Fabrication and Characterization of Bilayer ZnO/Cu_4O_3 Thin Films for Optoelectronic Application

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Abstract

Herein, we report the fabrication and characterization of pure ZnO, pure Cu_4O_3 and bilayer ZnO/Cu_4O_3 thin films using cost-effective nebulizer spray pyrolysis (NSP) method deposited on glass slide substrate. The microstructural, and optical, properties of the prepared films are studied using X-ray diffraction and UV–visible spectroscopy. The X-Ray diffraction (XRD) patterns revealed that all synthesized thin layer exhibit polycrystalline nature with würtzite hexagonal structure for pure ZnO sample and tetragonal structure for pure Cu_4O_3 film. However, the bilayer film revealed a domination of the ZnO and Cu_4O_3 with (002) diffraction plane present the preferential orientation. The obtained results indicate that the crystallite size of the deposited films vary from 7.47 to 10.45 nm. From UV-vis analysis, it was found that all thin layers exhibit highly optical transmission, and bilayer films present the maximum transmission more than 80% in the visible region. The Eg values of the prepared films were ranged between 2.92 and 3.18 eV. In addition, the optical parameters such as, the refractive index and extinction coefficient of all films were determined.

Keywords: ZnO, Cu_4O_3, Thin films, nebulized spray pyrolysis (NSP), X-ray diffraction, Optical properties.

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1. Introduction:

In the past decade, Transition metal oxides (TMOs) such as ZnO, NiO, SnO_2 played a significant role due to its vast potential applications such as: transparent electronics [1], electrochemical capacitors [2], gas sensor [3], heterojunction solar cells [4], catalysis [5]and electrodes in lithium batteries [6]. Zinc oxide (ZnO) is one of the important n-type semiconductor which is cost-effective, non-toxic, stable, abundance, high excitonic binding energy (60 meV), good mechanical and chemical stability and has a wide band gap of 3.2 eV [7,8]. Therefore, it is widely used in different fields such as; microelectronic devices, light-emitting diodes, laser devices and optoelectronic devices [9-12]. Whereas, copper oxides (CuO) received significant attention because of its low cost and abundant metal, non-toxic and favorable environment [13]. their oxides such as CuO, Cu_2O and Cu_4O_3 are natural p-type semiconductors with a direct band gap close ~1.4 eV suitable to PV applications as absorber layer [14]. For the fabrication of ZnO and Cu_4O_3 thin films, various methods were employed such as; electrochemical deposition, hydrothermal, thermal evaporation, sol-gel method, and nebulizer spray pyrolysis [15-19]. Among these methods nebulizer spray pyrolysis routes is a low-cost and easy to control the deposition parameters such as film deposition rate, concentration, thickness, etc [20]. The aim of this work focused on fabrication of pure ZnO pure, pure Cu_4O_3 and bilayer ZnO/Cu_4O_3 thin films using nebulizer spray pyrolysis (NSP) method deposited on glass slide substrate at temperature maintained at 400°C.The structural and optical properties of the prepared films were investigated.

2. Experimental details

2.1. Synthesis of thin films

pure ZnO, pure Cu_4O_3 and bilayer ZnO/Cu_4O_3 thin films were synthesized using nebulizer spray pyrolysis (NSP) technique. First the ZnO precursor solution was obtained by dissolving 30 ml of de-ionized water and the required mass of dehydrated zinc acetate (Zn $(CH_3COO)_2$, $2H_2O$) to get concentration of 0.1 mol/L-1. For preparing pure Cu_4O_3 solution, dissolving 0.1 mol/L-1 of copper chloride dehydrate ($CuCl_2.2H_2O$) in de-ionized water to obtain a final transparent solution. These starting solutions were stirred for about 30 min with a magnetic stirrer at room temperature a few drops of acetic acid was added separately to obtain homogenous solution. Before deposition process, microscopic glass slide (R217102) were cleaned with acetone and distilled water respectively for 10min, and then blowing dry with a compressed air. After that, the solution was sprayed onto heated substrates at 400°C in the air atmosphere. The distance between nozzle and the substrate was kept constant at 20 cm. After deposition of the ZnO and Cu_4O_3 thin films, the same procedure was repeated to get bilayer ZnO/Cu_4O_3 films. Finally, all prepared thin films were allowed to cool slowly at room temperature.

