

Thickness effect on nano-multilayered Sb/As₂S₃ chalcogenide thin films

Ramakanta Naik*

Department of Physics, Utkal University, Bhubaneswar 751004, India

*Corresponding author. Tel: (+91) 674 2507079; E-mail: ramakanta.naik@gmail.com

Received: 03 December 2015, Revised: 17 February 2016 and Accepted: 01 June 2016

ABSTRACT

The nano multilayered thin films of Sb/As₂S₃ metal chalcogenide were prepared by thermal evaporation technique under high vacuum. The optical parameters such as optical band gap, tauc parameter, urbach energy were determined from the transmission spectra using Fourier Transform Infrared Spectroscopy. These properties are greatly influenced by the thickness of the nano layered Sb/As₂S₃ thin film. The Small Angle X-ray diffraction study reveals the amorphous nature of these films. The analysis reveals that the optical band gap decreases with increase in thickness due to Sb metal. The tauc parameter and urbach energy supports the optical property change. Such type of dependence is attributed to quantum size effect in semiconductors. Copyright © 2016 VBRI Press.

Keywords: Chalcogenides; thin film; EDAX; FTIR; optical properties.

Introduction

Metal chalcogenide nano multilayered thin films are currently attracting considerable attention due to its wide range of applications in holographic recording and fabrication of phase gratings [1, 2]. These amorphous nanolayered chalcogenide structures are similar to the crystalline superlattices yet distinct from ideal crystalline superlattices produced by molecular beam epitaxy. Recently, chalcogenide glasses were prepared in the form of high quality multilayers with nano modulation which established the possibilities for tailoring the optical properties [3]. Nanostructure processing in chalcogenide glasses offers new possibilities for tailoring the electrical, optical and thermal properties. These nanostructures are zero-dimensional quantum dots, one-dimensional chalcogenide molecules embedded in nanoscale channels and two dimensional structures like ultra-thin films and multilayers [4]. The multilayer film of Si has significant role is solar cell applications [5].

Among these, Sb/As₂S₃ nano multilayered films are attractive because of its prominent application in efficient amplitude phase modulated optical relief holograms [6]. Nevertheless, the availability of amorphous semiconductors in the form of high quality multilayers provides potential applications in the field of micro and optoelectronics. The change in their optical properties like refractive index, optical bandgap and absorption coefficients has to be taken into account for some applications in opto-electronics. These films may be used for modeling solid state synthesis, optical recording and one step fabrication of optical relief with high intensity laser beams in the spectral range of high optical absorption [7]. Dielectric mirrors can be made from high refractive index contrast amorphous chalcogenide multilayered films [8]. There is a much interest in physical properties of nanometer size (10–80 nm) semiconductor

clusters. This size regime is interesting because it is where the transition from molecular to bulk electronic behaviour occurs [9].

In our previous paper, we have shown the optical properties change due to photo induced effect in Bi/As₂S₃ bilayer thin films [10]. Takats *et al.* have studied the structural and optical changes in the Bi(Sb)/As₂S₃ multilayers thin films which have potential applications in efficient amplitude-phase modulated optical relief recording as well as for creating surface patterns with modified electrical parameters [11]. The quantum size effect due to thickness variation is observed in In-Bi-Te film [12]. We have shown in our previous paper that the light stimulated diffusion of Te into As₂S₃ matrix resulted to photo-darkening in Te/As₂S₃ bilayer film. The solid solution of Te-As₂S₃ formed after intermixing reduces the optical band gap [13]. So, selecting suitable pairs of chalcogenide glasses with different optical gaps, one can modify the parameters of the light sensitive layers and use them for optical recording. For this reason, we have taken two important materials such as As₂S₃ and Sb for their wide usefulness.

