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Physical Properties of Undoped and Doped ZnO Thin Films Prepared by Spray Pyrolysis for Photovoltaic Application

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Abstract: Al doped ZnO thin films were synthesized by ultrasonic spray pyrolysis technique. The concentration ratio of [Al]/[Zn] was varied from 1 to 5 %mol in the starting solution, in order to investigate the effect of doping ratio on the structural optical and electrical films properties. The films thicknesse was found in the range 900-1100 nm. X-ray diffraction analysis indicates that the films doped with Al using aluminium chloride ($AlCl_3.H_2O$) has a textured structure with (002) preferred orientation, .The grain size increases with Al concentration from 28.91 to 59.11 nm. The average optical transmittance of all films, regardless the doping concentration, was higher than 80% in the visible range, the values of optical direct band gap and disorder energy(Urbach energy) were deduced from the absorption spectra . From the electrical measurements carried by two probes technique, we concluded that the electrical conductivity of doped ZnO layers higher than that of undoped layers.

Keywords: Spray pyrolysis, Thin films, Urbach energy, XRD, Zinc oxide.

1. INTRODUCTION

Zinc oxide is the most promising transparent conductive oxide (TCO) for its application as front electrode in photovoltaic technology based on amorphous and microcrystalline silicon solar cells [1]. It is characterised by low resistivity and high transparency in the visible wavelength range, The resistivity value of ZnO can be tuned between 10^{-4} and $10^{-9}\Omega$cm by doping or controlling the preparation parameters [2]. intrinsic and doped ZnO materials have been used as laser diodes [3], solar cells [4,5], sensors [6]catalysts for liquid phase hydrogenation [7]

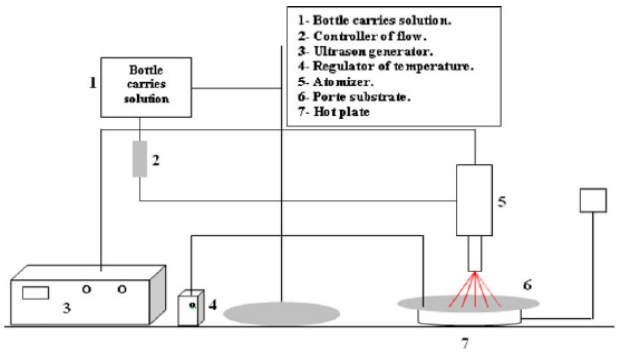
transparent electrodes [8], surface acoustic wave (SAW), and acoustic-optic devices [9]ZnO thin films have been deposited by various techniques, such as thermal evaporation [10, 11], sputtering [12, 13], chemical vapor deposition [14,15], sol–gel [16, 17], pulsed laser deposition [18,19], electrochemical deposition [20,21] etc.… In addition to these techniques, spray pyrolysis method has received much attention because of its simplicity and cost-effectiveness as it does not require sophisticated vacuum apparatus. By this technique, ZnO thin films can be prepared from various spray solution precursor such as zinc nitrate [22], or zinc chloride [23], or zinc acetate [24,25]. The aim of this work is to study

theinfluence of doping ratio on structural, optical and electrical properties of undopedZnO and Al doped ZnOthin films prepared by ultrasonic spray pyrolysis technique.

2. EXPERIMENTAL DETAILS

ZnO thin films were prepared by ultrasonic spray pyrolysis using a starting solution of zinc acetate dehydrate (Zn(CH3COO)2.2H2O) with 0.02 M concentrations diluted in methanol (CH3OH), Aluminum chloride salt used as dopant source is added with a small amount in the starting solution. The doping level is varied by changing the weight ratio [Al/Zn], in the solution, from 0 to 5 wt%. Glass and monocrystalline silicon substrates were used, the substrate temperature was fixed at 350 °C. The distance between the substrates and the spray gun nozzle was fixed at 5 cm. A schematic drawn of the spray pyrolysis apparatus for the synthesis of the ZAO particles is depicted in Fig (1).
The structural properties of the films were studied by X-Ray Diffraction (XRD), using Cu-kα radiation of wavelength k = 0.15418 nm. The size D of the crystallites was calculated from the Scherer's formula [26].The thickness was determined from ellipsometric measurements performed on ZnO films deposited onto the Si substrates. The transmittance of the layers deposited on glass was measured in the UV–Visible region using the Shimadzu 3101PC double beam

spectrophotometer. The gap energy Eg of the ZnO films, deposited on glass substrates, was determined from Tauc formula [27].



