Annealing effect on the properties of indium tin oxides (In2O3 :Sn) thin films prepared by ultrasonic spray technic

9 authors, including:

Abdallah Attaf
Université de Biskra
52 PUBLICATIONS   344 CITATIONS

SEE PROFILE

A. Bouhdjer
Université Batna 2
25 PUBLICATIONS   137 CITATIONS

SEE PROFILE

Hanane Saidi
Mohamed Khider University
42 PUBLICATIONS   211 CITATIONS

SEE PROFILE

Nadia Messei
Université de Biskra
3 PUBLICATIONS   0 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:

Project   treatment of water and pollution View project

Project   Using quadratic method in quantum physics View project

Research Article

ANNEALING EFFECT ON THE PROPERTIES OF INDIUM TIN OXIDES (IN₂O₃ :SN) THIN FILMS PREPARED BY ULTRASONIC SPRAY TECHNIC

N. Hamani[1], A. Attaf[1*], H. Saidi[1], K. G. Temmam[1], A. Bouhdjer[1], K. Bennaceur[1], N. Messei[1], Y. Benkhatta[1], N. Attaf[2]

[1]Physics of Thin Films and Applications Laboratory, University of Biskra, BP 145 RP, Biskra 07000, Algeria

[2]Laboratoire de Couches Minces et Interfaces Faculté des Sciences Université de Constantine, Algeria

ABSTRACT

Indium tin oxide (ITO) films were deposited on glass substrates using ultrasonic spray technic. The ITO films (with 4% Sn-doping concentration at substrate temperature 400°C) were annealed in the air at 450, 500, and 550 °C for 2 h. The structural, morphological, electrical and optical properties of ITO films were investigated using: XRD, SEM, four-point probe and UV–visible. The XRD analysis reveals that the films are polycrystalline with body-centered cubic structure, and the cristaline state of the films improve with the increase of annealing temperature. Surface morphology of the films changes with the change of the annealing temperature. The high optical transmittance observed in the films annealed at 500 °C. The films annealed at 550°C shows the low electrical resistivity 25 10^{-4} Ωcm due to the decrease of the odsorbed oxygen on the surface morphology of this films.

Key words: indium tin oxide; High transparency; Surface morphology; electrical resistivity.

1.   INTRODUCTION

Indium tin oxide (ITO) is widely utilized in different industrial applications due to its unique combined properties of transparency to visible light and electrical conductivity and wide band gap (>3.5 eV) [1]. ITO films are highly degenerate n-type semiconductors, low electrical resistivity (~10^{-4} Ω-cm) [2,3], and high carrier concentration. high transmittance (>80%) in the visible range of the electromagnetic spectrum [4]. Due to their physical properties, it has potential applications in many devices, such as flat panel displays, solar cells, surface heaters for automobile windows, energy efficient windows, camera lenses, gas sensors, antireflection coatings and heat reflecting mirrors [5,6]. For these applications, the film should be a high electrical conductivity and a high visible transparency film.

The TTO films can be elaborated by various preparation techniques such as thermal/electron beam evaporation [7], radiofrequency/direct current sputtering [8], pulsed laser deposition [9], chemical vapor deposition [10], sol–gel process [11], and spray pyrolysis [12]. In this paper, we chose the spray ultrasonic technic to elaborate the ITO films due to several reasons such as: the low cost, it is possible to alter the electrical, mechanical, optical and magnetic properties of ITO nanostructures. And the simple deposition on glass substrate.

In this study, we prepared ITO films (with 4% Sn-doping concentration) by ultrasonic spray and investigated the structural, electrical and optical properties of the ITO films as a function of annealing temperature.

