STUDY OF ELECTRICAL AND OPTICAL PROPERTIES OF SPRAYEDCUINTE$_{2(1-X)}$S$_{2X}$ THIN FILMS

Y. D. Tembhurkar[1],A. S. Meshram[2], O. P. Chimankar[3] and A. R. Khobragade[4]
[1,2]Department of Physics, S. K. Porwal College Kamptee, Nagpur (M.S) -441002 India
[3]Department of Physics, R. T. M. Nagpur University, Nagpur (M.S) - 440033 India
[4]Department of Electronics, S. K. Porwal College Kamptee, Nagpur (M.S) -441002 India
Corresponding author:ameshram138@gmail.com,

Abstract

The spray pyrolysis technique developed thin films of good stoichiometric $CuInTe_{2(1-x)}S_{2x}$ for the composition of x = 0 to x = 1 at the interval of 0.25.The thin films of $CuInTe_{2(1-x)}S_{2x}$ were prepared by spray pyrolysis technique on biological glass slide at various composition of x and deposition gradient from an aqueous solutions containing $CuCl_2$, $InCl_3$, $TeCl_4$ and thiourea respectively. From absorption spectra of the films, the band gap values are found to be 0.96 to 1.43 eV which shows the films direct allowed transition.Conductivity of thin films tested by hot probe method and was of p-type. Electrical resistivity determined by four probe method in the temperature range 77 K to 473 K. The activation energy was calculated from Arrhenius plot. All the films has attributed to copper vacancies.

Keywords- $CuInTe_{2(1-x)}S_{2x}$ thin films, Arrhenius plot, optical absorption spectra by spectrophotometer, etc.

1. Introduction

There has been growing interest in the application of I-III-VI_2 ternary compound semiconductors in various electronic devices. $CuInTe_2$and $CuInS_2$ are the ternary compounds for the use in thin film solar cells because of its optimum direct band gap energy [1, 2] and its controllable conduction type. The influence of growth parameters and the subsequent etch conditions on the electrical properties of $A^{I}B^{III}C_2^{VI}$ have been published in the literature [3].

In the recent years the ternary group compounds have high conversion efficiency that exceeds 15 to 19 %. This means that CIS/Se/Te-based solar cells are able to complete with poly si-based solar cells even though their cost of production is high. Thin films of ternary compound have been prepared by several methods such as electroplated [1], flash evaporation [4], Hot injection method [5],spray pyrolysis [2] [6] [7], Vertical Bridgman technique [8] [9]and electrodeposition method [10]. Among these method, spray pyrolysis method is a simplest, easiest method, inexpensive to deposition and deposition thin films in large area, which would be suitable for large scale industrial production of thin film solar cells [11].

We chose spray pyrolysis method because the films can be made at temperature 350^0C with large area and low processing cost and that is require only very pure starting materials. This paper is focused on the study of electrical and optical properties of $CuInTe_{2(1-x)}S_{2x}$thin films with the composition of x = 0 to x = 1 at the interval of 0.25 in air atmosphere.In this paper we reported optical band gap energy study for two different thicknesses and also studied the chemical composition of the element in $CuInTe_{2(1-x)}S_{2x}$the thin films.

2. Experimental Details

The aqueous solution of Cupric chloride, Indium tri-chloride, Tellurium tetra-chloride and thiourea were prepared of 0.02 M. Chemical used as AR grade. Solution of Cu:In:Te/S were mixed together in the ratio 1:1:3.2 by volume. Excess Tellurium and Sulfur required to reduce the deficiency of tellurium/Sulfur [2 and 7]. If ratio of Cu:In:Te/S used in the ratio 1:1:2, shows the tellurium/sulfur deficiency. Temperature of the substrate was maintained at 300^0C and it was measured by pre-calibrated copper constantan thermocouple. Thicknesses of the films were calculated by Michelson-interferometer. Electrical resistivity calculated by Four-probe technique and the type of conductivity was tested by hot probe method[7] [12].UV-1800 Shimadzu spectrophotometer were used to measured optical absorption from optical spectra and then using these spectra calculates optical band gap by plotting the graph between $(\alpha h\nu)^2$ versus hν for each films [2].

