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Aluminum Doped Zinc Oxide via Facile Pneumatic Spray Pyrolysis for Photovoltaic Applications

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Undoped and Aluminum-doped Zinc Oxide (AZO) were grown on a glass substrate using a facile home developed pneumatic spray pyrolysis technique. Four samples were prepared with Aluminum percentage weight ratios of 0, 0.5, 0.75 and 1. The structural, electrical and optical properties of the grown films were characterized using X-ray diffraction (XRD), the four-point and Ultraviolet–visible (UV-vis) spectroscopy methods respectively. XRD characterization revealed that the undoped and doped Zinc Oxide (ZnO) films have a polycrystalline structure with a strong preferential growth orientation along the (002) direction and the crystallite size increases and then decrease and ranges from 31.66 to 84.93 nm indicating the reduction increase again of defects. UV-vis spectroscopy has shown that the 0.1 % Al portion slightly enhanced the film transmission while larger amounts drastically deteriorated it which is probably due to the behavior of defect and the surface roughness. The band gap energy was almost unaffected varying between 3.21 and 3.29 eV. The defect's behavior has also affected the sheet resistance which showed a huge decrease of for increasing Al ratio until the last ratio where it has slightly increased. Although, most of the obtained results behave in their usual way, the transmittance behavior is the most remarkable where it can be useful in designing solar cells where the lightly doped AZO can be used as a window while the highly doped AZO can be used as part of the heterojunction with a *p*-type semiconductor (like Si, GaAs or another oxide) to increase generation and collection of carriers.

Keywords: Al doped ZnO, Spray pyrolysis, Electrical characterization, Optical characterization, Structural characterization.

1. INTRODUCTION

Transparent conductive oxides (TCO) are semiconductors with a wide gap (> 3 eV) [1]. Their importance lies in a compromise between good electrical conductivity and optical transmission in the visible spectrum [2]. One the most widely studied TCOs is Zinc Oxide (ZnO) due to its remarkable characteristics such as its large exciton binding energy (~ 60 meV), wide bandgap (~ 3.4 eV), natural abundance, non-toxicity, and strong thermal and chemical durability [3]. In recent years, it has been used as a wide–band gap semiconductor for optical and electronic applications such as solar cells as a window layer [4]. Its electrical, optical and other properties can be easily and conveniently controlled for targeted applications by metallic doping [5]. In particular, Aluminum (Al) doped Zinc Oxide (AZO) has emerged as a cheaper alternative to replace other TCOs such as Indium Tin Oxide (ITO) and Fluorine Tin Oxide (FTO) in several applications [6]. Different preparation methods and treatments were used to enhance ZnO thin films properties by Al doping [7-9]. In photovoltaics, AZO has played a major role in enhancing the performance of solar cells, in particular as a window layer. AZO can replace ITO in heterojunction Silicon solar cells (SCs) because of its low cost, abundant material reserves in nature and capability of achieving comparable efficiencies to the ITO-based SHJ solar cells [10]. ZnO as well as AZO were examined in view of their use both as TCO and the *n*-type partner for the p-type gallium arsenide (GaAs) substrate, that resulted in creation of the p-n heterojunction-based photovoltaic device [11]. The CdTe solar cell performance can be greatly improved by adjusting the carrier concentration of the AZO layer, as potential material to replace CdS window layer [12]. Furthermore, AZO can be used as an effective mean to improve a device performance [13]. The performance of an IGZO thin film transistor (TFT) was influenced by the conductivity of the AZO film, related to its structural properties, used as the source and drain electrodes [14]. AZO can also be used in different types of sensors [15].

