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Spray pyrolysised tin disulphide thin film and characterisation

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Abstract

Thin film of tin disulphide on glass substrate is prepared by spray pyrolysis technique at a substrate temperature of 458 K. Using the hot probe technique the type of semiconductor is found to be n-type. X-ray diffraction analysis revealed the polycrystalline nature of the film with hexagonal structure and a preferential orientation along the (0 0 1) plane. Fibre-like surface morphology has been observed on the film. The surface composition of the elements is analysed with EDAX spectrum. A value of $3.85 \times 10^{-7}\,\Omega^{-1}\,cm^{-1}$ for the room temperature (302 K) conductivity is determined using the four-probe method. Activation energy of about 0.25 eV is determined by plotting a graph between log (conductivity) versus reciprocal temperature. The optical absorption and transmittance spectra have been recorded for this film in the wavelength range 380–900 nm. Thickness of the film and variation of absorption coefficient with wavelength are determined using these spectral data. Band gap values of 2.16 eV with indirect allowed and 1.82 eV with indirect forbidden nature are observed for this pyrolysised SnS_2 thin film. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Several binary sulphides of tin such as SnS (orthorhombic), SnS_2 (hexagonal), Sn_2S_3 (rhombic) and Sn_3S_4 (tetragonal) were studied for their respective properties [1–7]. Mixed phases of the compound Sn_xS was also studied in detail [8]. Among them SnS_2 is a semiconducting material exhibiting n-type conductivity [9]. It is a layered semiconductor with CdI_2-type structure composed of sheets of tin atoms sandwiched between two close-packed sheets of sulphur atoms and it can exist in a number of different poly types [10–12]. Along with the important properties like, high optical absorption coefficient in the visible region ($> 10^4\,cm^{-1}$) [9], wide optical band gap (2.88 eV) [13], semiconducting nature of electricity and strong photo-conducting behaviour [4,13–15], this compound SnS_2 in the bulk form has other interesting properties like electrical switching and conduction mechanism [16], Raman spectral shift [17] and

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refractive index (n, k) variation [11]. These properties suggest this compound to be a promising material in the development of thin film solar cells [9].

Studies were done by many authors on SnS_2 single crystals like the crystals grown by physical vapour transport [13,18] and chemical vapour transport [14,16]. A number of thin film deposition techniques like chemical deposition [8,19], vacuum evaporation [5,20], chemical vapour transport [21], dip deposition [4], and chemical spray pyrolysis [9,22] have been used for preparing SnS_2 thin films. But only a few reports are available on SnS_2 thin films prepared by spray pyrolysis technique, which is a low cost technique that can be used to deposit uniform coatings on large surface area [23].

We present, in this paper, the results of the physical investigations carried out on thin films of SnS_2 prepared by spray pyrolysis technique using $SnCl_4.5H_2O$ and thiourea as the starting materials, with a different concentration.

2. Experimental details

A double nozzle sprayer made of glass was designed and fabricated in our laboratory to prepare thin film samples by spray pyrolysis technique. It is a coaxial assembly of two corning glass tubes, in which the diameters of inner and outer tubes are 6 and 14 mm, respectively. Both the tubes were tapered at one end with a tapering angle of 30° to form the spray nozzle. Well cleaned and degreased glass substrates were kept inside a tubular furnace designed for this technique. The furnace was resistively heated with kanthal wire and the temperature was controlled by a dimmerstat. A temperature controller automatically maintained the required temperature in which the setting could be made manually. A chromel–alumel thermocouple was used to sense the temperature inside the oven, which was in contact with the substrate holder. Inner tube of the spray nozzle was connected to the air compressor and the outer tube to the solution reservoir. The pressure of the carrier gas was monitored through the valve flow meter set. The solution flow rate was determined with the help of a stop clock and a graduated burette as the reservoir.

The deposition conditions were optimised in order to obtain reproducible and good quality films. Its colour, adhesion, surface smoothness and chemical treatment determine the quality of the film. Purified compressed air at a pressure of $10^4\,Nm^{-2}$ was used as the carrier gas. The nozzle was kept vertically above the substrate at a distance of 30 cm.

High purity $SnCl_4 \cdot 5H_2O$ and thiourea were dissolved separately in a solution containing deionised water and isopropyl alcohol in the ratio of 1:3 by volume. The molarities of tin and thiourea solutions were 1 and 2 M, respectively. A few drops of concentrated hydrochloric acid were added for complete dissolution. Equal volume of these two solutions were mixed and sprayed on to the glass substrates with an effective area of $75 \times 25\,mm^2$. The substrate temperature was maintained at 458 ± 2 K. The flow rate of the solution during spraying was adjusted to be $0.5\,ml\,min^{-1}$ and kept constant throughout the experiment. After depositing the film, it was allowed to cool to room temperature, cleaned with distilled water and then dried.