The effect of thickness on the optical properties of As₂Se₃ film was studied which results in the increase in optical band gap with increase in thickness [14]. The influence of thickness on various optical properties of GeSe₂ film was probed by various techniques [15]. The decrease in optical band gap with increase in thickness is reported for InSb film [16]. So, various authors have studied the thickness effect on the optical properties of single layer film. But, in the present work, we report the effect of Sb layer thickness on the optical properties of Sb/As₂S₃ thin films where we have compared three different thicknesses such as 470 nm, 630 nm and 870 nm. The top Sb layer thickness modifies the contact surface between the two layers and makes the changes in optical

properties. The optical band gap, refractive index, extinction coefficient and dielectric properties are significantly dependent on the film thickness. So, by using the properties which are changed due to the thickness of the film, we can fabricate the integrated optical materials. By selecting suitable thickness of the film, one can make devices which are sensitive to thickness of the film and use them for optical recording materials and holographic study material. The changes were characterized by various experimental techniques such as Small Angle X-ray Diffraction and Fourier Transform Infrared spectroscopy as discussed in the present paper.

Experimental

Materials

High purity As_2S_3 (99.999 % pure) and Sb (99.999 % pure) were purchased from Sigma-Aldrich Chemical Co. and used as received. Sb/ As_2S_3 nano-multilayered films with a total thickness of 470 nm, 630 nm and 870 nm were prepared by conventional cyclic thermal evaporation technique from high pure Sb and As_2S_3 . The modulation period was different for different film thickness. The total thickness of the film was measured by Alpha Step 500 as well as by the optical method using the interference pattern of the optical transmission spectra. The sub layer thickness of Sb and As_2S_3 are 1.8 nm and 2.9 nm (470 nm), 2.4 nm and 4.9 nm (630 nm) and 2.9 nm and 5.8 nm (870 nm) respectively. The deposition rate was 1–10 nm/s in a vacuum of 5×10^{-4} Pa. To avoid thickness in homogeneity, the substrates were rotated during evaporation.

Methods

The periodicity and the quality of the multilayer was monitored by the Small Angle X-ray Diffraction (SAXRD) method (Siemens, Cu K_α , $\lambda = 1.54 \text{ \AA}$). The elemental presence in the as-prepared film was checked by energy dispersive X-ray analysis (EDAX) in Sirion XL 40 in which EDAX is attached. The scan was done at 20 kV with 40 μA emission current exposing a sample of 1 cm^2 size at 2×10^{-7} Torr pressure. The optical transmission spectra were taken by using the Fourier Transform Infrared (FTIR) spectrometer from Bruker Optics (IFS66v/S) in the visible wavelength range 400–1200 nm. The measurement was done at room temperature. The measurement was done inside the sample chamber of the spectrometer in dark condition. The reflection loss was not that much as compared to the high absorption in the band gap region. The sample chamber was in vacuum condition to avoid oxidation.

Results and discussion

The quality of the nano multilayered films (NML) were characterized by SAXRD spectra as shown in Fig. 1. Although the SAXRD spectra did not show very well-defined, highly periodic structure, the periodicity calculated from these experiments and from the data of thickness measurements for the given number of deposition cycles were in good accordance. Since the interfaces and the periodicity in such a structure are not perfect the surface

roughness of the as-prepared NML also is about 1 nm. It may be concluded that probably this NLF consists of layer-arranged metal clusters separated by As_2S_3 layers. Additional transition layers may appear at interfaces or the period may change a little during the deposition. This may be the reason of the double maximum diffraction peak, presented in Fig. 1. The absence of sharp peaks confirms the amorphous nature of the multilayered films.

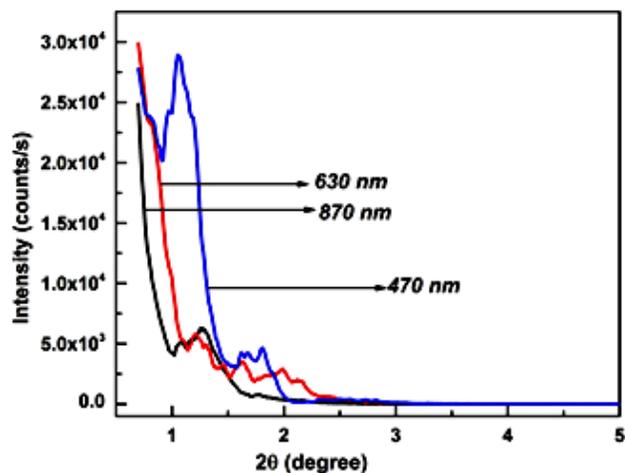


Fig. 1. XRD patterns of the Sb/ As_2S_3 nano-multilayered films.