Fig(1) Schematic diagram of the used spraying system

The absorption coefficient α(hγ), in the spectral region of the light's absorption, was deduced from the Beer–Lambert law [28]. The

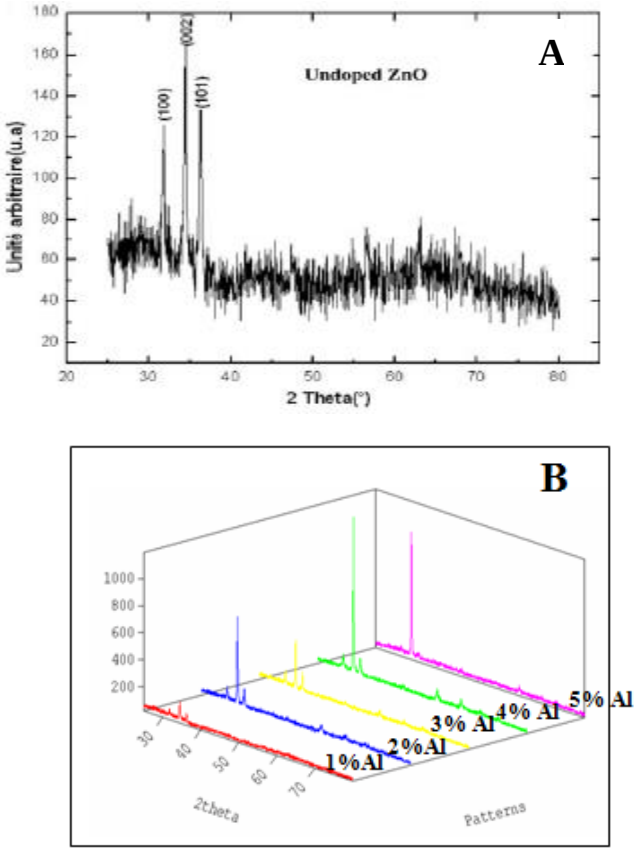
Urbach tail was determined from the variation of log(λ) with the incident photon energy hγ [29]. The electrical properties of the layers were determined using the I(V) characteristics by the two probes technique in a coplanar structure with two evaporated gold electrodes.

3. RESULTS AND DISCUSSION

3.1 Structural characterization

We employed the X-ray diffraction technique to get a first impression of the main crystalline phases and the possible orientation of crystalline in the films prepared at optimum conditions. The films prepared on glass substrates had good adhesion to the substrate. No chipping or delaminating were observed. Figure (2) shows X-ray diffractograms of the spray pyrolysis synthesized undoped (Fig(2a)) and Al doped ZnO thin films (Fig(2b)). This analysis reveals the existence of a ZnO single-phase with a hexagonal wurtzite structure. No peak originating from other compounds is detected beside those from ZnO, S.A.Studenikin and al [30] and A.S. Riad and al. [31]. report that it would be necessary to deposit the ZnO layers by spray pyrolysis technique at temperatures higher than 180 °C (in our case 350°C ¶), to ensure the total decomposition of the precursors and then to complete the pyrolysis reaction.