The film obtained was in golden yellow colour with good adhesion. The structural properties of the film were studied by the computer controlled JEOL JDX 803a X-ray diffractometer using Cu K_α radiation ($\lambda = 1.5418$ Å). The scanning angle 2θ was varied in the range of 10–80° in steps of 0.1°. The surface morphological studies were done with the SEM photographs taken with JEOL JSM 5300 scanning microscope. To have an idea about the surface elemental composition of the film, energy dispersive analysis by X-rays (EDAX) was carried out using Philips EDX spectrometer (XL30 ESEM TMP). Electrical conductivity at room temperature (303 K) was determined using the four-probe technique with Keithley 2000 electrometer. The variation of electrical conductivity with temperature was studied from 303 to 368 K. Optical absorption spectrum was recorded in the wavelength range 380–900 nm using Shimadzu-UV410S double beam spectrophotometer. As the effect of multiple interference was seen in the longer wavelength side, transmittance spectrum was also recorded in that wavelength region to determine the thickness of the film.

3. Results and discussion

The XRD profile of the spray pyrolysised SnS_2 thin film on glass substrate is shown in Fig. 1. The prominent Bragg reflection occurring at $2\theta = 15.4^\circ$ along with many other weak peaks confirms the polycrystalline nature of the film and d-value corresponding to this peak is 5.782 Å. Similarly the d-values of the other peaks are also determined and tabulated as in Table 1.

Assuming the 2T-hexagonal structure for the observed profile by comparing the obtained Bragg peaks positions and intensities with JCPDS data,[1] the peak at $2\theta = 15.4^\circ$ was identified to be (0 0 1) plane reflection. Hence, the preferential orientation growth of the film is along the c-direction. Sekar C. Ray et al. [4] also had obtained a single peak in their XRD pattern for their dip deposited SnS_2 thin film due to (0 0 1) plane reflection at $2\theta = 15.0^\circ$. The XRD pattern recorded by Thangaraju and Kaliannan [9] for their 1 μm thick SnS_2 thin film prepared by the same spray pyrolysis method but with different starting material, also had a prominent Bragg peak with d-value 5.901 Å which was identified to be due to (0 0 2) plane reflection. The lattice parameters determined in the present case are, $a = 3.621$ Å and $c = 5.749$ Å, whereas the reported values[1] are $a = 3.648$ Å and $c = 5.899$ Å. These values suggest that the unit cell being compressed in all the three directions resulting to a volume of 65.28 $Å^3$ whereas the reported value being 68.01 $Å^3$.[1]

The SEM photograph of the spray pyrolysised SnS_2 thin film is shown in Fig. 2 which shows the fibre-like formation of crystallites. The average length of the cross linked fibre are 0.5 μm. This type of formation of the crystallites was observed by Engelken [8] for SnS_2 thin films prepared by an electroless chemical precipitation and chemical vapour deposition techniques. In the study of particle morphology it was understood that it is diffusion drying after crust shell formation in spray pyrolysis plays an important role. The crust thus formed will result into fragment particles while it reaches the hot substrate, resulting in irregular shape [24]. The structure seen in Fig. 2 may be attributed to the above said fragmentation.

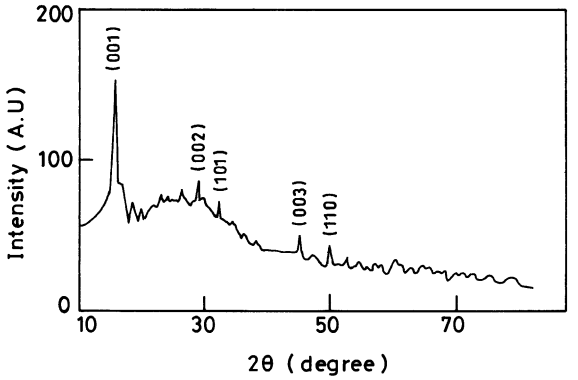

Fig. 1. X-ray diffraction pattern of SnS_2 thin film on glass substrate.

