

A comparative study on physical properties of Al-doped zinc oxide thin films deposited from zinc acetate and zinc acetylacetonate by spray pyrolysis

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Herein we present a comparative study on highly transparent, conductive aluminium-doped ZnO (AZO) thin films deposited by pneumatic spray pyrolysis (PSP) of a zinc acetate based solution and a zinc acetylacetonate based solution on soda lime glass. The structural, optical and electrical properties of the films were studied depending on aluminium content in the precursor solution and substrate temperature during deposition (T_s). The solution used to prepare AZO thin films contained 0.2 M zinc acetate or 0.2 M zinc acetylacetonate and aluminium acetylacetonate between 0–15 at.% [Al]/[Zn]. Substrate temperature was varied from 275 to 450 °C. Transmittance and reflectance spectra were recorded by UV-VIS-NIR spectroscopy. Resistivity, mobility and charge carrier density were determined by four point probe measurements in ambient conditions. According to X-ray diffraction analysis, AZO films are highly *c*-axis oriented until 2–3 at.% [Al]/[Zn] in the spray solution, depending on zinc precursor. Crystallite size is 25–30 nm for AZO films deposited at T_s 400 °C. All AZO films exhibited high average optical transmittance of 76–94% in the visible spectrum 400–800 nm wavelength range. E_g values ranged from 3.32 eV in undoped ZnO to 3.58 eV in highly doped AZO films deposited from zinc acetylacetonate due to the formation of secondary AlO_3 phases. The lowest resistivities were obtained at T_s 400 °C for films deposited from zinc acetate, 3–7.5 at.% [Al]/[Zn] in solution (0.40 Ω cm) and at T_s 400 °C, 3–7.5 at.% [Al]/[Zn] in solution for films deposited from zinc acetylacetonate (0.47 Ω cm).

Keywords: AZO, Al-doped ZnO, pneumatic spray pyrolysis, thin films

INTRODUCTION

Indium tin oxide (ITO) is one of the most popular transparent conductive oxides (TCO) in industry,

but expensive and toxic due to its high concentration of indium [1]. Zinc oxide (ZnO) is a suitable candidate for replacing ITO due to its low price, wide band gap of 3.27 eV, good electrical,

optical properties and stability in a hydrogen plasma atmosphere [2, 3]. Doped zinc oxide thin films can be applied as window layers in solar cells, electrical contacts in liquid crystals, sensors, optical coatings, transparent electrodes, light emitting diodes among other uses [4–6]. Doped zinc oxide thin film TCOs have been extensively studied as non-toxic and cheaper alternatives to ITO.

Several methods have been used to produce doped and undoped ZnO thin films, such as magnetron sputtering, pulsed laser deposition (PLD), chemical vapour deposition (CVD), chemical bath deposition (CBD) and spray pyrolysis (SP) [7–9].

Spray pyrolysis deposition (SP) uses a precursor solution which is nebulized by pressure, ultrasonication or an electric field and guided onto a hot plate to deposit metal oxide (MO) thin films. The solvent evaporates during transport, allowing the precursor to thermally decompose into a more stable product. SP is a simple, yet effective method with many advantages. More precisely, easy incorporation of any dopant element by adding it to the feed solution, easily controllable film growth rate and thickness, no need for vacuum or pristine substrates, possibility of layered or composition graded films, wide substrate temperature (T_s) range, low operation costs, no local overheating of the substrate, no constraints on the surface profile, material or dimension of the substrate and seamless integration in a standard complementary metal-oxide-semiconductor (CMOS) process [10, 11]. The research group at our laboratory has extensive experience in spray depositing indium doped ZnO [7, 12]. Al-doping effect on ZnO films deposited by SP had yet to be studied with this method as part of a larger research topic. For these reasons SP was used in this study to deposit Al-doped ZnO thin films.

Doping with transition metals using spray deposition has yielded ZnO films with comparably good optical transmittance and electrical conductivity, although many transition metals are toxic heavy metals [13–18]. The best optical and electrical conductivity results are commonly achieved by doping ZnO with elements from the boron group (B, Al, Ga, In) which act as +3 oxidation state electron donors when substituting Zn^{2+} [5, 19]. Indium is the best dopant in terms of optical and electric properties and improved crystallinity of the (002) preferred orientation of doped ZnO thin films [10]. Aluminium salts are considered inexpensive for

doping ZnO due to the prevalence of aluminium in the environment as well as its low toxicity [3]. Hence, aluminium was chosen as the doping element in this study.

The most common zinc precursors for depositing ZnO thin films are zinc chloride, zinc acetate and zinc acetylacetonate [5]. Aluminium chloride, aluminium nitrate and aluminium acetylacetonate are the most used Al dopants for AZO spray deposition. These compounds are preferred because they are cheap, highly soluble and decompose at suitable temperatures [10]. Similar results ($\rho = 10^{-1}$ – 10^{-3} Ωcm , $T = 80$ – 97%) have been obtained with different combinations of the aforementioned zinc and aluminium sources [5].

