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Physical properties of V_2O_5 sprayed films

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Thin films of V_2O_5 have been deposited by spray pyrolysis technique on glasses substrate with different solution concentrations (molarities) at temperature equal 300 °C. The structural, electrical and optical characteristics of the V_2O_5 films were examined by X-ray diffraction (XRD), Van der Pauw technique and double-beam spectrophotometry. X-ray diffraction reveals that the films, which have been deposited at T_S = 300 °C with different solution molarities are polycrystalline in nature having orthorhombic type crystal structure and a preferential orientation along <001> direction. The electrical resistivity at room temperature is decreased as the solution molarity increased. Transmission measurements showed that the transmission decreased as the molarity increased. The dependence of the refractive index, n, and extinction coefficient, k, on the wavelength for a sprayed film is also reported. Optical bandgap, Eg, has been reported for the V_2O_5 films and is equal to 2.50 eV.

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1. Introduction

The vanadium oxygen system (V_2O_5 and VO_2) has been widely studied. Indeed the system shows metal-semiconductor transitions, which imply an abrupt change in their optical and electrical properties. For example, VO_2 exhibits a change in electrical resistivity in the order of 10^5 Ω cm over a temperature change of 0.1 at 68 °C in a single crystal [1]. It is why this oxide is used in thermal sensing and switching. V_2O_5, made object of several theoretical and applied studies, due to their industrial importance for many technological applications, such as heterogeneous catalyst [1]. V_2O_5 plays also the role of active electrode in a rechargeable lithium battery [2], indeed high electrochemical activity, high stability and ease of thin film formation by numerous deposition techniques led to its use as a highly promising intercalation material in solid state micro-battery applications. However, stoichiometric vanadium oxide films are difficult to obtained [3].

The V_2O_5 thin film was prepared by different techniques such as RF-sputtering [4, 5], dc-magnetron sputtering [6] flash evaporation [7, 8], sol-gel technique [9] and pulsed laser deposition [10]. However, techniques with a relatively low cost and large area as the spray pyrolysis have been used to prepare this material.

In this work, the preparation of V_2O_5 by spray pyrolysis technique was investigated at different concentrations of spray solution. XRD technique is used to determine the film structure. Also, the electrical and optical properties of films are reported.

2. Experimental details

The spray pyrolysis is a cheap and simple technique based on different deposition process. In this technique, the V_2O_5 thin films were obtained on glass substrates by spraying a amonem meta vanadat solution from 0.1 to 0.5 M. Deionized water was used as solvent. Slides of glass microscope ultrasonically cleaned were used as the substrates to support the V_2O_5 films. The substrate temperature was fixed at 300 °C and controlled through a thermocouple (Chrome-Nickel) and controlled by 871 digital Kethley thermometer connected to the heater. Compressed air of pressure 6 N/cm^2 has been used as a carrier gas, the solution flow rate is 5 cm^3/min and spray nozzle to glass substrate distance of 25 cm. The schematic diagram of the apparatus we used for our sprayed process is shown in Fig.1, and has been described in references [11, 12].

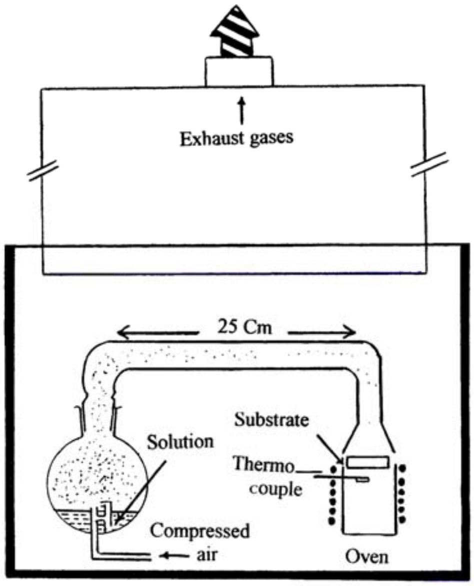

Fig. 1. Schematic diagram of the spraying pyrolysis process.

