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Influence of precursor ball milling in enhancing the structural, morphological, optical and electrical properties of AIZO thin films

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ABSTRACT

In this work, we report the effect of deposition time on the physical properties such as structural, morphological, optical and electrical properties of aluminium and indium co-doped ZnO (AIZO) thin films. AIZO films were deposited by ultrasonic spray pyrolysis technique on glass substrates at different deposition times (10, 12 and 15 min) using ball milled zinc precursor. A change in crystalline nature was observed from structural analysis with respect to growth time. AIZO thin films with hexagonal nanostructures and optical transmittance higher than 70% were confirmed from the morphological and optical studies. AIZO films showed an electrical resistivity varying in the range of 2.35–4.59 $\times 10^{-3}$ Ω cm. Finally, when we compared these results with AIZO films deposited using unmilled zinc precursor; we found that ball milling the precursor has a beneficial effect in enhancing the physical properties.

1. Introduction

Zinc oxide (ZnO) is a wide band gap (3.37 eV) compound semiconductor material that has received great attention in recent times due to its properties that fit well for several applications [1]. ZnO can be used in light emitting diodes, lasers, chemical gas sensors and transparent conductive oxide electrodes, etc. [2–5]. By native, ZnO is an n-type semiconductor and highly resistive. In order to enhance its electrical properties, doping with a suitable element (Aluminium/indium/gallium etc.) is mandatory [6]. Recent studies show that using two dopants helps in improving the properties [7]. Several techniques like chemical vapor deposition, thermal evaporation, sputtering, laser ablation and ultrasonic spray pyrolysis (USP) are available to fabricate ZnO thin films [8–12].

However, investigators are continuously searching for a new synthesis route for ZnO thin film fabrication to obtain minimum resistivity and high transmittance. In this respect, scientists found that mechanical milling of raw precursors results in nanocrystalline materials which in turn enhance the properties. Ramireddy et al. found that milling time influenced in minimizing the resistivity by one order magnitude (10^{-1}–10^{-2} Ω cm) for Al doped ZnO thin films [13] and Christine et al. reported that milling helps to reduce the reaction time and to gain high yield [14].

By considering the advantages of ball milling from earlier findings, we have opted to ball mill the zinc precursor and then to fabricate the AIZO thin films using USP. In addition, no work has been reported for the preparation of co-doped ZnO thin films, starting from milled zinc acetate dihydrate. In this work, we have investigated the structural, morphological, optical and electrical properties of AIZO thin films by varying the deposition times. Additionally to confirm the effect of ball milling we have compared these results with an AIZO film prepared using unmilled zinc acetate dihydrate.

2. Experimental

AIZO thin films were deposited on soda lime glass substrates by USP. Zinc acetate dihydrate ($Zn(OOCCH_3)_2 \cdot 2H_2O$, Alfa Aesar, 98–101%), aluminium acetylacetonate ($C_{15}H_{21}AlO_6$, Alfa Aesar, 99%) and indium acetate ($In(OOCCH_3)_3$, Alfa Aesar, 99.99%) were the precursors of Zn, Al and In respectively. Prior to the preparation of starting solution, zinc precursor was milled for an hour in a Pulverissette 7 (Fritsch) planetary ball milling equipment, using the following conditions: volume of the vessel-250 ml, ball to powder ratio-5:1 and angular speed-300 rpm. After milling, the Zn

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precursor (0.2 M) was dissolved in a mix of acetic acid, water and methanol using 50:50:900 vol (ml) proportions for making 1 L solution. In dopant solution of 0.2 M concentration was prepared by dissolving indium precursor in a mix of deionized water and acetic acid of 1:1 ratio. Al dopant solution of 0.1 M concentration was prepared by adding Al precursor in 100 ml of methanol. Finally, 1.5 at% of Al and 1.5 at% of In were added to the zinc precursor solution and depositions were carried out in USP. The solution flow was set at a rate of 1 ml/min. AIZO films were grown for three different growth times (10, 12 and 15 min) by maintaining a constant substrate temperature (475 °C). These films were identified according to their deposition times, namely T10, T12 and T15.

For comparison purpose, one AIZO thin film was grown on glass substrate using unmilled zinc precursor. The Zn and dopants solutions were prepared with the same conditions as mentioned earlier. This deposition was carried out for 10 min at 475 °C and labelled as U10. Thin films characterization details are given in ESI.

3. Results and discussion

The X-ray diffraction patterns of the Al and In co-doped ZnO thin films are shown in Fig. 1. The peaks of the samples are slightly shifted from the JCPDS data (01-089-0510) card of ZnO. This shift might be attributed to strain in the films. In addition peaks belonging to Al and In are not observed in the spectra, which confirm that the dopants are incorporated into the lattice of ZnO. The spectra show a dominating peak along (002) plane indicating that AIZO thin films are grown along *c*-direction of hexagonal wurtzite structure. All spectra present other weak peaks, corresponding to the planes (100), (101), (102), (103) and (004). In XRD analysis, FWHM (full-width at half maximum), is an important aspect in examining the crystallinity of the thin films. The T15 film presented the smallest FWHM (full-width at half maximum), in turn showed the highest crystallinity. The FWHM (in deg) of the samples T10, T12, T15 and U10 were 0.1683, 0.1682, 0.1679 and 0.2019 respectively. It is worth to mention that, this sample presented the highest thickness. Similar crystallinity improvement with respect to thickness was previously reported by other authors [15]. And also, T10 presented less FWHM than U10, which signifies that the milling of the precursor improves the crystallinity. By using Scherrer's formula $d=0.9\lambda/\beta\cos\theta$ crystallite sizes were estimated, where d indicates the crystallite size, λ denotes radiation wavelength used (1.5406 Å) and β is the FWHM in radians [16]. The obtained crystallite size of the samples T10, T12, T15 and U10 were 49.41, 49.44, 49.54 and 41.19 nm, respectively.