2.2 Thin films characterization

The structural properties of prepared thin films were investigated using X-ray diffraction Bruker D8 Advance equipped with X'Pert High Score under Cu Kα (λ=1.5406Å) radiation in the range of 20° and 60°.The optical transmission spectra were carried out by through Agilent technologies cray series UV-Vis spectrophotometer (cray 100 UV-Vis) in the wavelength between 300 and 900 nm.

3. Result and discussions

3.1 Structural properties

The structural properties of the deposited pure ZnO, pure Cu_4O_3 and bilayer ZnO/Cu_4O_3 thin films are analyzed by using the X-ray Diffraction technique (XRD). Fig.1 represents the XRD patterns of all prepared samples. As can be seen from pure ZnO sample, we can distinct three fundamental diffraction angle located at 31.74°, 34.42° and 47.53° which correspond to the diffraction planes (100), (002) and (102), respectively. All these diffraction peaks can be indexed to the hexagonal würtzite structure (JCPDS card no. 36–1451) [21]. A strong diffraction peak is observed at (100) plane which demonstrates that there is a high degree of crystallinity for the pure ZnO film. On other hand, the pure Cu_4O_3 film reveals peaks detected at 2θ=28.21°, 30.69°, 35.78° and 61.45° which corresponds to the Cu_4O_3 plane orientation of (112), (200), and (211), respectively, however the diffraction angle appeared at 2θ=50.42° corresponding to diffractions plane of (112), of monoclinic structure of CuO [22]. All detected peaks are matched well with the tetragonal structure of Cu_4O_3 (Paramelaconite, JCPDS 49-1830) and monoclinic structure of CuO (Tenorite, JCPDS 45-0936) respectively [23]. From the XRD patterns the intensity of the plane (200) present the strongest peaks which can considered as the preferred orientation. In addition, we can see from XRD patterns that the characteristic peaks of ZnO and Cu_4O_3 structure are detected, with appearance of new diffractions plane (004) and (301) corresponding to the tetragonal structure of Cu_4O_3. Also it is clearly seen that the preferential orientation from this sample display at (002) peak corresponding to ZnO lattice structure plane, which indicating a perpendicular alignment of the c-axis.

The estimated average crystallite size of pure ZnO, pure Cu_4O_3 and bilayer films can be calculated using the well-known Scherrer's formula [24]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

Where D is the crystallite size, β is the full width at half-maximum (FWHM) of the most intense diffraction peak, λ is the X-ray wavelength (1.54056 Å) and θ is the Bragg angle at (100), (200), and (002) peak plane corresponding to pure ZnO, pure Cu_4O_3 and bilayer sample respectively. The calculated crystallite size values were found to be 10.45, 7.47, and 9.25 nm corresponding to pure ZnO, pure Cu4O3 and bilayer sample respectively. It can be seen that the maximum values of crystallite size have been determined for pure ZnO film that indicates the better crystallinity,

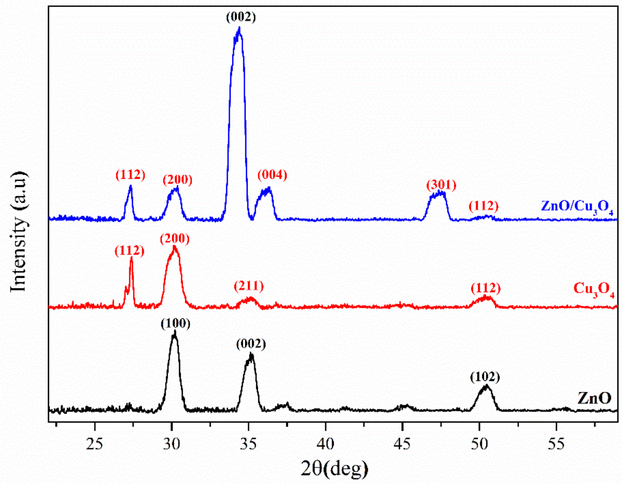

Fig.1: X-ray diffraction patterns of pure ZnO, pure Cu_4O_3 and bilayer ZnO / Cu_4O_3 thin films.