It has been found in earlier studies that alongside other parameters, e.g. T_s , dopant concentration, solvent composition [20], deposition time, zinc sources and dopant sources also have an effect on the physical properties of sprayed zinc oxide films [5]. Replacing part of zinc acetate with zinc chloride to essentially co-dope with Al and Cl has yielded larger crystallites, higher carrier mobility and consequently lower resistivity in sprayed AZO thin films compared to single zinc source films [21, 22]. Based on previous studies the critical [Al]/[Zn] at.% ratio for electrically conductive AZO films is considered to be below 6% with the majority of the results indicating 1–3% as the optimum [5, 19, 20].

Previous works by other research groups regarding spray deposited AZO have focused mainly on methanol-water and somewhat less on ethanol-water solvent mixtures. Isopropanol-water solvents have been previously used in our laboratory to deposit In-doped ZnO, but not Al-doped ZnO [7, 12]. Therefore, the aim of this study is to provide comparative information on physical parameters of as-deposited AZO thin films grown by pneumatic SP from an isopropanol-water solution using $Zn(acac)_2$ or $Zn(ac)_2$ as the precursor and $Al(acac)_3$ as the dopant.

METHODOLOGY

AZO thin films were deposited onto $15 \times 25 \times 1$ mm³ previously cleaned soda lime glass substrates by PSP in ambient atmosphere. The inner diameter of the two-fluid nozzle was 16 μm . The average distance between the nozzle and

the substrate was 25 cm at an incident angle of 30°. Compressed air with a fixed flow rate of 8 L/min was used as carrier gas. The solution flow rate was fixed at 3 ml/min. A molten tin bath was used for substrate heating. The substrate temperature (T_s) was varied from 275 °C to 450 °C with ± 5 °C accuracy.

The solvent used consisted of 50 ml of a mixture of isopropanol (99.5% v/v, Sigma-Aldrich), deionized water and acetic acid (99.8 v/v, Sigma-Aldrich) in a ratio of 30:19:1, respectively. Acetic acid was added to prevent the formation of zinc hydroxide in the solution.

Zinc acetate dihydrate (99% w/w) ($\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, abbreviated here as $\text{Zn}(\text{ac})_2$), and zinc acetylacetonate hydrate (95% w/w) ($\text{Zn}(\text{CH}_3\text{COCHCOCH}_3)_2 \cdot \text{H}_2\text{O}$, abbreviated here as $\text{Zn}(\text{acac})_2$), from Sigma-Aldrich were used as precursors for spray depositing AZO thin films due to their low cost, low decomposition temperature and high solubility [10]. The zinc precursor concentration in the solution was 0.2 M in all cases.

Aluminium acetylacetonate ($\text{Al}(\text{CH}_3\text{COCHCOCH}_3)_3$, abbreviated here as $\text{Al}(\text{acac})_3$) (99% w/w), from Sigma-Aldrich was used as an additive to both precursors (1–15 at.% $[\text{Al}]/[\text{Zn}]$). The following $[\text{Al}]/[\text{Zn}]$ ratios were used: 1, 2, 3, 5, 7.5 and 15 at.%.

The film structure and phase composition were characterised by X-ray diffraction analysis (XRD), optical transmittance spectra and van der Pauw and Hall measurements. XRD measurements were executed on a Rigaku Ultima IV diffractometer with $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$, 40 kV at 40 mA) in the range of 25–60°, step width 0.02°, by the θ –2 θ method using the silicon strip detector

D/teX Ultra. Crystallite size and lattice constants were calculated using proprietary Rigaku software (PDXL Version 2).

Optical total transmittance and total reflectance spectra were measured in the wavelength range 300–900 nm on a Jasco V-670 UV-VIS-NIR spectrophotometer using an integrated sphere. The thickness of the films was calculated from the total reflectance spectra (400–800 nm range) using an estimated refractive index of 2.00 in the automated envelope method provided in the Jasco SpectraManager software suite. The average film thickness was $530 \pm 130 \text{ nm}$.

Electrical properties were measured by the four point probe method (MMR Tech Variable Temperature Hall System and H50) at room temperature in the dark using gold plated probe contacts and by applying graphite ink on the samples for a better contact. A 0.64T permanent magnet was used for Hall measurements. Individual film thickness was taken into account when measuring electrical properties to reduce error.

RESULTS AND DISCUSSION

The most important parameters for aluminium-doped ZnO thin film TCO applications are optical transmittance and resistivity. Therefore, the optimal $[\text{Al}]/[\text{Zn}]$ ratios in the starting solution and T_s for AZO films deposited from $\text{Zn}(\text{acac})_2$ and $\text{Zn}(\text{ac})_2$ were sought.

