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TAILORING OF OPTICAL, COMPOSITIONAL AND ELECTRICAL PROPERTIES OF THE $In_xZn_{1-x}O$ THIN FILMS OBTAINED BY COMBINATORIAL PULSED LASER DEPOSITION

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Indium Zinc Oxide compositional libraries were fabricated by combinatorial pulsed laser deposition technique on glass substrate at room temperature. Two pairs of targets with In atomic concentrations, In/(In+Zn), of 28 at.% and 56 at.% or 42 at.% and 70 at.% were employed. A high transparency was observed for all the coatings with transmittance values better than 95%. The maximum thicknesses of the samples, inferred by spectroscopic ellipsometry, were within the 174-310 nm range for the simple PLD films, whereas in case of combinatorial PLD coatings were 341 or 467 nm. Energy dispersive X-ray spectroscopy revealed that In content in the combinatorial films was in the 27-52 at. % range. From atomic force microscopy histograms we evidenced a decrease of the RMS roughness down to 1 nm with the increase of the In content. As a result of the compositional library studies two minimum values of the electrical resistivity were identified at 2.3×10^{-3} Ω·cm and 8.6×10^{-4} Ω·cm, which correspond to 28.8-29.5 at.% and 44-49 at% range of Indium content.

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1. Introduction

During the last decade, great efforts have been directed to discover and develop new materials with improved optical, electronic and physical properties. As a result, extraordinary progresses have been made in synthesis of the novel compounds with remarkable features. However, the conventional “step by step” investigations are time consuming and expensive due to the requirements and the complexity of the materials used for the prospective technologies. Recently, the combinatorial approach has offered a comprehensive manner to overcome this barrier. This solution has been applied for the first time in the chemistry for a number of purposes generally related to the discovery of novel pharmacologically active molecules or investigating biological functions [1,2]. Combinatorial chemistry implies the rapid synthesis of a large number of different but structurally related compounds. The collection of these synthesized compounds is referred to as a combinatorial library [2]. This main advantage has inspired different uses, employing many variants of the technology. The concept has been successfully extended to the solid state materials such as semiconductors [3], metals [4], oxides [5], catalysts [6] or polymers [7]. Moreover, there are numerous publications which report combinatorial studies of materials as thin films. Deposition techniques like magnetron sputtering (MS) [8,9], pulsed laser deposition (PLD) [5,10], arc plasma deposition (APD) [4], chemical vapor deposition (CVD) [11,12], chemical solution deposition (CSD) [13] or ion beam-assisted deposition (IBAD) [14] have been successfully used to obtained coatings with tailored properties and libraries of composition. Combinatorial PLD (CPLD) offers a large versatility to design materials with purposely engineered physical properties and a rigorous control of the stoichiometry or to synthesize films that cannot be fabricated with conventional setups.

Transparent conductive oxides constitute a class of materials widely used in the solar cells [15] or thin film transistor (TFT) technology [16]. Among them, Indium Zinc Oxide (IZO) is a very attractive compound due to its high transparency, low resistivity, high carrier density and large electrical mobility [17, 18]. Using a combinatorial magnetron sputtering approach, Taylor et al. [19] found that amorphous IZO thin films with In/(In+Zn) concentrations from 45 % to 70 % exhibited better electrical properties than pure In_2O_3 or doped ZnO films. In our experiments, we investigated electrical, elemental composition, morphology and optical features of IZO films grown by CPLD. As a result of this study a compositional library was generated for each combinatorial sample.