Table 1
Comparison of d-values and relative intensities with literature data

Observed		SnS_2[a]	
d-values (Å)	I/I_0	d-values (Å)	($h\,k\,l$)
5.782	100	5.89	0 0 1
3.004	—	2.951	0 0 2
2.753	—	2.784	1 0 1
2.013	—	1.967	0 0 3
1.823	—	1.824	1 1 0

[a] X-ray powder diffraction file JCPDS File reference number 23–677.

The EDAX spectrum of the SnS_2 film was recorded in the binding energy region of 0.5–5.0 eV as shown in Fig. 3. It is found that tin and sulphur are present in almost stoichiometric ratio and is observed as 35% and 65%, respectively.

The as-prepared SnS_2 films exhibited n-type semiconductor nature through the hot probe technique, which agrees well with the reported literatures [11,13,25]. The DC electrical conductivity of SnS_2 single crystal reported by Domingo et al. [13] was that $10^{-7}\,\Omega^{-1}\,cm^{-1}$. Lee et al. [11] found that the same varies between 10^{-12} and $10^{-2}\,\Omega^{-1}\,cm^{-1}$ and concluded that the variation critically depends on the small departures from the stoichiometry.

[1] X-ray powder diffraction file JCPDS File reference number 23-677.

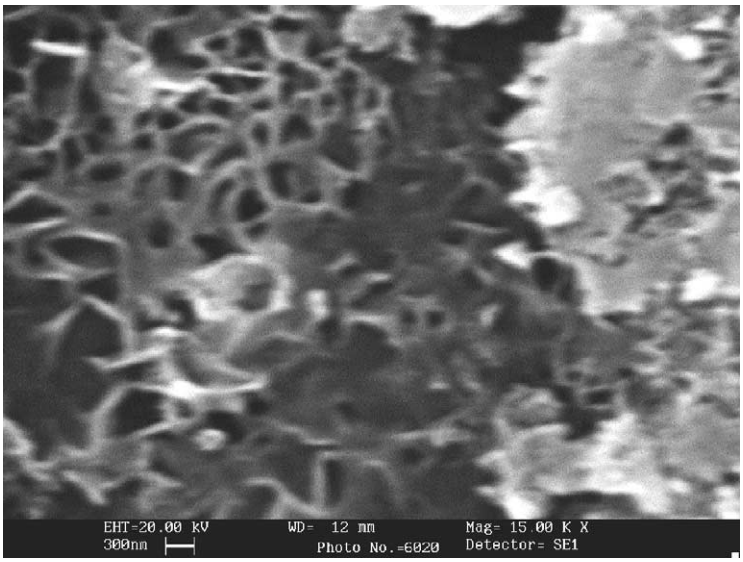

Fig. 2. Scanning electron micrograph of SnS_2 thin film.

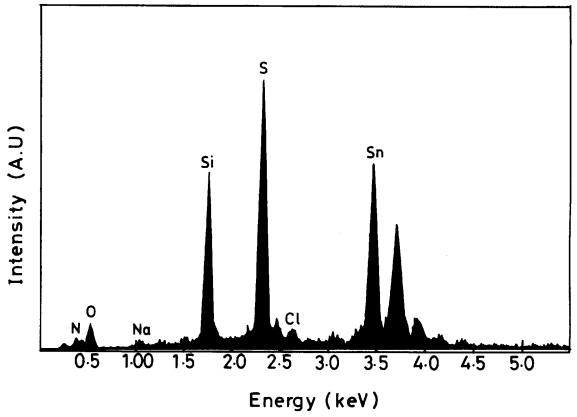

Fig. 3. EDAX spectrum of the as-deposited SnS_2 thin film on glass substrate.

The value of DC electrical conductivity of the as-prepared and polycrystalline SnS_2 thin film at room temperature is about $3.85 \times 10^{-7}\,\Omega^{-1}\,cm^{-1}$. The value reported by Thangaraju and Kaliannan [9] for their 1 μm thick spray pyrolysised SnS_2 thin film was $2.5 \times 10^{-4}\,\Omega^{-1}\,cm^{-1}$. The reduced conductivity value in the present case may be attributed to the inclusion of oxygen molecules and variations in stoichiometry. However, the amorphous SnS_2 thin films showed a wide scattered conductivity values ranging from about 10^{-11}–$10^{-2}\,\Omega^{-1}\,cm^{-1}$. Lokhande [25] reported a very low conductivity of 10^{-7}–$10^{-8}\,\Omega^{-1}\,cm^{-1}$ for 0.10–0.12 μm thin amorphous SnS_2 films prepared by a chemical method. Joy George and Joseph [26] observed a much lower conductivity of 10^{-9}–$10^{-11}\,\Omega^{-1}\,cm^{-1}$ for 2 μm thick vacuum deposited films. The conductivity of these films suddenly increased to 10^{-3}–$10^{-2}\,\Omega^{-1}\,cm^{-1}$ because of annealing which was attributed to the re-crystallisation processes taking place at elevated temperature. But, Kawano et al. [5] observed a high conductivity of $10^{-2}\,\Omega^{-1}\,cm^{-1}$ at room temperature and a lower conductivity of $10^{-7}\,\Omega^{-1}\,cm^{-1}$ at a reduced temperature of 200 K. The high value of conductivity at RT for their amorphous films was explained due to the presence of localised states inside the band gap.