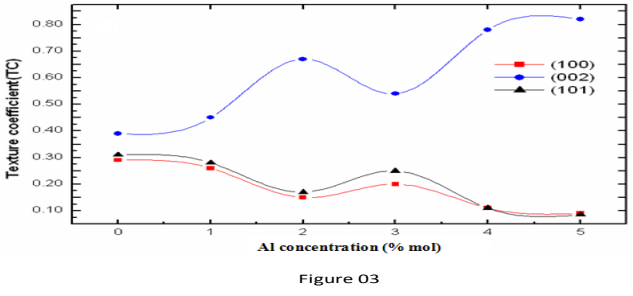
The diffraction patterns show the deposited ZAO films exhibit a hexagonal structure, which indicates that Al^{3+} ions substituting Zn^{2+} ions did not change the hexagonal wurtzite structure in Al-doped ZnO films. It is generally reported that ZnO thin films have a polycrystalline wurtzite structure regardless the deposition technique, with the (002) as a preferential direction. [32-35] The latter corresponds to the growth along the direction c normal to the substrate surface. This preferential orientation is believed to be due to the low energy of this plane [36].



Fig(2) A: XRD spectrum of undopedZnO thin film, B: XRD spectrum of Al doped ZnO films.

The texture coefficient is calculated to describe the preferential orientation using the following expression [37]:

$$TC_{hkl} = I_{(hkl)} / [\, I_{(100)} + I_{(002)} + I_{(101)} \,] \qquad (1)$$



Fig(3)Variation of texture coefficient TC(1 0 0) ,TC(0 0 2) and TC(1 0 1) of ZAO films

It was observed that the undopedZnO film had a preferred (0 0 2) orientation. However, the intensity of the (0 0 2) peak increases by increasing the doping concentration. In the case of ZAO layers, the value of the texture coefficient TC (002) (figure (3)) is maximum for the high doping concentrations (5% Al), it is equal to 0.90. We conclude that the incorporation of aluminium controls the arrangement of the atoms in the

ZnOmatrix.¶This result is confirmed by the increase in the size the grain size with the doping ratio. This improvement is possible due to the difference in size between the aluminium ion and the zinc ion radiuses (rZn2 + > rAl3 +).¶

XRD patterns was used to calculate the grain size (d) of the crystallites with the help of Scherrer's relation

$$D \equiv \frac{0.9}{\beta.Cos\theta_{hkl}}\lambda \qquad (2)$$

where λ is the X-ray wavelength (0.15418 nm), θ is the Bragg angle expressed in radians, and β is the full width at half-maximum (FWHM) of the most intense peak in our case is (002), K is the constant which depends on the shape of the crystallite was taken equal to 0.9. The full width at half-maximum and grain size variation with Al concentration are shown in Fig(4)

The grains size of undopedZnO film is estimated equal to 18.86 nm.¶ This value is lower compared to the sizes of crystallites of ZAO layers; this result confirms the incorporation of (Al) doping in the matrix of Zinc oxide in substitutional or interstitial position.

¶In the case of doping, The grains size increases with the concentration of Al dopant. ¶This result can confirm that Aluminium strongly supports the crystalline growth.

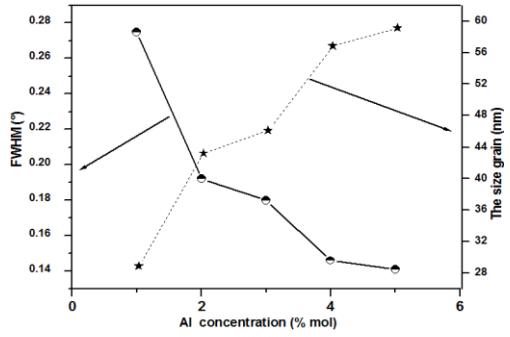


Fig (4)Variation of Crystallite size and full width at half-maximum (FWHM) with Al concentration.