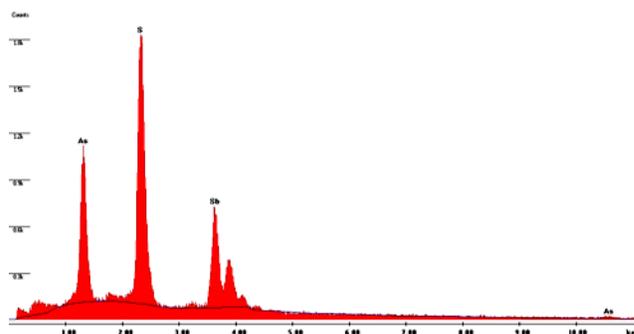


Fig. 2. EDAX spectrum of Sb/ As_2S_3 nano-multilayered film.

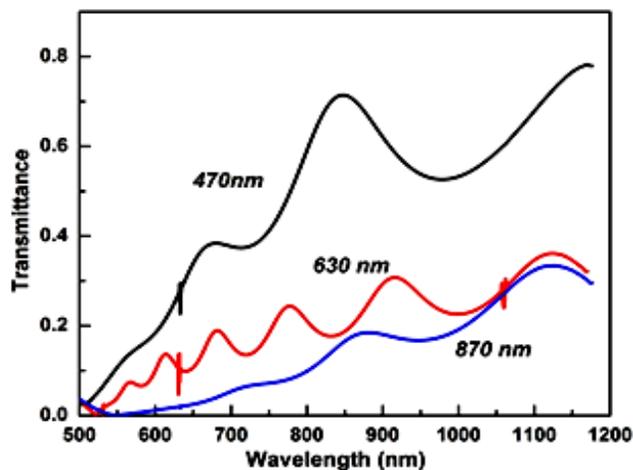


Fig. 3. Transmission spectra of Sb/ As_2S_3 nano-multilayered film.

The presence of As, Sb and S was confirmed from the EDAX spectrum as shown in **Fig. 2**. The transmittance spectra of the NML films as a function of wavelength are plotted in **Fig. 3**. It can be seen that the ‘non-shrinking’ interference fringes observed in the transmittance spectra at higher wavelength (500–1100 nm) indicate the homogeneity and smoothness of the deposited films.

The absorption coefficient of the NML films was calculated from the experimental data of transmittance and reflectance in the strong absorption region using the relation [17],

$$\alpha = \frac{1}{d} \ln \left(\frac{(1-R)^2}{T} \right) \quad (1)$$

where, T is the transmittance, R is the reflectance and d is the thickness of the deposited film. **Fig. 4** shows the dependence of the absorption coefficient on wavelength for the films. It has been observed that the absorption coefficient increases with thickness. In crystalline materials, the fundamental edge is directly related to transitions from the conduction and valence band, and associated with direct and indirect band gaps, whereas in the case of amorphous material the transitions are termed non-direct owing to the absence of an electronic band structure in k-space.

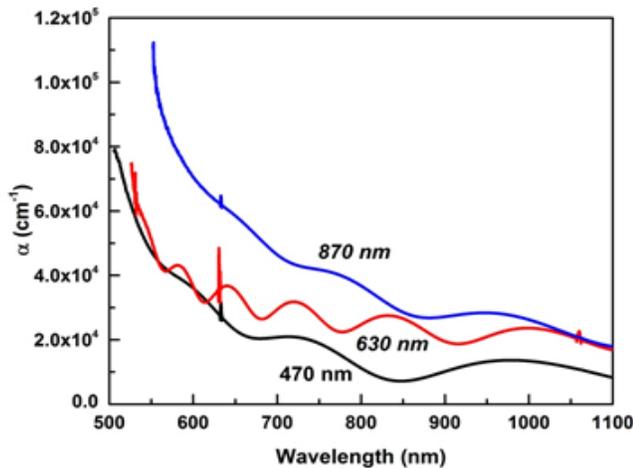


Fig. 4. Absorption spectra of Sb/As₂S₃ nano-multilayered film.

