The Influence of Substrate Temperature on In$_2$O$_3$ being Structured

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ABSTRACT

In$_2$O$_3$ thin films were grown by the chemical spray pyrolysis (CSP) method using the pneumatic spray set-up and compressed air as a carrier gas. Aqueous solutions containing InCl$_3$.4H$_2$O were deposited onto preheated glass sheets at substrate temperatures Ts=423–573K. X-ray differection (XRD) analysis confirmed the cubic bixbyite structure of indium oxide. The preferred growth orientation along the (211) plane for thin films. The crystallite size extracted from the XRD data corroborates the changes in full width at half maximum due to the variation in substrate temperature. It was shown that grain size of In$_2$O$_3$ thin film was (30)nm. Optical properties of In$_2$O$_3$ was studies and showed that the optical parameters (n, k α) were affected by substrate temperature.
Key word: Indium oxide, optical properties, nanostructure.

تأثير درجة حرارة القاعدة على تركيب الغشاء In$_2$O$_3$

الخلاصة

تم تحضير اغشية رقيقة من In$_2$O$_3$ باستخدام طريقة الترسيب الكيميائي الحراري . المحلول المستخدم يحتوي على كلوريد الانديوم المائي والذي يرسب على على قواعد زجاجية وبدرجات حرارية تتراوح من 423 الى 573 كلفن. تم دراسة حيود الاشعة السينية لايجاد تركيب غشاء اوكسيد الانديوم. الطور السائد هو (211) لهذه الاغشية الرقيقة. تم حساب الحجم البلوري من قياس حيود الاشعة السينية وان التغير الحاصل في نتيجة للتغير في درجة حرارة القاعدة. لقد وجد ان الحجم الحبيبي لغشاء In$_2$O$_3$ يساوي 30 نانومتر. اما الخصائص البصرية لاغشية In$_2$O$_3$ والمبينة بالثوابت البصرية (معامل الانكسار، معامل الخمود و معامل الامتصاص) والتي تتأثر بدرجة حرارة القاعدة.

INTRODUCTION

T he oxide layers such as SnO$_2$, In$_2$O$_3$, ZnO, Sb$_2$O$_5$, CdO etc are important semiconductors with the band-gap values of about (2.8-4) eV. Owing to their unique catalytic, optical, electronic and gas-sensing properties, In$_2$O$_3$ can be used as catalyst, luminophore, electrode, solar cell and gas sensor, etc [1,2].

In particular, the nanostructures of In$_2$O$_3$ often demonstrated shape- and size-dependent physical and chemical properties that were of technological importance

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and scientific research interest. Accordingly, so far, considerable effort has been devoted to designing novel methods for the synthesis of In_2O_3 nanomaterials with different characteristics [3-5]

Transparent conducting oxide (TCO) thin films with a unique combination of low resistivity ρ, high carrier mobility μ, and near-infrared (NIR) transmittance are desired for optoelectronics applications. Transparent thin film transistors require high channel mobility to improve device performance, and solar cells require high NIR transparency to widen the spectral sensitivity in the entire visible-NIR region. Numerical simulation using the Drude model authenticates that the higher NIR transparency (*T)* can be achieved by increasing the μ of TCO films. A number of TCOs, including zinc oxide ZnO, indium oxide In_2O_3 and tin oxide SnO_2, are known to exist for many years. However, commercial TCOs (SnO_2 : In, SnO_2 :F, and ZnO:Al) suffer from free-carrier absorption in the NIR region and hence limit μ Photovoltaic industry demands TCOs to transmit the entire solar spectrum for electrode applications [6]. The short-wavelength (ultraviolet UV) cutoff corresponds to the fundamental band gap energy of the materials, whereas the long-wavelength (infrared IR) edge corresponds to the free-carrier plasma resonance frequency. In general, for a material to be transparent across the visible spectrum, its band gap must be greater than 3 eV to enable transmission up to the near UV 400 nm wavelength, and its free-carrier plasma resonance frequency absorption must lie in the NIR 1500 nm or IR. Increasing *n* decreases ρ but also has the drawback of shifting the IR absorption edge toward the visible region, thus narrowing the window. This phenomenon is determined by the plasma oscillation of the free carriers that screen incident electromagnetic wave via intraband transitions within the conduction band. The IR reflection in ITO is well predicted by the Drude model [7]. The position of the UV edge depends, in part, on the *n* in the material. A straightforward analysis of the density of states in the conduction band reveals that the UV edge will shift to shorter wavelengths with increasing *n* because the change in the optical band gap *Eg* increases the carrier density as $\Delta E \sim n^{3/2}$ [8].