The different properties of AZO thin films are greatly affected by the different preparation conditions. For example, the grain size and the roughness difference of can affect the optical properties [16]. Transmission may be reduced because of increased thickness and increased roughness [17] since Al doping create more defects and

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affects randomly transmittance and resistivity [18]. The transmittance decrease is usually correlated with grain and defect density increase indicating the substitution of Zn^{2+} with Al ions indeed facilitates the formation of zinc vacancy (VZn) and increasing the oxygen vacancy (VO) concentration in the thin films, hence; the fewer the defects the better the crystallinity of the film and the smaller the resistivity [19]. In summary, Al may substitute Zn atoms in the ZnO matrix and may have different and wide range effects such increasing then reducing conductivity, reducing mobility, affecting transmission and other electrical and mechanical properties, but the remaining challenges are how the different preparation conditions and techniques affect these properties [20]. In this work, AZO thin films were prepared using a facile spray deposition on glass substrate with different Al weight percentages ranging from 0 to 1 %. The structural, optical and electrical properties were characterized by XRD, UV-vis spectroscopy and four-point respectively. The obtained results were analyzed for possible utilization of these films in designing solar cells based on AZO as a dual-function layer or a combination of a window layer and a heterojunction with other semiconductors such as Si, GaAs or CdTe as suggested recently [21].

2. MATERIALS AND METHODS

Glass substrates are used to allow good optical characterization of the films and because of the good thermal expansion that it presents with ZnO. The glass substrates were cleaned to remove organic contamination using organic solvents (ethanol, acetone) and then intensively rinsing with distilled water. A gentle cleaning of the two surfaces of the blades is carried out using a soft lint-free paper (optical paper) before it was immersed in a bath of distilled water, then an ethanol bath. The degreasing in each bath lasts five minutes and is followed by a rinsing with distilled water. The thin AZO layers were prepared from hydrated zinc acetate ($C_4H_6O_4Zn2H_2O$) dissolved in distilled water according to a molar concentration of the solution equal to 0.15 M. An addition of a few drops of hydrochloric acid (HCl) is necessary to ensure maximum dissolution of zinc acetate, and then stirred for 1 hour. For the Al doping, quantities of hydrated aluminum nitrate ($AlN_3O_9.9H_2O$), according to the desired Al doping, in were dissolved in the starting precursor. The doping percentage is varied in the range 0-1 wt%. The deposition conditions are shown in Table 1.

The grown thin films were characterized using a Rigaku mini Flex 600 XRD diffractometer for structural properties, a JASCO V-770 UV-Vis spectrometer for the optical properties while a four- probe with a Pico Amperemeter Keithley 485 and a 2182 Nanovoltmeter.
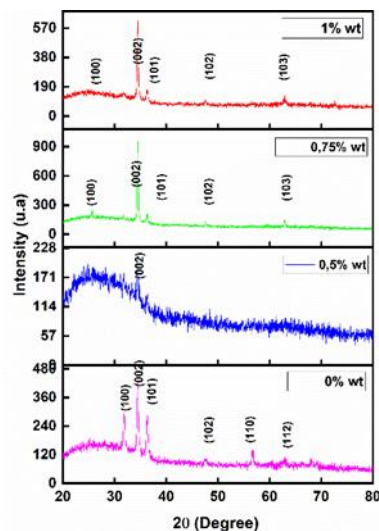
Table 1 – The deposition conditions of the sprayed AZO thin films

Al doping ratio: (wt%)	Substrate temperature (°C)	Deposition time (min)	Distance sprayer-substrate (cm)	Pressure of compressor	Molarity of the solution (mol/l)
0-1	300	3	12	Moderate	0.15