2. EXPERIMENTAL PROCEDURE

In the present work, Indium tin oxide films are prepared using an ultrasonic spray. In_2O_3:Sn solution were prepared by dissolving 0.1 M indium chloride ($InCl_3$) was used as the source of Indium source, dissolved in an appropriate amount of methanol CH_3OH solution (99.995%) purity and tin chloride penta-hydrate ($SnCl4.5H_2O$) (99.0%) was used as tin (Sn) doped . Some drops of HCl solution have been added as stabilizer. The ITO films (with 4% Sn-doping concentration at 400°C) were annealed in the air at 450, 500, and 550 °C for 2 h. All Substrates were cleaned and degreased successively using Acetone, propanol, and distilled water. The solution flow rate was chosen to be 50 mL/h. Films structure was analyzed using

X-ray spectroscopy on a D8 ADVANCE Diffract meter by a Cu Kα radiation (λ =1.5405 Å), the optical transmittance spectra were obtained by a UV–VIS spectrophotometer (Perkin Elmer Lambda 25 UV-Visible) and these measurements were carried using glass as reference in a wavelength range of 200–1000 nm. Electrical resistivity was measured by four-point method. The morphology was analyzed by JOEL model JSM 6301F scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1. X-Ray diffraction studies

Fig1 shows XRD patterns of indium tin oxide films deposited on glass substrates annealed at different temperature 450, 500 and 550 °C for 2 h. All the films shows two strong reflection peaks at 30.80° and 35.66° which can be attributed respectively to the (222) and (400) plane suggesting that film is polycrystalline in nature having a cubic crystal structure.in addition to the presence of an others weak peaks such as (440) and (662). However, it is clear that the intensity of diffraction peaks increase with the increase of annealing temperature to 550 °C.This reveals the development of crystallinity due to having a sufficient amount of kinetic energy and mobility of the grains; the large grains absorb the small grains [13].on the other hand, The XRD results suggest that the annealing temperature has not segnificant effect on the preferred grothe orientation of ITO films; generally the (222) plane is the preferred growthe orientation due to the low surface energy[14]. This result goes in harmonic with the results of our erlier work [15]. Table 1 shows a comparison between XRD results and standard pattern for pure indium oxide In_2O_3.

The average grain size D of ITO thin films is calculated using Scherrer's formula [16]:

$$G = \frac{K\lambda}{\beta \cos\theta} \qquad (1)$$

Where θ is the Bragg angle and β is the full width at half maximum (FWHM) of the peak, while λ is the X-ray wavelength. As can be seen from figure 2, the grains size increase with

the increase of annealing tamperature. This is owig to the increase of the kinetic energy of the grains by increasing the annealing temperature; coalescence of small grains [15]. The same values of grains size obtained by others researches [17.18]. On the other hand, increase of the grains size as observed by SEM analysis (explained later).
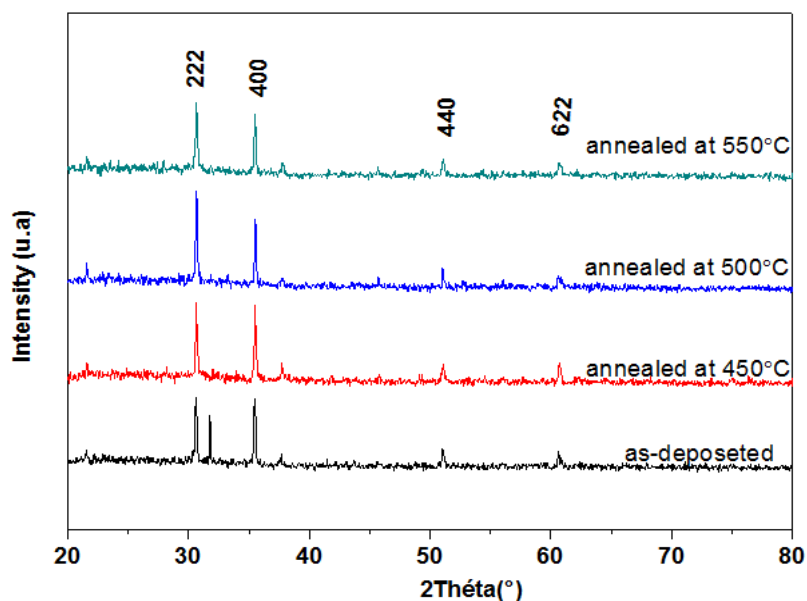

