Applied Surface Science 255 (2009) 5288–5291

Contents lists available at ScienceDirect

Applied Surface Science

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

Structural investigations of ITO-ZnO films grown by the combinatorial pulsed laser deposition technique

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ARTICLE INFO

Article history:
Available online 31 July 2008

Keywords:
Pulsed laser deposition
Combinatorial
TCO
ITO
ZnO

ABSTRACT

Mixtures of transparent and conductive oxides such as ITO-ZnO have been grown by a combinatorial pulsed laser deposition technique from two targets that were located 15 mm apart. The films were deposited on (1 0 0)Si and quartz substrates that were heated at temperatures from 300 to 500 °C. Measurements of the In to Zn ratios along the transversal axis of the substrates, which passes through the maximum thickness points corresponding to each target position were performed using energy dispersive X-ray spectroscopy and spectroscopic ellipsometry. From simulations of the X-ray reflectivity spectra, collected with a 2 mm mask on different locations along the transversal axis of the samples, the density and thickness of the deposited films were calculated and then the In to Zn ratios. The crystalline structure and electrical properties of the deposited films were also investigated along the same axis. Changes in the ratio of In/Zn along this axis resulted in changes of the film lattice constant and texture.

1. Introduction

One of the best-known and most used methods to obtain new and better properties or functionalities from a material is by doping or alloying it with other materials. Since it is not yet possible to predict, based on first principles, the right amount of doping or alloying element required to optimize a specific property of the new phase or material studied, one must design ways to find the right recipe with minimum effort and cost. The combinatorial method, where two or more sources of atomized materials are simultaneously or alternatively used for deposition on a single substrate is an great example of such optimization work [1–5]. By changing both the direction and the dose of the atomized incoming fluxes, one has control upon the lateral and vertical compositional gradients of the deposited thin film material. Depending on the resolution of the analytical techniques used for characterization, a single sample could now provide a rather large range of various compositions and/or thicknesses. We have used the combinatorial pulsed laser deposition (C-PLD) method to obtain transparent and conductive oxides films by mixing indium tin oxide (ITO) with pure zinc oxide. Such films are used for the top transparent electrode for solar cells, controlling also the amount of light that is captured and protecting the cell from the ambient. Pure ITO is the most used material for transparent and conducting electrodes [6,7]. Unfortunately, it is rather expensive and scarce, which limit its use in a large scale, industrial production of solar cells. There were many studies and investigation aiming at replacing or mixing ITO with inexpensive and abundant ZnO [8–10]. By mixing these two components we also wanted to tailor the mechanical, crystalline, electrical and optical properties of these films.

2. Experiment

The mixed films were deposited using the C-PLD technique, where ITO and ZnO targets were located in two different positions 15 mm apart and ablated sequentially using a KrF laser. The deposition sequence was 20 pulses from the ITO target followed by 20 pulses from the ZnO target to ensure a good atomic mixing of the components. The total number of pulses was varied from 1000 to 5000, which resulted in films thicknesses from around 50 to 250 nm across a 50 mm long substrate. The material was collected on Si or quartz substrates heated from 300 up to 500 °C. Films grown separately from each target will have their maximum thickness positioned at the intersection between the perpendiculars from the laser impact area on the targets with the substrate.

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doi:10.1016/j.apsusc.2008.07.120

On the line passing through the maximum thickness points, samples will exhibit a continuous gradient of concentrations. All the reported investigations were performed along this line, hereafter called the transversal axis.

The films crystalline structure was investigated by symmetrical and grazing incidence X-ray diffraction (XRD and GIXD) in a Panalytical MRD X'Pert system, while the density, thickness and surface roughness were extracted from simulations of the acquired X-ray reflectivity (XRR) spectra using the Panalytical WinGixa software. Thickness and phase concentration were also obtained from simulations of the optical data acquired by spectroscopic ellipsometry (SE) (Woollam VASE) using the instrument database for optical constants. The elemental concentration was also measured by X-ray dispersive energy spectroscopy (EDS) in a JEOL 6400 instrument. Optical measurements were performed by measuring the optical transmittance of films deposited on quartz (spectrophotometer GBC-Cintra 10).

3. Results and discussion

We firstly investigated the deposition of pure ITO and ZnO films to obtain information about the growth rate, lateral thickness variations, mass density and surface roughness. Spectroscopic ellipsometry and XRR spectra were recorded using a various apertures along the transversal axis. Fig. 1 displays the thickness variation across the transversal axis for a pure ZnO film obtained from simulations of the acquired SE spectra.

Fig. 2 displays XRR spectra acquired from several locations for the same pure ZnO films. It is evident that, regardless of locations, the critical angle value for a pure film remained unchanged, which implies that the film density, which is proportional to the critical angle, was also unchanged. The XRR spectra were modeled, using the WinGixa program by Panalytical, to extract information about the density, thickness and roughness of the deposited films. The maximum film thickness value was found to be 198 nm, in excellent agreement with the SE measured value of 198.7 nm. The ZnO and ITO thin films densities were found to be 5.35 and 6.87 g/cm^3, respectively.