3. Results and Discussion

3.1 Electrical properties

Thin films as checked by hot probe method showed p-type conductivity. The resistivity is determined for two different ranges of temperature range (a) from 300 K to 473 K and range (b) is from 77 K to 273 K. The resistivity for range (a) is measured at atmospheric pressure. The resistivity for range (b) is measured at 10^{-2}torr pressure for which a four-probe arrangement together with sample film was enclosed in a specially prepared stainless steel container, which was immersed in a liquid nitrogen bath [2] as shown in fig. 1. The resistivity was calculated for two different ranges of temperature: - Range (I) is from 300-473 K and range (II) is from 77 K (liquid Nitrogen temperature) to 273 K using relation given below,

$$\rho = \frac{\pi t}{\log_e 2} \times \frac{V}{I} (1)$$

Fig. 2shows the Arrhenius plot of conductivity versus inverse temperature of as deposited $CuInTe_2$ and $CuInS_2$ thin films for the composition x = 0 and x = 1 respectively. The annealed films showed that the atoms are arranged in more regular form than as deposited films. It was observed from fig 2 and 3, three distinct regions of conductivity are seen

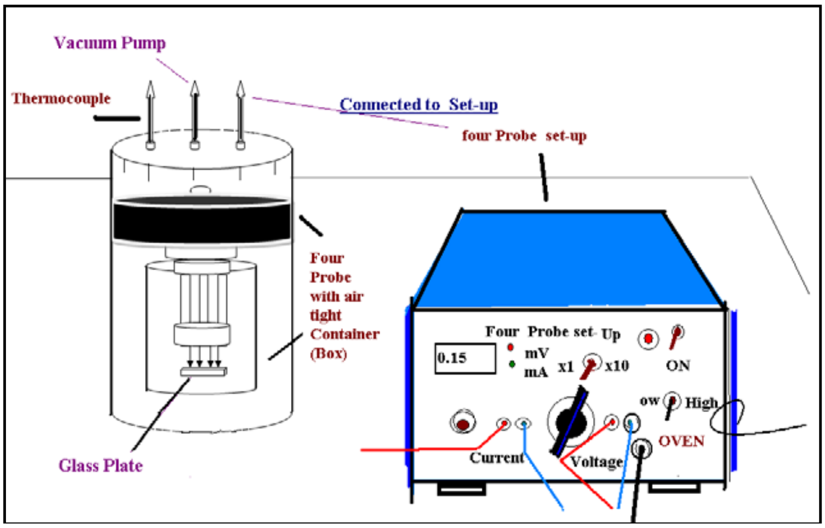

Fig .1 Experimental Set-up of Four Probe methods

The activation energy (E_a) in p-type film can be calculated using the relation [13],

$$\sigma = \sigma_0 \exp\left[\frac{-E_a}{KT}\right] (2)$$

Activation energies calculated using above equation for these three regions (From fig 2) are 86 meV, 38 meV and 3 meV for the temperature range 300 K-473K, 160 K- 250 K and 90 K- 125 K respectively of the composition x = 0 ($CuInTe_2$) and from fig.3, the activation energies are 96 meV, 60 meV and 8.2meVfor x = 1 ($CuInS_2$) the above temperature ranges. Activation energy values of other composition of x (0.25, 0.5 and 0.75) are listed in table 1.

The Arrhenius plot can yield the different levels which are responsible for different donor or acceptor mechanisms. The change in the carrier mechanism is indicated by the change in slope of the curve [14]. Films are not doped intentionally and therefore the defect observed in intrinsic nature. As the conductivity is p-type, acceptors like levels are expected to be present [14].