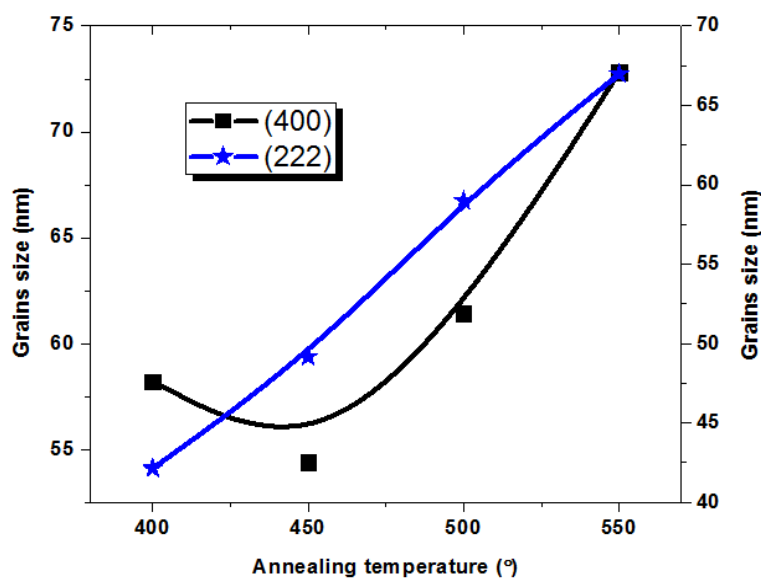**Fig.1.** XRD patterns of ITO films annealed at different temperatures

Fig.2. Variation of grain size with annealing temperature

Table 1. Comparison between XRD results and standard pattern for pure indium oxide

	Standard 2θ (°)	Observed 2θ (°)	hkl	FWHM
Without annealing	30.580	30.6052	(222)	0.1476
	35.451	35.4435	(400)	0.2066
	51.049	51.0429	(440)	0.1771
	60.662	60.6971	(622)	0.4320
Annealed at 450°	30.580	30.6108	(222)	0.1181
	35.451	35.4791	(400)	0.1771
	51.049	51.0387	(440)	0.3542
	60.662	60.7162	(622)	0.2880
Annealed at 500°	30.580	30.6504	(222)	0.1476
	35.451	35.5083	(400)	0.1476
	60.662	60.8000	(622)	0.8640
Annealed at 550°	30.580	30.6361	(222)	0,1181
	35.451	35.4640	(400)	0.2066
	51.049	51.0659	(440)	0.3542
	60.662	60.7333	(622)	0.4320

The dislocation density (δ) and strain (ε) were calculated using the following formula [19]:

$$\delta = \frac{1}{G^2} \tag{2}$$

$$\varepsilon = \frac{\beta \cos \theta}{4} \tag{3}$$

The calculated structural parameters of prepared indium tin oxide thin films using the above are listed in Table 2. The calculated structural parameters of prepared indium tin oxide thin are listed in Table 2. The calculated values of lattice constant of prepared ITO films annealed at 450 and 500°C are a= 10,1073A˚ and 10, 1145A˚,respectively.They are slightly smaller than the reported value 10.118 A˚ for pure indium oxide (JCPDS Card No. 06-0416) [20]. Obtained lattice constant value is slightly increased for the film annealed at 550°c. This can

be attributed to the oxygen deficiency [21] because the In_2O_3 thin films tend toward reduction when they were annealed at high temperature [22].The dislocation density (δ) and strain (ε) show a decreasing with increasing in annealing temperature. This is owing to recrystallization process in the films at high annealing temperature [23].

Table 2. Variation of grain size, strain, lattice parameter and dislocation density with annealing temperature

Ts (°C)		D_{moy} (nm)	a (A°)	$\varepsilon*10^{-4}$	δ (lines/m^2)*10^{14}
Without annealing		50.182	10.1191	6.9048	3.9710
Annealed at	450	51.78	10.1073	6.6995	3.4012
	500	60.21	10.1145	5.6726	2.7584
	550	69.89	10.1191	4.9663	2.472

3.2. Surface morphological analysis

The scanning electron microscope (SEM) pictures in Figure 3 shows the typical surface morphology of the ITO films annealed at different temperature. It can be seen from the images that the films are dense and the grain size along sample surface increases as the annealing temperature is increased as we found in the XRD analysis. The surface of the film exhibited a polycrystalline nature with a grain size of about 70 nm after annealing. The micrograph shows a uniform film nature with distinct grain boundaries but the films prepared at 400°C have non-uniform particles (or clusters), the films annealed at 500 °C has both small and big grains and the film annealed at 550 °C has only big grains due to the high temperature.