The crystal structure of the films was investigated by X-ray diffraction (XRD), and was performed in a JEOL JDX-60PA X-ray diffractometer using of CuKα radiation (1.5405 Å) and operating at 40 KV. The analysis was made with CuKα radiation in the range of 5° to 90° with slow scanning speed (2°/min) and step width of 0.02°, respectively. The films deposited on the glass substrates were used for the XRD analyses.

The electrical resistivity of the prepared films was measured under vacuum by the Van der Pauw's method [13] in conjunction with the corresponding correction tables [14]. The current is passing through the sample at a fixed voltage with a Keithley 616 electrometer. For the current measurement, thin film electrodes of aluminium were deposited on the surface of the V_2O_5 films. The electrodes were connected to copper wires using silver paste.

The optical parameters of the V_2O_5 films were calculated from the optical transmission and reflection data recorded in the wavelength range from 200 to 2500 nm using a UV/visible double beam spectrophotometer Shimadzu-3101PC.

3. Results and discussion

When the spraying the films at higher substrate temperature, three processes may take place, recovery, recrystallization, and grain growth at higher temperatures. During recovery, both macro and micro residual stresses are liable to decrease in magnitude. During recrystallization new grains are formed and residual stress is practically eliminated, while strength and hardness decrease [15], for this; we sprayed V_2O_5 at higher optimum substrate temperature (300 °C).

The surface of V_2O_5 thin film for 0.5 M of spray solution is rougher than the surface corresponding of the 0.1 M. This parameter is important for optical properties of materials [16] and plays a fundamental role in terms of charge transfer capability and cycle life [17]. It depends of the deposition method and post-deposition temperature treatment.

Fig. 2 shows the X-ray diffraction (XRD) patterns for samples prepared on the glass substrate at Ts = 250 and 300 °C with different solution molarities. The films were amorphous at substrate temperature equal 250 °C, but higher this value (300 °C) the films are crystalline. For as-prepared samples (Fig. 2), the lines are attributed to the (200), (001) and (002) lattice planes and characteristics of V_2O_5 [18] as indexed in comparing with the JPCDS cards (no. 09-0387) of X-ray powder. The XRD spectrum exhibits an intense (001) peak indicating preferential orientation in the <001> direction, this result revealed that the structure is such that the crystallographic c-axis is perpendicular to the substrate surface and the crystalline orientation is favoured. Similar results were obtained in previous works [19, 20].

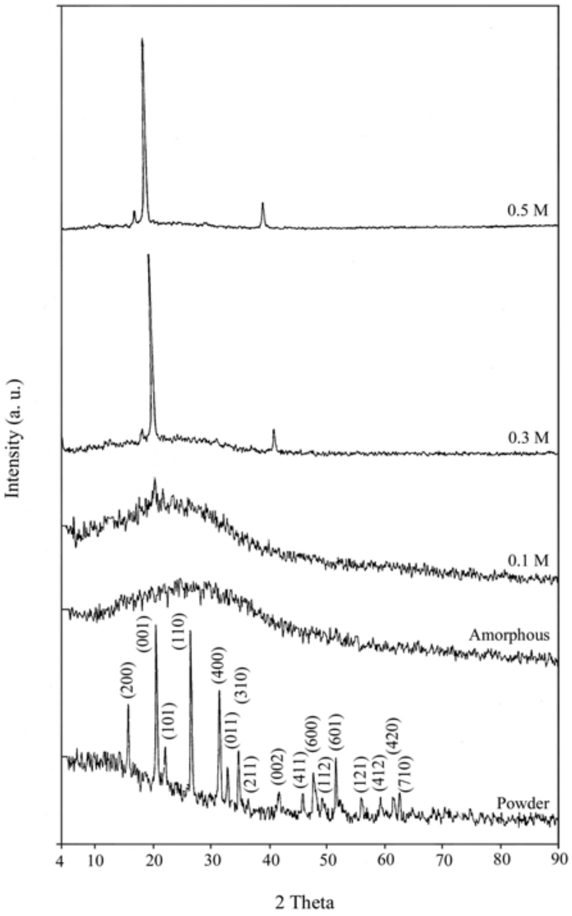

Fig. 2. XRD spectra of V_2O_5 powder and thin films sprayed with different solution molarities. (amorphous at Ts = 250 °C - crystalline at Ts = 300 °C, t = 200 nm)