However, for film mixtures the critical angle was found to be a function of the location where the measurement was performed. By inspecting Fig. 3a, where spectra collected from a mixed film are displayed along those collected from pure films, one can see that the mixed film possesses a density that changes along with the location on the transversal axis. The calculated values were from 5.63 g/cm^3 in the ZnO rich region up to 6.51 g/cm^3 in the ITO rich region, between those calculated for pure ZnO and ITO films. The amplitude of the oscillations observed in the XRR spectra, which are related to the roughness of the films, was also depending on the location, as shown in Fig. 3b: the pure ITO is very smooth, with a surface rms (root mean square) below 1.0 nm, whereas ZnO films exhibited rms values of several nm. The mixed film exhibited roughness values between those estimated for pure films. From the calculated average density of the film on a particular location on the transversal axis and the densities of pure films we then calculated the fractions of ITO and ZnO at that particular location and then the Zn/In ratio. The obtained results agreed quite well with those estimated by EDS and presented in Fig. 4. It is clear that by using this C-PLD technique we were able to grow films with

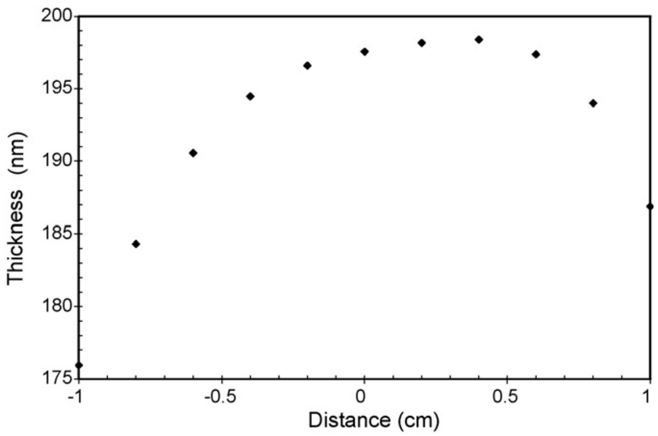

Fig. 1. Thickness dependence estimated by SE for a pure ZnO film.

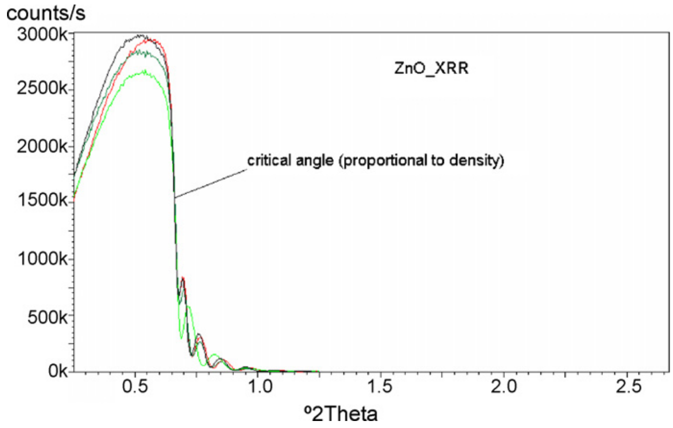

Fig. 2. The critical angle region for XRR spectra acquired from various locations on a ZnO film.

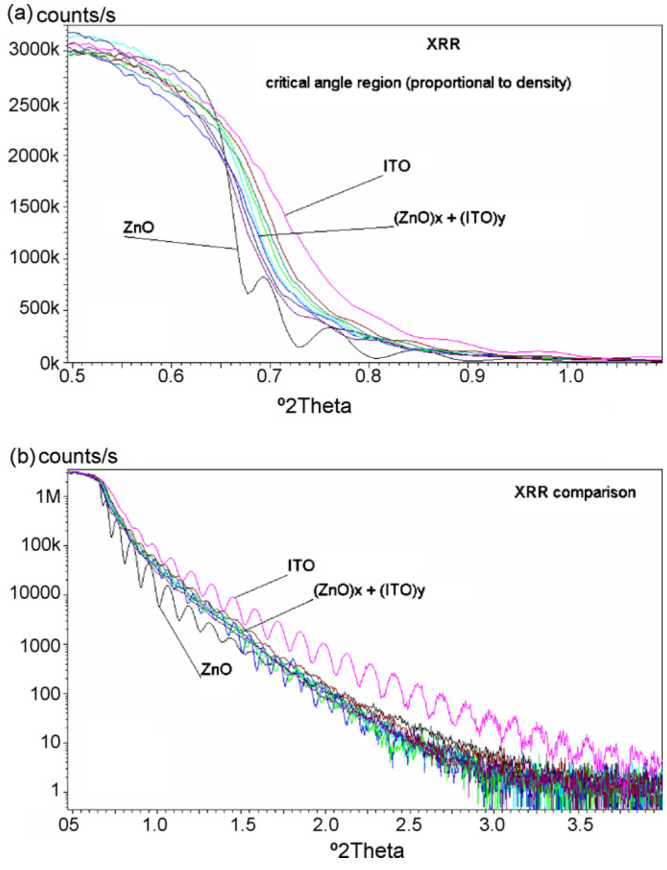

Fig. 3. XRR spectra acquired from various locations on a ITO-ZnO mixed film: (a) critical angle region and (b) complete spectra; the XRR spectra from pure ZnO and ITO films are also displayed.