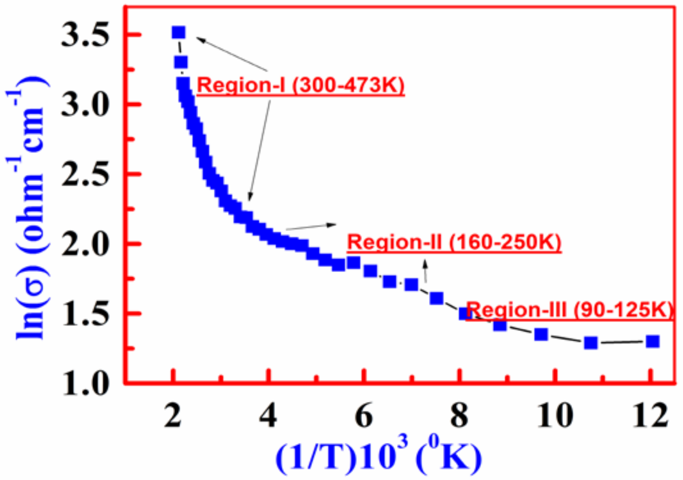

Fig. 2 Arrhenius plots of conductivity of as-deposited $CuInTe_2$ thin film

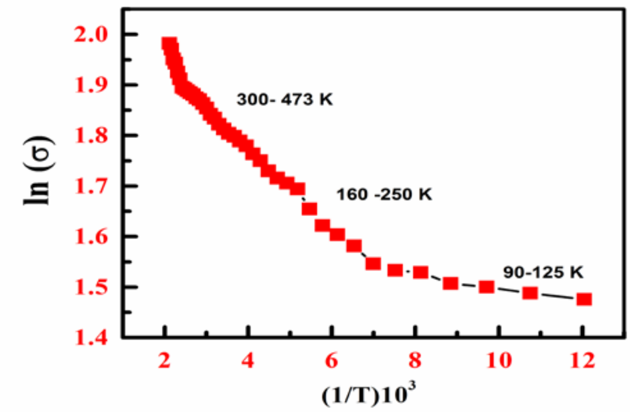

Fig. 3 Arrhenius plots of conductivity of as-deposited $CuInS_2$ thin film.

The activation energy of 86 meV obtained in our investigation is agreed well with 88 meV calculated by hydrogenic approximation [4] which may be due to the acceptor like levels produced by tellurium interstitials at high temperature regions above 250 K. our value 86 meV are smaller than Sridevi and Reddy [4] who was reported activation energy 100 meV for the temperature range 250 K to 300K for flash evaporated $CuInTe_2$ thin films. Dawar et al [15] studied the similar works on vacuum deposited $CuInTe_2$ thin films in the temperature range 77 K to 300K. They stated that the films would have a large deficiency in copper than indium which consistent with higher carrier concentration. Since the films are polycrystalline, the activation energy compounds to the potential barrier of the grain boundary.It is known for long time that defects play a very important role in determining the transport properties of compound semiconductors [16, 17]. The p –type conductivity in $CuInTe_{2(1-X)}S_{2x}$ thin films is mainly due to the presence of Cu-vacancies whereas n-type conductivity results due to formation of Cu interstitials or S, Se and Te vacancies [18].

Table .1 Activation energies of calculated from Arrhenius plots for as deposited films

(x)	Films	Activation Energy (meV) at different Temperature			Resistivity (Ωm)
		300-473K	160-250K	90-125K	
0	$CuInTe_2$	86	38	3	3.669-33.638
0.25	$CuInTe_{1.5}S_{0.5}$	52	18	4	311.716 -1085
0.5	$CuInTe_{1.0}S_{1.0}$	61	19	7	0.045-0.008
0.75	$CuInTe_{0.5}S_{1.5}$	100	56	5	2.066-17.458
1.0	$CuInS_2$	180	70	7	4.373-7.25

This shows that, there is nearly varies conductivity with decreasing temperature with low values 33.3–3.70 Ω^{-1} cm^{-1}. This result is in well agree with Sridevi and Reddy [4] who reported that $CuInTe_2$ is naturally p–type semiconductor[4, 19], acceptor-like levels are expected to be present.The high temperature region is connected to the band conductivity whereas the low-temperature one to the hopping conductivity over localized states of the impurity band/ionic band [20,21]. Our activation energy of 86 meV (Table 4.1) may be due to the acceptor–like levels produced by selenium interstitials [4, 22, 23, 24]. It is also observed that different scattering mechanisms [25, 26] are operative in two temperature regimes (for high temperature). The Seebeck coefficient only a weakdependence of the solar cell parameters; higher Seebeck coefficientsare correlated with higher solar cell efficiencies.

3.2 Optical Properties

Optical absorption study of a material provides useful information to analyze some features concerning the band structure of materials. The optical band gap energy of the semiconductor is an important parameter that plays a major role in the construction of photovoltaic cells.

Optical transmission studies of all as deposited thin films samples were carried out in the wavelength range 350 nm to 1100 nm at room temperature on UV-1800 Shimadzu spectrophotometer. In the absorption measurements, we are concerned with the lightintensity I after traversal of a thickness (t) of material as compared with the incidentintensity I_0, thereby defining the absorption coefficient (α),

$\alpha = 1/t \log (I_0/I)$ (3)

The optical band gap can be calculated by using Tauc relation [27] given by,

$\alpha h\nu = A(h\nu - Eg)^n$(4)

Here, α is the absorption coefficient, n is the integer and has a values 1/2, 3/2 and 2 are thedirectallowed, indirectallowed, forbidden direct and forbidden indirecttransition respectively [5, 28].