When the molarity increases, the preferential orientation ($I_{(001)}/I_{(002)}$) increased as shown in Figure 3, indicating coexistence of <001> and <002> textures. As shown from the previous Figure (Fig. 2), the appearance of the peaks is attributed to recovery and recrystallization of the films due to higher temperature of the substrate temperature (Ts = 300 °C). Moreover, the produced data for all films prepared at different molarities of spray solution showed a good agreement with the data of V_2O_5 powder file (JCPDS data number 09-0387) which corresponding to the orthorhombic crystalline structure. Indeed, the typical peaks of the single polycrystalline phase in V_2O_5 films appear in XRD spectra. Also the colour of as-prepared films not having undergone treatment is pale yellow, which could indicate that vanadium was incorporated as V^{5+} in V_2O_5 lattice (it is known that V^{4+} presents a brown or black colour) [21].

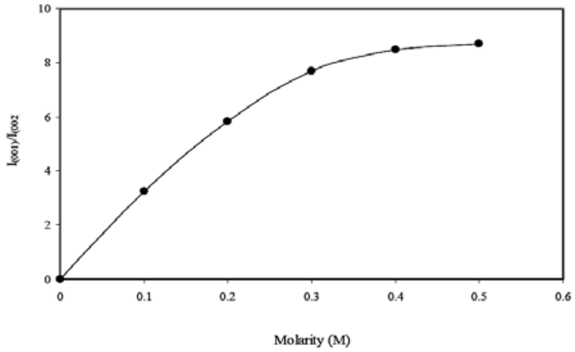

Fig. 3. The variation of intensity ratio of the (0 0 1) and (0 0 2) of V_2O_5 thin films as a function of solution molarities. (Ts = 300 ^oC, t = 200 nm, molarity = 0,1 M).

It is observed that the crystallinity of the film increases with increasing the solution molarity. The increase in the intensity of the peaks may be attributed to either grain growth associated with larger thickness or increase in the degree of crystallinity by increasing the solution molarity or both. For evaluation of lattice parameters we have used the relation:

$$d_{hkl} = 1 / (h^2/a^2 + k^2/b^2 + l^2/c^2)^{½} \qquad (1)$$

So a, b and c are the orthorhombic lattice parameters. In this relation (h, k, l) are miller indices of reflector plans appearing on the diffraction spectra and d_{hkl} their inter-reticular distances. The obtained values of lattice parameters are equal, a = 0.986 nm, b = 0.3634 nm and c = 0.4367 nm, the results are comparable with the other results [22, 23].

The current - voltage (I-V) characteristics of V_2O_5 films are ohmic at room temperature up to a large applied field. The hot-point probe method showed that all the investigated V_2O_5 films were n-type semiconductors. The room temperature electrical resistivity of V_2O_5 films was studied by four-probe technique of Van der Pauw method

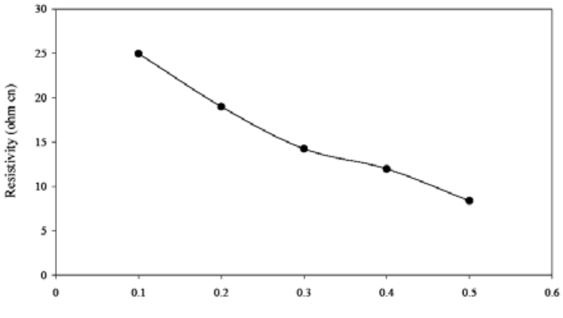

Fig. 4. Variation of electrical resistivity with different solution molarity for V_2O_5 thin films. (Ts = 300 ^oC, t = 200 nm, molarity = 0,1 M).