2. Experiment

The experiments have been conducted in a pulsed laser deposition chamber using a combinatorial geometry described below (Fig. 1). Two batches of combinatorial samples have been deposited using home made targets with atomic In concentrations, In/(In+Zn), of 28 at.% and 56 at.% or 42 at.% and 70 at.%, respectively. A planetary ball mill (model Retsch S 100) was used to obtain a homogeneous mixing of the In_2O_3 (Aldrich, 99.9% purity) and ZnO (Aldrich, 99.99% purity) powders. In order to obtain compact pellets, the grinded powder was pressed at 5 MPa and sintered for 12 hours at 1100 ^{o}C in air. All the depositions have been performed by alternative ablation of targets using a KrF* (λ= 248 nm, τ_{FWHM} = 25 ns) laser source (model COMPexPro 205, Lambda Physics-Coherent) under 1 Pa oxygen atmosphere. The laser fluence onto the target surface was around 3 J/cm^2. The films were deposited at room temperature (RT) on typical microscope glass slides with (26x76) mm^2 size. Prior to introduction inside the deposition chamber, the substrates were successively cleaned into an ultrasonic bath in acetone, ethanol and deionized water for 15 min and then blown dry with high purity nitrogen. The distance between the substrates and the targets was set at 5 cm (see Table I). In order to obtain comparable results, the positions of the targets and the substrates with respect to the focus laser beam were the same for all the samples presented in the paper (Figure 1). Just for the sake of comparison, apart from the films obtained by CPLD we synthesized films from each target in a typical PLD setup. The number of applied laser pulses for every type of target was 3000 at a laser repetition rate of 10 Hz.

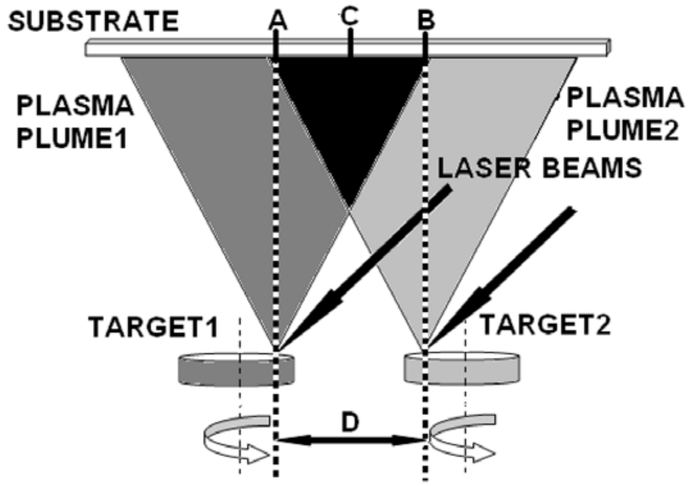

Fig. 1. Combinatorial pulsed laser deposition setup;

Table I. Deposition conditions of the PLD and CPLD grown thin films and the maximum thickness value of each sample;

Sample	Target1 In/(In+Zn) (at.%)	Target2 In/(In+Zn) (at.%)	No. of laser pulses applied onto Target1	No. of laser pulses applied onto Target2	Maximum thickness value (nm)
IZOC1	28	56	25×120=3000	25×120=3000	467
IZOFC1	28		3000		280
IZOEC1		56		3000	310
IZOC2	42	70	25×120=3000	25×120=3000	341
IZOFC2	42		3000		174
IZOEC2		70		3000	246

In the case of combinatorial films, for each target we applied series of successively 25 laser pulses in 120 consecutive steps. The laser beam impinged on the targets at a separation distance between the laser spots of D=22 mm (see Figure 1). As depicted in figure 1, A and B positions on the substrate correspond to mirror positions of the laser spots on the target 1 (with lower In content) and target 2 (with higher In content), respectively, whereas the C point is the middle in-between A and B positions. Using CPLD in this geometry we deposited films having only one well-defined composition gradient across the length of the glass slide.

Optical spectra were recorded with a double beam spectrophotometer (GBS, Cintra 10e) in the 300–1200 nm wavelength range.

The morphological features of the IZO films were examined by atomic force microscopy (AFM) in a non-contact mode with a Nanonics MV 4000 Microscope. All the AFM scans were performed on a 30×30 μm^2 area.

The energy dispersive X-ray spectroscopy (EDX, FEI model Inspect S) with a SiLi detector (model EDAX Inc.) was used to determine the chemical composition of the combinatorial films and of all targets.

The thickness and the optical properties of the films were inferred from spectroscopic ellipsometry (SE) measurements with a Woollam V-VASE equipment. A Cauchy model was used to fit the experimental data in the 1.5-2.5 eV spectral range, where the thin films were highly transparent (k=0).

The electric resistivities were measured at RT with a four point probe head from Jandel, a Keithley 2182A nanovoltmeter and a current that was generated by a Keithley 6220 precision current source.

