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Room temperature deposition of high figure of merit Al-doped zinc oxide by pulsed-direct current magnetron sputtering: Influence of energetic negative ion bombardment on film's optoelectronic properties

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ABSTRACT

Aluminum-doped zinc oxide is regarded as a promising indium-free transparent conductive oxide for photovoltaic and transparent electronics. In this study high transmittance (up to 90,6%) and low resistivity (down to 8,4°1^{-4} Ω cm) AZO films were fabricated at room temperature on thermoplastic and soda-lime glass substrates by means of pulsed-DC magnetron sputtering in argon gas. Morphological, optical and electrical film properties were characterized using scanning electron microscopy, UV–vis–nIR photo-spectrometer, X-ray spectroscopy and four probes method. Optimal deposition conditions were found to be strongly related to substrate position. The dependence of functional properties on substrate off-axis position was investigated and correlated to the angular distributions of negative ions fluxes emerging from the plasma discharge. Figure of merit as high as 2,15 ± 0,14 Ω^{-1} were obtained outside the negative oxygen ions confinement region. Combination of high quality AZO films deposited on flexible polymers substrates by means of a solid and scalable fabrication technique is of interest for application in cost-effective optoelectrical devices, organic photovoltaics and polymer based electronics.

1. Introduction

Transparent conductive oxides (TCOs) are a class of oxide semiconductors combining good electrical conductivity properties and high transparency in the visible region of the electromagnetic spectrum. Important technological applications of TCOs, such as light emitting diodes [1,2], transparent contacts for solar cells [3], for liquid crystal displays [4], and low thermal emissivity coatings [5] or electro-chromatic windows [6] have driven extensive research efforts towards improved properties control through material synthesis and, at the same time, deposition schemes allowing TCO's growth on a wide range of substrates.

Aluminum-doped zinc-oxide (AZO) films have been recently considered as a promising alternative to the indium-doped tin oxide (ITO) industrial standard. Several researchers demonstrated state-of the-art visible transmittance and resistivity [7] approaching record ITO's performances while being non-toxic materials, cheap to manufacture and with a low environmental impact. Intensive research efforts have been devoted in the past decade to improve TCO's films optoelectrical performances using soda lime glass as a substrate [8]. The crucial processing parameter to be optimized in order to obtain low resistivity films is generally the substrate temperature and the optimal value for crystalline films formation has been assessed to be around 250–500 °C depending on TCOs and deposition technique [9].

Room temperature fabrication of high quality TCO thin films has become, in the last few years, the necessary route of technical development due to the rapid expansion of polymer based electronics: proliferation of polymeric components in photovoltaic devices impose severe restrictions on the energy flux delivered to substrates and nanometer-scale systems require minimal atoms interdiffusion between thin films deposited during consecutive fabrication steps.

Different physical deposition technologies for room temperature processing such as atomic layer deposition [10], pulsed laser deposition [11], DC [12] and RF magnetron sputtering [13] have been reported to produce thin films of Al-doped zinc oxide (AZO) with performances adequate for applications. Due to its high deposition rates, low cost, scalability to large areas and possibility of low temperature processing, the magnetron sputtering synthesis remains one of the most interesting growth techniques. Pulsed direct current driven magnetron sputtering discharges (pDCMS) are especially interesting due to limited scale-up costs for large areas deposition reactors. Although radio frequency driven magnetron sputtering discharges (RF-MS) could provide a sputtering deposition with a lower dc sputter voltage, the obtainable deposition rate of AZO films prepared by this method is often too low for high throughput fabrication of transparent electrode. On the other hand, the deposition rate of AZO films prepared by pDCMS deposition is adequately high, but inferior electrical performances are generally

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obtained, compared with AZO films prepared by RF-MS. In conventional pDCMS and RF-MS deposition, low processing temperatures are also detrimental for film properties. In literature optimal deposition conditions have been identified for substrate temperatures around 300 °C [14,15] while, below this limit, poor electrical and optical properties are generally observed. Such high temperature processing conditions prevent high quality AZO film deposition on most of the conventional polymeric materials of interest for optoelectrical applications.

In this study we investigate an off-axis deposition approach for room temperature pulsed DC magnetron sputtering of AZO thin films deposited both on glass and polymeric (polyethylene terephthalate, PET) substrates with competitive optical and electrical properties. Optical and electrical film properties are analyzed as a function of the substrate position with respect to the sputtering target and the influence of negative ions bombardment on film properties is discussed, the details of the negative ions angular distributions are calculated and taken into account for deposition process optimization. Although other authors reported the influence of ion bombardment on magnetron sputtered thin film, its role on films growth is still the subject of discussion.

