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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 $2.35\text{--}4.59 \times 10^{-3} \Omega \text{ cm}$. 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.

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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 ($10^{-1}\text{--}10^{-2} \Omega \text{ cm}$) 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 ($\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$, Alfa Aesar, 98–101%), aluminium acetylacetonate ($\text{C}_{15}\text{H}_{21}\text{AlO}_6$, Alfa Aesar, 99%) and indium acetate ($\text{In}(\text{OOCCH}_3)_3$, 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 Pulverisette 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. AlZO 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 AlZO 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 AlZO 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 AlZO 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

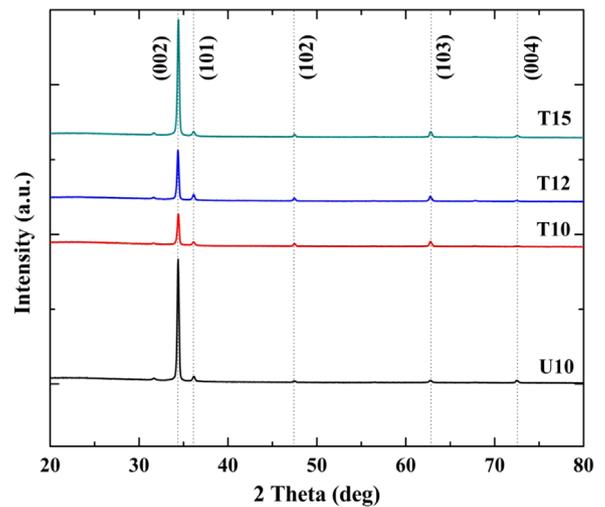


Fig. 1. XRD patterns of AlZO films with different experimental conditions.

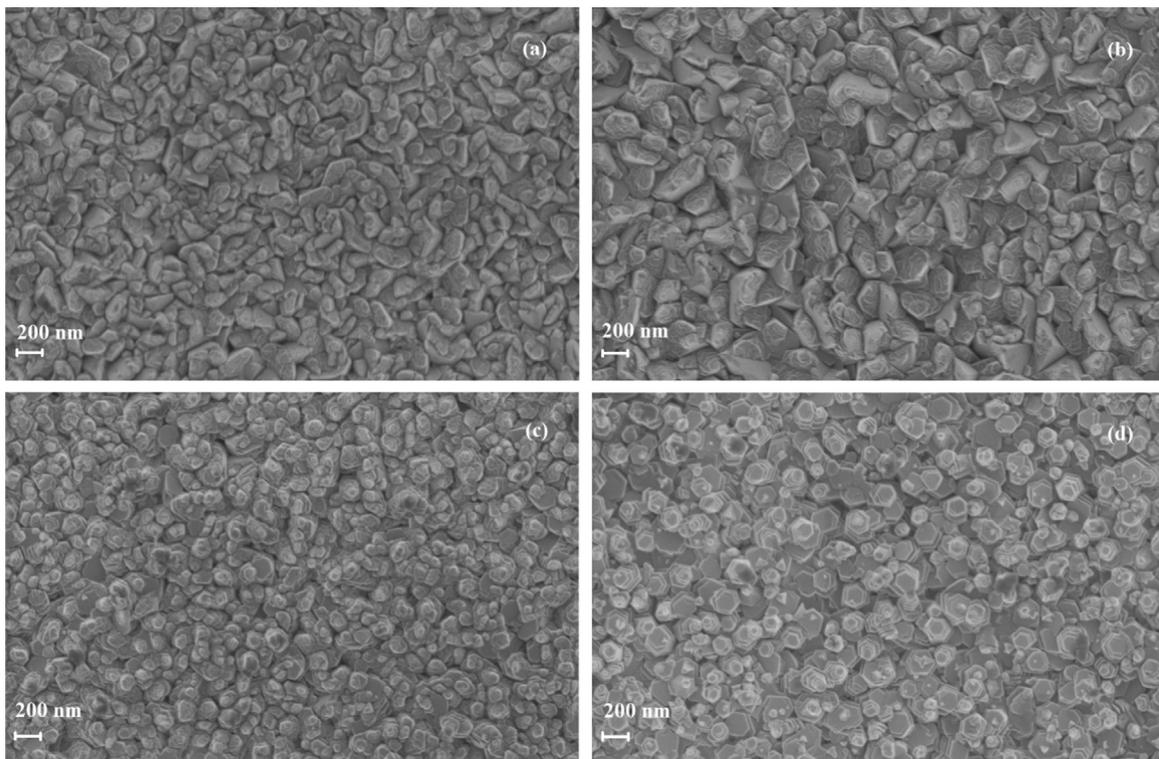


Fig. 2. Surface morphology of AlZO thin films (a) T10, (b) T12 (c) T15 and (d) U10.