3. Results and discussion

The optical transmission of the films (Fig. 2) showed a high transparency (> 95%) in the visible and near infrared (NIR) region. All the transmittance spectra are given without substrate contribution. Due to the reduced thickness, just a few interference fringes were observed in the measured spectral range.

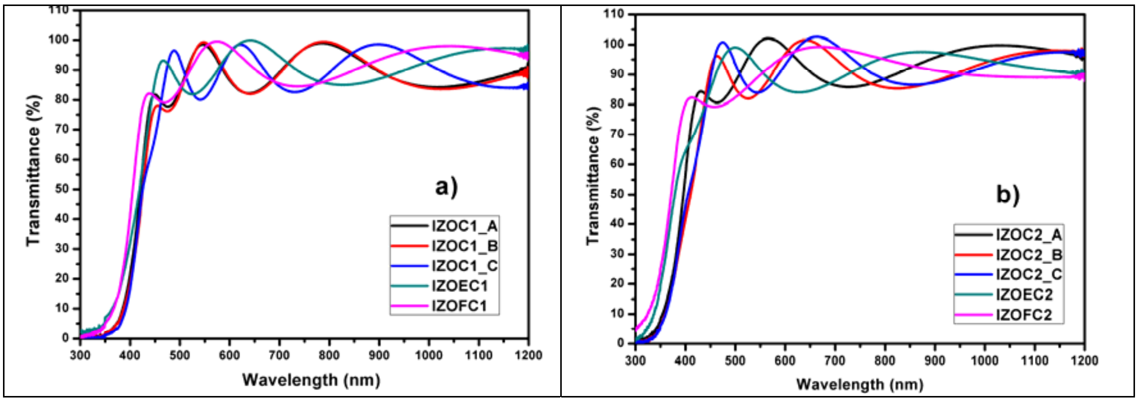

Fig. 2. Optical spectra of thin films deposited from targets with (a) 28 at. % or 56 at. % and (b) 42 at. % or 70at. % In content, respectively;

Spectroscopic ellipsometry measurements were employed to determine the thickness profiles of the thin films. In order to plot the accurate profiles, the thickness of all the samples was determined in 26 equidistant points on the same row.

The measurements were performed along a 55 mm long line drawn through A and B points which correspond to the maximum of compositions for the target 1 and 2, respectively. In Fig. 3 the thickness profiles are given for the films obtained by ablation of the targets 1 and 2, in PLD and CPLD geometries. SE measurements performed for the first batch of samples deposited from the targets with 28 at. % and 56 at.% In content showed that the largest thickness values inferred for the coatings deposited in PLD geometry were 280 nm (IZOFC1) and 310 nm (IZOEC1), whereas for the film grown in the CPLD geometry (IZOC1) the maximum thickness was of 467 nm. In the case of the second set of coatings deposited from the targets with 42 at.% and 70 at.% In content, the maximum values of thickness for the IZOFC2, IZOEC2 and IZOC2 samples were 174 nm, 246 nm and 341 nm, respectively (Table I). The thickness profiles of the deposited samples were obtained by the fitting of the experimental data with a 9th order polynomial distribution. An excellent matching and overlapping of the values and curve shapes was obtained between the thickness profiles of the combinatorial samples IZOC1 and IZOC2 and the sum of the thickness curves IZOFC1+IZOEC1 and IZOFC2+IZOEC2, which correspond to the simple PLD coatings (see Figures 3a and 3b).