In the absorption process, a photon of known energy excites an electron from a lower to a higher energy state, corresponding to an absorption edge. In chalcogenide glasses, a typical absorption edge can be broadly ascribed to one of the three processes: (i) Residual below-gap absorption (ii) Urbach tails and (iii) interband absorption. Chalcogenide glasses have been found to exhibit highly reproducible optical edges, which are relatively insensitive to preparation conditions and only the observable absorption [18] with a gap under equilibrium conditions account for the first process. In amorphous materials, a different type of optical absorption edge is observed and absorption coefficient increases exponentially with the photon energy near the energy gap. This type of behavior has also been observed in other chalcogenides [18, 19]. This optical absorption edge is known as the Urbach edge and is given by,

$$\alpha(h\nu) = \alpha_0 \exp \left(\frac{h\nu}{E_e} \right) \quad (2)$$

where, α_0 is a constant and E_e corresponds to the Urbach energy (the width of the band tail of the localized states in the band gap). In this region, transition between (defect) states in the gap and the bands take place [20]. Plotting the dependence of $\log(\alpha)$ on photon energy will give a straight line. The calculated value of E_e , the inverse of the slope of the straight line, gives the width of the tails of the localized states into the gap at band edges. In evidence, the Urbach energy of 870 nm film exhibits a higher value of 501 ± 2 meV, whereas Urbach energy decreases with decrease in thickness to 387 ± 1 meV (for 630 nm) 200 ± 3 meV for thinner film of thickness 470 nm. From the above results, it is concluded that the film of 470 nm thickness possesses structural randomness and as the thickness increases the defects are increased.

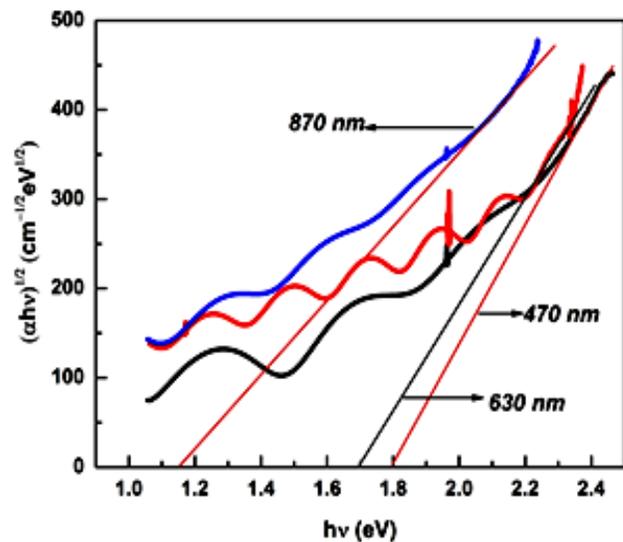


Fig. 5. Band gap variation with thickness.

The fundamental absorption edge in most amorphous semiconductors follows an exponential law. Above the exponential tail, the absorption coefficient has been reported [21] to obey the following equation:

$$(\alpha h\nu)^{1/2} = B^{1/2} (h\nu - E_g) \quad (3)$$

where, ν is the frequency of the incident beam, B is a constant, E_g is optical band gap. By plotting $(\alpha h\nu)^{1/2}$ vs $(h\nu)$ and fitting the distinct linear regime which denotes the onset of absorption, with straight line fitting, the x-intercept will give the value of optical band gap as shown in **Fig. 5**. The slope of the fitting will give the value of $B^{1/2}$. The constant B includes information on the convolution of the valence band and conduction band states and on the matrix element of optical transitions, which reflects not only the k selection rule, but also the disorder induced spatial correlation of optical transitions between the valence band and conduction band [22]. Moreover, B is highly dependent on the character of the bonding. The above equation is valid for a number of amorphous materials in the spectral region of large (10^4 - 10^5 cm⁻¹), i.e., Tauc region. The error