3.3. Optical analysis

The effect of annealing temperature on the optical property of ITO films was examined. The ITO films with thickness of 184 nm were annealed at 450, 500 and 550 °C for 2 h. Fig 4 shows the transmittance spectra of ITO films for different annealing temperatures and Table 1 shows the average transmittance in the visible region (λ= 400-700 nm). It is clear that the transmittance increases with increasing the annealing temperature from 450 to 550 °C. The
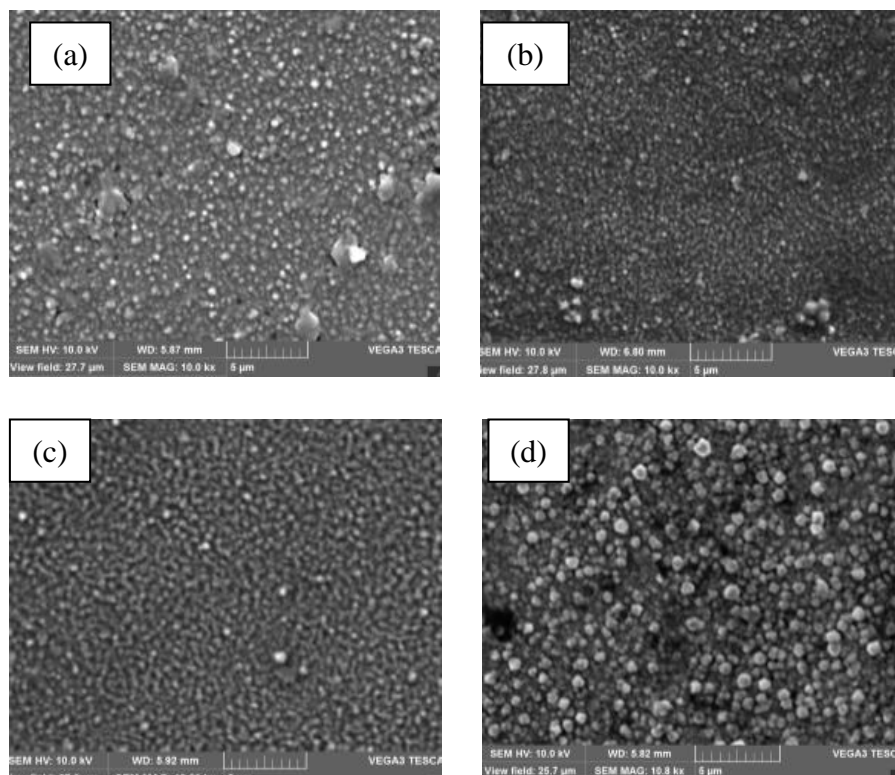
Fig 3. SEM surface morphology of ITO films at various annealing temperatures: (a) as deposited at 400°C; (b) Annealed at 450 °C; (c) 500 °C; (d) 550 °C for 2h

Transmittance higher than 80% after annealing, and such results may be related to low scattering of light. The optical band gap of ITO thin films was calculated by the following expression [24],

$$(\alpha h\upsilon) = A\left(h\upsilon - E_g\right)^{\frac{1}{2}} \tag{4}$$

Where α is absorption coefficient, A is the constant independent of photon energy ($h\upsilon$), h is the Planck constant and Eg is the energy band gap of the semiconductor equals the energy which provide an electron; in order to do a direct transition between valence and conduction bands. The value of optical band gap can be found by extrapolation of the linear region to $(\alpha h\upsilon)^2 = 0$ (fig 5) [16,24].