3.4 Optical properties

Optical transmittance spectra of the ZnO, Cu_4O_3 and ZnO/ Cu_4O_3 bilayer thin films are shown in Fig. 2. The analysis of these figures revealed that the transmittance of the bilayer samples has been display high average transmittance of (~80%) in the range of 300–900 nm compared to pure ZnO and Cu_4O_3 films, this behavior indicating high quality, and low dispersion of light [25]. Whereas the lower transmittance around (~74%) presented in the pure ZnO films. An abrupt diminution can be observing in the transmittance spectra from all samples has been found in the range around 350–380 nm region that indicates the inter-band absorption edges [26].

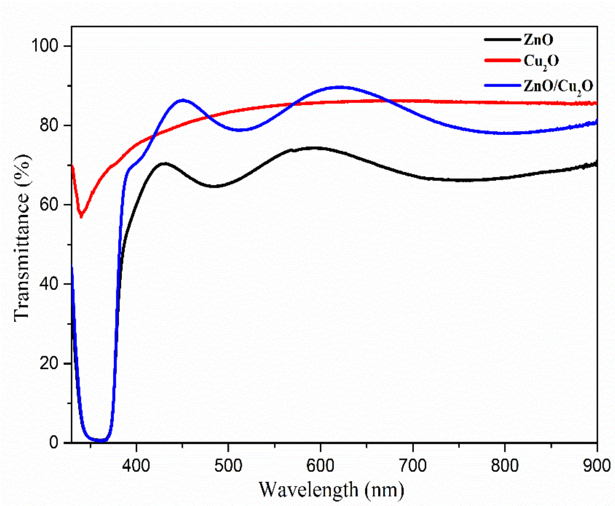

Fig.2: Transmittance spectra of pure ZnO, pure Cu_4O_3 and bilayer ZnO / Cu_4O_3 thin films.

In order to evaluate the band gap energy (Eg) of all deposited films, the Tauc formula can be used which imply the relationship between the absorption coefficient (α) and the incident photon energy (hν) as follows [27]:

$$\alpha = \frac{B}{h\nu}\left(h\nu - E_g\right)^{\frac{1}{2}} \qquad (2)$$

Where B is constant related with the nature of transition, α is the absorption coefficient, hν is the photon energy and Eg is the band gap energy.

the absorption coefficient α can be estimated from the transmittance T, and the films thickness d using the following equation [27]:

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \qquad (3)$$

The optical band gap values of pure ZnO, Cu_4O_3 and bilayer ZnO/ Cu_4O_3 films have been evaluated by extrapolating the linear portion of the plot of (αhν)2 versus (hν) as illustrated in Fig.3. The obtained results show that the Eg values for pure ZnO (2.92 eV) and for pure Cu_4O_3

(3.18 eV). However, from bilayer ZnO/Cu_4O_3 films are (3.17 eV), which authorizes its use as an optical window in solar cells.

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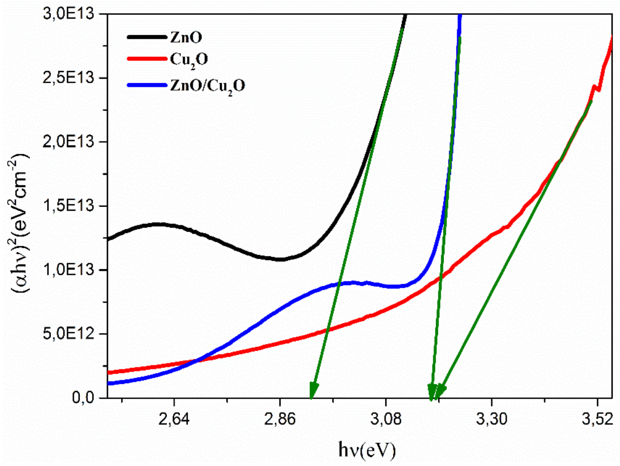

Fig.3: Tauc's plot of pure ZnO, pure Cu_4O_3 and bilayer ZnO / Cu_4O_3 thin films.

The refractive index (n) plays significant factors in optical devices, optoelectronic applications optical communication, and optical amplifiers etc. The refractive index (n) of all prepared thin films are calculated using the following equations [27]:

$$n = \frac{(1+R)}{(1-R)} \pm \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad \text{and} \quad k = \frac{\alpha\lambda}{4\pi} \qquad (4)$$

Where, k, R, λ and α are Extinction coefficient, the reflectance, wavelength and absorption coefficient respectively. The variation of n and k values as a function of wavelength is shown in Fig. 4 and Fig. 5 respectively.