The stress in our films was estimated from the observed shift, in the diffraction peak, between their position in recorded XRD spectra and in ASTM cards and by using the formula of Hoffmann [38].

$$\sigma = \left[2C_{13}\frac{(C_{11}+C_{12})C_{33}^{Couche}}{C_{13}}\right] \text{ eZZ} \qquad (3)$$

$$C_{33}^{Couche} \equiv \frac{0.99C_{33}^{Cristal}}{1-e_{ZZ}} \qquad (4)$$

where

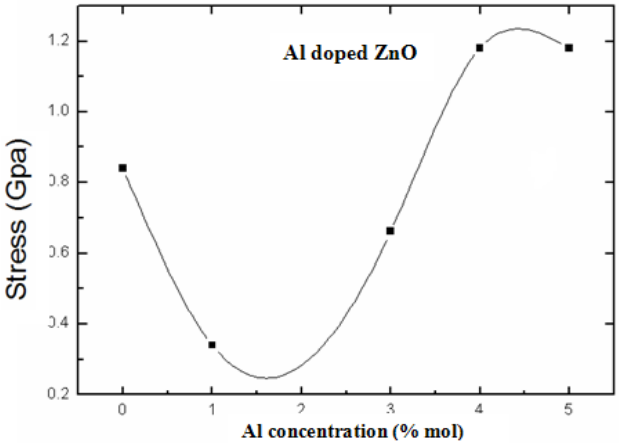
$$e_{zz} \equiv \frac{c_0 - c}{c_0} \qquad (5)$$

and

Cij are the elastic constants of ZnO given by the following values [39]:

C_{11} =209,7 GPa ; C_{12} =121,1 GPa;

C_{13} =105,1 GPa ; C_{33} =210,9 GPa:

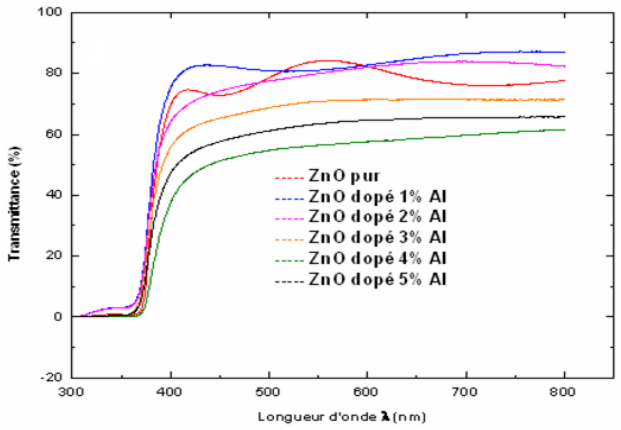


Fig(5)Stress of undopedZnO and ZAO thin films deposited by Spray pyrolysis.

The origin of the stress in undopedZnO thin films is due to the deposition technique and the temperature of the substrate. However, in the case of the ZAO films, it is due to the incorporation of Al atoms in the film network. As seen in Fig(5)With low concentration of Al the constraints decrease with doping ratio, this is due to the occupation of the substitutional sites by the Al ions knowing that (rZn2 + < rAl3 +).¶ On the other hand, the increase in the constraints starting from a certain percentage is interpreted by the saturation of the substitutional sites what obliges the aluminium ions to occupy of the interstitial sites.

3.2 Optical characterization

In Fig (6) we have reported the UV-VIS optical transmission spectra of ZnO and ZAO thin films deposited with spray technique. The obtained films are highly transparent in the visible range. Their transmission is ranged from 70 to 90%. This value is reported by several authors; this enables ZnO films the character of transparent material and justify its application as front windows in optoelectronic devices [40,41] . The presence of the interference fringes in spectra is due to the multiple reflections at the interfaces films/substrate and film/air. The presence of the fringes translates that our films are sufficiently thick and smooth light scattering at the film surface and enhances the light transmission.



Fig(6)Optical transmission spectra of ZAO films .

All the films exhibit a sharp absorption edge below 400 nm, this is due to the onset of fundamental absorption of ZnO . From these spectra, one can inferred that the doping (Al) concentration slightly affects the transmittance of the films.