Electrical properties

Resistivity, mobility and charge carrier density were measured for all films, results are presented in Fig. 1. Both undoped and Al-doped ZnO

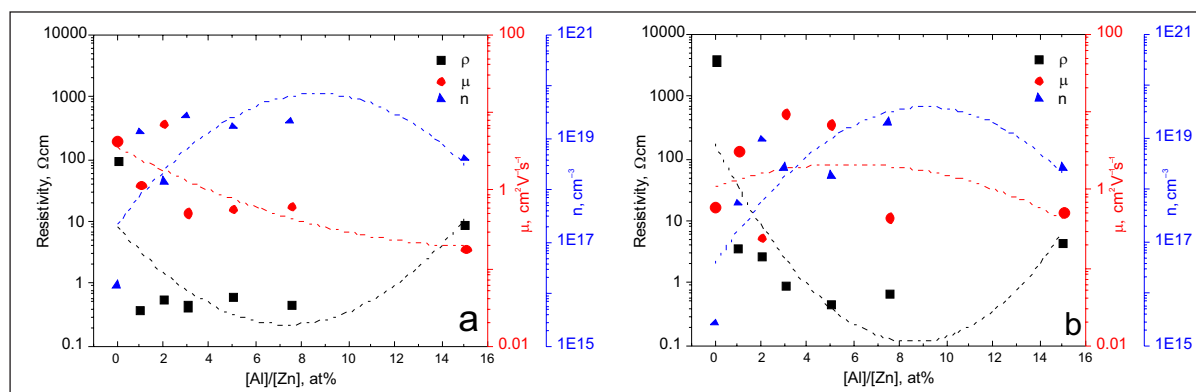


Fig. 1. Electrical parameters of AZO films deposited at T_s 400 °C from (a) $\text{Zn}(\text{ac})_2$ or (b) $\text{Zn}(\text{acac})_2$, $[\text{Al}]/[\text{Zn}]$ ratios in solution: 0, 1, 2, 3, 5, 7.5, 15 at.%

films exhibit n-type conductivity, as it was determined before and observed in Hall measurements in the current study (Hall constant mark $-$) [5, 23]. The effect of Al doping was first investigated based on the best achieved results in literature at $T_s = 400$ °C [5]. Doping with Al decreases AZO film resistivity by 4–5 orders of magnitude (Fig. 1b). The difference in resistivity, mobility and charge carrier concentration for films deposited from either zinc precursor is relatively small in the 1–7.5 at.% Al region (Fig. 1). Minimum resistivity at 400 °C is obtained for $\text{Zn}(\text{acac})_2$ based films ($0.5 \Omega\text{cm}$) between 5–7.5 at.% $[\text{Al}]/[\text{Zn}]$ and between 3–7.5 at.% Al ($0.4 \Omega\text{cm}$) in films grown from $\text{Zn}(\text{ac})_2$. Gómez et al. obtained minimum resistivity $0.02 \Omega\text{cm}$ with both precursors at 2.5 at.% Al in methanol solution and T_s 475 °C, which may be due to many different deposition parameters [9].

At 15 at.% $[\text{Al}]/[\text{Zn}]$ the film resistivity rises by more than an order of magnitude when 15 at.% $[\text{Al}]/[\text{Zn}]$ is added to the solution compared to 7.5 at.% (Fig. 1a, b), possibly due to exceeding the maximum Al incorporation limit in the ZnO lattice [5, 9]. Excess Al atoms over the critical level may cause intragrain congregation and/or grain boundary segregation forming Al-O clusters (AlO_x) from the inevitable thermal decomposition of $\text{Al}(\text{acac})_3$ partially into AlO_x [6, 23]. Therefore, 7.5 at.% Al was chosen for the temperature series, because the lowest resistivities as well as the highest charge carrier concentrations were obtained for both types of films at this Al doping level in solution ($2.1\text{E}19$ for $\text{Zn}(\text{ac})_2$, $2.0\text{E}19$ for $\text{Zn}(\text{acac})_2$, Fig. 1a, b).

As seen in Fig. 2a, b, minimum resistivity for 7.5 at.% AZO films deposited from both zinc pre-

cursors is attained at 400 °C ($0.7 \Omega\text{cm}$ for $\text{Zn}(\text{acac})_2$ and $0.5 \Omega\text{cm}$ for $\text{Zn}(\text{ac})_2$). The optimal deposition temperature derived from literature is thereby verified as correct. The same conclusion was reached by many others [5].

Structural properties

The effect of T_s and the ratio of $[\text{Al}]/[\text{Zn}]$ in the starting solution on crystallite sizes and crystallographic orientations was investigated by X-ray diffraction (XRD). The diffraction patterns of AZO thin films deposited from $\text{Zn}(\text{ac})_2$ and $\text{Zn}(\text{acac})_2$ in different conditions are shown on Figs. 3 and 4. All diffraction patterns are in their original linear scale. According to the XRD patterns (Figs. 3, 4), all films exhibit diffraction peaks at 2θ of 31.84, 34.50, 36.34, 47.65 and 56.73, corresponding to the reflections from the (100), (002), (101), (102) and (110) planes of hexagonal wurtzite type ZnO (PDF 01-075-0576) [24]. The crystallite sizes were estimated using the (100), (101) and (002) diffraction peak data and the Scherrer equation [25]:

$$D = \frac{0.94\lambda}{B\cos\theta}, \quad (1)$$

where λ is the wavelength value for the Cu-K $_{\alpha 1}$ line (1.5406 \AA), β is the FWHM in radians, and θ is the Bragg diffraction angle.