in different optical parameters was calculated by the χ^2 fitting values. These values are automatically calculated as standard errors after straight line fitting of different plots. The optical band gap of the As_2S_3 film is found to be 2.38 ± 0.002 eV whereas the band gap reduced to 1.80 ± 0.001 eV for $\text{Sb}/\text{As}_2\text{S}_3$ 470 nm film. Since the optical absorption depends on short-range order in the amorphous states and defects associated with it, the decrease in optical band gap may be explained on the basis of “density of state model” proposed by Mott and Davis [23]. It is found that the optical band gap decreased from $E_g = 1.80 \pm 0.001$ eV for 470 nm film to $E_g = 1.69 \pm 0.001$ eV for 630 nm film as the absorption edge shifts to lower photon energies with the deposition of more Sb on it. The modulation period of 630 nm film is more than that of 470 nm film. The optical energy gap decreased to 1.15 ± 0.002 eV for 870 nm films with increasing thickness and these changes can be attributed due to the presence of defects in amorphous materials [24]. The initial formation of films is significantly affected to a great extent by the structure of the substrate. During the deposition of As_2S_3 film on the glass substrate, some defects were present in the lower surface and it decreases as the thickness increases. When we have deposited Sb layer on the As_2S_3 layer, then again the defects were created near the surface. In particular, it is known that unsaturated bonds (Sb-Sb) together with some saturated bonds (As-S) are produced as a result of an insufficient number of atoms deposited in amorphous films. These unsaturated bonds are responsible for the formation of defects in the film which produce localized states in the amorphous solids. The presence of a high concentration of localized states in the bond structure is responsible for the low values of the optical energy gap in the case higher thickness film. By increasing the thickness of the Sb layer from 1.8 nm to 2.9 nm, the formation of unsaturated defects is greatly enhanced and produces a large number of unsaturated bonds such as Sb-Sb, S-S and As-As. The reduction in the number of saturated defects increases the density of localized states in the band structure and consequently decreases the band gap. This is well supported by the Tauc parameter and the Urbach energy. $B^{1/2}$ exhibits a higher value of $709 \pm 1 \text{ cm}^{-1/2} \text{ eV}^{-1/2}$ for the NML film of lower thickness (470 nm) as compared to 870 nm film $418 \pm 3 \text{ cm}^{-1/2} \text{ eV}^{-1/2}$. But as the thickness increases, $B^{1/2}$ also decreases and exhibits a lower value of $553 \pm 1 \text{ cm}^{-1/2} \text{ eV}^{-1/2}$ for the 630 nm NML film. In evidence, the Urbach energy of lower thickness film of 470 nm exhibits a lower value of 200 ± 3 meV, whereas Urbach energy increases with increase in thickness. The smaller the $B^{1/2}$ value, the higher the structural disorder [25]. So, the decrease in E_g in the amorphous films can be explained by the increased tailing of the band tails in the gap. The Sb metal deposition decreases the transmission and the optical band gap making the film more conducting. The decrease in band gap with increase in thickness of these multilayer films may also be due to the quantum size effect as observed in Se [26].

Conclusion

The NML films have amorphous nature as confirmed from the SAXRD. Various parameters related to optical

properties were calculated for different thickness NML films of $\text{Sb}/\text{As}_2\text{S}_3$. The optical transmittance decreased with thickness of Sb layer. The absorption mechanism in the film is due to indirect allowed transition. The decrease in optical band gap is due to the change in localized states near to the band edges which is attributed to the increased tailing of the band tails in the gap. This deposition of more Sb layer thickness creates more homopolar bonds which are responsible for the decrease of band gap as well as the increase in disorder that we have seen from the decrease value of $B^{1/2}$ and increase value of Urbach energy. So, by using the properties which are changed due to the thickness of the film, we can fabricate the integrated optical materials. By selecting suitable thickness of the film, one can make devices which are sensitive to thickness of the film and use them for optical recording materials and holographic study material.