Scanning electron microscopy images of AIZO films are shown in Fig. 2(a-d). Sample T10 surface appears compact with small and half-grown hexagonal structures (Fig. 2(a)), of size oscillating between 100 and 200 nm. The surface of sample T12 (Fig. 2(b)) is

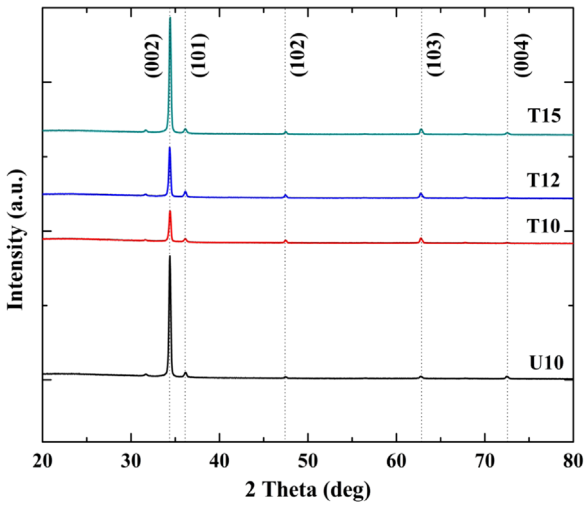

Fig. 1. XRD patterns of AIZO films with different experimental conditions.

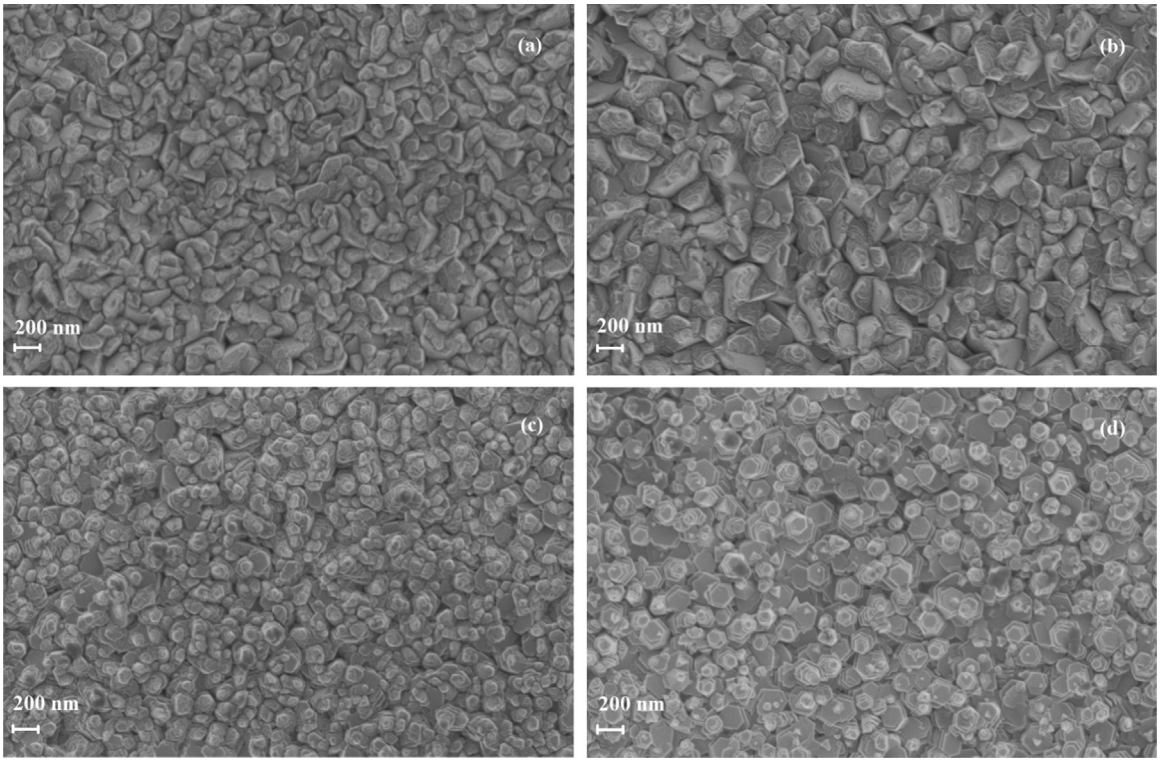

Fig. 2. Surface morphology of AIZO thin films (a) T10, (b) T12 (c) T15 and (d) U10.