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Effect of annealing temperature on the structural and optical properties of SnO_2 thin films elaborated by sol-gel technique

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In this study, the influence of annealing temperature on the structural and optical properties of SnO_2 thin films was investigated. SnO_2 thin films were prepared by sol–gel deposition on glass substrates at room temperature and then annealed at different temperatures (300, 400 and 500°C) in air for two hours. The obtained films were characterized by Raman spectroscopy and UV–Vis spectrophotometry techniques. A single-phase rutile structure was revealed by Raman spectroscopy analysis. The optical measurements have shown that all the films have a high transparency (75-85%) in the visible spectral range, and the optical band gap increases from 3.68 to 3.89 eV with increasing annealing temperature.

Keywords: SnO_2 thin films, sol-gel, annealing, Raman spectroscopy, UV-Vis.

Вплив температури відпалу на структурні та оптичні властивості тонких плівок SnO_2, отриманих золь-гель методом. *M. Khechba, A. Hafdallah, A. Soualhia, F. Hanin*

Досліджено вплив температури відпалу на структурні та оптичні властивості тонких плівок SnO_2. Тонкі плівки SnO_2 готували методом золь-гель осадження на скляні підкладки при кімнатній температурі, а потім відпалювали при різних температурах (300, 400 і 500°C) на повітрі протягом двох годин. Отримані плівки були охарактеризовані методами раманівської спектроскопії та спектрофотометрії УФ у видимому діапазоні. Однофазну структуру рутилу було виявлено раманівським спектроскопічним аналізом. Оптичні вимірювання показали, що всі плівки мають високу прозорість (75-85%) у видимому діапазоні, а ширина забороненої зони збільшується з 3,68 до 3,89 еВ зі збільшенням температури відпалу.

1. Introduction

Thin films of materials with high optical transmittance and electrical conductivity have a lot of applications in advanced technologies [1]. Tin oxide (SnO_2) is one of these materials used in numerous applications in modern technologies, such as solar cells [2], conductive transparent electrode [3], transistors [4], varistors [5] and sensors [6]. It has a wide band gap (in the range of 3.5 – 4.0 eV [7]), a high transparency in the visible range (90%) and a high reflectivity in the infrared energy range [8]. SnO_2 crystallizes in the rutile structure with

the symmetry of the P4/nmm space group and has lattice constants a=4.738Å and c= 3.184Å [9–10].

The physicochemical properties of tin oxide thin films depend on the method and conditions of preparation [11–13]. A number of studies have focused on the influence of certain parameters, such as heat treatment and the substrate nature, on the physical properties of SnO_2 thin films [7, 14]. Various techniques are used to prepare SnO_2 thin films, namely, spray pyrolysis [15], sol–gel process [16], chemical vapour deposition [17], sputtering [18] and pulsed laser deposition [19].

In this work, Sol–Gel Dip Coating (SGDC) was employed to deposit SnO_2 thin films at room temperature on glass substrates. The structural and optical properties of the obtained films were studied and the effect of annealing temperature was investigated.

2. Experimental

Tin dioxide sols were prepared by dissolving of 2g of tin chloride dehydrate precursor $SnCl_2$ $2H_2O$ in 20 mL of absolute ethanol in the presence of acetic acid (5 ml). The solution was stirred at 60°C for 2 h in a closed container until homogeneous, i.e. until the solids were dissolved. The thin films were deposited by the dip-coating technique on glass substrates previously cleaned with ultrasound in acetone. The cleaned glass substrates were vertically and carefully immersed into the sol for a short time and withdrawn from the bath at a pulling speed ranging from 1 mm/s to 10 mm/s. Then the films were dried and sintered at different temperatures [300, 400 and 500°C] for 2 hours. However, the sintering was carried out only after the final dipping.

Raman spectra were recorded at room temperature using a Renishaw In Via Raman micro-spectrometer equipped with a neon laser (λ_0 = 632 nm) as an excitation source and a motorized x-y stage and autofocus. Optical transmittance was measured using a Shimadzu 3011 PC UV-Vis spectrophotometer at room temperature in the spectral range 300-800 nm.

3. Results and discussion

3.1. Structural properties

SnO_2 is known to have six atoms per unit cell (space group D_{4h}^{14}) giving 18 vibrations modes. Among these modes, two are IR active (A_{2u}, E_u) and four are Raman active (E_g, A_{1g}, B_{1g}, B_{2g}) [20]. The microstructure, shape, size and defects can affect the intensity and shape of IR and Raman peaks.