On the other hand, we have used the Urbach energy (Eu), which is related to the disorder in the film network; as it is expressed follow [24],

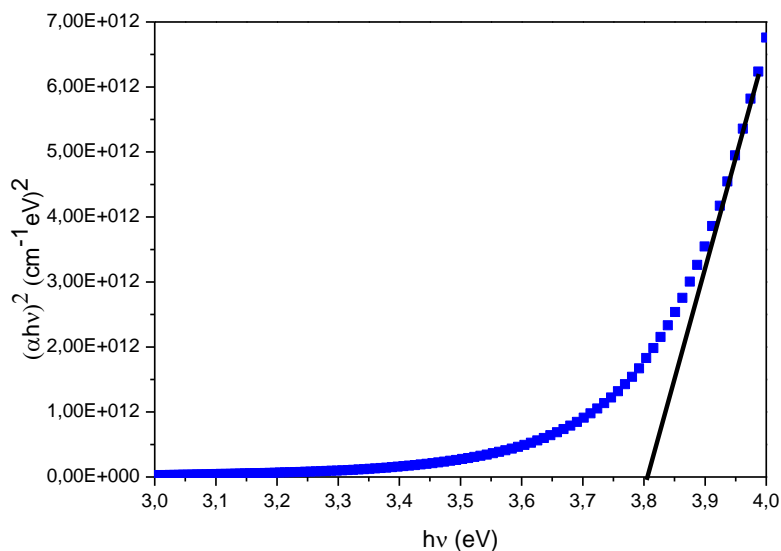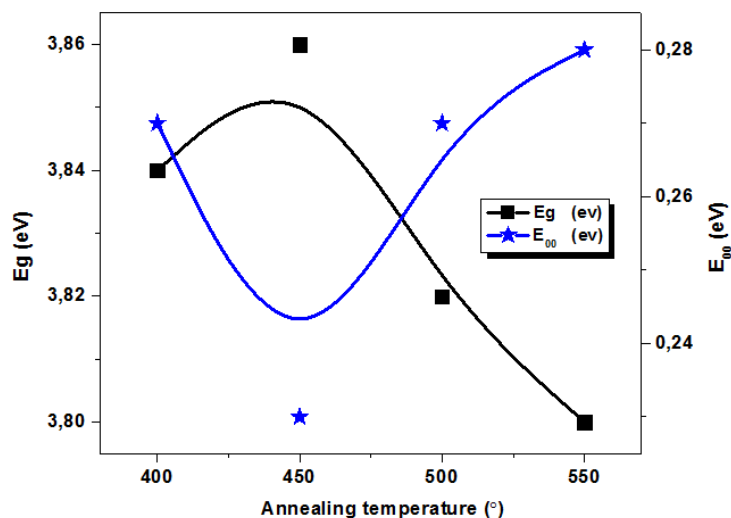$$A = A_0 \exp\left(\frac{h\upsilon}{E_u}\right) \qquad (5)$$

Where A_0 is a constant and E_u is the Urbach energy.
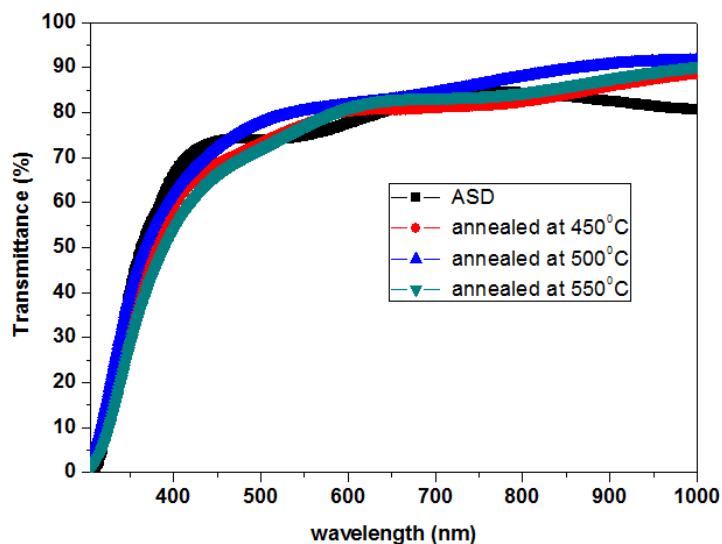
Fig.4. Transmittance spectra of ITO films annealed at different temperatures

**Fig.5.** The plot of $(\alpha h\upsilon)^2$ vs.$(h\upsilon)$

Fig.6. Variations of optical band gap and urbach energy as function of annealing temperature

The optical properties of the films are influenced by the oxygen diffusion with annealing temperature, the band gap decreases with increasing the annealing temperature from 500 to 550 °C (see figure6). Further annealing temperature (450 °C), the band gap decreased; however, the oxygen vacancy for the decrease of gap energy after annealed [25,26].