In_2O_3 thin films have been explored by various deposition techniques such as thermal reactive evaporation, rf magnetron sputtering, dc magnetron sputtering, hollow cathode sputtering, pulsed laser ablation, and spray pyrolysis [4-9].

In this study we report the effect of substrate temperature on the structural of thin films and optical characteristics of In_2O_3 thin films deposited by ultrasonic spray pyrolysis technique,

EXPERIMENTAL DETAILS
Film preparation

In_2O_3 thin films were deposited by the chemical spray pyrolysis CSP technique from aqueous solutions containing indium chloride ($InCl_3.4H_2O$), using a pneumatic spray set-up and compressed air as a carrier gas. Glass sheets with a size of $20 \times 20 \times 0.1$ mm³ were used as substrates placed on a molten tin bath. Deposition temperatures were varied from 423 to 573K, and kept within an accuracy of ±5 °C using a feedback control system for the heater supply. The film deposition temperature was measured from the glass surface when deionised water was

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sprayed. Total volume of the solution sprayed was 50 ml and the rate of spray was 2.5 ml/min in all cases. The scheme of the spray pyrolysis set-up used in this research is presented in Figure (1).
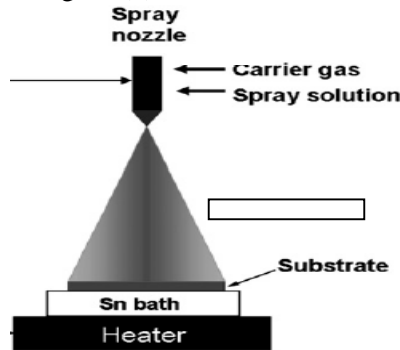

Figure (1): Spray pyrolysis set up used for thin film preparation.

Film characterization

The deposited thin films were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM) and optical transmission spectra. XRD measurements were performed on a Rigaku Ultima IV diffractometer with Cu Kα radiation (λ=1.5406 Å, 40 kV at 30mA) using the silicon strip detector. Crystallite size (g) and lattice constants (a) were calculated using equations (1 & 2). The crystallite size was calculated using the Debye- Scherrer method [6,7].

$$a = d \times \sqrt{h^2 + k^2 + l^2} \quad \text{............ (1)}$$

Where d is a distance between atomic levels and h, k, l miller constants.

$$g = \frac{k\lambda}{\beta cos\theta} \quad\quad\quad \text{............ (2)}$$

Where k is the shape factor (scherer constant of 0.94), λ is the x-ray wavelength, β is the line broaden in at half the maximum intensity (FWHM) and θ is the Bragg angle.

The optical total transmittance spectra of the films were measured in the wavelength range of 250–900 nm on a Jasco V-670 UV–VIS–NIR spectrophotometer equipped with an integrating sphere.

RESULTS AND DISCUSSION
Optical properties

Figure (2) shows the variation of transmittance spectra of the In₂O₃ thin films deposited with different substrate temperature Ts. The transmittance increased with increasing substrate temperature up to 523 K and the further increase of Ts decreased the transmittance. Table 1 shows the value of optical transmittance in 900 nm of In₂O₃ thin films at different Ts, which have an obvious influence on the

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transmittance. Below 523K Ts, an increase of the optical transmittance is observed. The optical transmittance can be increased with a reasonable increase in the Ts.

When the Ts 523K the optical transmittance of In_2O_3 thin films with 120 nm thickness shows the highest value. If the Ts above 523 K, the optical transmittance will begin to decrease. The results can be explained as following: when the Ts is lower, the particles evaporated from the target cannot be oxidized enough so the prepared In_2O_3 thin films are anoxic and sub-oxides such as $InOx$. The transmittance of In_2O_3 thin films were higher because sub-oxides can be oxidated with an increasing substrate temperature.

When the Ts is over a maximum, the redundant oxygen can be absorbed in the defects such as grain boundaries and microcracks, which is affirmed by Hamberg and Granqvist [5]. The redundant oxygen can cause optical absorption and scattering. Furthermore, we calculated the optical band gap values of In_2O_3 thin films from transmittance spectra, results are tabulated in table (1). In the strong absorption region, the absorption coefficient (α) can be calculated from Lambert's formula [2,3]:

$$\alpha = d^{-1}\ln(1/T) \qquad \ldots\ldots\ldots\ldots(3)$$

where T and d are transmittance and film thickness, respectively.