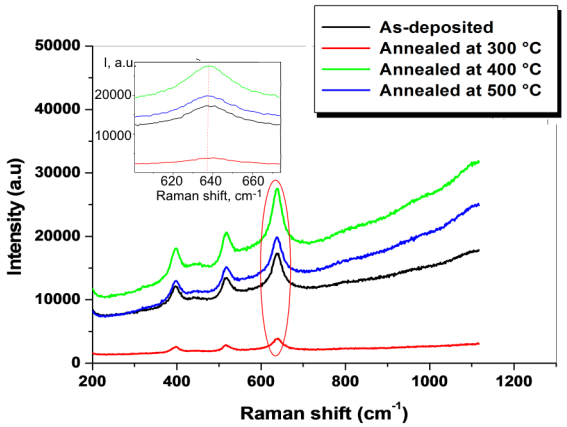

Fig 1. Raman spectra of tin oxide thin films annealed at different temperatures.

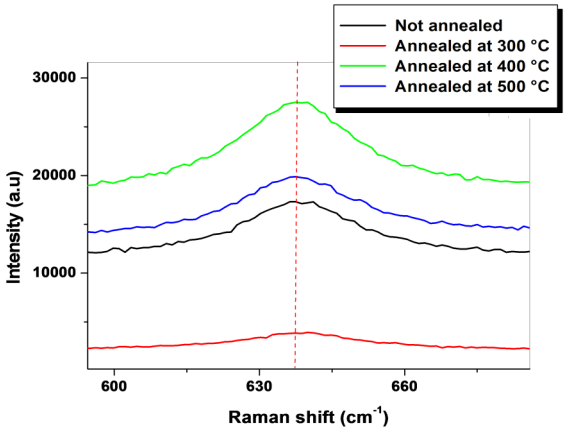

Fig 2. Evolution in intensity of the peak observed at 638.04 cm^{-1} depending on different temperatures

Fig. 1 shows the Raman spectra of as-deposited and annealed SnO_2 films. The spectrum shows three peaks at about 398.68 cm^{-1}, 516.22 cm^{-1} and 638.04 cm^{-1} which can be attributed to SnO_2 optical phonons [21]. It is clear from Fig. 1 that, in all cases, the most intense peak is observed at 638.04 cm^{-1}.This peak corresponds to the principal mode A_{1g} of the rutile phase of SnO_2 which is a characteristic of the expansion and contraction vibrations of the Sn-O bonds. This result is in good agreement with the literature data [10, 11, 15]. The peak localized at 398.68 cm^{-1} is attributed to the A_{2g} vibration mode and corresponds to the vibration of the Sn and O atoms in the plane perpendicular to the c axis [22]. In addition to these peaks, we notice the appearance of another peak at 516.22 cm^{-1}.

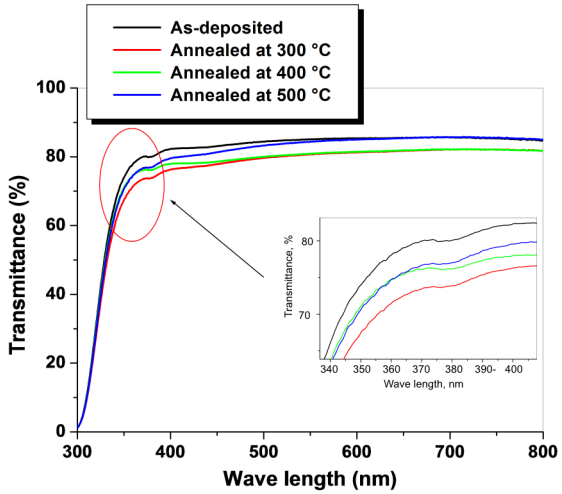

Fig 3. Optical transmittance of SnO_2 thin films annealed at different temperatures as a function of wavelength

The analysis of the all Raman scattering spectra of SnO_2 before and after thermal treatment at different temperatures shows that all the spectra do not have significant peak shifts and their profiles are identical. However, we can note the influence of the annealing temperature on the intensity of the observed peaks.

If we compare the Raman spectra of SnO_2 before and after heat treatment at different temperatures, we can say that all the spectra do not show any significant shift of the peaks (as an example, the peak located at 638.04 cm^{-1}, Fig 2). In addition, we can also note the influence of the annealing temperature on the intensity of the observed peaks. This is due to a slight change in grain size.