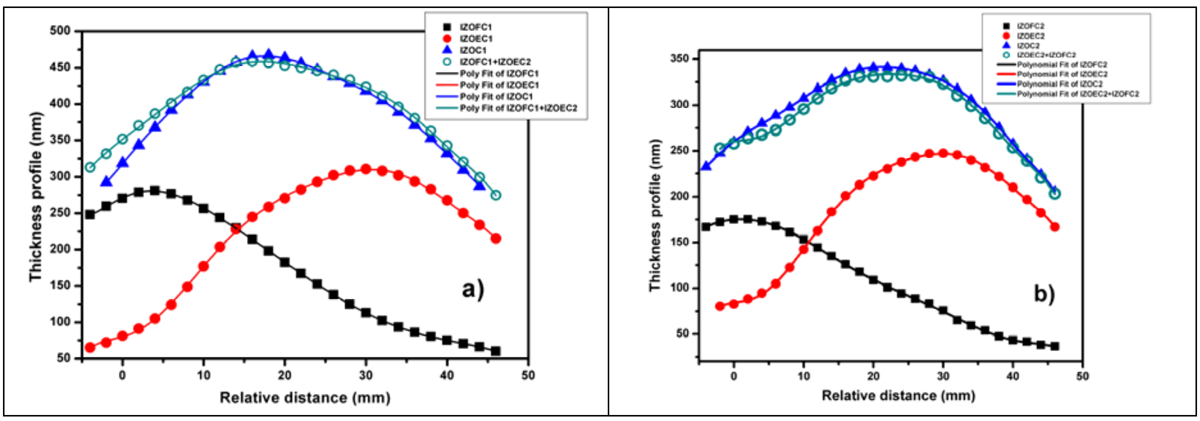

Fig. 3. Thickness profiles of the thin films deposited from targets with (a) 28 at. % or 56 at. % and (b) 42 at. % or 70xat. % In content, respectively;

The EDS results of elemental composition showed that a nonlinear variation of the composition of the films can be achieved by the CPLD. The corresponding In content, In/(In+Zn), along the line defined by A and B positions was determined by averaging the data collected from successive segments of 2.5 mm length. In addition, the In content of the targets 1 and 2 was established as a mean of the values recorded from 4 different areas. We found out that the atomic concentration of In, In/(In+Zn), in the target 1 and 2 used in our experiments was of 28 at.% and 56 at.% or 42 at.% and 70 at.% for the first or the second batch of samples, respectively (see Table I). Figures 4 a) and b) show the results of a line-scan for the In content measured from an edge scan along the length of the film. The compositional profiles of IZOC1 and IZOC2 samples obtained by fitting the experimental data are described by a nonlinear distribution given as the hereinafter function:

$$C_{at.\%}[In/(In+Zn)] = A1 + (A2 - A1)\cdot\left[\frac{p}{1+10^{(LOGx01-x)\cdot h1}} + \frac{1-p}{1+10^{(LOGx02-x)\cdot h2}}\right] \quad (1)$$

where, A1, A2, p, h1, LOG_x01, h2, LOG_x02 are the fitting parameters.

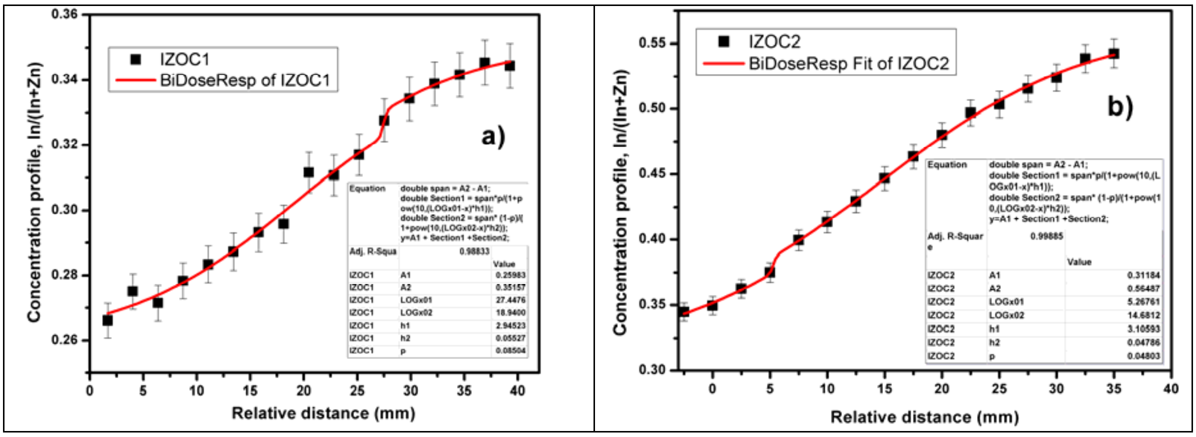

Fig. 4. Elemental composition profiles of (a) IZOC1 and (b) IZOC2 samples determined by EDS;