Fig 4 shows the transmittance versus wavelength plots of the $CuInTe_{2(1-x)}S_{2x}$ thin filmsas-deposited using different chemical composition parameter x = 0 to x = 1. As expected transmittance of spray deposited films increases with changing value of 'x' in above mention proportion. The onset of decrease of transmittance depends upon the concentration and represents the fundamental absorption edge [2, 19, 26, 29].

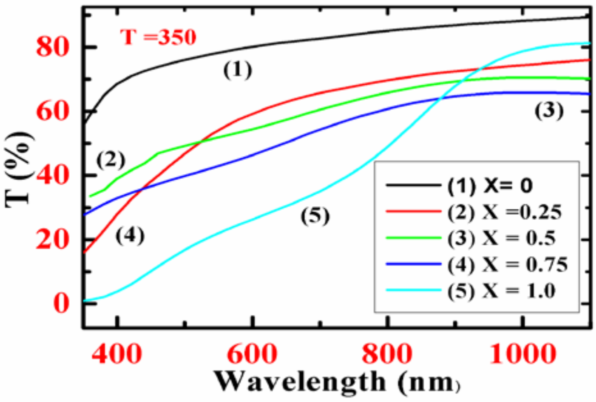

Fig .4Variation of Transmittance versus wavelength plots of $CuInTe_{2(1-x)}S_{2x}$ thin filmsdeposited at 350^{0}C with 1) x = 0, 2) 0.25, 3) 0.5, 4) 0.75, 5) 1.0

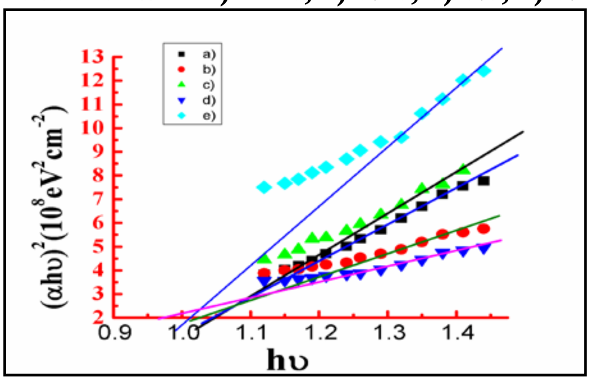

Fig .5Variation of Transmittance versus wavelength plots of $CuInTe_{2(1-x)}S_{2x}$ thin filmsdeposited at 350^{0}C with a) x = 0, b) 0.25, c) 0.5, d) 0.75, e) 1.0

Fig 5 illustrates$(\alpha h\upsilon)^2$ as a function of photon energy ($h\upsilon$) for all thin films of as-deposited and $CuInTe_{2(1-x)}S_{2x}$ film with temperature 350^{0}C and meet energy (hv) axis given the values of band gap Eg[30]. All the film showshigher value of band gap as compare to bulk CIS (1.53eV).This increase in band gap maybe due to thesecondary phase which increases the density of localized state.The absorption coefficient is calculated by using these values of band gap (Eg_1) and slope A of the linear portion of the curves, for hv values corresponding to the non-linear portion of the curve. It is observed that the calculated absorption coefficient (α_1) is always less than the observed optical absorption coefficient (α) of higher values of hv.

This can only be explained, if we assume the presence of an additional absorption process. Using this value Eg_1 and the slope A_1 of the curve, α_1 is calculated for hν. It was observed that calculated the value of α_1 is always less than observed absorption coefficient α for this range of wavelength. This can be only explained if we assume an additional absorption process [2, 4,29].The absorption due to this additional process is denoted by α_2, defined by,

$$\alpha_2 = \alpha_{exp} - \alpha_{1cal} \quad (5)$$

The energy band gap is measured in tail of the spectra with the help of absorption spectra, a graph $(\alpha h\nu)^2$versus hv is plotted as shown in fig 5. The extrapolation of the straight line to (hν) axis gives the value of the energy band gap [30, 31, 32].