In the present study, the conductivity is found to increase up to $1.133 \times 10^{-6}\,\Omega^{-1}\,cm^{-1}$ as the temperature increases from RT to 368 K. which shows the semiconductor nature of the film. The result is being analysed by a thermally activated process,

$$\sigma = \sigma_0 \exp(-E_a/KT), \quad (1)$$

where σ_0 is a pre-exponential factor and E_a is the activation energy, both of which are determined by the best fit of the experimental data to Eq. (1). The Arhenious plot is drawn as shown in Fig. 4, from which it can be predicted that the variation of conductivity of the SnS2 film under study is being assisted by a single activation process with an activation energy of $E_a = 0.25$ eV. It is approximately equal to one-ninth of the optical band gap of 2.16 eV as determined from the optical analysis. This indicates the presence of a shallow donor level, which might have been situated very close to the conduction band. The value of the pre-exponential factor σ_0 is found to be $3.521 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$. Joy George and Joseph [26] had observed a two-step activation process with activation energy values of E_a being 0.20 and 0.25 eV for their annealed and re-crystallised SnS_2 thin film in two different temperature regions of 300–365 K and 365–400 K, respectively. Kawano et al. [5] also had observed a two-step processes of activation for their vacuum deposited amorphous SnS_2 thin film. They found an activation energy of 0.26 eV below 242 K and 0.47 eV above 242 K with pre-exponential values of 2.4×10^{-1} and $2.3 \times 10^{3}\,\Omega^{-1}\,cm^{-1}$, respectively. Lokhande [25] also had observed a two-step activation process with activation energies of 0.43 and 1.52 eV in two different temperature regions for amorphous SnS_2 films.

The optical absorption spectrum of the SnS_2 thin film predicts that this compound absorbs less amount of photons in the low energy region corresponding to the wavelength range of 900–540 nm. In this region, due to this low absorption multiple interference effect is predominant. Thickness of the film 't' is calculated using the wavelengths corresponding to the two successive transmittance maxima (λ_1, λ_2) or the minima (λ_1', λ_2') observed in the transmittance spectrum, in the formula [27]

$$t = \lambda_1\lambda_2/2n(\lambda_2 - \lambda_1) = \lambda_1'\lambda_2'/[2n(\lambda_2' - \lambda_1')]. \quad (2)$$

Here, the refractive index n, is assumed to be equal to the refractive index of SnS_2 in the bulk form. The variation of n with wavelength is assumed to be negligible. The average value of the thickness thus determined is equal to 445 nm. Knowing the thickness, the absorption coefficient α, is calculated from the absorption spectrum. The variation of α with wavelength is plotted as shown in Fig. 5. The absorption spectrum itself predicts that this compound SnS_2 begins to absorb photons of higher energy corresponding to the wavelength region 540–400 nm and hence the effect of multiple interference is not observed. The values of α obtained in the present study agree well with that of the values reported by Joy George and Joseph [20] for their SnS_2 films prepared by vacuum evaporation method.

The optical absorption data of tin disulphide film have been elaborately investigated for the evidence of either allowed or forbidden indirect

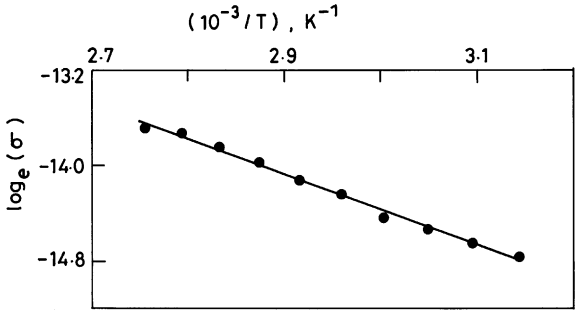

Fig. 4. Variation of electrical conductivity of spray pyrolysised SnS_2 thin film.