Table 1
Resume of opto-electronic properties of AlZO thin films.

Characteristics	Sample ID			
	T10	T12	T15	U10
Thickness, <i>t</i> (nm)	360	718	860	659
Average transmittance (%)	79.62	77.27	72.30	65.29
Bandgap, E_g (eV)	3.53	3.51	3.50	3.48
Sheet resistance, R_s (Ω/\square)	76.20	64.00	27.38	93.40
Figure of Merit, Φ_{TC} ($\times 10^{-3}/\Omega$)	1.34	1.18	1.42	0.27
Resistivity, ρ (Ω cm)	2.74×10^{-3}	4.59×10^{-3}	2.35×10^{-3}	6.15×10^{-3}

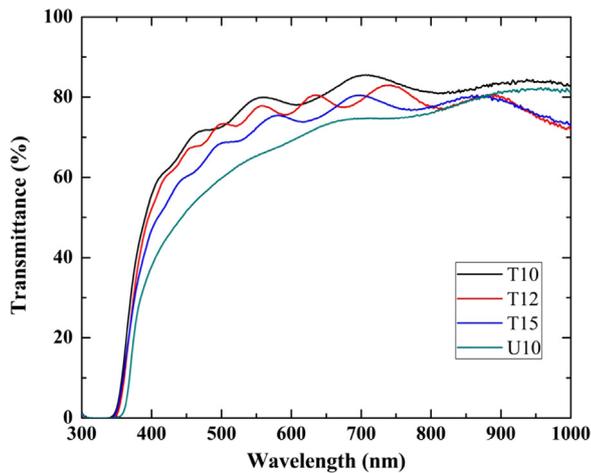


Fig. 3. Transmittance spectra of AlZO thin films.

with better defined hexagonal structures with size variations between 100 and 200 nm. When the deposition time is increased to 15 min, AlZO films present a surface covered with well-defined hexagonal tower like structures of sizes between 100 and 150 nm (Fig. 2(c)). In the case of film (U10) deposited with unmilled precursor, the surface is covered with hexagonal pyramids. The size of base of the pyramids is in the range ~ 50 –250 nm (Fig. 2(d)). And also, this sample is not closely packed like ball milled sample. From the SEM observations it is clear that milling of Zn precursor play an important role in changing the surface morphology.

All the AlZO thin films deposited with milled precursor exhibits an optical transmittance higher than 70% (Table 1) in the UV–vis region, as shown in Fig. 3. The curves of T10, T12 and T15 present interference fringes, confirm the uniformity and good quality of the thin films [17]. A drastic decrease in transmittance with deposition time of AlZO films can be observed. This decreasing behavior is associated with the increase in film thickness (Table 1). Kumar's team also observed similar transmittance changes for ZnO thin films with different thicknesses [18]. Furthermore, Ramamoorthy et al. revealed that incorporation of dopants into the ZnO lattice also plays a role in achieving high transmittance [19].

When we compare the average transmittances of milled and unmilled samples, lesser transmittance is observed for U10 than T10. This would have occurred due to the size of the grains (Fig. 2 (a) and (d)). Koo's group also reported that larger grains show less transmittance [20]. In addition, U10 doesn't present interference fringes like T10, in turn assures that surface of the film is not uniform. Earlier, Ilican expressed the quality of indium doped ZnO films based on interference fringes [17]. By extrapolating the linear portion of the plot $(\alpha h \gamma)^2$ versus $h \gamma$, the band gap, E_g can be obtained. The E_g values are reported in Table 1. The shift in bandgap with respect to the bandgap of undoped ZnO ($E_g = 3.37$ eV) [1] suggests that co-dopants are embedded into the ZnO lattice [21].

This optical phenomenon is referred as Burstein-Moss effect [22].