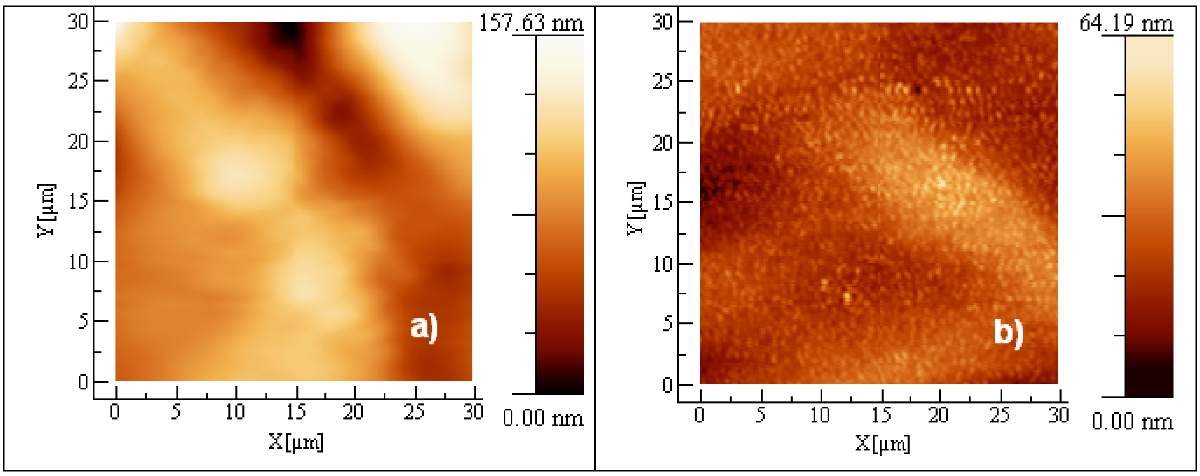

Fig. 5. Typical AFM images of the (a) IZOC1 and (b) IZOC2 samples;

The variation in the concentration of each element reflects exactly the composition of the combinatorial thin films. Indium atomic concentration into the combinatorial ZnO thin films, in between A and B positions, varied in the 27-33 at % and 36-52 at % range for the IZOC1 and IZOC2 sample, respectively. It is worth mentioning as direct observation that a lower Indium content was determined in the composition of the combinatorial thin films. These results can be explained by the preferential nucleation of the ZnO at the interface with the glass substrate. Previous investigations (elsewhere reported) by X-ray reflectometry simulations (XRR) showed that a lower mass density was estimated for thinner films. In the case of thicker samples, this behavior wasn't noticeable.

The morphology of the combinatorial samples was investigated by AFM measurements from different areas between the A and B positions. In Figure 5 typical AFM images are displayed for the (a) IZOC1 and (b) IZOC2 samples. The analysis of AFM histograms showed that the films are smooth, with RMS roughness values which varied between the A and B positions for IZOC1 (Figure 6 curve a) and IZOC2 (Figure 6 curve b) sample in the 7.1-26.2 nm and 1.0-7.3 nm range, respectively. Each plotted point in Figure 6 was obtained as the mean of the RMS roughness values collected from 3 adjacent areas. One may observe that RMS roughness values decrease between the A and B positions [18]. Considering the profiles of the elemental composition (Figure 7) across the surface of the sample in the direction of A to B positions, the decreasing of RMS roughness is related with the increase of Indium content as compared to Zn.

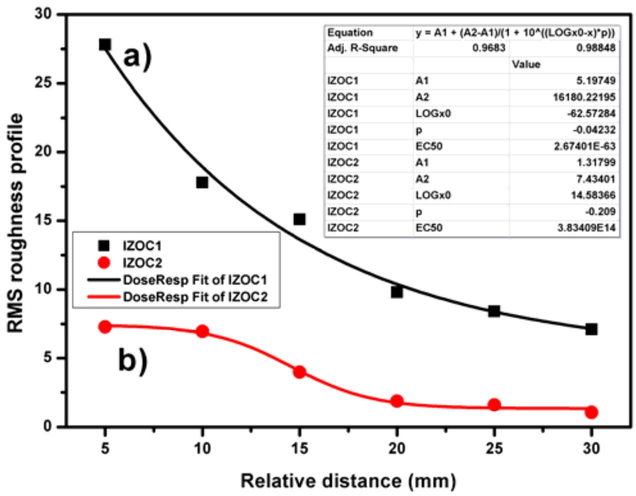

Fig. 6. RMS roughness profiles between A and B positions of the (curve a) IZOC1 and (curve b) IZOC2 samples;

The RMS roughness profiles exhibit a nonlinear distribution (Figure 6 and 7)) described by the function (2):

$$y = A1 + (A2 - A1)/\left(1 + 10^{(LOGx0 - x) \cdot p}\right) \tag{2}$$

where A1, A2, p and LOG_x0 are the fitting parameters.