3. RESULTS AND DISCUSSION

The XRD spectra of ZnO films doped with Al with different doping percentages (undoped, 0.5 %, 0.75 %, 1 %) are presented in Fig. 1. The (100), (002) and (101) diffraction peaks were observed. These peaks are in good agreement with the JCPDS reference file (No 36-1451) which confirms the hexagonal structure of wurtzite type for all the elaborated layers and the polycrystalline structure with a strong preferential growth orientation perpendicular to the crystallographic planes (002) of the hexagonal structure of ZnO (the c axis is perpendicular to the substrate). Other peaks around $2\theta = 31°$ and $2\theta = 36°$ correspond to the (100) and (101) planes respectively of the ZnO system, they appear intensively in the spectrum of pure ZnO then they decrease with increasing doping. An increase in the intensity of the dominant peak (002) with the doping ratio is observed. The maximum intensity is noted for the 0.75 % Al doping, which explains that the high concentration of the dopant promotes growth according to (002) because of its low energy. No corresponding additional Aluminum peaks were observed, probably indicating that Al atoms occupy interstitial sites of ZnO [22]. Fig. 2 represents the variation of the size of the crystallites (D) and the deformation (ε) variation with Al doping ratio. The crystallite size increases from 31.66 to 84.93 nm with increasing Al doping ratio in good agreement with other studies [16]. The increase in *D* can be explained by the fact as

Fig. 1 – XRD spectra of the different elaborated AZO thin films

the ratio of doping increases, the electrostatic interaction between atoms becomes greater, thus increasing the probability of more solute gathering to form a crystallite [17]. Furthermore, the deformations vary inversely with the size of the crystallites. This decrease indicates a decrease in lattice imperfections in the grain boundaries [18]. We obtained the best crystallization of the hexagonal phase of ZnO on the film doped with 1 wt % Al with a crystallite size of 84.93 nm and a strain of – 0.4304 %. If authors have the appropriate experience, they can

continue to develop the existing two-level list starting from the third level.

Fig. 3 shows the optical transmittance (a) and its corresponding average (b) of the AZO prepared thin films for different doping concentrations of Al in the wavelength range 400-800 nm. All spectra are transparent in the visible range ranges and its average between (49-84%). The transmission is over 80% for low Al doping values (0%, 0.5%) and then drops drastically to just under 50% for the 0.75% ratio. This behavior can be attributed to the roughness of the film surface and defects. For smaller Al doping; defects are reduced since Al substitute Zn^{2+} sites and hence annihilate the oxygen vacancies. For larger doping; probably oxygen vacancies (VO) are annihilated hence the additional Al atoms contribute to creating more defecting by occupying interstadial sites or oxygen Zn^{2+} vacancies (VZn) [22].
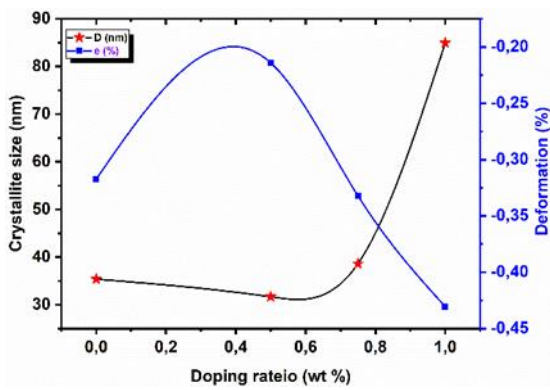

Fig. 2 – The variation of the crystallites size (*D*) and the deformation (ε) variation with Al doping ratio
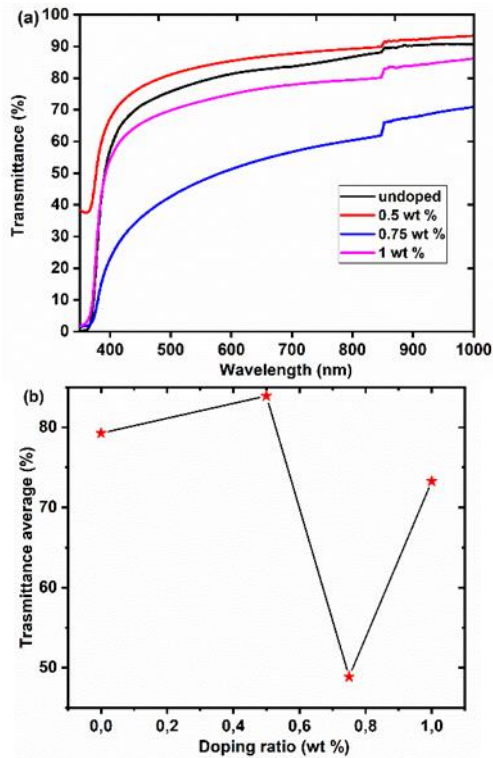

