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Effects of annealing and structural phase transformation on the Urbach absorption in thin silver sulphide films

P. Chattopadhyay and S. Guha Roy
Department of Electronic Science, University of Calcutta, 92, A.P.C. Road, Kolkata-700009, India

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The sub-band gap optical absorption in silver sulphide thin films prepared by chemical conversion technique has been studied in the light of Urbach absorption law at different annealing temperatures. The study reveals the Urbach absorption parameters and band gap of the material are sensitive to annealing temperature. Interestingly, these parameters undergo a sudden change as the annealing temperature exceeds a certain critical value. The observed changes in the values of absorption parameters have been attributed to the structural phase transition and the modification of grain boundary interfaces and/or changes in the crystallographic orientation due to annealing. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4896971]

I. INTRODUCTION

Silver sulphide is an important member in the family of semiconducting metal sulphides having interesting physical and chemical properties, namely, photographic sensitivity,[1] gas sensing properties,[2–4] important optical properties being exploited in semiconductor sensitized solar cells,[5,6] and photocatalytic properties applied to hydrogen generation.[7] The applications of silver sulphide in realizing atomic/resistance switches,[8–11] core-shell coaxial nano-structures[12,13] have made this material even more attractive and a promising candidate for nano-scale electronics.

However, despite of diverse applications, there seems to be inadequacies in the understanding of the optical absorption properties of this material, including when the material is in the form of thin film. For example, the band gap of Ag_2S thin film is found to be dependent on different processing conditions. Ezema *et al.*[14] reported an increase in the band gap of chemically deposited Ag_2S thin films from 1.10 eV to 1.40 eV when the samples are annealed at 420 K. However, Sankapal *et al.*[15] reported a decrease in the value of band gap of the material upon annealing. Moreover, the effect of annealing may lead to a change in the grain size or reorganization of the material as observed in other polycrystalline thin films.[16,17] It is also well known that silver sulphide undergoes a phase transition around a temperature of 180 °C, which results in a structural change from monoclinic to body centered cubic phase. Such a structural phase transition is likely to influence the optical absorption parameters of the material, including the parameters of sub-band gap optical absorption spectra described by Urbach law.[18] It is therefore a matter of concern how the Urbach law in the sub-band gap absorption region of the material is influenced under such annealing conditions.

In a recent paper,[19] the sub-band gap optical spectra of as-deposited and annealed cadmium sulphide films have been analyzed by segmenting the absorption curves into three regions, namely, a region of constant absorption, the region described by Urbach law and a band-to-band transition region. It has been found that the Urbach absorption region yields a steepness constant, which is much different from the theoretical value of its single crystal counterpart. Similar effects are likely to be present in other polycrystalline materials, e.g., silver sulphide thin films, as in the present case. Moreover, for polycrystalline Ag_2S films, the effect of annealing and structural phase transformation on the Urbach absorption parameters and their correlations to the band gap energy of the material is still a matter of concern. It is therefore important to study the above effects of annealing on the optical absorption spectra of silver sulphide thin films. In this work, an attempt has been made to explore the consequences of annealing and structural phase transformation on the Urbach absorption in chemically prepared thin Ag_2S films. The results are analyzed by applying the scheme of segmentation of the absorption curve discussed in Ref. 19.

II. SAMPLE PREPARATION AND MEASUREMENTS

In order to prepare thin films of Ag_2S, we have used chemical bath deposited polycrystalline CdS thin films as the source material. The method of deposition has been discussed in our previous publication.[20] The chemical bath prepared for the deposition of the source CdS films contained cadmium chloride, ammonium acetate, ammonium hydroxide, and thiourea. The deposition temperature has been maintained within 65 °C to 75 °C. The solution is continuously stirred at a constant speed to obtain uniform films on glass substrates. The process has been repeated several times until good quality CdS films are obtained. Subsequently, as-deposited CdS films have been chemically converted into Ag_2S films applying a chemical conversion technique discussed earlier.[20] The source films are immersed into an aqueous $AgNO_3$ (1.47×10^{-1} M) solution. An adequate immersion time (~24h) has been given to obtain grey-black coloured Ag_2S films. The converted Ag_2S thin films are taken out of the solution, cleaned in distilled water and dried. The thickness of the film has been measured and found to be 9.5 μm. The converted Ag_2S samples are then heat treated for 15 min in open air in the temperature range of 50 °C to 300 °C, at intervals of 50 °C. The surface morphology of the film so prepared is studied by