1–3 at.% $[\text{Al}]/[\text{Zn}]$ films deposited from $\text{Zn}(\text{ac})_2$ at 400 °C are highly c-axis orientated, i.e. the preferred orientation is (002) while crystallites in 5–7.5 at.% films are (101) orientated (Fig. 3a), which is consistent with previous publications [19, 26]. Even in the 15 at.% Al film no secondary AlO_x phases were detected.

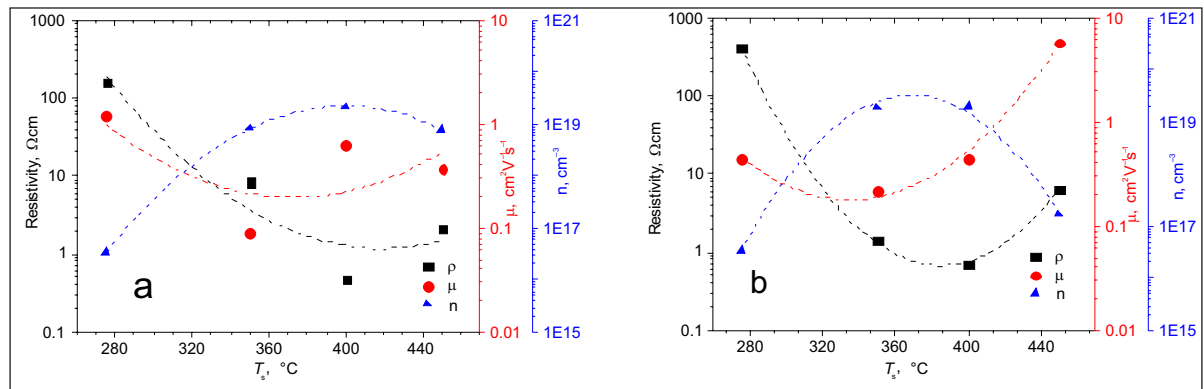


Fig. 2. Electrical parameters of AZO films deposited at various temperatures from (a) $\text{Zn}(\text{ac})_2$ or (b) $\text{Zn}(\text{acac})_2$, $[\text{Al}]/[\text{Zn}]$ ratio 7.5 at.% in solution

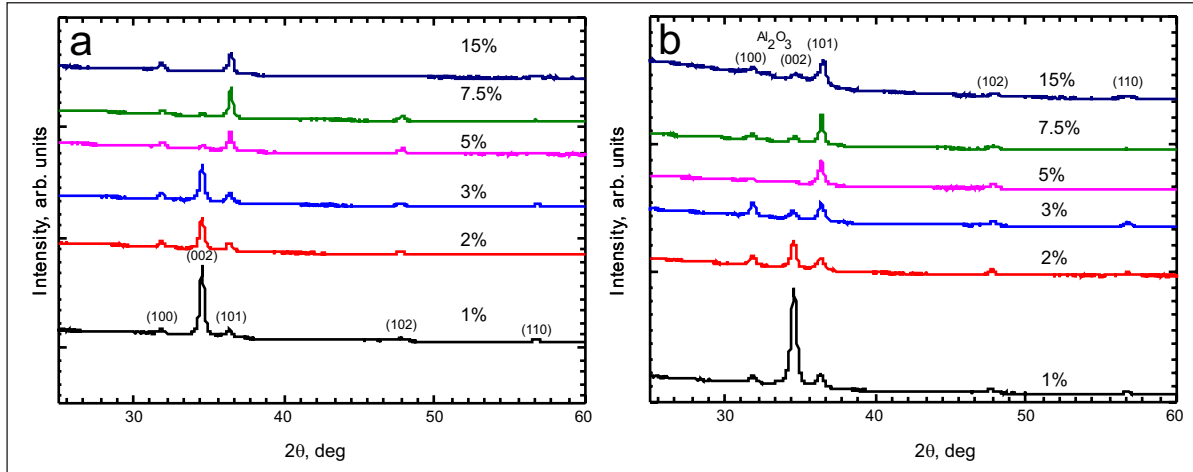


Fig. 3. XRD patterns of AZO thin films prepared from 50 ml of 0.2 M (a) $\text{Zn}(\text{ac})_2$ or (b) $\text{Zn}(\text{acac})_2$ doped with $\text{Al}(\text{acac})_3$ at T_s 400 °C. $[\text{Al}]/[\text{Zn}]$ ratios in the solution: 1, 2, 3, 5, 7.5, 15 at.%

The gradual degradation for film crystallinity, indicated by smaller peak intensities, is attributed to increased Al doping levels in the AZO film [5].