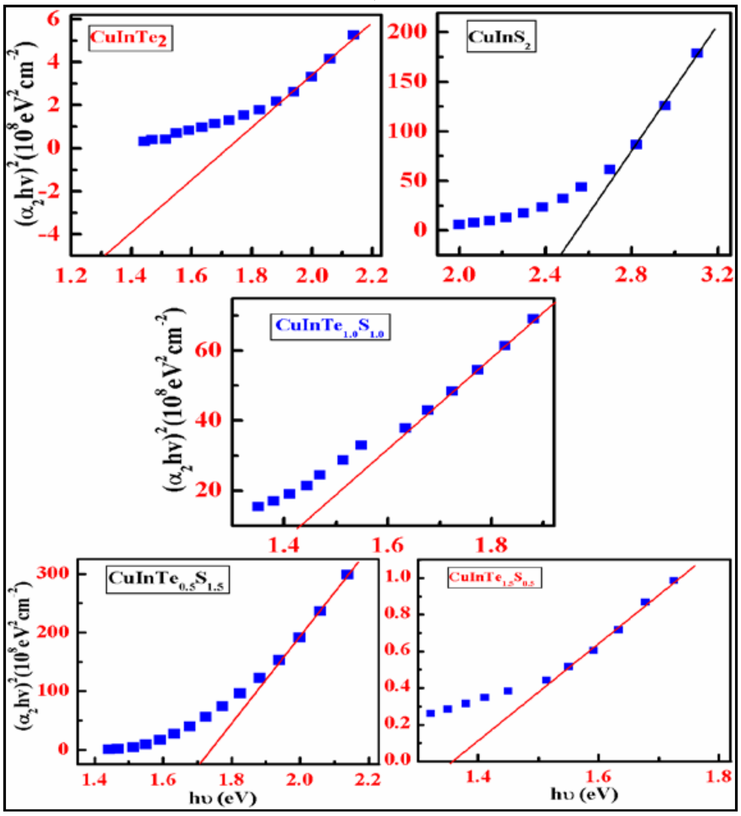

Fig .6 Plot of $(\alpha_2 h\nu)^2$ against incident photon energy (hv) of as deposited $CuInTe_{2(1-x)}S_{2x}$ thin films for x = 0, 0.25, 0.5, 0.75 and 1.0

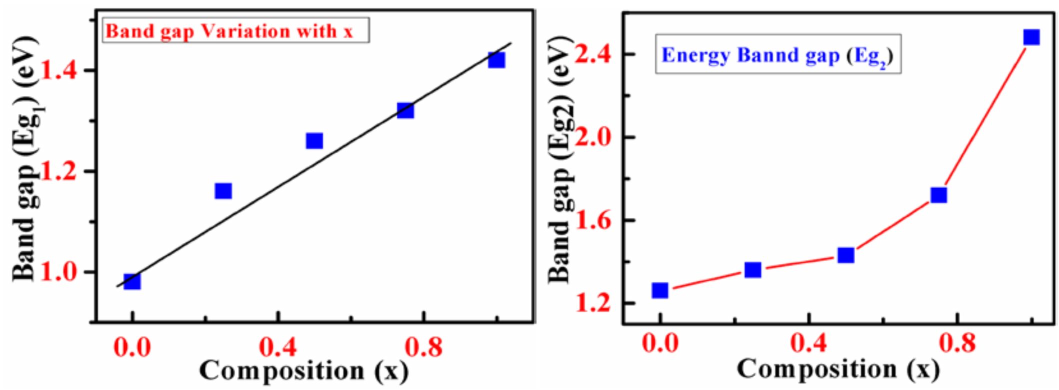

Fig. 7 Plot graph energy band gap (Eg_1) and (Eg_2) against composition x.

Table .2 Tabulated values of optical band gap (Eg), Thickness (t) with composition of x of $CuInTe_{2(1-x)}S_{2x}$ as deposited thin films

x	Films	Thickness (µm)	Optical Band gap (eV)
0	$CuInTe_2$	0.1752	0.98
0.25	$CuInTe_{1.5}S_{0.5}$	0.1821	1.16
0.50	$CuInTe_{1.0}S_{1.0}$	0.2012	1.26
0.75	$CuInTe_{0.5}S_{1.5}$	0.2103	1.32
1	$CuInS_2$	0.1862	1.43

From fig 5 shows that the band gap (Eg_1) values obtained were 0.98 eV, 1.16 eV, 1.26 eV, 1.32 eV and 1.42 eV for x = 0, 0.25, 0.5, 0.75 and 1 respectively. From fig (7), it is observed that the band gap (Eg_1 and Eg_2) varied linearly with the composition of x. our results indicating linear variation of band gap with the composition (x) tailed with the observation of Tembhurkar et al [2] by plotting iso-band gap plots.