Fig. 4 shows the resistivity vs. solution molarity for the prepared V_2O_5 films. It is observed that, the electrical resistivity tend to decrease with increasing the solution molarity [22]. This behavior indicates that V_2O_5 is a good material for making the resistors. The lower resistivity with the solution molarity may be attributed to the removal of water molecules leading to a decrease in the (hkl) d-spacing [24]. Also, oxygen vacancies are believed to be the source of conduction electrons. Since the electrical transport depends upon the vanadium present in the V^{4+} state and the transport mechanism involves the exchange of electrons between V^{4+} and V^{5+} ions [25]. The variable electrical transport properties of V_2O_5 thin films is very interesting, since it enables to determine many parameters such as the Seebeck coefficient, activation energy, band structure and the temperature coefficient of resistance.

The spectral variations of transmissions for the V_2O_5 films sprayed onto glass substrates at Ts = 300 ^oC and different solution molarities were measured in the wavelength range 200 - 2500 nm using a Shimadzu-3101PC Spectrophotometer and are shown in Fig. 5. It was observed that, the surface of the films prepared at solution molarity from 0.2 to 0.5 M appears to be rougher due to the increase of scattered light and decrease of the film transmission and specular reflection. From Fig. 5, it is clear that as the solution molarity decreases, the film transmission increases all over the whole spectral region. For a molarity equal to 0.1 M, the spectra show a higher optical transmission value reaches 80%. Also, the absorption edge is shifted toward higher energy by decreasing solution.

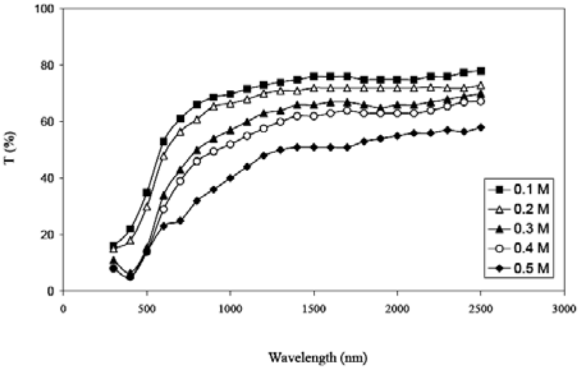

Fig. 5. Optical transmittance spectra of sprayed V_2O_5 thin films formed at different solutionmolarities. (Ts = 300 ^oC, t = 200 nm).

A method for the determination of the refractive (n) and absorption (k) indices of thin absorbing films on transparent substrates (with refractive index n) were reported earlier by Denton et. al. [26]. It requires measurement, at normal incidence, of the reflectance (R) and the transmittance (T) from a film on the substrate as a function of wavelength (λ). Then, the refractive indices (n) were determined from the reflectance (R) data using [27]:

$$R = [(n-1)^2] / [(n+1)^2] \quad (2)$$

As shown in Fig. 6, the refractive indices of the films decrease as the wavelength increases. The obtained results show that the refractive index decreases from 2.7 to 2.0 over the spectral range from 500 until 800 nm, and then become nearly constant with increasing wavelength, but decreases again at higher wavelength (2000 nm). Also, the maximum value of refractive index is observed at short wavelengths (λ = 500 nm), which is good agreement with the data obtained by others [28, 29] for like phase.