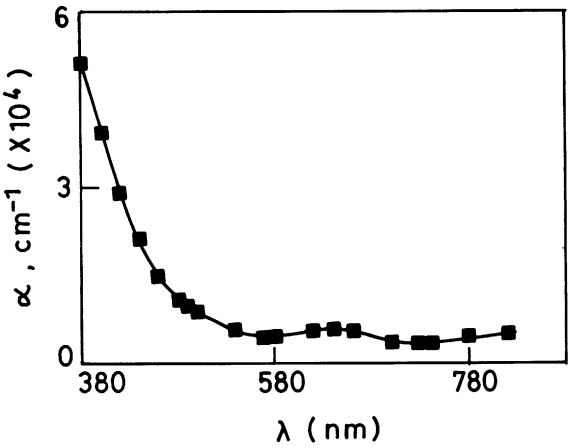

Fig. 5. Absorption coefficient α versus wavelength for SnS_2 thin film.

transition in accordance with the theory of Bardeen et al. [28]. An analysis of Eq. (3) which relates the absorption coefficient α, with the band gap E'_g as

$$\alpha = A(h\nu - E'_g \pm E_p)^r/[h\nu] \quad (3)$$

provides information about the type of optical transition taking place in semiconductor thin films. Allowed indirect transitions and forbidden indirect transitions are assigned when Eq. (3) is substituted with $r = 2$ and 3, respectively. E'_g is the indirect band gap and E_p the absorbed (+) or emitted (−) phonon energy. Both $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ versus photon energy $h\nu$ have been plotted. In Fig. 6,

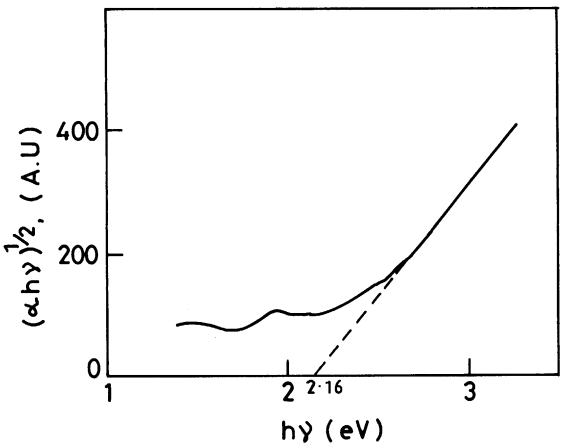

Fig. 6. A typical plot of $(\alpha h\nu)^{1/2}$ against photon energy $h\nu$ for SnS_2 thin film.

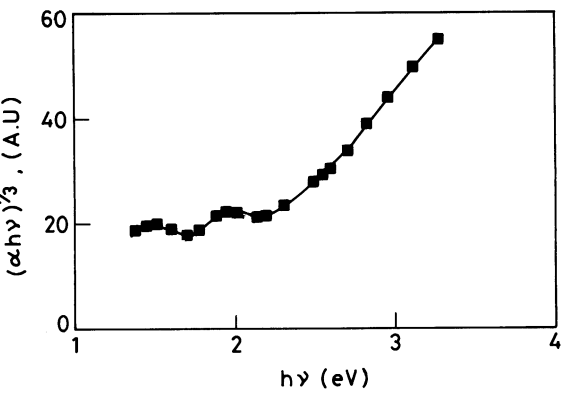

Fig. 7. Plot showing $(\alpha h\nu)^{1/3}$ against photon energy $h\nu$.

where $(\alpha h\nu)^{1/2}$ vs $(h\nu)$ is plotted, a straight line portion is obtained corresponding to the photon energy values extending from 2.56 to 3.19 eV. The energy intercept of this line gives an indirect allowed band gap of 2.16 eV. In the other curve in Fig. 7 corresponding to the value of $r = 3$, a straight line is observed which extends for the energy values between 2.59 and 3.12 eV. The energy intercept of this line predicts an indirect forbidden transition with an energy gap of 1.82 eV. The obtained indirect allowed band gap value agrees with the value of 2.12 eV reported by Joy George and Joseph [20]. They have observed another indirect allowed transition also with a band gap of 2.31 eV. Domingo et al. [13] had reported a threshold for possible indirect phonon assisted transition at 2.07 eV while Greenaway and Nitche [10] and Lee et al. [11] had reported that the fundamental absorption edge at 2.21 eV is due to an allowed indirect transition. The presence of forbidden indirect transition with a band gap of 1.82 eV may be due to the inclusion of oxygen inside the film.