Fig. 3 – The optical transmittance (a) and its corresponding average (b) of the AZO prepared thin films for different doping concentrations of Al in the wavelength range 400-800 nm

The band gap of the AZO thin films was determined from the transmission spectra by means of a graphical method using the Tauc relation (1). The Tauc plot transform the transmittance curve to $(\alpha h\nu)^2$ versus $h\nu$. The determination of the optical gap of the films is deduced by extrapolation of the linear part to the $h\nu$ axis as shown in Fig. 4 (a) and the corresponding energy gap are shown in Fig. 4 (b) as a function of the doping rate.

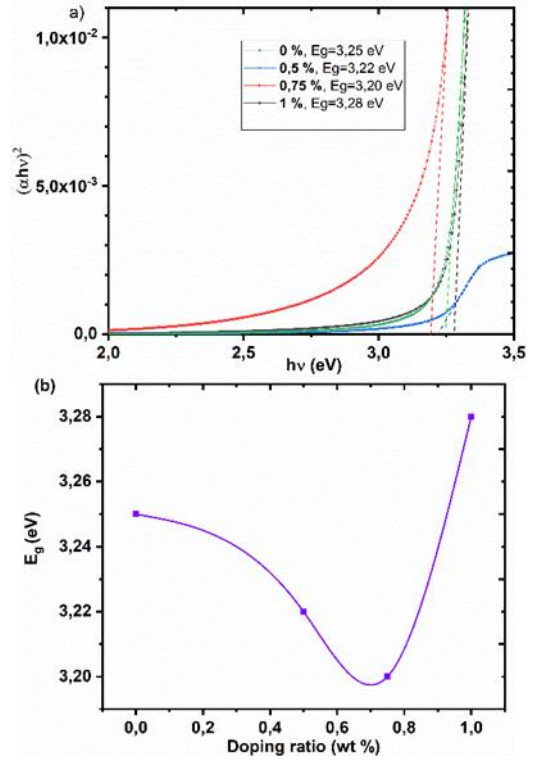$$(\alpha h\nu)^2 = A(h\nu - E_g) \tag{1}$$

Fig. 4 – a) The Tauc plot: $(\alpha h\nu)^2$ vs $h\nu$ and b) the calculated energy band gap of the differently doped AZO thin films

The variation in the energy gap can be attributed to the variation in grain size [21, 22]. We observe a decrease and then an increase in the band gap, this widening of can be interpreted by the Burstein-Moss effect. This phenomenon is linked to the increase in the number of majorities. This increase leads to a shift in the fermi level just below the level of the conduction band causing the band gap to increase.
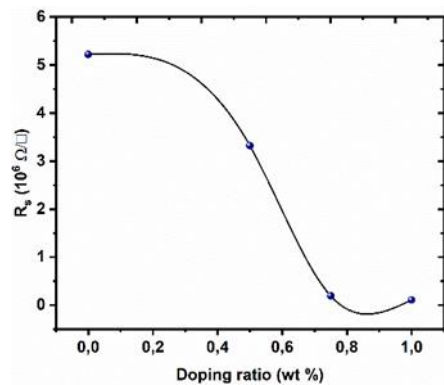

Fig. 5 – The sheet resistance variation (R_s) as a function of the doping concentration

The sheet resistance variation (R_s) as a function of the doping concentration is represented in Fig. 5. R_s was found to decrease with Al doping concentration to a minimum value obtained at 1 wt %, Rs = $1.09 \times 10^5 \, \Omega/\square$. The decrease in R_s can be explained by the increase in crystallite size leading to a reduction in grain boundary scattering as well as defect creation and annihilation by Al atoms and/or reduced mobility due to increased scattering by higher Al atoms. The decrease in the sheet resistance of the film due to the increase in the carrier concentration in AZO thin films, due to the incorporation by substitution of Al^{3+} ions on the Zn^{2+} cationic sites. This explanation is in good agreement with the XRD analysis, which shows an improvement in the crystallinity for the prepared films.