The absorption has its minimum at low energy and increases with optical energy in a manner similar to the absorption edge of the semiconductors. The absorption coefficient for directly allowed transition for simple parabolic scheme can be ascribed as a function of incident photon energy as [3]:

$$\alpha h v = (h v - E_g)^{1/2} \qquad \ldots\ldots\ldots\ldots (4)$$

where hv is the photon energy. The optical band gap of In_2O_3 thin films can be determined by plotting $(\alpha h v)^2$ versus hv, and extrapolation method. Figure 3 indicates the variation of $(\alpha h v)^2$ versus hv for In_2O_3 thin films prepared in the present study. It is observed that the optical band gap increased from 3.55 to 3.7 eV corresponding to the increase of Ts flow rates from 423 to 573 K, shows in table (1).

Table (1): optical properties of In₂O₃ thin films prepared at different Ts.

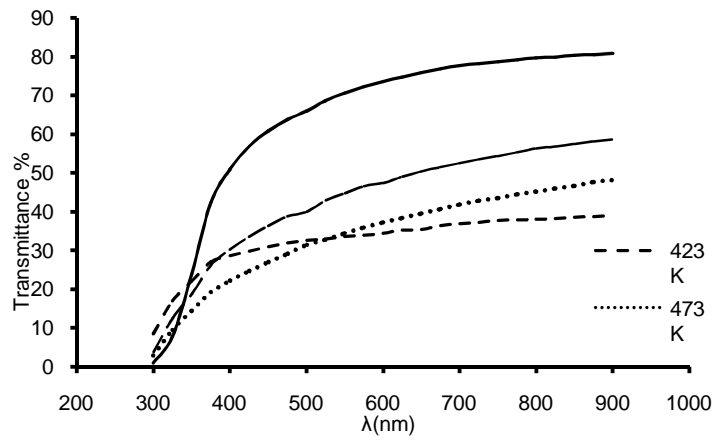| Substrate temperature (K)	Optical band gab (eV)	Transmittance %	Absorption coefficient (cm⁻¹)	
			300nm	900nm
423	3.55	39.6	2.46	0.92
473	3.61	48.4	3.5	0.73
523	3.7	80.3	4.6	0.21
573	3.6	58.7	3.24	0.53

Figure (2): Transmittance spectra of the In$_2$O$_3$ thin films in Different substrate temperature.
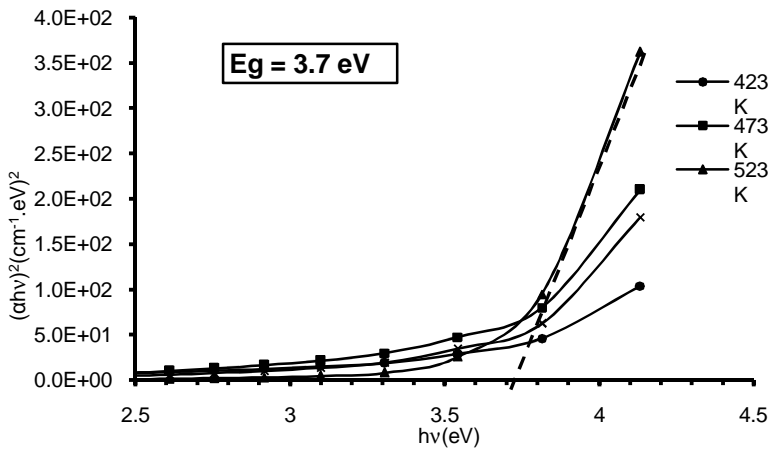

Figure (3): Plot of $(\alpha h\nu)^2$ against hν for indium oxide thin films at different substrate temperature.