AZO films deposited from $\text{Zn}(\text{acac})_2$ lose their c-axis orientation between 2 and 3 at.% $[\text{Al}]/[\text{Zn}]$ (Fig. 3b). Crystallites are randomly oriented in films grown from $\text{Zn}(\text{acac})_2$ beyond 3 at.% Al (Fig. 3b). This could mean that the zinc precursor affects the shift in preferred orientation from the (002) plane to the (101) plane. This change in preferred orientation of doped ZnO was previously reported by numerous other research groups [5, 9, 27]. Also, in the 15 at.% Al film a sec-

ondary peak was detected at 32.91 degrees, indicative of the presence of a separate Al_2O_3 phase.

The relative intensities of diffraction peaks for films grown from both precursors are somewhat different, with $\text{Zn}(\text{ac})_2$ producing higher crystallinity and stronger (101) preferred orientation than $\text{Zn}(\text{acac})_2$ in AZO films deposited by SP at T_s 350–450 °C (Fig. 4a, b). AZO films deposited at 275 °C from both precursors are randomly oriented. $\text{Zn}(\text{acac})_2$ based film diffractograms exhibit wider and lower diffraction peaks, meaning the average crystallite size must be smaller. This is confirmed in Table 1 with 7.5 at.% films deposited from $\text{Zn}(\text{acac})_2$ containing on average

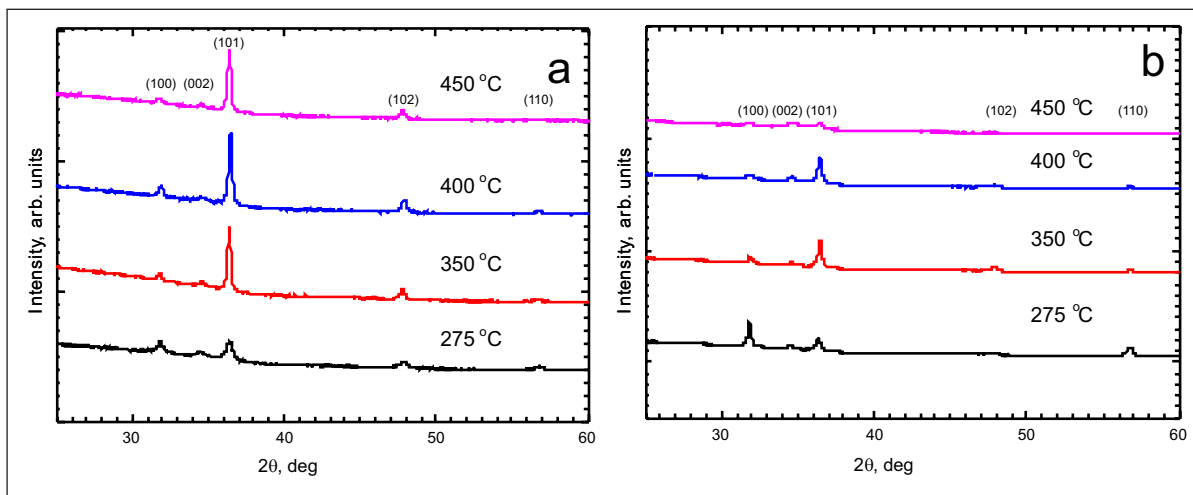


Fig. 4. XRD patterns of AZO thin films prepared from 50 ml of 0.2 M (a) $\text{Zn}(\text{ac})_2$ or (b) $\text{Zn}(\text{acac})_2$ doped by $\text{Al}(\text{acac})_3$ at different T_s with $[\text{Al}]/[\text{Zn}]$ ratio 7.5 at.% in solution

30 vs 40 nm sized crystallites in films deposited from Zn(ac)₂.

The only anomaly is the randomly oriented film grown from Zn(acac)₂ at 450 °C in contrast to the strongly (101) oriented film grown from Zn(ac)₂ (Fig. 4a, b). The anomalous film shows strong broadening and reduced intensity of the diffraction peaks. The PDXL software determined the diffraction peaks at 2θ of 31.65, 34.57, 36.37, 47.72 and 56.72 degrees, which probably belong to ZnO and Zn₆Al₂O₉ (PDF No. 00-051-0037). This discrepancy needs to be studied further.

The crystallite size in 7.5 at.% Al AZO films deposited from Zn(ac)₂ is about 20 nm at T_s 275 °C, increasing to about 40 nm between T_s 350–450 °C (Table 1). This could mean that the films grown below T_s 350 °C are formed of smaller crystallites containing impurities, which hinder film conductivity (Fig. 2), [5]. Crystallite size for films deposited from Zn(acac)₂ is consistently about 30 nm at T_s 275–400 °C (Table 1). Undoped ZnO films deposited from Zn(ac)₂ exhibit somewhat larger crystallites (58 nm) than their counterparts from Zn(acac)₂ (40 nm). Crystallite size in films deposited at T_s 400 °C from 1–5 at.% Al solutions is on average 29 nm in Zn(ac)₂ based films and 22 nm in Zn(acac)₂ based films. Similar crystallite sizes for AZO films grown from Zn(acac)₂ and Al(acac)₃ have

been reported in literature (33 nm at 1 at.% Al to 20 nm at 5 at.% Al at T_s 500 °C) [6].