The minimum Urbach energy was reached at annealed temperature 450°C, which means the adequate temperature for less disorder. As expressed in the literatures [27, 28].

3.4. Electrical analysis

The annealing temperature has influences on the electrical property of the ITO films. Fig 7 shows the variation of resistivity as a function of annealing temperature for the ITO films with thickness of 184 nm. The resistivity of the ITO films decreased as the annealing temperature was increased from 450 to 550 °C. It indicates that the minimum resistivity is 0.0025 Ω .cm at 550 °C with annealing time of 120 min as shown in Fig. 7. When the composition in the crystallite of the thin films reaches optimal stoichiometric fraction, the crystallites gradually grow completely. The improved crystal performance and the reduction of grain boundary lead to the reduction of the absorption of donor SnO_2 in dislocation and crystal defects conditions. Therefore, the carrier concentration and carrier mobility also increased and with the subsequent reduction of the resistivity of the thin films [29].
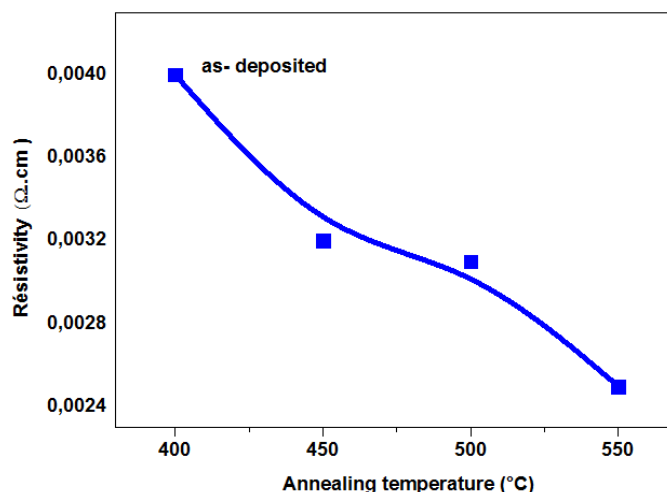
Fig 7. Resistivity of ITO films annealed at different temperatures

4. CONCLUSIONS

The ITO films were deposited onto glass substrates by ultrasonic spray (with 4 wt% Sn and substrate temperature 400°C) and annealing at temperatures range 450-550 °C. The structural, electrical and optical properties of the films were studied as a function of annealing temperature. The XRD patterns exhibited a preferential orientation along the (2 2 2) and (4 0 0) directions. SEM indicated the spherical grain growth with sizes ranging between 51.78 to 69.89 nm. From the transmittance measurement using a spectrophotometer, it was found that optical transparency of ITO films were up to 83% in the visible region as the annealing temperature increased. The resistivity of the films had a minimum value of 0.0025 Ωcm when annealed at 550 °C.

5. REFERENCES

[1] M. Thirumoorthi, J. Thomas Joseph Prakash .Journal of Asian Ceramic Societies 4 (2016) 124–132

[2] Artorn Pokaipisit, Mati Horprathum   and Pichet Limsuwan , Kasetsart J. (Nat. Sci.) 42 : 362 - 366 (2008).

[3] Yoonsuk Kim , Seungho Park , Byung-Kuk Kim , Hyoung June Kim , Jin-Ha Hwang . International Journal of Heat and Mass Transfer 91 (2015) 543–551

[4] A.El Hichou, A.Kachouane , J.L.Bubendorff , M.Addou , J.Ebothe , M.T

royon,A.Bougrine. Thin Solid Films 458   (2004) 263–268

[5] C.G. Granqvist*, A. Hulta˚ker. Thin Solid Films 411 (2002) 1–5.

