties using reactive magnetron sputtering [4]. Another issue is the homogeneity of the electrical properties. Weltzel and Ellmer reviewed this problem [5] that can be traced back to the initial report by Minami et al. in 1982 that the resistivity of the deposited films increases in front of the target axis [6]. This degradation has been related to the bombardment with negative oxygen ions that introduces point defects such as zinc vacancies and oxygen interstitials that can compensate the donors [7,8]. It is worth noting that such bombardment could cause damages to any materials in contact with the zinc oxide layer and might be the reason why CdSe buffer layers are required between the absorber layer and the insulating zinc oxide layer (i-ZnO) covered by the AZO transparent electrode of CIGS solar cells [3]. Another possible reason is the change in the local environment of the Al atoms that can lead to an deactivation of the dopants which is more pronounced in more resistive films [9,10]. An $Al_2O_3(ZnO)_m$ homologous phase can be formed where the Al atoms are in an octahedral configuration and do not contribute to the conductivity.

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

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To improve the properties of the films without heating the substrate, high power impulse magnetron sputtering (HiPIMS) could be used [11,12]. HiPIMS uses short pulses of high current density, that lead to a denser plasma and a large ionized fraction of the sputtered material [13]. The dynamics of the HiPIMS process leads to several effects such as self-sputtering [14], strong gas compression followed by rarefaction [15] and regions of strong ionization (spokes) [16]. It has also been shown that the hysteresis effect can be reduced or completely suppressed using a reactive HiPIMS process [17,18].

In the present work AZO films were deposited without thermal assistance using reactive HiPIMS from a metallic Zn/Al target. Their optical, electrical and structural properties were investigated as a function of the position of the substrate during the deposition in order to evaluate the homogeneity of the process. The properties were also compared to the properties of a sample deposited by DC sputtering with similar average current. In a second part, the HiPIMS process was investigated, to explain the difference in the properties of the films between the different deposition methods.

2. Experimental

AZO films were grown without thermal assistance on glass substrates by reactive HiPIMS from a $Zn_{0.97}Al_{0.03}$ target. The target had a diameter of 5 cm and the distance between substrate and target was 8 cm. A schematic representation of the sputtering chamber is shown in Fig. 1. The gas flow rate was fixed at 80 sccm for argon and between 0 and 20 sccm for oxygen. This led to a total pressure of 1 Pa for the highest oxygen flow rate. The substrates were placed on a rotating substrate holder to ensure a homogeneous deposition. The magnetron was placed eccentric to the rotation axis of the substrate holder at a horizontal distance of 8 cm in order to reach good lateral homogeneity of the chemical composition [19].

The HiPIMS pulses were supplied by a Melec SPIK 2000A that was connected to an Advanced Energy Pinnacle Plus DC power supply. The discharge current waveforms were recorded using a Pearson Current Monitor model 110 connected to a Tektronix TDS 2024B oscilloscope. For most of the experiments, the pulse length was 100 μs with a frequency of 1000 Hz. This corresponds to a duty cycle of 10%. Depositions were done at discharge voltages of 540 V, 555 V and 570 V for 15 min. The corresponding discharge current waveforms are shown in Fig. 2. The peak current increased with the discharge voltage from 2 A at 540 V to 3 A at 570 V. This corresponded to an average current of about 200 mA. Some experiments were also performed at 570 V, using the same duty cycle but pulse lengths of 80 and 120 μs. The average current ranged from 0.18 A to 0.26 A as a function of the voltage and pulse lengths. For comparison, another sample was fabricated using DC magnetron sputtering with a current of 0.2 A and a corresponding voltage of 335 V. The oxygen flow rate was set to 8 sccm to adjust to the lower sputtering power of 67 W. The substrate temperature does not exceed 45 °C during the deposition process as measured by thermal level stripes (Thermax).