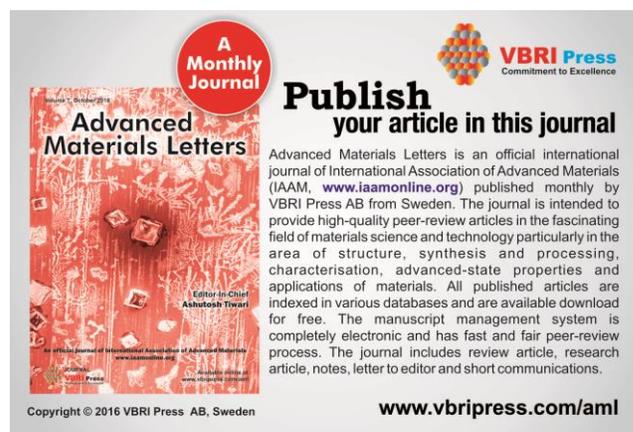
Acknowledgements

The authors thank Department of Science and Technology (DST), Govt of India for DST-INSPIRE Research grant and using the National Facility for Optical Spectrometry at Department of Physics, Indian Institute of Science (IISc).

References

- Malyovanik, M.; Ivan S; Csik A; Langer G A; Beke D L; Kokenyesi S; *J. Appl. Phys.* **2003**, *93*, 139.
DOI: [10.1063/1.1526157](https://doi.org/10.1063/1.1526157)
- Adarsh, K. V.; Naik, R.; Sangunni, K. S.; Kokenyesi, S.; Jain, H.; Miller, A. C.; *J. Appl. Phys.* **2008**, *104*, 053501.
DOI: [10.1063/1.2973460](https://doi.org/10.1063/1.2973460)
- Naik, R.; Ganesan, R.; Adarsh, K. V.; Sangunni, K. S.; Takats, V.; Kokenyesi, S.; *J. Non-Cryst. Solid*, **2009**, *355*, 1943.
DOI: [10.1016/j.jnoncrysol.2009.05.061](https://doi.org/10.1016/j.jnoncrysol.2009.05.061)
- Tanaka, K.; *J. Non-Cryst. Solids* **2003**, *326*, 21.
DOI: [10.1016/S0022-3093\(03\)00371-5](https://doi.org/10.1016/S0022-3093(03)00371-5)
- Khanna, K. M.; Ekai, R.; Ronno, C. K.; Rotich, S. K.; Torongey, P. K.; *Indian J Pure & Appl. Phys.*, **2005**, *43*, 432.
- Wagner, T; Ewen, P. J. S.; *J. Non-Cryst. Solids* **2000**, *266*, 979.
DOI: [10.1016/S0022-3093\(99\)00890-X](https://doi.org/10.1016/S0022-3093(99)00890-X)
- Vojnarovych, I.; Takach, V.; Cheresnyia, V.; Pynzenik, V.; Makauz, I.; Chernovich, S.; *Phys. Chem. Solid State*, **2007**, *8*, 722.
- Kohoutek, T.; Orava, J.; Wagner, T.; Hrdlicka, M.; Vlcek, M.; Frumar, M.; *J. Phys. Chem.* **2008**, *69*, 2070.
DOI: [10.1016/j.jpcc.2008.03.003](https://doi.org/10.1016/j.jpcc.2008.03.003)
- Mane, R. S.; Sankapal, B. R.; Lokhande, C. D., *Mat. Chem. Phys.* **2000**, *64*, 215.
DOI: [10.1016/S0254-0584\(99\)00261-8](https://doi.org/10.1016/S0254-0584(99)00261-8)
- Naik, R.; Ganesan, R.; Sangunni, K. S., *J. Alloys Comp.* **2013**, *554*, 293.
DOI: [10.1016/j.jallcom.2012.11.198](https://doi.org/10.1016/j.jallcom.2012.11.198)
- Takats, V.; Vojnarovich, I.; Pinzenik, V.; Mojzes, I.; Kokenyesi, S.; Sangunni, K. S., *J. Phys. Chem. Solids* **2007**, *68*, 943.
DOI: [10.1016/j.jpcc.2007.01.021](https://doi.org/10.1016/j.jpcc.2007.01.021)
- Soni, P. H.; Bhavsar, S. R.; Pandya, G. R.; Desai, C. F., *Indian J Pure & Appl Phys.* **2008**, *46*, 806.
- Naik, R.; Kumar, C.; Ganesan, R.; Sangunni, K. S., *Mater. Chem. Phys.* **2011**, *130*, 750.
DOI: [10.1016/j.matchemphys.2011.07.062](https://doi.org/10.1016/j.matchemphys.2011.07.062)
- Sati, D. C.; Kumar, R.; Mehera, R. K., *Turk. J. Phys.*, 2006, *30*, 519.
ISSN: [1300-0101](https://doi.org/10.1300-0101).
<http://journals.tubitak.gov.tr/physics/issue.htm?id=684>
- Ananth R T, Chithra lekhhab P, Sundarakannana B, Pathinettam D P, *Philos. Mag.* **2012**, *92*,
DOI: [10.1080/14786435.2011.647104](https://doi.org/10.1080/14786435.2011.647104)
- Viswakarma, S. R.; Kumar, A.; Tripathi, R. S. N.; Das, S., *Indian J Pure & Appl. Phys.*, **2013**, *51*, 260.
- Othman, A. A.; Osman, M. A.; Amer, H. H.; Dahshan, A., *Thin Solid Films*, **2004**, *457*, 253.
DOI: [10.1016/j.tsf.2003.10.158](https://doi.org/10.1016/j.tsf.2003.10.158)