In Fig (7) we have reported the variation of the optical gap of undoped and doped ZnO thin films. The optical gap was estimated from the well used linear extrapolation of the variation of $(\alpha h\gamma)2$ as function of the incident photon energy $h\gamma$ where α is the coefficient absorption calculated from the transmission spectra (calculated as (1/d) Ln (1/T) ; d: thickness film, and T: optical transmittance) and $h\gamma$ is the photon energy. This estimation procedure is widely used for direct transition semiconductors, which obeys the following relation [42]:

$(\alpha h\upsilon)2 \sim (h\upsilon - Eg)$ (6)

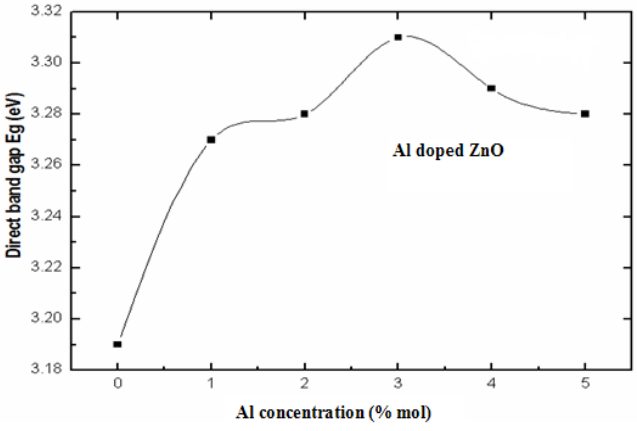


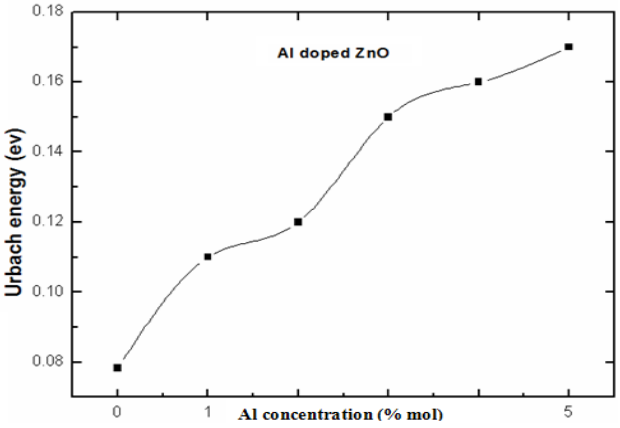
Fig (7)Evolution of the optical gap of ZAO films with Al concentration.

With low concentration of the doping agent, the value of Eg increases by 3.19 eV up to 3.31 eV. ¶This variation is interpreted by the Burstein-Moss effect [43,44].,the gap reduction in the 4%-5 % interval is the result of the occupation of the interstitial sites by the the Al doping atoms, since the latter, represent the principal native donors in the ZnO films [45]. The interpretation of the variation of the gap with the Al doping level corroborate well with the statement in the last section , where it is mentioned that with 3 % of doping ratio , Al atoms occupy the interstitial sites in the matrix of Zinc oxide ¶.¶The latter is compatible with the interpretation of the reduction in transmittance to strong percentage of aluminium.

In Fig(8)is shows the evolution of Urbach energy (Eu) of ZAO films with doping ratio, the Eu reflects the disorder in the film network; it is related to the absorption coefficient by the following expression [46]:

$\alpha = \alpha 0 \exp(h\upsilon / Eu)$ (7)

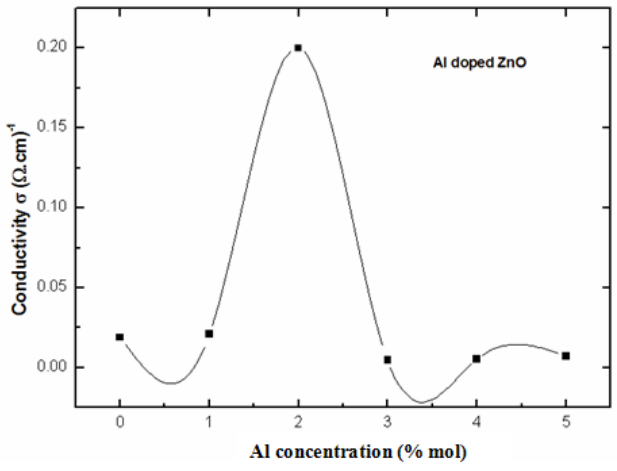
where $\alpha 0$ is a constant; Eu is the Urbach energy. The calculated Urbach energy in our films varies from 78 to 170 meV .These results are comparable with Bourgine et al ones [28].