The estimated electrical resistivity ($\rho = R_s \cdot t$) of the samples T10, T12, T15 and U10 are given in Table 1. The obtained resistivity values signifies that Al^{3+} and In^{3+} ions would have well substituted some Zn^{2+} ions, in turn would have increased carrier concentration [21]. The film (T15) shows the lowest resistivity among others, could be attributed from fully grown compact nanostructures (Fig. 2(c)). The quality of the films can be estimated using Haacke's figure of merit $\Phi_{TC} = T^{10}/R_s$, where T indicates the transmittance at 550 nm and R_s refers the sheet resistance [23]. The highest figure of merit of $1.42 \times 10^{-3}/\Omega$, is achieved for the films deposited for 15 min

4. Conclusions

We used a cost-effective ultrasonic spray pyrolysis technique to fabricate aluminium and indium co-doped ZnO thin films on glass substrates. AlZO films were grown at a substrate temperature of 475 °C using ball milled and unmilled zinc precursor. The effect of deposition time on structural, morphological, optical and electrical properties were investigated on AlZO films prepared using ball milled precursor. The structural properties showed that films were crystalline and grown along the plane (002). Morphological studies confirmed that AlZO films were compact and homogeneous. Optical transmittance analysis proved that films were highly transparent ($> 70\%$) and the electrical measurements showed that AlZO films exhibited low resistivity values (2.35 – $4.59 \times 10^{-3} \Omega$ cm). In the end, when we correlated the results of films prepared with milled and unmilled zinc precursor, we observed that milling a precursor before thin film fabrication results in minimizing the resistivity and in enhancing the crystallinity, homogeneity and optical transmittance. From our results, we conclude that AlZO thin films grown by USP are efficient, reliable and highly suitable for TCO applications.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.matlet.2016.06.007>.

References

- [1] Z.L. Wang, *J. Phys. Condens. Matter* 16 (2004) R829–R858.
- [2] B. Sundarakannan, M. Kottaisamy, *Mater. Lett.* 165 (2016) 153–155.
- [3] T.P.H. Sidiropoulos, R. Röder, S. Geburt, et al., *Nat. Phys.* 10 (2014) 870–876.
- [4] J.V. Kumar, A. Maldonado, M. Olvera, *Mater. Lett.* 157 (2015) 169–171.
- [5] A. Mondal, N. Mukherjee, S. Kumar, *Mater. Lett.* 60 (2006) 1748–1752.
- [6] S. Benramache, O. Belahssen, H. Ben Temam, *J. Semicond.* 35 (2014) 073001.
- [7] V.K. Jayaraman, A.M. Álvarez, Y.M. Kuwabara, et al., *Mater. Sci. Semicond. Process.* 47 (2016) 32–36.
- [8] J.G. Lu, T. Kawaharamura, et al., *J. Cryst. Growth* 299 (2007) 1–10.
- [9] D. Chhikara, M. Senthil Kumar, K.M.K. Srivatsa, *Superlattices Microstruct.* 82 (2015) 368–377.
- [10] V.K. Jayaraman, Y.M. Kuwabara, A.M. Álvarez, et al., *Mater. Lett.* 169 (2016) 1–4.
- [11] N. Batra, M. Tomar, et al., *J. Appl. Phys.* 114 (2013).
- [12] Y. Lee, H. Kim, Y. Roh, *Jpn. J. Appl. Phys.* 40 (2001) 2423–2428.
- [13] T.R. Ramireddy, V. Venugopal, J.B. Bellam, et al., *Materials(Basel)* 5 (2012) 1404–1412.
- [14] C. Friederike, C.F. Burmeister, *Chem. Soc. Rev.* 42 (2013) 7660–7667.
- [15] T. Prasada Rao, M.C. Santhoshkumar, *Appl. Surf. Sci.* 255 (2009) 4579–4584.
- [16] A.L. Patterson, *Phys. Rev.* 56 (1939) 978–982.
- [17] S. Ilıcan, M. Caglar, Y. Caglar, *Mater. Sci.* 25 (2007) 709–718.
- [18] V. Kumar, N. Singh, R.M. Mehra, et al., *Thin Solid Films* 539 (2013) 161–165.
- [19] K. Ramamoorthy, et al., *Opt. Commun.* 262 (2006) 91–96.
- [20] Y.T.O, J.B. Koo, et al., *Mater. Sci. Eng. A* 374 (2004) 191–195.
- [21] T. Tohsophon, N. Wattanasupinyo, et al., *Thin Solid Films* 520 (2011) 726–729.
- [22] A.P. Roth, J.B. Webb, D.F. Williams, *Phys. Rev. B* 25 (1982) 7836–7839.
- [23] G. Haacke, *J. Appl. Phys.* 47 (1976) 4086–4089.