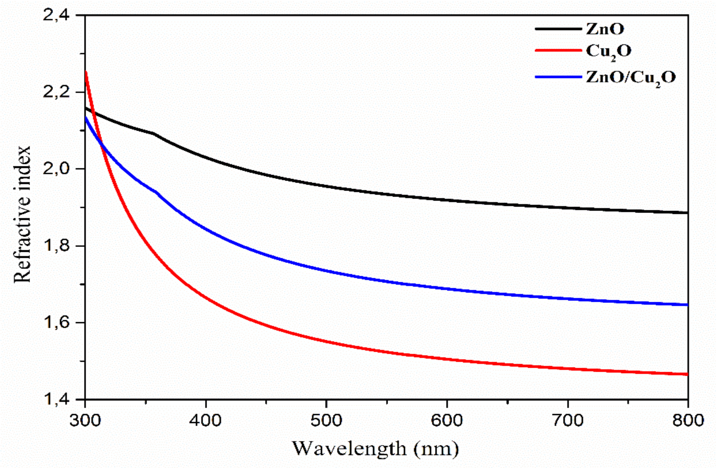

Fig.4: Refractive index as function of wavelength of pure ZnO, pure Cu_4O_3 and bilayer ZnO /Cu_4O_3 thin films.

It is can be seen that the refractive index (n) of all samples is decreased slightly with increase in wavelength, this behavior can be due to the reduction and the loss of light after passing through the required material [28]. In all thin layers, the extinction coefficient spectra were also decreased with increasing the wavelength of photon. Furthermore, the k values are very small and approximately behind to zero, this result support that the prepared films are transparent in visible region and with smooth surface [29].

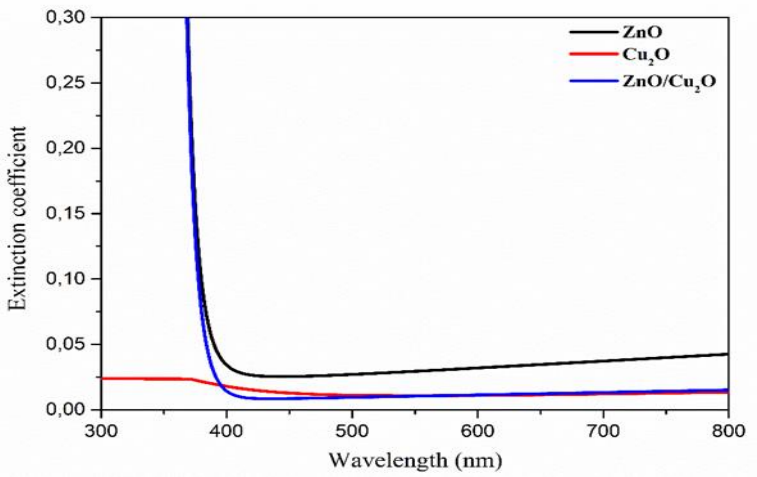

Fig.5: Extinction coefficient as function of wavelength of pure ZnO, pure Cu_4O_3 and bilayer ZnO/Cu_4O_3 thin films.

4. Conclusion

In this work, pure ZnO, pure Cu_4O_3 and bilayer ZnO /Cu_4O_3 thin films have been achieved using cost effective nebulizer spray pyrolysis (NSP) technique at 400˚C on glass slide substrates. Investigation of the prepared films has been done using X-ray diffraction and UV-visible spectrophotometer. X-ray diffraction patterns from pure ZnO sample indicate a polycrystalline nature with würtzite hexagonal crystal structure, and the preferred orientation was along (100) plane. Whereas, pure Cu_4O_3 film have tetragonal structure with (200) diffraction plane as preferential orientations. In addition, the XRD analysis of bilayer sample showed a domination of the ZnO and Cu_4O_3 with (002) diffraction plane present the preferential orientation. The crystallite size of all samples was found to vary from 7.47 to 10.45 nm. The bilayer ZnO/Cu_4O_3 thin film showed high average optical transmission around 80% in the visible region. Hence, the estimated optical band gap was found to be in the range 2.92-3.18 eV in all films. The other optical constants namely refractive index and extinction coefficient are found to decreases as function of wavelength. As a result, it can be assumed that the bilayer ZnO /Cu_4O_3 thin film can be considered as good candidate for optoelectronics devises.