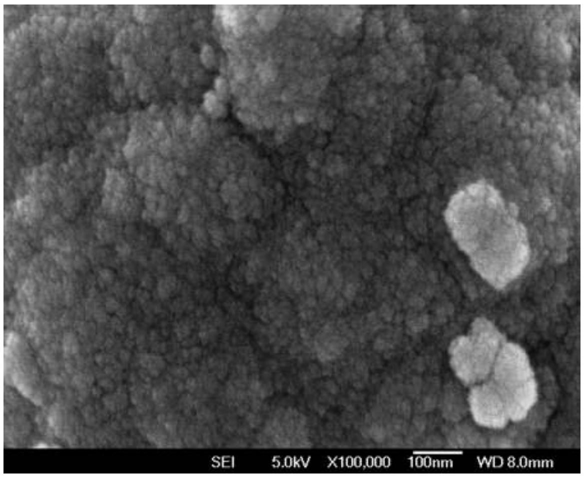


FIG. 1. The SEM image of as-deposited Ag_2S thin film prepared by chemical conversion method.

scanning electron microscope (SEM). The SEM image of the as-deposited Ag_2S film is shown in Fig. 1. The image reveals grain size varying over the range of ~9.7 nm to 16.2 nm. The compositional analysis of the sample has been carried out by energy dispersive X-ray analysis (EDS). The EDS results in Fig. 2 reveal the silver to sulphur atomic ratio to be 1.32:1, along with traces of cadmium and other elements.

The optical absorbance of the films is measured by spectrophotometer over a range of wavelength from 340 nm to 1100 nm. The absorption spectra of the samples annealed at different temperatures are shown in Fig. 3. The corresponding plots of absorption coefficient as a function of photon energy for the as-deposited and annealed samples are shown in Fig. 4.

III. EXTRACTION OF THE ABSORPTION PARAMETERS

To extract the optical absorption parameters of the Ag_2S films, the absorption spectra of the films may be divided into two different regions, one corresponds to the Urbach absorption region and the other is the typical band-to-band transition region. The variation of absorption coefficient of the film in the Urbach region is found to be nearly exponential, which can be described by the Urbach exponential rule in the following form:[19]

$$\alpha = \alpha_0 \exp(h\nu/E_0), \tag{1}$$

where E_0 is the Urbach energy and α_0 is a constant. The values of E_0 and α_0 of the Ag_2S films have been estimated from $\ln\alpha$ vs. $h\nu$ plots and are plotted in Fig. 5. It may be seen that, when the photon energy exceeds the band gap energy, the absorption coefficient increases sharply with the photon energy. Such a region is considered to determine the band gap of the Ag_2S films, by applying the well known relation[21]

$$\alpha = A\,(h\nu - E_g)^{\gamma}, \tag{2}$$

where E_g is the band gap of the material and A is a constant and $\gamma = 1/2$. The α^2 vs. $h\nu$ plots for band-to-band transition region for as-deposited and annealed Ag_2S films are shown in Fig. 6. The band gap of all the samples has been determined by extrapolating linear regions of all the curves to the $h\nu$-axis. The variation of the band gap energy with the annealing temperature is shown in Fig. 7.