- 18 Abkowitz, M., *Polym. Eng. Sci.* **1984**, 24, 1149.
DOI: [10.1002/pen.760241412](https://doi.org/10.1002/pen.760241412)
- 19 J. Tauc (Ed.), *Amorphous and Liquid Semiconductors*, Plenum Press New York **1979**, pp. 159
ISBN: [0-306-307774](https://www.isbn-international.org/product/0-306-30777-4)
- 20 Urbach, F., *Phys. Rev.* **1953**, 92, 1324.
DOI: [10.1103/PhysRev.92.1324](https://doi.org/10.1103/PhysRev.92.1324)
- 21 Elliot, S. R., *Materials Science and Technology: A Comprehensive Treatment*, Wiley, New, York, **1991**, pp. 376.
ISBN: [10.3527268251](https://www.isbn-international.org/product/10-3527268251)
- 22 Bindemann, R., Paetzold, O., *Phys. Status Solidi B*, **1990**, 160, 183.
DOI: [10.1002/pssb.2221600252](https://doi.org/10.1002/pssb.2221600252)
- 23 Mott, N. F., Davis, E. A., *Electronics Processes in Non-Crystalline Materials*, Clarendon, Oxford, **1979**, 428.
ISBN: [10:0198512880](https://www.isbn-international.org/product/10-0198512880)
- 24 Chaudhary, S.; Biswas, S. K.; Choudhary A.; *J. Mater. Sci.*, **1988**, 23, 4470.
DOI: [10.1007/BF00551946](https://doi.org/10.1007/BF00551946)
- 25 Pan, R. K.; Tao, H. Z.; Zang, H. C.; Zhao, X. J.; Zhang, T. J.; *J. Alloys Compd.* **2009**, 484, 645.
DOI: [10.1016/j.jallcom.2009.05.011](https://doi.org/10.1016/j.jallcom.2009.05.011)
- 26 Singh, M.; Bhahada, K. C.; Vijay, Y. K.; *Indian J Pure & Appl. Phys.*, **2005**, 43, 129.



A Monthly Journal

Advanced Materials Letters

Publish your article in this journal

Advanced Materials Letters is an official international journal of International Association of Advanced Materials (IAAM, www.iaamonline.org) published monthly by VBRI Press AB from Sweden. The journal is intended to provide high-quality peer-review articles in the fascinating field of materials science and technology particularly in the area of structure, synthesis and processing, characterisation, advanced-state properties and applications of materials. All published articles are indexed in various databases and are available download for free. The manuscript management system is completely electronic and has fast and fair peer-review process. The journal includes review article, research article, notes, letter to editor and short communications.

www.vbripress.com/aml

Copyright © 2016 VBRI Press AB, Sweden