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Relevance of annealing on the stoichiometry and morphology of transparent thin films

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ABSTRACT

Transparent thin films of SnO_2, ZnO:Al, and ITO were deposited onto glass substrate by vacuum thermal evaporation technique, from 0.5 cm diameter grains (i.e. ITO, ZnO:Al (3%) and SnO_2) with 99.99% purity. To improve the quality (i.e. stoichiometry and morphology) of these thin films, they were annealed at 400 °C in air for 2 h. Following this annealing, the samples become suitable to be used as contact electrodes for solar cells.

The investigations were performed on samples having a polycrystalline structure, as revealed by X-ray diffraction analysis after annealing process. Moreover, these thin films had a strong orientation with the following planes parallel to the substrate: (1 0 1) for SnO_2, (0 0 2) for ZnO:Al and (2 2 2) for ITO film respectively. Atomic force microscopy (AFM) investigations of the ZnO:Al (R_{rms} = 2.8 nm) and ITO samples (R_{rms} = 11 nm) show they are homogeneous and a slightly higher roughness (R_{rms} = 51 nm) for the SnO_2 thin film surface. The size and shape of the grains were also observed and investigated by scanning electron microscopy (SEM). All SnO_2, ZnO:Al and ITO transparent thin films are uniform and dense.The values obtained for electrical resistivity, transmission and energy bandgap as well as conductivity and transparency properties of these thin films, make them suitable to be used as transparent contact electrodes for solar cells.

1. Introduction

Transparent and conductive oxide (TCO) thin films, such as aluminum doped zinc oxide (ZnO:Al), indium tin oxide (ITO) and tin oxide (SnO_2), are the target for advanced research technologies due to their versatile properties than can be applied to gas sensors [1], optoelectronics [2], solar cells [3], and displays. Occupying one of the priority fields of the worldwide scientific research, these materials are integrated within the structures of solar cells as transparent contact electrodes. Equally, used as transparent contact electrodes, these layers illustrate a possible improvement in performance of the solar cell [3].

N. Baydogan [2] showed that ZnO thin films doped with 1.2 at% Al have decreasing resistivity with increasing annealing temperature, and T.L. Chen [4] obtained highly stable Al-doped ZnO transparent conductors using an oxidized ultrathin metal capping layer at its percolation thickness. The properties of ZnO:Al thin films make them suitable for their use in various electronic applications, as well as their integration in solar cells as window layer [5].

The excellent electrical and optical properties of ITO thin films have been exploited in many applications [6]. However, the thicker the layer the higher the charge carriers concentration as well as the conductivity, but the lower the transparency of the material. The conductivity of ITO thin films is increased by improvements in crystalline structure. Therefore, it is important to choose a proper deposition technique followed by an appropriate annealing treatment to further improve their optical and electrical properties [6,7]. Note that tin oxide (SnO_2) thin films have a bandgap of 3.6 eV, as well as other noteworthy properties [1,8].

All these oxide thin films can be deposited by several methods, such as: vacuum thermal evaporation [9], spray pyrolysis [10], pulsed laser deposition [6,11], sol gel [12], spin coating [13] or radio frequency (RF) magnetron sputtering [14].

Post-deposition annealing in various ambient conditions reduces defect concentration in amorphous and crystalline films, leading to a higher electron mobility. SnO_2 thin films showed a compact and homogeneous structure, with an optical transmission around 80% in the visible range of the spectrum [15]. It has been used as transparent conductive contact on glass substrate to achieve ZnTe/CdSe heterojounctions [9].

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In this paper we investigate the stoichiometry and morphology of transparent thin films such as: ZnO:Al, SnO_2 and ITO. All samples have the same thickness and are deposited onto glass substrate by vacuum thermal evaporation. Optical properties of the three different compounds, enumerated above, were investigated.

The aim of the study was to compare/assess the properties of each thin film regarding uniformity, transparency and conductivity. If integrated in solar cells as transparent contact electrodes, an increase in quantum efficiency will be possible with these high quality samples.

2. Experimental

The oxides thin films were deposited by vacuum thermal evaporation with a quasi-closed volume Baltzers deposition equipment. Thus, the ZnO:Al(3%), ITO and SnO_2 thin films were deposited onto glass substrate, from 0.5 cm diameter grains (i.e. ZnO:Al(3%), ITO and Sn) with 99.99% purity.

For deposition of ZnO:Al(3%), SnO_2 and ITO thin films, resistive evaporators made of tantalum with density of 16.6 g/cm^3 and atomic weight of 180.9, were used. The electrical current intensity in the evaporator had been increased gradually and slowly in order to achieve a thermal equilibrium between the evaporator and the substance there of. Until the evaporation process did not become stationary over the evaporator was placed a mobile screen. This is because, during the heating of the evaporator a quantity of adsorbed residual gases is released as well. The screen is removed as soon as the evaporation becomes stationary.