References

[1] Kang Chen, Junan Pan, Weinan Yin, Chiyu Ma, Longlu Wang, Flexible electronics based on one-dimensional inorganic semiconductor nanowires and two-dimensional transition metal dichalcogenides, Chinese Chemical Letters 34 (2023) 108226.

[2] Mao-Sung Wua, Der-Sheng Chan, Kun-Hao Lin, Jiin-Jiang Jow, A simple route to electrophoretic deposition of transition metal-coated nickel oxide films for electrochemical capacitors, Materials Chemistry and Physics 130 (2011) 1239– 1245.

[3] Aditya Kushwaha, Rahul Kumar, Neeraj Goel, Chemiresistive gas sensors beyond metal oxides: Using ultrathin two-dimensional nanomaterials, FlatChem (2023)100584.

[4] Luis G. Gerling, Somnath Mahato, Anna Morales-Vilches , Gerard Masmitja, Pablo Ortega, Cristobal Voz, Ramon Alcubilla, Joaquim Puigdollers, Transition metal oxides as hole-selective contacts in silicon heterojunctions solar cells, Solar EnergyMaterials&SolarCells145(2016)109–115.

[5] Mohammadreza Kosari, Morteza Golmohammadi, Seyed Javad Ahmadi, Jafar Towfighi, Ali Heidari Chenari, On the catalysis capability of transition metal oxide nanoparticles inupgrading of heavy petroleum residue by supercritical water, J. of Supercritical Fluids 126 (2017) 14–24.

[6] Shanshan Yan, Yejian Xue, Shihua Li, Guangjie Shao, Zhaoping Liu, Improving catalytic activity of layered lithium transition metal oxides for oxygen electrode in metal-air batteries, international journal of hydrogen energy 45 (2020)1846e1856.

[7] K.Deva Arun Kumar, V. Ganesh, S. Valanarasu, Mohd. Shkir, I. Kulandaisamy, A. Kathalingam, S. AlFaify, Effect of solvent on the key properties of Al doped ZnO films prepared by nebulized spray pyrolysis technique, Materials Chemistry and Physics 212, (2018)167-174.

[8] Meryem Polat Gonullu, Design and characterization of single bilayer ZnO/Al2O3 film by ultrasonically spray pyrolysis and its application in photocatalysis, Micro and Nanostructures 164 (2022) 107113.

[9] Shobhna Choudhary, R.J. Sengwa, ZnO nanoparticles dispersed PVA–PVP blend matrix based high performance flexible nanodielectrics for multifunctional microelectronic devices, Current Applied Physics 18 (2018) 1041–1058.

[10] Andreia de Morais, Wesley de Souza Rodrigues, Douglas Jos´e Coutinho, Ana Fl´avia Nogueira, Jilian Nei de Freitas, Investigation of nitrogen-doped carbon dot/ZnO

nanocomposites and their application as interlayer in solution-processed organic light emitting diodes, Materials Science and Engineering B 297 (2023) 116749.

[11] Cheng-Ying Chou, Shih-Feng Tseng, Tien-Li Chang, Chen-Ting Tu, Hsieh-Cheng Han, Controlled bridge growth of ZnO nanowires on laser-scribed graphene-based devices for NO gas detection, Applied Surface Science 508 (2020) 145204.

[12] Eya Kacem, Hanan A. Althobaiti, Maryam Al-Ejji, Nour Bader, Asma Abed, A. Rajeh, Structural, optical, and thermal studies of Poly(vinylidene fluoride-co-hexafluoropropylene) and Polyvinylpyrrolidone composite doped Ag/ZnO mixed nanoparticles for flexible optoelectronic devices, Optical Materials 146 (2023) 114560.

[13] S. Dolai, R. Dey, S. Hussain, R. Bhar, A.K. Pal, Synthesis, characterization and photo-response of p-type cupric oxide thin films prepared by sol-gel technique, Materials Science & Engineering B 236–237 (2018) 153–161.

[14] Yahya Alajlani, Frank Placido, Anders Barlow, Hin On Chu, Shigeng Song, Saeed Ur Rahman, Robert De Bold, Des Gibson, Characterisation of Cu2O, Cu4O3, and CuO mixed phase thin films produced by microwave-activated reactive sputtering, Vacuum 144 (2017) 217-228.