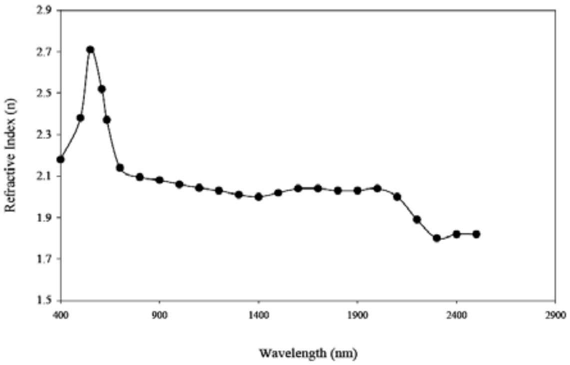

Fig. 6. Variation of the refractive index (n) with wavelength of sprayed V_2O_5 thin films. (Ts = 300 °C, t = 200 nm, molarity = 0,1 M).

The absorption coefficient, α, and the extinction coefficient (absorption index), k, were obtained from the transmittance, T, and reflectance, R, using the approximate formula [30]:

$$T = (1-R)^2 \exp(-\alpha t)/[1-R^2 \exp(-2\alpha t)] \quad (3)$$

where t is the thickness of the film and α is related to the extinction coefficient by:

$$\alpha = 4\pi k/\lambda \quad (4)$$

Fig. 7 shows the variation in k, as a function of the wavelength. The values of k are attributed to the fundamental band gap and the very low transmittance at short wavelength. The information, which used in the calculations, is mainly obtained from reflectance so that surface effects tend to dominate [29]. The variation of the optical constant of the films can be correlated with their structural characteristic [31], such as the improvement of stoichiometry [32], the increase in grain size [33] and the decrease in micro strain [31]. This behavior of the refractive index (n) and absorption constant (k) with wavelength is in agreements with studies reported by Akl [22] and Kaid [34].

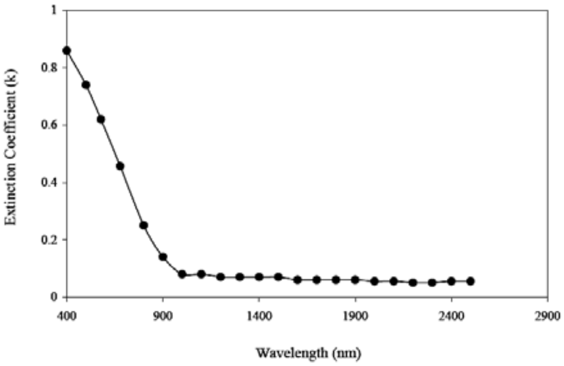

Fig. 7. Variation in absorption index with wavelength for sprayed V_2O_5 films. (Ts = 300 °C, t = 200 nm, molarity = 0,1 M).

The fundamental absorption edge of semiconductors corresponds to the threshold for charge transitions between the highest nearly filled band and the lowest nearly empty band. The absorption is very small for photon energy much less than the energy gap and increases significantly for higher photon energies. The inter-band absorption theory shows that, the absorption coefficient near the threshold versus incident energy, is given by the following relation [35]

$$(\alpha h\nu) = A (h\nu - Eg)^n \quad (5)$$

where A is the probability parameter for the transition and Eg the optical gap energy. For allowed direct transitions the coefficient n is equal to 1/2 and for indirect allowed transitions n = 2. Generally, for crystalline films, the above relationship is well obeyed, provided that n = 1/2**.** The curves $(\alpha h\nu)^2$ for allowed direct transition presents evident linearity, this seems to suggest that V_2O_5 has a direct gap. The value Eg corresponding to direct band gap transitions were calculated via the $(\alpha h\nu)^2$ versus hν, using the formula:

$$(\alpha h\nu)^2 = A (h\nu - Eg) \quad (6)$$

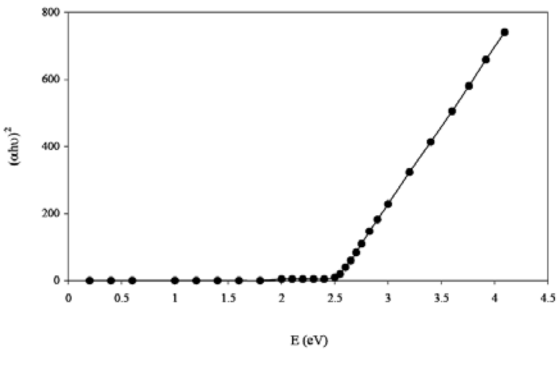

Fig. 8. Variation of $(\alpha h\nu)^2$ with photon energy of sprayed V_2O_5 films. (Ts = 300 °C, t = 200 nm, molarity = 0,1 M).