2. Experimental details

Film deposition was performed in a custom-built stainless steel cylindrical vacuum chamber evacuated by a turbo pump system backed by a membrane fore vacuum pump. Angstrom Science Onyx II magnetron sputtering cathode was used coupled with a pulsed-DC power supply with adjustable repetition frequency and duty cycle. An 0,250″ (≈6,4 mm) thick Al_2O_3(2 wt.%):ZnO sputtering target (diameter ≈ 51,2 mm, purity 99,99%) was used. The following processing parameters were found suitable for optimized film deposition and kept fixed throughout all the reported experiments unless stated otherwise in the text: high voltage pulses repetition frequency 50 kHz at 40% duty cycle (t_{ON} = 8 μs), discharge operating pressure 1,0 Pa and Argon gas flow 20 sccm, discharge absorbed power was kept below 5 W·cm^{-2} (typically 2,5 W·cm^{-2} at 6,4 mA·cm^{-2} and 450 V) in order to prevent passive heating of the substrate, target-substrate distance was fixed at 50 ± 5 mm. Polished n-Si (100) wafer, soda lime glass (SLG) and PET foils were used in parallel as deposition substrates. Thin films were deposited in an off-axis arrangement: substrates were placed parallel to the target surface plane with sample's center positioned at specific distances from the target axis. In the following discussion, off-axis radial displacements are indicated as compared to the target radius R_0 using the parameter R/R_0, where R_0 was fixed at 50 ± 5 mm. Micrographs of deposited films were acquired by a Zeiss SUPRA40 field-emission scanning electron microscope (SEM) using an operating voltage of 7 kV and structural characterization was performed via powder X-ray diffraction (P-XRD) (Bruker D8 Advance Diffractometer Cu Kα1, λ = 1,5406 Å) used in reflection mode, measurement parameters were: exposure time = 0,1 s, angular step size = 0,016°. Transmittance and reflectance spectra were acquired by a UV–Vis–nIR (PerkinElmer Lambda1050) spectrophotometer in the range 250–2500 nm, with a 150 mm diameter integrating sphere. All data presented in the following discussion has been normalized to remove bare substrates contributions. Electrical properties (resistivity, carrier densities and Hall mobility) were characterized by means of an Hall effect analyzer (Microworld, HMS5300), based on a four-probes Van der Pauw method [16], with a probing current of 1 mA and a mean magnetic field intensity of 0,56 T; silver contacts were fabricated at the edges of each sample to remove stray contact resistance between the AZO film and the gold probes.

3. Results and discussion

AZO films showed in this work were physically stable and presented very good adherence to the polymeric substrate, no cracking or peel-off was observed after deposition. Optoelectrical properties shown in the following text were found constant several weeks after thin film deposition, samples were stored exposed to air without control of temperature and humidity conditions. Growth rates in our deposition conditions are off-axis position dependent, [17] and for the low power deposition conditions chosen for our experiments, maximal growth rate was 65 nm min^{-1} at the center (R/R_0 = 0) of the collection region as measured by SEM images and profilometric measurements. Typical film thickness used for material characterization at different radial positions was 1,0 ± 0,2 μm obtained by varying the deposition time.

3.1. Negative ion confinement

It is known that the relative position of magnetron sputtering source and substrate can strongly influence the optoelectrical properties radial non-uniformity of the deposited oxides and TCOs films, [18,19] depending on cathode voltage and operating gas pressure, resulting in deposition of high resistivity films when the substrate is placed in front of the sputtering target and lower resistivity films when the substrate is placed away from the target axis. This behavior was likewise observed in our experiments, with the difference between inner and outer regions electrical properties being more pronounced for low pressure (P < 0,9 Pa) and high cathode voltage (650 V < U < 750 V) conditions.

These differences in film properties were observed for several binary transition metal oxide targets' materials [20] and they were attributed to the influence on film growth of negative ions (being O^- the dominant species for AZO targets but also comprising O_2^-, AlO^-, ZnO^-, and higher atomic mass species [21]) sputtered from the negatively biased target surface [18]. A negative charged particle created in the proximity of the target surface is accelerated, by the full cathode potential, across the plasma sheath in the direction of the substrate location gaining energies of the order of several hundreds of eV, according to $E \le e(V_{plasma} - V_{target})$. Because of their high kinetic energy the collision cross section with background gas atoms (argon) is low [22], implying that in the low pressure (mean free path of several millimeters) and short target-substrate distances (few centimeters) conditions typical for our experiments, thermalization processes are ineffective and energetic negative ions travel across the quasi-neutral plasma region bombarding the substrate surface while preserving almost all of their original energy. Despite the fact that a certain amount of kinetic energy from bombarding particles can be beneficial for film growth, by creation of surface mobile defects that assist epitaxial growth of film monolayers, excessively high energies can induce the formation of bulk defects, unwanted implantation of oxygen negative ions and damages in the material crystalline structure [23]. During deposition processes at high DC-bias voltage, decreased growth rates (resputtering) or erosion of the substrate materials was also observed [18]. In order to avoid unwanted film damage by energetic ion bombardment off axis conditions were chosen in order to avoid direct sight between target and substrate.

The angular distribution function of sputtered particles flux at each spot of the negatively biased target surface follows a cosine law [24,25] of the form (1):

$$\mathrm{PDF}(\alpha) = \mathrm{N}\left(c_1 \cos\alpha + c_2 \cos^2\alpha\right) \quad (1)$$

where α is the angle between an individual particle trajectory and the normal direction to the target surface, N is a normalization factor and $c_{1,2}$ are the empirical ($c_1 \approx 0{,}9 \cdot c_2$) weight factors estimated from measured profiles. The average velocity of an ejected particle is typically of the order of 10^3 m s^{-1} [26]. Neutral particles are not affected by plasma fields and follow this angular distribution, allowing for some broadening due to collisions at higher pressures. Charged particles, however, are affected by the plasma sheath electric fields, positive ions are accelerated back to the target surface driving the sputtering process, and negatively charged ions are accelerated away from the target in the direction of the substrate. Due to this additional velocity component normal to the target surface the final negative ions angular distribution