The only exception is the aforementioned anomalous film deposited at 450 °C from Zn(acac)₂ whose crystallites are much smaller than other 7.5 at.% [Al]/[Zn] films deposited from the same precursor (9 vs 30 nm) or at the same temperature from Zn(ac)₂ (9 vs 44 nm) (Table 1). The film is nearly amorphous and probably consists of a different phase altogether, as mentioned before. Mobility for the anomalous AZO film is an order of magnitude higher than for other films of the same temperature series or the 7.5 at.% [Al]/[Zn] sample deposited from Zn(ac)₂ (Fig. 2a, b). Usually, mobility decreases when grain size decreases, so some mobility enhancing phenomena must be affecting the anomalous film [5].

Optical properties

Figure 5 shows the optical total transmittance spectra of aluminium-doped ZnO films deposited at different T_s from (a) Zn(ac)₂ or (b) Zn(acac)₂ with constant [Al]/[Zn] ratio 7.5 at.%. All the films are highly transparent, exhibiting 76 to 94% average transmittance in the wavelength region (400–800 nm). The band edge does not shift significantly nor does average transmittance (~87%) decrease at any temperature for Zn(ac)₂ based AZO films in the films deposited at T_s 350–450 °C, 7.5 at.% [Al]/[Zn] in solution,

Table 1. Crystallite sizes for AZO films deposited at T_s 275–450 °C from 50 ml of isopropanol-water solution containing 0.2 M (a) Zn(ac)₂ or (b) Zn(acac)₂ doped with Al(acac)₃, [Al]/[Zn] ratios 0, 1, 2, 3, 5, 7.5, 15 at.%

T _s (°C)	[Al]/[Zn] ratio in solution (at.%)	Zn(ac) ₂		Zn(acac) ₂	
		Peak used in eq. (1)	Crystallite size (nm)	Peak used in eq. (1)	Crystallite size (nm)
275	7.5	(101)	18	(101)	28
350	7.5	(101)	46	(101)	32
400	0	(002)	58	(002)	40
400	1	(002)	30	(002)	22
400	2	(002)	27	(002)	25
400	3	(002)	29	(101)	19
400	5	(101)	30	(101)	25
400	7.5	(101)	36	(101)	31
400	15	(101)	26	(101)	19
450	7.5	(101)	44	(101)	9

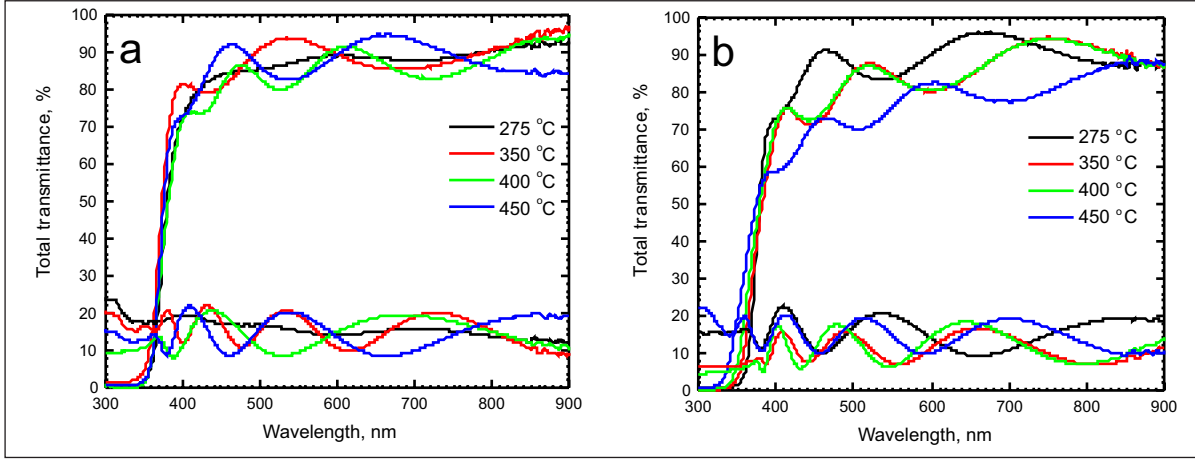


Fig. 5. Optical transmittance spectra of AZO thin films deposited from 50 ml of 0.2 M (a) $\text{Zn}(\text{ac})_2$ or (b) $\text{Zn}(\text{acac})_2$ doped with $\text{Al}(\text{acac})_3$ at different T_s using the $[\text{Al}]/[\text{Zn}]$ ratio 7.5 at.% in the solution

see Fig. 5a, b. On the other hand, average transmittance decreases from 85% at T_s 350–400 °C to 76% at 450 °C (400–800 nm range) for $\text{Zn}(\text{acac})_2$ based films (Fig. 5b). AZO films deposited from both precursors at T_s 400 °C have similar transmittance ~83% regardless of Al doping.