As shown in Fig. 8, the extrapolation of the linear part of the curve $(\alpha h\nu)^2$ crosses the energy axis at Eg. The obtained value of direct gaps for spray pyrolysed V_2O_5 polycrystalline thin films is equal to 2.50 eV. This factor confirms that these films may be semiconductors as described in the literature [36]. However, the obtained value of direct transition agrees with the values reported by several authors [37-41] for crystalline V_2O_5 thin film.

4. Conclusion

Polycrystalline V_2O_5 thin films with different solution molarity have been prepared by spray pyrolysis technique at substrate temperature of 300 ^oC. X-ray diffraction analysis shows that the sprayed V_2O_5 films are polycrystalline texture with orthorhombic structure and a preferential orientation along <001> direction. XRD results confirm the crystallinity of the films and the nature of their phases. V_2O_5 films prepared by spray pyrolysis technique behaved as n-type semiconductors. Films grown at different molarities showed an electrical resistivity in the range of $(0.8 – 2.5) \times 10^1$ Ω cm. The results show that the resistivity decreases as the molarity increases.

The optical investigations based on the spectrophotometric characteristics have confirmed that the V_2O_5 films sprayed on glass show low transparency. With increase in the solution molarity, transmittance decrease was observed. The optical parameters (n and k) have been calculated. The dependence of the refractive index, n, and extinction coefficient, k, on the wavelength for a sprayed film is also reported. The V_2O_5 films exhibited a direct transition and the optical energy gap (Eg) value was calculated to be 2.50 eV.