Fig(8)Evolution of Urbach energy of ZAO films with Al concentration.

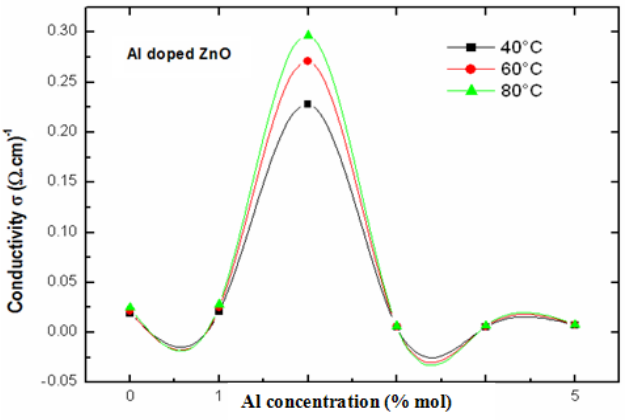
Given the minimal value of low dopant concentration reaffirms the stability of the films and the increase of Eu with the doping ratio is very logical and also ensures the incorporation of Al atoms in ZnO matrix, this increase is found by B.N.Pawar et al [45]. and interpreted by the donor levels of interstitial zinc atoms [47].

3.3 *Electrical characterization*

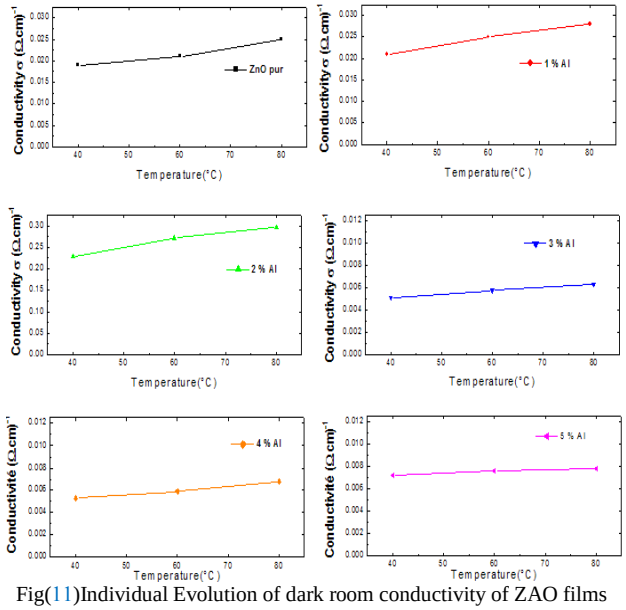


Fig(9)Evolution of dark room conductivity of ZAO films with Al concentration.

Fig (9), shows the evolution of dark conductivity measured at room temperature of ZAO films with Al concentration. As can be seen the conductivity enhances with the increase in of Al doping level and reached its maximal value of 0.2 (Ωcm)-1 at 2% of Aluminium concentration, then it decreases with further increase in the doping level. The enhancement in the conductivity with the increase in the Al concentration can be interpreted by the increase in the number of the free charge carriers (electrons) coming from the ions Al+3 donors incorporated in the substitutional site [48]. However, the reduction in the conductivity with further increase in Al concentration is¶ caused by the segregation of excess Al atoms in the grain boundaries. It is worth noting that the Al atoms segregation in the grain boundaries inhibits their electrical activity as doping atoms. The same behaviour of the reduction in the dark conductivity after a critical doping level is reported by many authors with different doping atoms [49, 50].