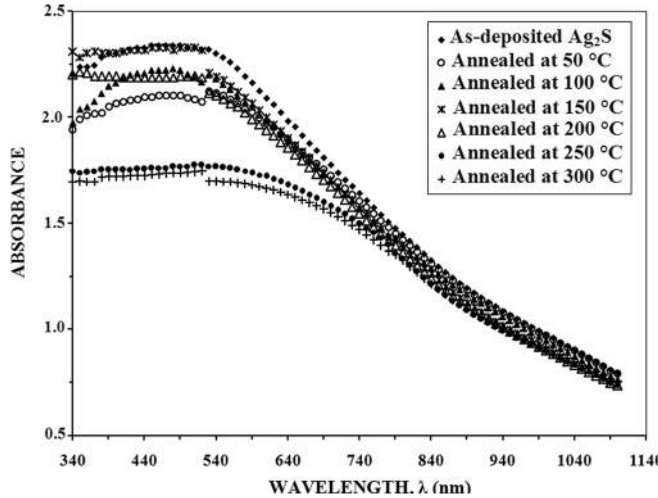
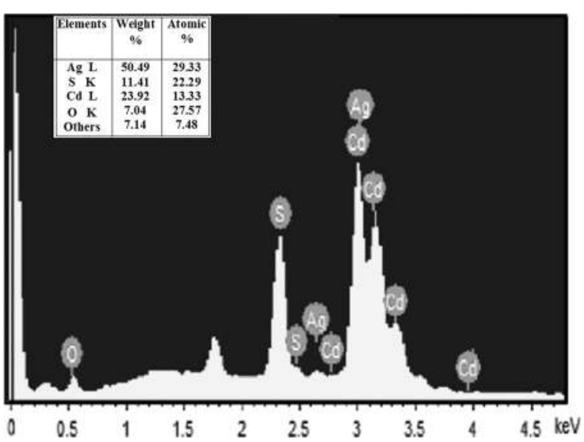


FIG. 3. Measured absorption spectra of the Ag_2S thin films, as-deposited and annealed prepared by chemical conversion method.



Elements	Weight %	Atomic %
Ag L	50.49	29.33
S K	11.41	22.29
Cd L	23.92	13.33
O K	7.04	27.57
Others	7.14	7.48

FIG. 2. The EDS results of as-deposited Ag_2S thin film prepared by chemical conversion method.

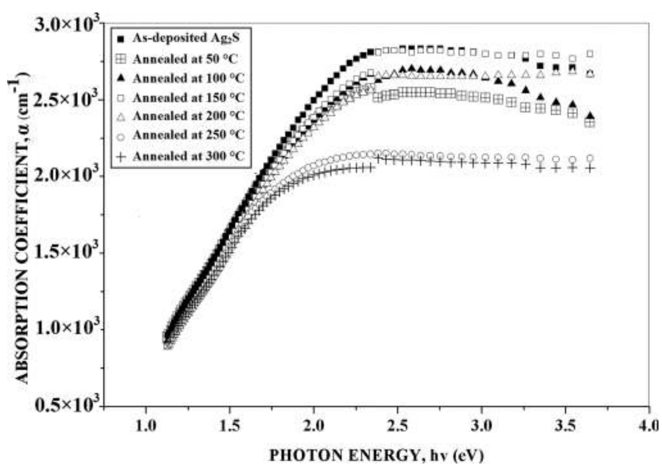


FIG. 4. Dependence of absorption coefficient, α, for as-deposited and annealed Ag_2S thin films on photon energy.

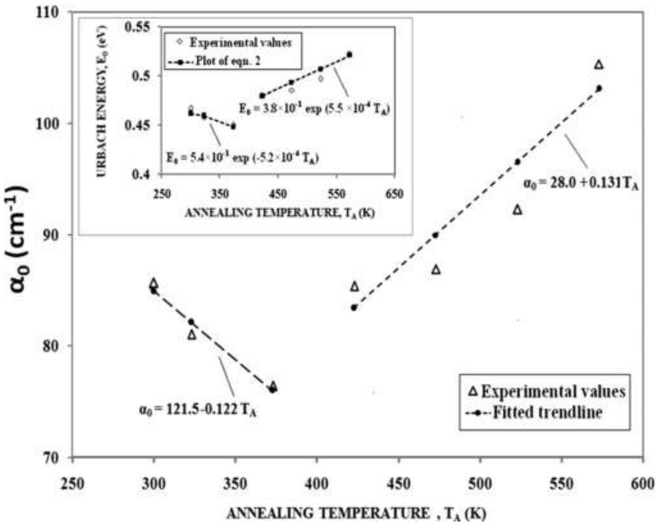


FIG. 5. Dependence of Urbach parameters, α_0 and E_0, on the temperature of annealing, T_A. Dashed line curves represent linearly fitted relations describing the experimental values of α_0. The inset shows the variation of Urbach energy, E_0 with annealing temperature, T_A. Dashed line curves represent exponentially fitted relations applying Eq. (2).