X-ray analysis

   Figure (1) shows the X-ray diffraction patterns of the In$_2$O$_3$ films. The positions of the peaks fit well with polycrystalline In$_2$O$_3$ with hexagonal wurtzite structure. We observed that the (211) peak is very sharp and other reflections (222), (411), (611) appear relatively weak. In all cases a preferential (211) growth appears indicating the crystallite structure of the films is oriented with their c-axis perpendicular to the substrate. This behavior is in good agreement with other researches [6, 7, 9]. This particular orientation follows the grain evolutionary selection model proposed by Van der Drift and usually correlates with the energies gained by the incident species on the substrate under appropriate experimental conditions. Regular alternating layers of indium and oxygen atoms linked along the *c*-axis as pseudodiatomic molecules thus constitute the In$_2$O$_3$ film's stable hexagonal, closely packed wurtzite crystal structure. However, nonoptimal

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experimental conditions, defects and other chemical impurities may hinder the (400) oriented growth as is the case in high temperature films.

A dominant signal associated with the (211) planes is found for In$_2$O$_3$ thin films. Using the (222) peak and the Debye-Scherrer formula [8] the crystallites size was estimated. The values obtained for three different substrate temperatures starting from 423 to 573 K was 11.45 nm to 45.76 nm respectively. The grain size broadening with substrate temperature correlates with the increase in Eg [6]. As the substrate temperature increased, the peak intensity and crystal size increased, which may be due to the decrease in stress with increasing temperature. Further, the XRD 2θ scattering angle at (222) peak increases slightly from 30.43° to 31.438° as the substrate temperature is varied from 423 K to 573 K. Such shift suggests that some strain and stress are induced in the film due to the film-substrate lattice mismatch [7]. The lattice constant (a) calculated from XRD patterns the range between 9.5 and 10.3 Å, (table (2)) and in agreementwith the standard data of the IO film. There is no significant variation in (a) by increase in substrate temperature Ts.
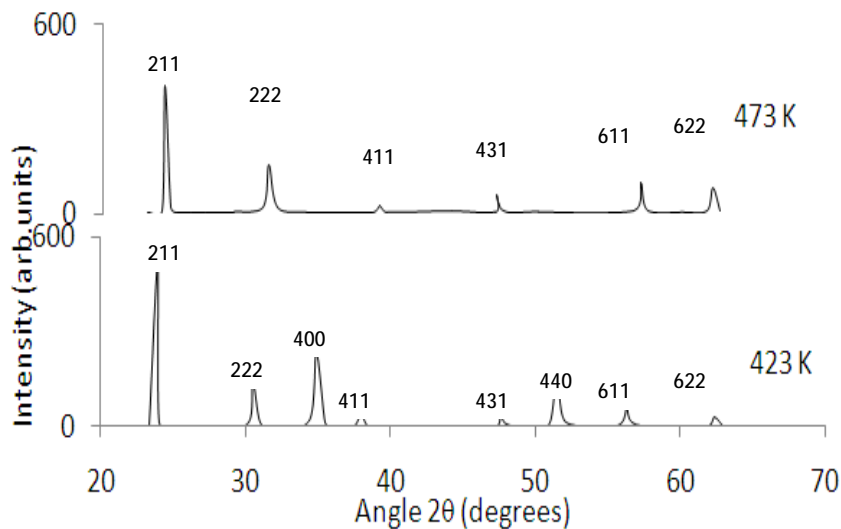

Figure (4): XRD patterns in In$_2$O$_3$ thin films with different substrate temperature.

Table (2): Data extracted from the XRD analysis as a function of substrate temperature.

Temperature(K)	Angleθ(deg)	hkl	Latticeconstant (Å)	FWHM (deg)	Crystal size (nm)
423	11.97	211	9.7	0.60	13.54
	15.24	222	10.3	0.18	45.76
473	11.1	211	9.5	0.76	10.66
	15.7	222	9.6	0.28	29.48
523	11.45	211	9.7	0.63	11.45
	15.5	222	10.1	0.21	33.48

CONCLUSIONS

Indium oxide films have been successfully prepared using the spray pyrolysis technique. The influence of various process parameters on the film properties has been carried out and the spray pyrolysis parameters have been optimized to give good quality films. The optimizedocess parameter for the preparation of device-quality In$_2$O$_3$ films are: concentration of InCl$_3$ is 2 g/100 ml, air-flow rate is 30 lpm, substrate–nozzle distance is 25 cm and the substrate temperature is 523K. The best In$_2$O$_3$ film prepared in this set of optimized conditions has a band gap value of 3.70 eV with a transmission of 80.3%. The XRD results show the cubic structure with (211) preferred orientation together with a less prominent (222) plane. At temperatures >573K, the peak intensities are found to be decreasing which may be due to the less uniform surfaces which might have been caused by the deteriorated crystalline nature of the films.

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