Fig(10)Evolution of dark room conductivity of ZAO films with measure temperature



Fig(11)Individual Evolution of dark room conductivity of ZAO films with measure temperature

In Figs(10)and (11), we have reported the results of dark conductivity measurement at different temperatures above room temperature. As seen, the conductivity variation exhibits an Arrhenius behavior, this is a normal behavior of the semiconductors. According to the literature, this effect is interpreted by the thermal activation energy. This energy causes the ionization which yields to the increase in the free electrons concentration in the conduction band.

4 CONCLUSIONS

ZnO and Al-doped ZnO (ZAO) films were prepared by a home-made spray pyrolysis technique, It is shown that the chemical spray technique is as efficient and reliable as another sophisticated growth technique X-ray diffraction analysis shows that the sprayed ZAO films are polycrystalline with a hexagonal structure and all films have (002) texture but the (002) peak of ZAO films shifts to different angles than ZnO films.

All films exhibit a transmittance higher than 80 % in the visible region and a sharp fundamental absorption edge. But the optical transmittance of ZAO films is slightly smaller than that of ZnO films , The optical direct band gap and Urbach energy of films increased from 3.19 to 3.31 eV and 78 to 170 meV.

Al-doped films had a lower resistivity than undoped films. For doped ZnO films, the 2% doped film deposited at 350 ◦C had a lower resistivity than any other film, the results presented are not the most extensive reported, we considered that these films are potentially attractive to be applied as transparent conductors in thin film solar cells.

REFERENCES

[1] J. Meier, J. Spitznagel, U. Kroll, C. Bucher, S. Fay, T. Moriarty, A. Shah, Thin Solid Films 451–452 (2004) 518.

[2] B. Dinghua , H. Gu, K. Anxiang , Thin Solid Films 312 (1998) 37.

[3] C. Liu, J.A. Zapien, Y. Yao, X. Meng, C.S. Lee, S. Fan, Y. Lifshitz, S.T. Lee, Adv. Mater. 15 (2003) 838−841.

[4] Z.S. Wang, C.H. Huang, Y.Y. Huang, Y.J. Hou, P.H. Xie, B.W. Zhang, H.M. Cheng, Chem. Mater. 13 (2001) 678−682.

[5] K. Westermark, H. Rensmo, T.A.C Lees, J.G. Vos, H.T. Siegbahn, J. Phys. Chem. B 106 (2002) 10108−10113.

[6] H.M. Lin, S.J. Tzeng, P.J. Hsiau, W.L. Tsai, Nanostruct. Mater. 10 (1998) 465−468.

[7] G.M. Hamminga, G. Mul, J.A. Moulijn, Chem. Eng. Sci. 59 (2004) 5479−5485.

[8] S. Jager, B. Szyszka, J. Szczyrbowski, G. Brauer, Surf. Coat. Technol. 98 (1998) 1304 .

[9] Y. Yoshino, T. Makino, Y. Katayama, T. Hata, Vacuum 59 (2000) 538.

[10] J. Ma, F. Ji, D. Zhang, H. Ma, S. Li, Thin Solid Films 357, 98 (1999)

[11] S.A. Aly, N.Z. El Sayed, M.A. Kaid, Vacuum 61, 1 (2001)

[12] T. Minami, Y. Ohtani, T. Miyata, T. Kuboi, J. Vac. Sci. Technol. A 25, 1172 (2007)

[13] B.Y. Oh, M.C. Jeong, J.M. Myoung, Appl. Surf. Sci. 253, 7157 (2007)

[14] J.G. Lu, T. Kawaharamura, H. Nishinaka, Y. Kamada, T. Ohshima, S. Fujita, J. Cryst. Growth 299, 1 (2007)