4. CONCLUSIONS

Aluminium doped zinc oxide thin films were elaborated on a glass substratiousing a facile pneumatic spray pyrolysis technique for different doping percentages. The grown films were characterised for their structural characteristics using X-ray diffraction, and their crystallite size and deformation were extracted. The undoped and doped zinc oxide (ZnO) films were found to have a polycrystalline structure with a strong preferential growth orientation along the (002) direction and the crystallite size increases and then decrease and ranges

from 31.66 to 84.93 nm. This behaviour was explained by the reduction increase again of defects since al atoms may substitute Zn atoms and may also occupy interstitial site. The four-point technique was used to reveal the electrical characteristics. The sheet resistance initially decreases and then decrease again. This was also related to the behaviour of defects as well as the increase in the free carriers generated by al doping which reduces defects. The slight increase of the sheet resistance may be due to the increased again defects or a reduced mobility due to increased scattering by higher al atoms. The optical properties of the prepared films were characterised using ultraviolet–visible (uv-vis) spectroscopy method respectively. Al doping has a drastic effect on the thin films' transmission. It increases initially due to crystallinity improvement and then it is reduced drastically before it improves slightly. This may be due to the combination effects of defects creation/annihilation, surface roughness and crystallinity. The findings of this work may be very important in designing windows as well as active layers of solar cells in photovoltaic applications.

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Оксид цинку, допований алюмінієм, шляхом легкого піролізу пневматичним розпиленням для фотоелектричних систем

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Нелегований і легований алюмінієм оксид цинку (AZO) вирощували на скляній підкладці за допомогою легкої, розробленої вдома технології піролізу з пневматичним розпиленням. Чотири зразки були підготовлені з масовим відношенням алюмінію в процентах 0, 0,5, 0,75 і 1. Структурні, електричні та оптичні властивості вирощених плівок були охарактеризовані за допомогою рентгенівської дифракції (XRD), чотириточкової та ультрафіолетової видимої (УФ) області. -vis методи спектроскопії відповідно. XRD показало, що нелеговані та леговані плівки оксиду цинку (ZnO) мають полікристалічну структуру з сильною переважною орієнтацією росту вздовж напрямку (002), а розмір кристалітів збільшується, а потім зменшується та коливається від 31,66 до 84,93 нм, що вказує на повторне збільшення зменшення. дефектів. Спектроскопія УФ-видимого діапазону показала, що частка 0,1 % Al дещо покращує пропускання плівки, тоді як більші кількості різко погіршують його, що, ймовірно, пов'язано з поведінкою дефекту та шорсткістю поверхні. Енергія забороненої зони майже не змінювалася, коливаючись між 3,21 і 3,29 еВ. Поведінка дефекту також вплинула на стійкість листа, яка показала значне зниження для збільшення співвідношення Al до останнього співвідношення, де воно трохи збільшилося. Незважаючи на те, що більшість отриманих результатів поводяться у звичайний спосіб, поведінка пропускання є найбільш примітною, коли вона може бути корисною при розробці сонячних елементів, де злегка легований AZO можна використовувати як вікно, а сильно легований AZO можна використовувати як частина гетеропереходу з напівпровідником *p*-типу (наприклад, Si, GaAs або іншим оксидом) для збільшення генерації та збору носіїв.

Ключові слова: ZnO, легований Al, Піроліз розпиленням, Електричні характеристики, Оптичні характеристики, Структурні характеристики.