The engineering of the band gap is paramount to meeting process specifications in solar cell applications. According to empiric and theoretical results, ZnO exhibits direct inter-band transitions and for allowed transitions between parabolic bands the following equation is valid [19]:

$$(\alpha h\nu)^2 = A(h\nu - E_g), \quad (2)$$

where α is the absorption coefficient, $h\nu$ is photon energy, A is a constant, and E_g is the band gap.

The interference fringes were eliminated if necessary by using the following equation [28]:

$$\alpha = \frac{1}{D} \ln \left(\frac{1-R}{T} \right), \quad (3)$$

where α is the absorption coefficient, d is film thickness, R is total reflectance, and T is total transmittance. E_g was determined by plotting $(\alpha h\nu)^2$ against $h\nu$ and extending a tangent line from the straight part of the resulting straight line portion of the plot as shown in Fig. 6.

E_g in undoped ZnO films was 3.31 eV when deposited from either zinc precursor. The increase in E_g is substantially greater in $\text{Zn}(\text{acac})_2$ based films (3.32–3.57 eV vs 3.30–3.43 eV, T_s 400 °C, 0–15 at.%) possibly due to the formation of inert phases at higher Al at.% levels in

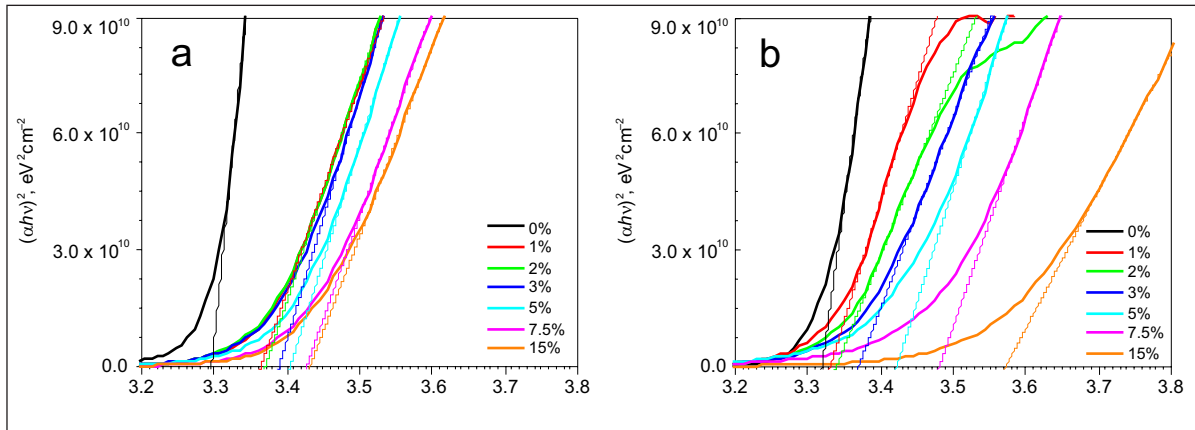


Fig. 6. Plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of AZO thin films prepared from 50 ml of 0.2 M (a) $\text{Zn}(\text{ac})_2$ or (b) $\text{Zn}(\text{acac})_2$ doped with $\text{Al}(\text{acac})_3$ at T_s 400 °C with the following $[\text{Al}]/[\text{Zn}]$ ratios in the solution: 0, 1, 2, 3, 5, 7.5, 15 at.%

the source solution (Fig. 6a, b). The E_g values obtained for 3 at.% Al-doped ZnO films deposited at T_s 400 °C from $\text{Zn}(\text{ac})_2$ (3.39 eV) and $\text{Zn}(\text{acac})_2$ (3.37 eV) are similar to those obtained by Gómez et al. (3.40–3.47 for 3 at.%) [9].

The increase in the band gap is mostly explained by the Moss-Burstein effect [5], which is caused by an increase in carrier concentration. Al is incorporated in the films in increasing quantities until a critical level above which the charge carrier concentration decreases. For the Moss-Burstein effect to manifest, the carrier concentration must exceed $1 \times 10^{20} \text{ cm}^{-3}$. The blue shift in the band gap in films deposited from $\text{Zn}(\text{acac})_2$ in this study is instead probably due to the formation of a wider band gap AlO_x phase (see Fig. 3b) [29]. This effect is often attributed to the formation of inactive clusters of AlO_x [5, 23].