References

[1] J. Haber, M. Witko, R. Tokarz, Appl. Catalysis A General, 157 (1997) 3.
[2] C. Julien, G.A. Nazri, in: Solids-State Batteries: Materials Design and Optimization, edited by Kluwer Academic Publishers, 1994.
[3] K.M. Park, S. Yi, S. Moon, S. Im, Optical Materials, **17**, 311 (2001).
[4] K. West, B. Zachau-Christiansen, T. Jacobsen, S. Skaarup, 6th Meeting on lithium Batteries, Munster, 1992, Extended Abst. TUE-11, p. 63.
[5] M. Benmoussa, E. Ibnouelghazi, A. Bennouna, E.L. Ameziane, Thin Solid Films, **265**, 22 (1995).
[6] M.G. Krishna, Y. Debauge, A.K. Bhattacharya, Thin Solid Films, **312**, 116 (1998).
[7] L. Murawski, C. Gledel, C. Sanchez, J. Livage, J.P. Audiers, J. Non-Cryst. Solids, 89 (1987) 98.
[8] L. Murawski, C. Sanchez, J. Livage, J.P. Audiers, J. Non-Cryst. Solids, **124**, 71 (1990).
[9] T. Yoshino, N. Baba, Y. Kouda, Jpn. J. Appl. Phys., **26**, 782 (1987).
[10] C. Julien, E. Haro-Poniatowski, M.A. Camacho-Lopez, L. Escobar-Alarcon, J. Jimenez-Jarquin, Mater. Sci. Eng., **B65**, 170 (1999).
[11] A. Ashour, Turk J Phys., **27**, 1 (2003).
[12] H. H. Afifi, S. A. Mahmoud and A. Ashour, Thin Solid Films, **263**, 248 (1995).
[13] L. J. Van der Pauw, Philos. Res. Rep. **13**, 1 (1958).
[14] A. A. Ramadan, R. D. Gould and A. Ashour, Thin Solid Films, **239**, 272 (1994).
[15] B.D. Culliry, Elements of X-ray Diffraction, Addison Wesley, London, 1978.
[16] H. Bach, D. Krause, Thin Films on Glass, Springer-Verlag, Berlin Heidelberg, 1997.
[17] C. Julien, E. Haro-Poniatowski, M. A. Camacho-Lopez, L. Escobar-Alarcon, J. Jimenez-Jarquin, Mater. Sci. Eng., **B65**, 170 (1999).
[18] P.V. Gel'd, S.I. Algamovskii, I.I. Matveenko, Russ. J. Inorg. Chem., **5**, 815 (1960).
[19] M.Benmoussa, E.Ibnouelghazi, A. Bennouna, E.L. Ameziane, Thin Solid Films, **265**, 22 (1995).
[20] M.Benmoussa, E.Ibnouelghazi, A. Bennouna, Y. Laaziz, E.L. Ameziane, Le vide **275**, 24 (1995).
[21] K. Melghit, S.P. Pillai, V.G. Kumar Das, J. Mater. Sci. Lett., **18,** 661 (1999).
[22] Alaa A. Akl, Applied Surface Science In Press, Available online 3 Feb. 2006.
[23] A. Bouzidi, N. Benramdane, A. Nakrela, C. Mathieu, B. Khelifa, R. Desfeux, A. Da Costa, Materials Science and Engineering, **B95**, 141 (2002)
[24] S. Krishnakumar, C.S. Menon, Phys. Stat. Solidi a, **153**, 439 (1996).
[25] C. Sanchez, J. Livage, J.P. Audier, A. Madi, J. Non-Cryst. Solids, **65**, 285 (1984).
[26] R.E. Denton, R.D. Campbell, S.G. Tomlin, J. Phys. D: Appl. Phys. **5**, 852 (1972).
[27] J. Gottesman and W. F. C. Ferguson, J. Opt. Soc. Am., **44**, 368 (1954).
[28] E. Masetti, F. Varsano, F. Decker, A. Krasilnikova, Electrochim. Acta, **46**, 2085 (2001).
[29] T. Rechardson, K. von Rottkay, J. Slack, F. Michalak, M. Rubin, Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, CA94720, USA.
[30] A. Ashour, H. H. Afifi and S. A. Mahmoud, Thin Solid Films, **248**, 253 (1994).
[31] A. Ashour, N. El-Kadry and S. A. Mahmoud, Vacuum, **46**, 1419 (1995).
[32] K. Yamaguchi, N. Nakayama, H. Matsumoto, S. Ikegami, Jpn. J. Appl. Phys., **16**, 1203 (1977).
[33] F. Tepehan and N. Ozer, Solar Energy Mater., Solar Cells, **30**, 353 (1993).
[34] M A Kaid, Physics Department, Faculty of Science, Minia university, Minia, EGYPT, private communication.
[35] P. Kireev, la physique des semiconducteurs, Mir ed., Moscou, 1975.
[36] C.V. Ramana, B.S. Naidu, O.M. Hussain, R. Pinto, J. Phys. D: Appl. Phys., **34**, L35 (2001).

[37] T. Maruyama, T. Kawaguchi, Thin Solid Films, **188,** 323 (1990).
[38] B. Yagoubi, C.A. Hogarth, J. Mater. Sci., **26**, 579 (1991).
[39] Z.S. El mandouh, M.S. Selim, Thin Solid Films, **371**, 259 (2000).
[40] C.V. Ramana, B.S. Naidu, O.M. Hussain, R. Pinto, J. Phys. D: Appl. Phys., **34**, L35 (2001).
[41] A. Bouzidi, N. Benramdane, A. Nakrela, C. Mathieu, B. Khelifa, R. Desfeux, A. Da Costa, Mater. Sci. Eng., **B95**, 141 (2002).

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