In order to establish the variation of electrical properties as function of the composition we measured by the four point probe technique the sheet resistance of the combinatorial coatings in different points in A-B direction, taking into account the geometrical approximations for thin films [20]. Using the thickness profiles (Figure 4) we calculated the corresponding electrical resistivity in each point (Figures 8a and 8b).

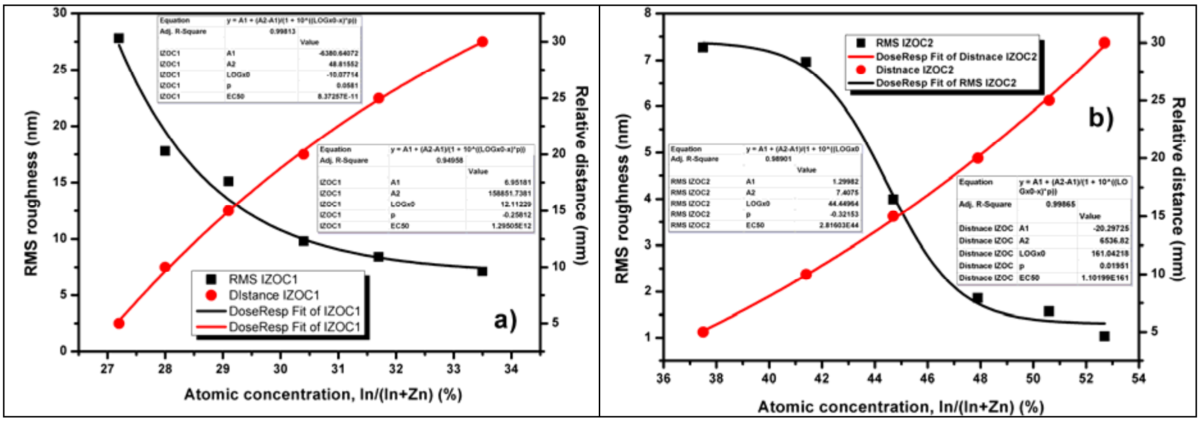

Fig. 7. The RMS roughness of the combinatorial thin films (a) IZOC1 and (b) IZOC2 as a function of the In atomic concentration.

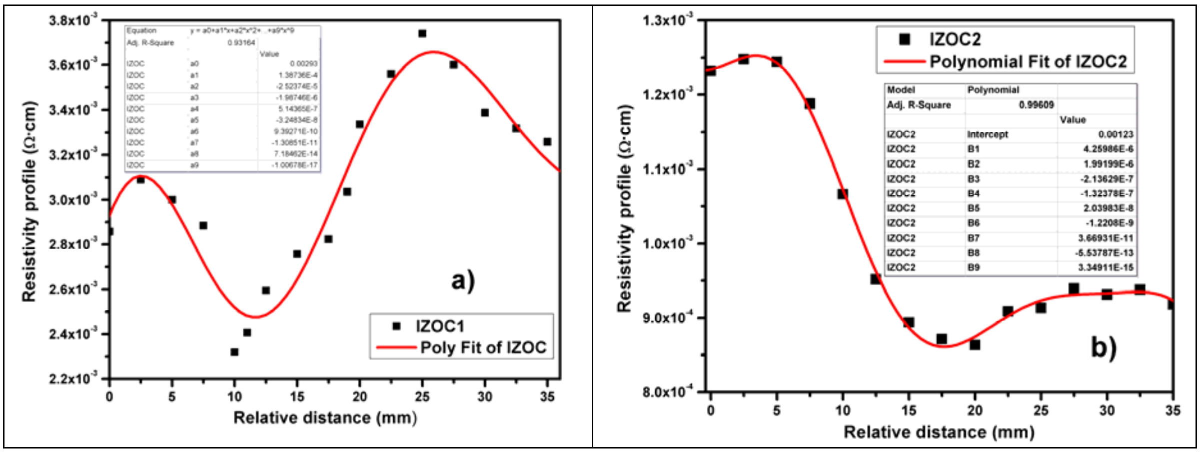

Fig. 8. Electrical resistivity profiles of the combinatorial thin films deposited from targets with (a) 28 at. % or 56 at. % and (b) 42 at. % or 70at. % In concentrations, respectively;

Due to the In concentration gradient, the resistivity profiles versus the relative distance (Figure 8) and resistivity versus In atomic composition (Figure 9), respectively, should be similar, which was confirmed by our results.