3.2. Optical properties

The optical transmittance spectra of as-deposited and annealed SnO_2 thin films recorded in the range 300–800 nm are plotted in Fig 3.

From the Fig.3 it is easy to observe that the behavior of transmittance for all the films is almost similar in the wavelength range of 350–800 nm and the values of the optical transmittance decrease with increasing annealing temperature from 300 to 400°C and then increase for the annealing temperature of 500°C. This might be attributed to a slight increase in grain size and the homogeneity of the structure. The average percentage of transmittance of all samples varies between 75% and 85% in the visible region. This high transparency is one of the essential characteristics which justify the practical interest in SnO_2 thin films [23]. The observed transmission values are compared with earlier reported data [24]. A slight shift of the absorption edge towards higher wavelengths was found with increasing annealing temperature.

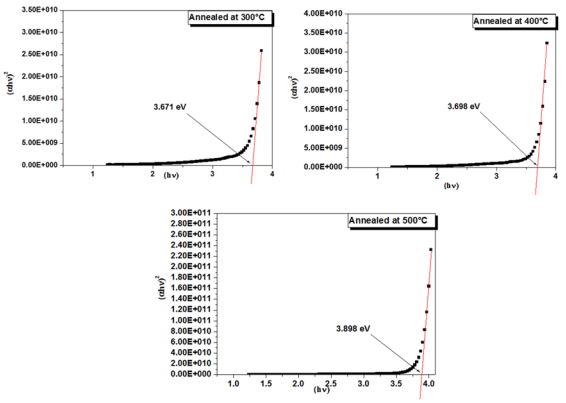

Fig 4: Typical variation of $(\alpha h\upsilon)^2$ as a function of photon energy.

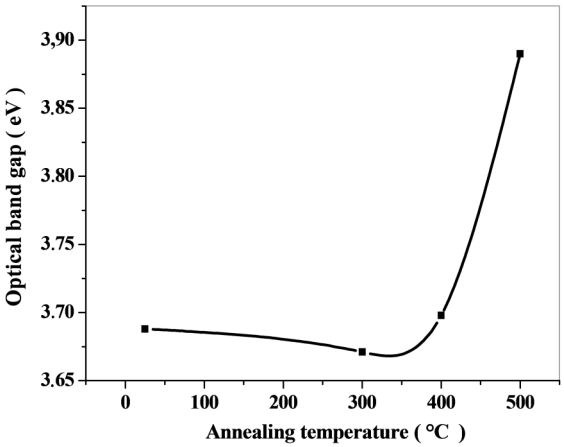

Fig 5. Variation of the optical band gap as a function of annealing temperature.

Higher energy electron transitions from the valence band to the conduction band confirm the direct semiconductor nature of the SnO_2 material [25]. The E_{opt} band gap of the deposited films is deduced by using the following Tauc formula [26]:

$$(\alpha h\nu) = A(h\nu - Eg)^m \quad (1)$$

where v is the frequency; A is a constant; m takes the values 1/2, 2, 3/2 and 3 depending on the interband transition mode, i.e. direct, allowed indirect, direct forbidden and indirect forbidden transition, respectively.

The optical band gap (E_{opt}) of the films is evaluated by extrapolating the straight line portion of the curve $(\alpha h\upsilon)^2$ *versus* hυ to α=0 (Fig. 4). The band gap energy is plotted in Fig. 5 as a function of annealing temperature. The calculated band gap values are shown in the Table.

Table. Optical band gap values of as-deposited and annealed SnO_2 thin films.

Annealing temperature (°C)	Optical band gap (eV)
As-deposited	3.68
300	3.67
400	3.69
500	3.89

The curve (Fig. 5) shows clearly that the optical energy gap increases with increasing annealing temperature. The obtained Eopt values are almost in agreement with results of S. K.Haza'a [27].

4. Conclusion

High quality tin oxide thin films have been fabricated by Sol Gel Dip Coating method on glass substrates. The Raman spectroscopy analysis showed that all SnO_2 thin films crystallized in the rutile structure with improved crystallinity with increasing annealing temperature. The optical UV-Vis transmittance measurements showed that the transparency of the obtained SnO_2 thin films increased with increasing annealing temperature. The optical absorption edges of all films were in the range of 300 to 400 nm and the calculated band gap values varied from 3.68 to 3.89 eV.