The optical transmittance of the films was measured in the ultraviolet, visible and near infrared ranges using a Cary 5000 UV-Vis-NIR spectrophotometer. The resistivity of the films was measured using a 4-point probe setup. The mobility and charge carrier density were measured using a HMS 5000 Hall effect measurement setup. Photoluminescence (PL) measurements have been performed with an excitation wavelength of 266 nm using a CryLas FQCW266–50 laser. The spectra were recorded using a Horiba iHR320 spectrometer equipped with a Horiba Syncerity multichannel CCD detector. The structural properties were measured using $\theta/2\theta$ x-ray diffraction (XRD) with an AXS Bruker D8 Advance

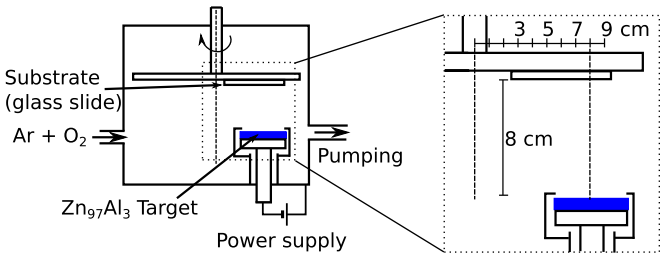

Fig. 1. Schematic representation of the sputtering chamber. The inset shows the position of the sample in the chamber.

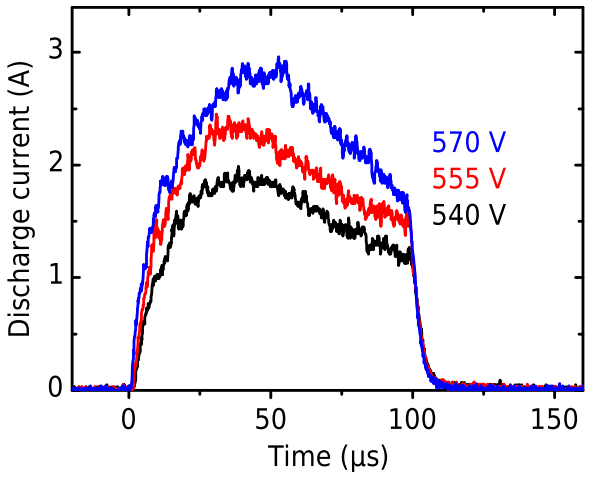

Fig. 2. Discharge current waveforms for three HiPIMS deposited samples using different discharge voltages with an oxygen flow rate of 20 sccm.

diffractometer with a Cu anode (Cu Kα=0.154 nm) and high resolution transmission electron microscopy (HRTEM) with a JEM-ARM200F cold FEG Cs probe corrected microscope (point resolution 0.19 nm in TEM mode and 0.078 nm in STEM mode). The TEM samples were prepared by a focussed ion beam (FIB)/scanning electron microscope (SEM) dual beam system (FEI Strata DB235). The oxygen content, characterized by O/(Zn+O) atomic ratio was measured using Rutherford backscattering spectrometry (RBS). RBS measurements have been performed with a 1.5 MeV $^4He^+$ beam produced by the Van de Graaff accelerator of the ACACIA platform at the ICube Laboratory. Special attention was paid to the charge collection during the analysis because of the non-conductive behavior of the glass substrates. A thin gold layer (2 nm) was deposited on all the samples together. The RBS contribution of this layer was used to check the efficiency of the ion beam current measurement. This thin layer does not alter the accuracy of the measurements.

3. Results and discussion

3.1. Optical, electrical and structural properties

The optical and electrical properties of the AZO films were investigated as a function of the position on the sample as shown in Fig. 1. The corresponding extracted values for the optical bandgap and resistivity along with the film thickness are reported in Table S1 in the supplementary material. The transmittance of the samples was measured between 200 nm and 3300 nm. The obtained spectra for the sample position of 4 cm are shown in Fig. 3. The average transmittance in the visible range is generally above 83% for all the films, but slightly higher in the case of the DC deposited film. For the HiPIMS deposited samples the transmittance close to