The thickness of the ZnO:Al, ITO and SnO_2 thin films was preset to 550 nm, given the installation is provided with a quartz monitor (i.e. quartz crystal thin films QSG 201) as well as with an optical thin film monitor (i.e. GSM 210). The distance between the substrate and evaporator was 10 cm and a high vacuum during deposition of 7×10^{-7} Torr (using a TURBOVAC MAG 1500 CT turbomolecular vacuum pump) was achieved within the deposition chamber. After deposition the ITO, ZnO:Al and SnO_2 thin films were annealed at 400 °C in air for 2 h. For the heat treatment we used a Type F21100 Tube Furnace oven. It is equipped with a chamber that is heated by heating elements embedded into a fire-resisting material.

The glass substrates were obtained from MENZEL-GLASER glass slides with dimensions of 22 mm × 64 mm and thickness of 1.13–1.17 mm. Each investigated glass substrate had a size of 15 mm × 15 mm, where the thin film coating was 13 mm × 13 mm given the desired topography of the applied mask. These glass substrates were cleaned before being placed in the mask. The cleaning process consisted of degreasing, cleaning with acetone and ethyl alcohol, ultrasonication for 10 min and drying under a nitrogen flux.

In determining the structure of the oxide thin films, X-ray diffraction (XRD) investigations using a Cu-Kα (λ = 0.15406 nm) radiation were carried out with a Bruker diffractometer, in the 2 theta angular range 20–70°.

The thickness of the samples was also measured with a contact Ambios high resolution profilometer (XP-2). Visual inspection of ZnO:Al, SnO_2 and ITO thin films was performed with a Zeiss microscope (Axio Imager model).

Topography of the surface of the thin films was investigated by atomic force microscopy (AFM). It was used to analyze the aspect and roughness of the surface of the samples. The AFM images have been obtained with an XE-100 Park Systems microscope, offering performances such as: maximum and minimum scanning areas of 50 μm × 50 μm and respectively 500 nm × 500 nm and height scale of maximum 12 μm. Measurements were carried out in non-contact mode, using a silicon tip with 10 nm radius of curvature, in order to analyze surface roughness and morphology of the films on different areas. In this paper we show images of 3 μm × 3 μm scanned area samples, containing topography information with nanoscale resolution. For the AFM image processing the XEI software version 1.5, Powerful image Processing Tool for SPM Data was used.

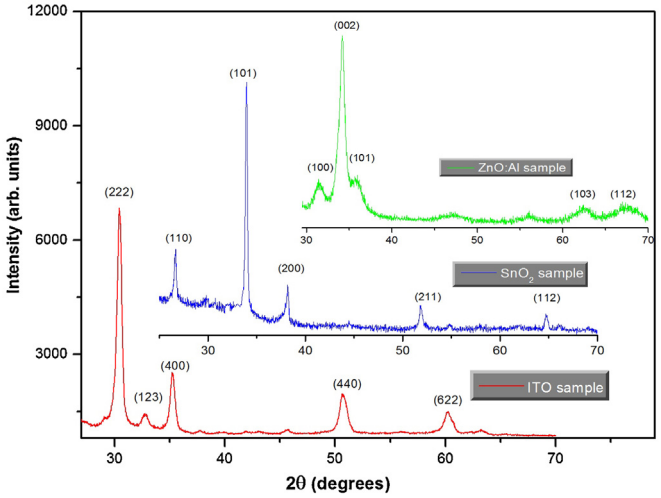

Fig. 1. XRD of the ITO, SnO_2 and ZnO:Al thin film (from bottom to top).

Also, scanning electron microscopy (SEM) was used to analyze the morphology of our samples. SEM images were obtained with FEI Quanta (E = 50 keV and 0–30 mm working distance) microscope.

Spectral properties in the range 190–1200 nm of ITO/glass, ZnO:Al/glass and SnO_2/glass were measured with a Perkin Elmer LAMBDA 950 UV/Vis/NIR Spectrophotometer.

3. Results

Diffractograms acquired from the ITO, ZnO:Al and SnO_2 samples are shown in Fig. 1, depicting diffraction maxima that were identified from standard ASTM (i.e. American Society for Testing Materials) diffraction charts.

The experimental interplanar distance, d_{hkl}, was determined using Bragg formula [16]. Following the analysis the ITO sample, shows a cubic structure and the value of lattice parameter (a) were determined with the following formula [17,18]:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}, \quad (1)$$

where h, k and l are Miller indices.

In the case of ZnO:Al thin film, with a wurtzite (hexagonal) structure, the lattice parameters (a and c) were determined with the formula [16,19]:

$$\frac{1}{d_{hkl}^2} = \frac{3}{4}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2}. \quad (2)$$

The SnO_2 thin film shows a tetragonal structure and the lattice parameters (a and c) were determined with the relation [16,20]:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}. \quad (3)$$

The values of the crystalline lattice constants for the three samples are given in Table 1. For the ZnO:Al thin film it was noticed the presence of crystallite content with diffraction maxima at angle $2\theta = 33.34°$, corresponding to reflection on the (0 0 2) crystalline plane, parallel with the surface of the substrate. The SnO_2 thin film has crystallites with diffraction maxima at angle $2\theta = 33.95°$, corresponding to reflection on the (1 0 1) crystalline plane. The ITO thin film, on the other hand, show these crystallites with maxima