4. Conclusion

Golden yellow coloured thin film of SnS_2 has been successfully deposited on to glass substrates by spray pyrolysis technique. Polycrystalline nature of the film with hexagonal structure and lattice parameter values has been determined, which agree with the standard data. The unit cell dimensions and hence it's volume corresponding to this polycrystalline SnS_2 thin film under study are found to be compressed while comparing with that of the powder diffraction file data. The surface morphological studies exhibited fibre-like structure in the film. The surface elemental compositional analysis of the film is carried out and shows near stoichiometry. This film is found to exhibit n-type electrical conduction. The activation process in the film due to thermal energy is studied and found that the determined activation energy value of 0.25 eV agrees exactly with the reported values. This predicts the presence of a donor level close to the conduction band. The vivid colours seen on the film by the reflected light proves the effect of

multiple interference. The transmittance maxima and minima are observed and hence the thickness of the film is determined to be 445 nm. This spray pyrolysised SnS_2 thin film shows both allowed and forbidden optical transitions of indirect nature with band gap values of 2.16 and 1.82 eV, respectively.

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References

[1] M. Sharon, K. Basavaswaran, Solar cells 25 (1988) 91.
[2] W. Hofmann, Kristallografiya 92 (1935) 161.
[3] S. Bucchia, J. Jumas, M. Maurir, Acta Crystallogr. B 37 (1981) 1903.
[4] Sekar, C. Ray, Malay K. Karanjai, Dhruba Das Gupta, Thin solid films 350 (1999) 72.
[5] K. Kawano, R. Nakata, M. Sumita, J. Phys. D: Appl. Phys. 22 (1989) 136.
[6] D. Mootz, A. Puh, Acta Crystallogr. 23 (3) (967) 471.
[7] L.D.C. Bok, J.C.A. Boeyens, J.S. Afric, Chem. Inst. 10 (2) (1935) 49.
[8] R.D. Engelken, H.E. Mc Claud, Chuan Lee, Mike Slayton, Hossein Ghoreishi, J. Electrochem. Soc. 134 (1987) 2696.
[9] B. Thangaraju, P. Kaliannan, J. Phys. D: Appl. Phys. 33 (2000) 1054.
[10] D.L. Greenaway, R. Nitsche, J. Phys. Chem. Solids 26 (1965) 1445.
[11] P.A. Lee, G. Said, R. Davis, T.H. Lim, J. Phys. Chem. Solids 30 (1969) 2719.
[12] S. Acharya, O.N. Srivastava, Phys. Status Solidi. A 56 (1979) K1.
[13] G. Domingo, R.S. Itoga, C.R. Kannewurf, Phys. Rev. 143 (1966) 536.
[14] S.G. Patil, R.H. Tredgold, J. Phys. D: Appl. Phys. 4 (1971) 718.
[15] R. Nakata, M. Yamaguchi, S. Zembutzu, M. Sumita, J. Phys. Soc. Japan 32 (1972) 1153.
[16] G. Said, P.A. Lee, Phys. Status Solidi. A 15 (1973) 99.
[17] D.G. Mead, J.C. Irwin, Solid State Commun. 20 (1976) 885.
[18] Joy George, C.K. Valsalakumari, J. Crystal Growth 63 (1983) 233.
[19] D. Lokhande, J. Phys. D: Appl. Phys. 23 (1990) 1703.
[20] Joy george, K.S. Joseph, J. Phys. D: Appl. Phys. 15 (1982) 1109.
[21] Koichi Matsumoto, Katsuki Takagi, J. Crystal Growth 63 (1983) 202.
[22] A.K. Abass, K.J. Majeid, H.A. Jassim, W.A. Murad, Solid State Commun. 57 (1986) 805.
[23] B. Thangaraju, P. Kaliannan, Cryst. Res. Technol. 35 (2000) 71.
[24] Jui-chen Lin, James W. Gentry, J. Aerosol Sci. 27 (1) (1996) S375.
[25] C.D. Lokhande, V.V. Bhad, S.S. Dhumure, J. Phys. D: Appl. Phys. 25 (1992) 315.
[26] Joy george, K.S. Joseph, J. Phys. D: Appl. Phys. 16 (1983) 33.
[27] O.S. Heavens, Optical Properties of Thin Solid Films, Dover Publications Inc., New York, 1965, p. 115.
[28] J. Bardeen, F.J. Blatt, L.H. Hall, Proceedings of the Photoconductivity conference, Atlantic city, Wiley, New York, 1956, p. 146.