[6] Fachun Lai , Limei Lin, Rongquan Gai, Yongzhong Lin, Zhigao Huang. Thin Solid Films 515 (2007) 7387–7392.

[7] M.H. Habibi,   N.Talebian, Acta Chim. Slov.52 (2005)53–59.

[8] M. Gulen, G.Yildirim, S.Bal,A.Varilci, I.Belenli, M.Oz, J.Mater.Sci.: Mater. Electron.24 (2013)467.

[9] A.Petukhov, A.N.Shatokhin, F.N.Putilin, M.N.Rumyantseva, V. F.Kozlovskii, A.M.Gaskov, D.A.Zuev .A.Lotin, O.A.Novodvorsky, A.D.Khramova, Inorg. Mater.48(10)(2012)1020–1025.

[10] J.M. Gaskell, D.W.Sheel, Thin Solid Films 520 (12)(2012)4110–4113.

[11] A.Ayeshamariam, M.Kashif, M.Bououdina, U.Hashim, M. Jayachandran, M.E.Ali, Ceram.Int.40 (2014)1321–1328.

[12] H. Bendjedidi, A. Attaf, H. Saidi, M. S. Aida, S. Semmari, A. Bouhdjar, and Y. Benkhetta, Journal of Semiconductors, vol.36, No.12 (2015)123002.

[13] A. Sudha, S.L. Sharma, T.K. Maity. Materials Letters, 157 (2015) 19–22.

[14] A. Bouhdjer, A. Attaf, H. Saidi, H. Bendjedidi, Y. Benkhetta, and I. Bouhaf. Journal of Semiconductors, Vol. 36, No. 8.

[15] A. Bouhdjer, H. Saidi, A. Attaf, M.S. Aida, Mohamed JlassI, I. Bouhaf, Y.Benkhetta, H. Bendjedidi, Optik,   127   (2016)   7319–7325.

[16] Y. Benkhetta, A. Attaf, H. Saidi, A. Bouhdjar, H. Benjdidi, I.B. Kherchachi,M. Nouadji, N. Lehraki, Optik,   127   (2016)   3005–3008.

[17] A. Amarala, b, P. Brogueirab, C. Nunes de Carvalhoa, c, G. Lavareda, Surface and Coatings Technology, 125 (2000) 151–156

[18] Zhaohui Qiao, Dieter Mergel, Thin Solid Films, 484 (2005) 146 – 153.

[19] I. B. Kherchachi, A. Attaf, H. Saidi, A. Bouhdjer, H. Bendjedidi, Y. Benkhetta, and R. Azizi, Journal of Semiconductors, Vol. 37, No. 3.

[20] V.G. Rajeshmon, M.R. Rajesh Menon, C. Sudha Kartha, K.P. Vijayakumar, Journal of Analytical and Applied Pyrolysis 110 (2014) 448–454.

[21] N.G. Pramod,S.N. Pandey, P.P. Sahay .Ceramics International 38 (2012) 4151– 4158

[22] Kazuhiro Kato, Hideo Omoto, Takao Tomioka. Thin Solid Films 520 (2011) 110–116.

[23] A. Moses EzhilRaja, K.C. Lalithambika. Physica B 403 (2007) 544.

[24] Imen Bouhaf Kherchachi, Abdallah Attaf, Hanane Saidi, Adel bouhdjar, Hamza bendjdidi,Benkhetta Youcef and Rahil Azizi, Main Group Chemistry, 15 (2016) 231–242

[25] C. Guillén, J. Herrero, Vacuum 84 (2010) 924–929.

[26] N. Bouhssira, S. Abed, E. Tomasella, J. Cellier, A. Mosbah, M.S. Aida, M. Jacquet, Appl. Surf. Sci. 252 (2006) 5594–5597

[27] M. Subramanian, M. Tanemura, T. Hihara, T. Jimbo, Chem. Phys. Lett. 487 (2010) 97–101.

[28] A. Jain, P. Sagar, R.M. Mehra, Solid-State Electron. 50 (2006) 1420–1424.