CONCLUSIONS

The effects of zinc precursor, $[\text{Al}]/[\text{Zn}]$ atomic ratio in the source solution and T_s on the physical properties of Al-doped ZnO thin films were studied. From the structural, optical and electrical measurement results a complex dependence on the aforementioned deposition parameters is established. Zinc acetylacetonate is unsuitable for PSP deposition of highly transparent and conductive AZO films at substrate temperatures higher than 400 °C due to higher resistivity ($7 \text{ } \Omega\text{cm}$ at T_s 450 °C vs $0.7 \text{ } \Omega\text{cm}$ at T_s 400 °C) caused by a smaller crystallite size (9 vs 31 nm) and reduced optical transmittance in the visible region (10% lower average transmittance at T_s 450 °C – 76% in 400–800 nm range) due to the formation of a wider band gap, less transparent $\text{Zn}_6\text{Al}_2\text{O}_9$ and Al_2O_3 phases. The average crystallite size for 1–5 at.% Al in solution $\text{Zn}(\text{acac})_2$ based films deposited at T_s 400 °C is 22 nm and 29 nm for $\text{Zn}(\text{ac})_2$ based films. Transmittance, mobility and charge carrier concentration are similar for films grown at T_s 400 °C. The lowest resistivity is achieved for both types of AZO films at 400 °C: 3–7.5 at.% $[\text{Al}]/[\text{Zn}]$ in the source solution for zinc acetate based films ($0.4 \text{ } \Omega\text{cm}$) and 3–7.5 at.% $[\text{Al}]/[\text{Zn}]$ in the source solution for zinc acetylacetonate based films ($0.5 \text{ } \Omega\text{cm}$). Increasing the $[\text{Al}]/[\text{Zn}]$ ratio to higher than 7.5 at.% results in higher resistivity films probably due to exceeding critical Al solubility in

the ZnO lattice and formation of inert secondary AlO_x phases. Due to stability, higher crystallinity and generally better results in optical and electric properties, zinc acetate is a better zinc precursor for PSP deposition of conductive AZO films at T_s 400 °C using isopropanol-water mixture as solvent.

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**ALIUMINIU LEGIRUOTŲ CINKO OKSIDO
PLONŲJŲ DANGŲ FORMAVIMAS
PNEUMATINIO PURŠKIMO PIROLIZĖS
METODU NAUDOJANT CINKO ACETATĄ
IR CINKO ACETILACETONATĄ BEI
PALYGINAMASIS GAUTŲ JUNGINIŲ
FIZIKINIŲ SAVYBIŲ VERTINIMAS**

Santrauka

Darbe pristatoma didelio optinio pralaidumo, laidžių aliuminiu legiruoto cinko oksido (AZO) dangų palyginamoji analizė formuojant jas pneumatinio purškimo pirolizės metodu. Dangos buvo formuojamos ant natrio-kalcio silikatinio stiklo purškimo metu naudojant cinko acetato ir cinko acetilacetono pagrindo tirpalus. Struktūrinės, optinės ir elektrinės dangų savybės buvo analizuojamos priklausomai nuo aliuminio kiekio pirminiame tirpale ir padėklo temperatūros dan-

gų formavimo metu (T_s). Tirpalas, naudojamas formuojant dangas, sudarytas iš 0,2 M cinko acetato arba 0,2 M cinko acetilacetono ir aliuminio acetilacetono (Al/Zn santykis: 0–15 atom. %). Padėklo temperatūra kito nuo 275 iki 450 °C. Optinio pralaidumo ir atspindžio spektrai buvo matuojami UV-VIS-NIR spektroskopu. Varža, krūvio judrumas ir pernašos tankis įvertinti naudojant keturių zonų metodą esant standartinėms aplinkos sąlygoms. Rentgeno spindulių difrakcijos analizė parodė, kad AZO dangos yra labiausiai orientuotos c-ašimi, kai Al/Zn koncentracijų santykis pirminiame tirpale siekia 2–3 atom. %. Kristalitių dydis, kai padėklo temperatūra T_s dangų formavimo metu 400 °C, yra 25–30 nm. Visos suformuotos AZO dangos pasižymi dideliu vidutiniu optiniu pralaidumu (76–94 %) regimajame 400–800 nm bangų spektre. Eg vertė kito nuo 3,32 eV nelegiruotame ZnO junginyje iki 3,58 eV itin legiruotose AZO dangose naudojant cinko acetilacetono pagrindo tirpalą. Šis pokytis įvyko dėl antrinių AlO_x fazių formavimosi. Mažiausia varžos vertė ($0,40 \Omega \times cm$) fiksuota, kai temperatūra dangos formavimo metu buvo 400 °C naudojant cinko acetatą (Al/Zn santykis tirpale 3–7,5 atom. %) ir $0,47 \Omega \times cm$ naudojant cinko acetilacetoną (koncentracija 3–7,5 atom. %, kai temperatūra dangos formavimo metu – 400 °C).

Raktažodžiai: aliuminiu legiruotas cinko oksidas (AZO), Al legiruotas ZnO, pneumatinis purškimo pirolizės metodas, plonosios dangos