[15] Yanhong Zhang, Hu Bai, Jiaming Chu, Haiyang Lan, Qi Zhou, Zixian Wang, Weitao Jin, Juan Zhou, Effect of CuO-ZnO catalyst layer on proton-conducting electrochemical cell reactor for CO2 reduction reaction, International Journal of Hydrogen Energy (2023).

[16] Cong Qin, Yan Wang, Yuxiao Gong, Zhanying Zhang, Jianliang Cao, CuO-ZnO hetero-junctions decorated graphitic carbon nitride hybrid nanocomposite: Hydrothermal synthesis and ethanol gas sensing
application, Journal of Alloys and Compounds 770 (2019) 972-980.

[17] Roberto L´opez, Gerardo Villa-S´anchez, Israel Vivaldo de la Cruz,Cecilia Encarnaci´on-G´omez, Víctor Hugo Castrej´on-S´anchez, Antonio Coyopol,Jorge Edmundo Mastache, Cesar Leyva-Porras, Cupric oxide (CuO)/zinc oxide (ZnO) heterojunction diode with low turn-on voltage, Results in Physics 22 (2021) 103891.

[18] Prerna Mahajan, Anoop Singh, Sandeep Arya, Improved performance of solution processed organic solar cells with an additive layer of sol-gel synthesized ZnO/CuO core/shell nanoparticles, Journal of Alloys and Compounds 814 (2020) 152292.

[19] Abbas S. Pathan, Deepak L. Gapale, Shivaji V. Bhosale, Abhijit S. Landge, Sandesh R. Jadkar, Sandeep A Arote, Studies on resistive-type humidity sensing properties of copper-zinc mixed metal oxide nanostructures, Inorganic Chemistry Communications 153 (2023) 110824.

[20] K. Deva Arun Kumar, S. Valanarasu, A. Kathalingam, K. Jeyadheepan, Nd3+ doping effect on the optical and electrical properties of SnO2 thin films prepared by nebulizer spray pyrolysis for opto-electronic application, Materials Research Bulletin 101 (2010) 264-271.

[21] S. Uday Balegar, N. Srinatha, R. Shashidhar, A Raghu, Annealing temperature-dependent structural and optical characteristics of spray pyrolyzed ZnO thin films, Materials Today: Proceedings (2023).

[22] Hong-Sik Kim, Pankaj Yadav, Malkeshkumar Patel, Joondong Kim, Kavita Pandey, Donggun Lim, Chaehwan Jeong, Transparent Cu4O3/ZnO heterojunction photoelectric devices, Superlattices and Microstructures 112 (2017) 262-268.
[23] Hong-Sik Kim, Melvin David Kumar, Wang-Hee Park, Malkeshkumar Patel, Joondong Kim, Cu4O3-based all metal oxides for transparent photodetectors, Sensors and Actuators A 253 (2017) 35–40.
[24] C. Mrabet, A. Boukhachem, M. Amlouk, T. Manoubi, Improvement of the Optoelectronic Properties of Tin Oxide Transparent Conductive Thin Films through Lanthanum Doping, Journal of Alloys and Compounds 666 (2016) 392-405.
[25] V. Dhanasekaran, T. Mahalingam, Physical properties evaluation of various substrates coated cupric oxide thin films by dip method, Journal of Alloys and Compounds 539 (2012) 50–56.
[26] R. Sathish Kumar,S. Johnson Jeyakumar, M. Jothibas, Kartharinal Punithavathy, J. Prince Richard, Influence of molar concentration on structural, optical and magnetic properties of NiO nanoparticles, J Mater Sci: Mater Electron 28 (2017) 15668–15675.
[27] M. Anithaa, K. Saravanakumar, N. Anitha, I. Kulandaisamy, L. Amalraj, Influence of annealing temperature on physical properties of Sn-doped CdO thin films by nebulized spray pyrolysis technique, Materials Science & Engineering B 243 (2019) 54–64.
[28] Z. Serbetci, R.K. Gupta, F. Yakuphanoglu, Preparation and characterization of nanorods Sb doped CdO films by sol–gel technique, J. Sol-Gel Sci. Technol. 61 (2012) 477–483.
[29] M. Anitha, L. Amalraj, N. Anitha, Applied Physics A 123 (12), 764 (2017).