Fig 6 shows the graph $(\alpha_2 h\nu)^2$ versus hν for the composition of parameter x,it is observed that the each graph is linear. When it is extrapolated to (hν) axis, the optical band gap is found to be 1.26 eV, 1.36 eV, 1.43 eV, 1.72 eV and 2.43 eV for x = 0, 0.25, 0.5, 0.75 and 1.0 respectively. This also indicates the presence of second direct allowed transition. This is due to onset of an additional absorption process. The difference between these two direct allowed transitions at 0.98 eV and 1.26 eV is 0.28 eV for $CuInTe_2$. Higher values of Eg_2 are obtained at present works compared to other researchers, it was calculates Eg_3 values nearly 1.26 eV [4].

The band gap for x = 0 i.e $CuInTe_2$ was fairly in good agreement with result obtained by Boustani et al [19] produced by evaporation method; the energy gap is calculated to be 0.97 eV and higher values reported by Sridevi et al [4]. The other researchers [33, 30] also reported the values of the band gap lies between 0.93 to 1.03 eV for different preparation technique This lower value of optical band gap may be due to the existence of tailstates and traps [4].

Similarly the optical band gap for x =1 i.e. $CuInS_2$ was close agreement with other workers [34]who demonstrated that the optical band gap was 1.44 eV and 1.38- 1.5 eV respectively for spraypyrolytically deposited films[35]. Therefore, the observed band gap of 1.43 eV of $CuInS_2$ thin films, which are very close to the theoretical values of 1.55 eV [5]and others [7, 36].

The calculation of the optical parameters of the structure of $CuInS_2$ thin films on glass substrate were obtained by mean transmittance values only using a method previously reported by Jackson Lontchiet al [12].He was noted a decrease of band gap value with the annealing temperature due the improvement of the crystallinity of the films. Values are between 1.3 eV and 1.6 eV around the optimal band gap value for the un-doped and the Na-doped $CuInS_2$.

In case of $CuInS_2$, the difference between two direct allowed transitions namely 1.43 and 2.48 eV is 1.06. Sridevi and Reddy [4] have reported thins value as 0.24 and have stated that this is spin-orbit splitting for flash evaporated $CuInSe_2$ thin films.

4. Conclusion

The $CuInTe_{2(1-x)}S_{2x}$ thin films have been successfully prepared by a simple and inexpensive spray pyrolysis deposition method. The conductivity of the films of p-type was obtained. Opticalmeasurement showsthattheCuInTe$_{2(1-x)}S_{2x}$film with the composition of x (x = 0 to x =1 at the interval of 0.25) hasabandgapof 0.98 to 2.43 eV,satisfyingtherequirementoftheabsorberlayers insolar cells. Our energy difference (1.06 eV) is more than the other researchers. $CuInTe_{2(1-x)}S_{2x}$ has absorption coefficient in the order of 10^4 cm^{-1} and has transmittance 70% in the visible region of the solar spectrum.The films are not doped intentionally hence the defect observed in intrinsic nature. The acceptor like levels are appears to be produced by tellurium and sulfur interstitials. At low temperature a variable range hopping conduction mechanism appears to be operative.

Acknowledgements

Authors would like to express his thanks to Principal, S. K. Porwal College Kamptee for providing research facilitates in the respective laboratories.