References

1. Y. Mouchaal, G. Louarn, A. Khelil, M. Morsli, N. Stephant, A. Bou, T. Abachi, L. Cattin, M. Makha, P. Torchio, J.C. Bernède, Vacuum, 111 (2015) 32-41.
2. C.Y. Kim, D.H. Riu, *Thin Solid Films*, 519 (2011) 3081–3085.
3. R. E. Presley, C.L. Munsee, C.H. Park, D. Hong, J.F. Wager, D.A. Keszler, *J. Phys. D: Appl. Phys.*, 37 (2004) 2810–2813.
4. M. L.L.Chi, J. K.Chou, W.Y. Chung, , T. P. Sun, S.K.Hsiung, Mater. *Chem. Phys.*, 63 (2000) 19–23.
5. M. R.Cassia-Santos, V. C. Sousa, M. M.Oliveir, F. R. Sensato, W. K.Bacelar J. W. Gomes, *Mater. Chem. Phys.*, 90 (2005) 1–9.
6. X. Du, Y. Du, S. M. George, *J. Phys. Chem. A*, 112 (2008) 9211–9219.
7. A. F. Khan, M. Mehmood, M. Aslam, M. Ashraf, *Applied Surface Science*, 256 (2010) 2252–2258.
8. M. Batzill, U. Diebold, *Prog. Surf. Sci.*, 79 (2005) 47–154.
9. P. D. Borges, L. M. R. Scolfaro, H. W. Leite Alves, E. F. da Silva, *Theor. Chem. Acc.*, 2010, 126, 39–44.
10. C. M. Ghimbeu, R.C.V. Landschoot, J. Schoonman, M. Lumbreras, *Journal of the European Ceramic Society*, 27 (2007) 207–213.
11. Z. Jiang, Z. Guo, B. Sun, Y. Jia, M. Li, J. Liu, *Sensors and Actuators B*, 145 (2010) 667–673.
12. Z.W. Chen, H.J. Zhang, Z. Li, Z. Jiao, M.H. Wu, C.H. Shek, C.M.L. Wu, J.K.L. Lai, *Acta Materialia*, 57 (2009) 5078–5082.
13. J. Zhao, X.J. Zhao, J.M. Ni, H.Z. Tao, *Acta Materialia*, 58 (2010) 6243–6248.
14. S. Shukla, S. Patil, S.C. Kuiry, Z. Rahman, T. Du, L. Ludwig, C. Parish, S. Seal, *Sensors and Actuators*, B 96 (2003) 343–353.
15. R. L. Mishra, K.M. Sheo, S. G. Prakash, *J. Ovonic. Res*, 5(4) (2009) 77-85.
16. M. Khechba, A. Bouabellou, F. Hanini, S. Touati, *J. New Technol. Mater.*, 07(02) (2017) 72-75.
17. M. Maleki, S. M. Rozati, *Bull. Mater. Sci.*, 36(2) (2013) 217-221.
18. V. Kumar, A. Jain, D. Pratap, D.C. Agarwal, I. Sulania, V. V. Siva Kumar, A. Tripathi, S.Varma, R.S. Chauhan, *Adv. Mat. Lett.*, 4(6) (2013) 428-432.
19. H. Kim, R.C.Y. Auyeung, A. Piqué, *Thin Solid Films*, 516 (2008) 5052–5056.
20. P. Venkateswara Reddy, B. Sankara Reddy, S. Venkatramana Reddy, *Inter. J. of Chem. Tech. Res.*, 6 (3) (2014) 2168-2170.
21. A.F. Khan, M. Mehmood, A.M. Rana, M.T. Bhatti, A. Mahmood, *Chin. Phys. Lett.*, 7 (2009) 077803.
22. A. Dieguez, A. R. Rodrıguez, A. Vila, J.R. Morante, *Journal of Applied Physics*, 90(3) (2001) 1550–1557.
23. D.C. Woo, C.Y. Koo, H.C. Ma, H.Y. Lee, *Transactions on electrical and electronic materials*, 13 (5) (2012) 241-244.
24. R. Mariappan, V.Ponnuswamy, P.Suresh, R.Suresh, M.Ragavendar, C. Sankar, *Materials Science in Semiconductor Processing*, 16 (2013) 825–832.
25. B. Pejova, I. Grozdanov, *Thin Solid Films*, 515(13) (2007) 5203-5211.
26. J. Tauc, Amorphous and liquid semiconductors, *Plenum Press*, 1974, London.
27. S. K. Haza'a, *IOSR Journal of Applied Physics*, 7(1) (2015) 59-63.