[15] A. Martın, J.P. Espinos, A. Justo, J.P. Holgado, F. Yubero, A.R.G. Elipe, Surf. Coat. Technol. 151, 289 (2002)
[16] V. Musat, B. Teixeira, E. Fortunato, R.C.C. Monteiro, Thin Solid Films 502, 219 (2006)
[17] H.M. Zhou, D.Q. Yi, Z.M. Yu, L.R. Xiao, J. Li, Thin Solid Films 515, 6909 (2007)
[18] Y. Liu, J. Lian, Appl. Surf. Sci. 253, 3727 (2007)
[19] Y. Liu, L. Zhao, J. Lian, Vacuum 81, 18 (2006)
[20] N. Fathy, M. Ichimura, J. Cryst. Growth 294, 191 (2006)
[21] Y. Takashige, T. Nebiki, T. Narusawa, Solid State Phenom. 124–126, 135 (2007)
[22] P. Singh, A. Kumar, Deepak, D. Kaur, J. Cryst. Growth 306, 303 (2007)
[23] C. Messaoudi, D. Sayan, M.A. Lefdil, Phys. Stat. Sol. (a) 151, 93 (1995)
[24] M. Krunks, E. Mellikov, Thin Solid Films 270, 33 (1995)
[25] M.A. Kaid, A. Ashour, Appl. Surf. Sci. 253, 3029–3033 (2007)
[26] P. Scherrers, Gott. Nachr. 2, 98 (1918)
[27] J.J. Tauc, Amorphous and Liquid Semiconductor (Plenum, New York, 1976)
[28] A. Bougrine, A. El Hichou, M. Addou, J. Ebothe´, A. Kachouna, M. Troyon, Mater. Chem. Phys. 80, 438–445 (2003)
[29] M.V. Kurik, Phys. Status solidi (a) 8–9 (1971)
[30] S.A. Studenikin, N. Golego, M. Cocivera, J. Appl. Phys. 83 (1998) 2104.
[31] A.S. Riad, S.A. Mahmoud, A.A. Ibraim, Physica B 296 (2001) 319.
[32] B.J. Lokhand,P.S. Patil and M.D. Uplane, Mater.Lett.57(200)573
[33] J.Mass, P.Bhattacharya and R.S. Katiyar, Mater.Sci. and Eng.B103(2003)9.
[34] R.Ondo-Ndong,F. Pascal-Delannoy,A. Boyer,A.Giani and A. Foucaran,Mater.Sci. Eng.B97(2003)68.
[35] Y. Nakanishi, A. Miyake,H. Kominami,T.aoki, Y. Hatanaka and G. Shimaoka, Appl.Surf.Sci.142(1999)233.
[36] S.Y. Shu, W. Water and J.T. Liaw, J.Eur.Ceram.Soc.23(2003)1593.
[37] X. Jiwei, Z. Liangying, Y. Xi, Ceram.Lnt. 26, 883 (2000)
[38] K.T. Ramakrisha Reddy, T.B.S. Reddy, I. Forbes, R.W. Miles, Surf. Coat. Technol. 151–152, 110–113 (2002)
[39] T.B. Bateman, Appl. Phys. 33(11), 3309 (1962)
[40] R. Scheer, T. Walter, H.W. Schock, M.L. Fearheiley and H.J. Lewerenz, Appl. Phys Lett.63(1993)3294.
[41] J.Hu and R.G. Gordon, J. Appl. Phys. 71(1992)880.
[42] P. Sreedhara Reddy, et al., Solid State Commun. 12 (1991) 899.
[43] T.S. Moss, Proc. Phys. Soc. Lond. B67 (1954) 775
[44] E. Burstein; Phys. Rev. 93 (1954) 632.
[45] B.N. Pawar, S.R. Jadkar, M.G. Takwal. Solar Energy Materials & solar cell.
[46] M.V. Kurik, Phys. Status Solidi (a) 8, 9 (1971)
[47] J. Song, I-Jun Park and Kyung-HoonYoon,Journal of the Korean Physical Society (1996) pp. 219-224.
[48] S.S. Lin, J.L. Hung, P. Sajgalik, Surf. Coat. Technol. 185, 254 (2004) J Mater Sci: Mater Electron
[49] D.J. Goyal, C. Agashe, M.G. Takwale, V.G. Bhide, J. Mater. Res. 8, 1052 (1993)
[50] B. Choi, H.B. Im, Thin Solid Films 193&194, 712 (1990)

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