References

1] Mahalingam, T., Thanikaikarasan, S., Sanjeeviraja, C., Taekyu, K., Sebastian, P. J and Yong, D. K, J. New Mater. Electrochem. Syst., 2010, 13, 77-82.
2] Tembhurkar, Y. D and Hirde, J. P, Bull. Mater. Sci., 1992, 15, 2, 143-148.
3] Fernandez, B. J., Dàvila. R and Belandria, E, Inst. Phys. Conf. Ser. NO152, Section G, Magnetic Materials, 1998.
4] Sridevi, D and Reddy, K. V, Thin Solid Films, 1986, 141,157-164.
5] Vahishad, Y., Ghasemzadeh, R.,Irajizad, A and Mirkazemi, S. M, J. Nanostructures, 2013, 3, 145-154.
6] Suriyanarayanan, N and Mahendran, C, Arch. Phy. Res., 2012, 3, 1, 54-59.
7] Parameshwari, P. M., Bhat, S., Gopalakrishna, N. K, Arch. Phy. Res., 2012, 3, 6, 441-451
8] Essaleh, L., Galibert, J., Wasim, S. M and Marin, G, 2003, 240, 3, 625-633.
9] Wasim, S. M., Essaleh, L., Rincon, C., Marin, G., Galibert, J., Leotin, J, J. Phys. Chem. Solid, 2005, 66, 1887-1890.
10] Xu, X. H., Wang, F., Liu, J. J., Park, K. C., Fujishige, M, Sol. Energy Mater. Sol. Cells, 2011,95, 791–796.
11] Nakamura, S., Yamamoto, A., Sol. Energy Mater. Sol. Cells, 2004, 81, 147-154.
12] Lontchi, J., Khalfallah, B., Abaab, M.,Inter. J. Renew. Energy Res.,2016, 6, 2, 520-526.
13] Sudha L. K., Roy. S., and Rao, K. U, Inter. J. Mater., Mecha. Manufac., 2014, 2, 1, 96-100.
14] Mott, N. F, Phil. Mag. 1969, 19, 835.
15] Dawar, A. L., Kumar, A, Mall, R. P and Mathur, P. C, Thin Solid Films, 1984, 112, 107-119.
16] Wasim, S. M, Rinco´n, C and Mari´n, G, Phys. Stat. Sol. (a), 2002, 194, 1, 244–252.
17] Zachmann, H., Puttnins, S., Daume,F.,Rahm, A and Otte, H, Thin Solid Films, 2011, 519 7317-7320.
18] Marin, G., Wasim, S. M., Sánchez Pèrez, G., Bocaranda, P and Mora, A. E, J. Electro. Mater. 1998, 27, 1351-1357.
19] Boustani, M., Assali, K. El., Bekkay, T., A., Khiara, A., Sol.Energy Mater. Sol. Cell., 1997, 45, 369-376.
20] Kotbi, A., Hartiti, B., Ridah. A., and Thevenin, P., Optical and Quantum Electronics, 2016, 48, 1-9.
21] Iqbal, M., Galibert, J., Wasim, S. M., Herna´ndez, E., Bocaranda, P., Le´otin, J.,Phys. Stat. Soli. (b), 2000, 219, 351.
22] Wasim, S. M., Rincon, C., Marin, G., Marquez, R., J. Phys. Chem. Solids, 2003, 64, 1627.
23] Wasim, S. M., Essaleh, L., Rincon, C., Marin, G., Galibert, J and Leotin, J., J. Phys.Chemi. Sol., 2005, 66, 1887-1890.
24] Bouloufa, A., Messous, Yakushev, M. V., Tomlinson, R. D and Zegadi, A., J. Electr. Dev., 2003, 2, 34-39.
25] Ellmer, K., Hinze, J., Klaer, J., Thin Solid Films, 2002, 413, 92-97.
26] Roy, S., Guha, P., Chaudhuri, S., Pal, A. K., Vacuum, 2002, 65, 27-37.
27] Shay, J. L and Wernick, J. K., Ternary chalcopyrite Semiconductors Growth, Electronic Properties and Applications (Pergamon Oxford, 1975).
28] Ubale, A.U., Chipade, K.S.,Bhute, M. V., Raut, P. P., Malpe, G. P., Sakhare, Y.S., Belkhedkar, M. R.,Inter. J. Mater. Chem., 2012, 2, 4, 165-172.
29] Tembhurkar Y. D., and Hirde, J. P., Bull. Meter. Sci. 16 (3) June (1993) 177-186.
30] Mise, T., Nakada, T.,Thin Solid Films, 2010, 518, 5604–5609.
31] Lakhe M.,and Chaure**,**N. B.,J. Mater. Sci. Eng., 2015, 4, 6, 1-6.
32] In-Hwan Choi and Jang-Il Kim, Journal of the Korean Physical Society, 2001, 39, 2, 336-339
33] Hussain, K. M. A., Podder, J., Saha, D. K., and Ichimura, M.,Ind. J. Pure and Appl. Phys., 2012, 50, 117-122.
34] Onnagawa. Hand Miyashita, K., Jap. J. Appl. Phys., 1984, 23, 8, 965-969.
35] Kotbi, A, Hartiti, B.,Ridah, A and Thevenin, P., Optical and Quantum Electronics, 2016, 48, 1-9
36] Rabeh, M., Kanzari, M and Rezig, B J. Optoelectronic and Biomedical Mater. 2009, 1, 1, 70-78.