This compositional dependence consisting of one row of data points defines a compositional library. The experimental data of the resistivity were fitted with a 9th order polynomial distribution. Further examinations of the compositional libraries revealed a minimum of the electrical resistivity values for each combinatorial sample. Unlike the IZOC1 film, where the electrical resistivity decreased merely at a minimum value of 2.3×10^{-3} Ω·cm in the 28.8-29.5 at.% region of In content (Figure 9a), the IZOC2 coating exhibited the lowest resistivity value of 8.6×10^{-4} Ω·cm corresponding to the 44-49 at% region of In content (Figure 9b). Similar behaviors of the minimum in the resistivity have also been reported by other authors using typical magnetron sputtering setups for the comparable In atomic concentration values [21, 22].

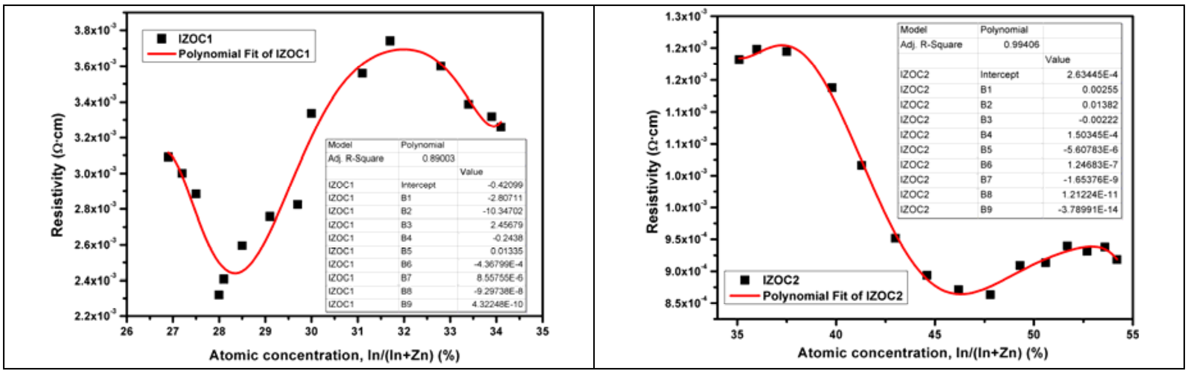

Fig. 9. The resistivity of the combinatorial thin films (a) IZOC1 and (b) IZOC2 as a function of the In atomic concentration.

The combinatorial experiments conducted in our study allowed us to emphasize in a comprehensive manner the potential of this approach to characterize the properties of the $In_xZn_{1-x}O$ systems by the deposition of only few libraries. The effects of the substrate temperature on the properties of the combinatorial coatings and the deposition of thin films from the In at. % optimized targets, as inferred from the compositional libraries, will be further performed in the typical PLD experiments.

4. Conclusions

We successfully applied the combinatorial pulsed laser deposition technique to investigate the optical, compositional, morphological and electrical properties of $In_xZn_{1-x}O$ ($27 \leq x \leq 52$) system. Two batches of samples were deposited using two pair of targets with Indium atomic concentrations, In/(In+Zn), of 28 at.% and 56 at.% or 42 at.% and 70 at.%. All the coatings showed high optical transmission (>95%) in VIS-NIR spectrum. AFM histograms indicated the decrease of the RMS roughness down to 1 nm with the increase of the In content. The analysis of the compositional libraries evidenced two minimum values of the electrical resistivity at 2.3×10^{-3} Ω·cm and 8.6×10^{-4} Ω·cm corresponding to 28.8-29.5 at.% and 44-49 at% region of Indium content.

Acknowledgments

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