IV. DISCUSSIONS

The absorption spectra of Ag_2S thin films shown in Fig. 3 reveal optical absorption in Urbach and band-to-band transition regions to be dependent upon the annealing temperature. Interestingly, for all the samples, the value of E_0 has been found to be much larger in magnitude compared to a value of kT of Urbach's original exponential rule.[18] This has also been observed in the case of thin CdS films and attributed to a characteristic feature for polycrystalline material.[19] The present results on the absorption coefficient of the Ag_2S films further corroborate the above conclusion. The measurements also indicate the sensitivity of sub-band gap absorption parameters and band gap of the material to be dependent on annealing temperature. The variation of E_0 with annealing temperature has been shown in Fig. 5. It is found that the E_0 values can be fitted by an exponential relation given by

$$E_0(T_A) = E_0(0)\ \exp(BT_A), \tag{3}$$

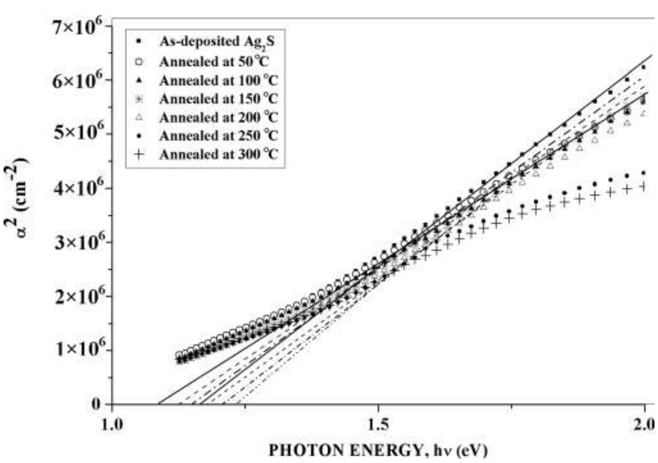


FIG. 6. The plot of α^2 as a function of photon energy, $h\nu$ for the as-deposited and annealed Ag_2S thin films.

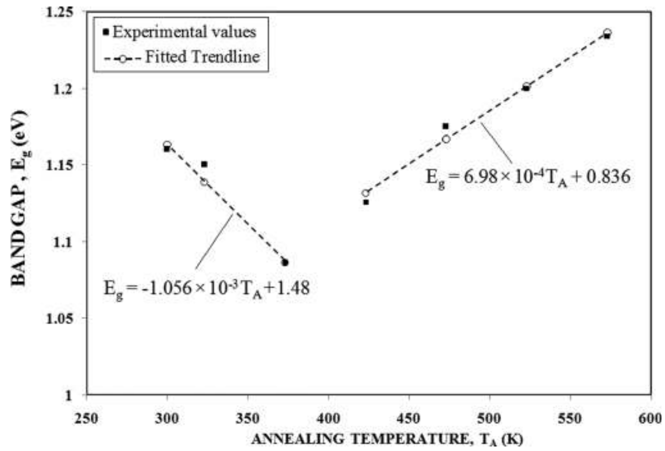


FIG. 7. The variation of the band gap energy with the annealing temperature.

where $E_0(0)$ and B are constants and T_A is the annealing temperature. As may be seen from the figure, the Urbach energy initially decreases with the annealing temperature, which can be described by Eq. (2) with $E_0\ (0) = 5.4 \times 10^{-1}$ eV and $B = -5.2 \times 10^{-4}\ K^{-1}$. However, an opposite trend in the variation of E_0 (0) is noticed as the annealing temperature exceeds a certain value. The values of E_0 (0) and B in this case have been found to be 3.8×10^{-1} eV and 5.5×10^{-4} K^{-1}, respectively. A reversal in the sign of the constant B suggests an important role of a critical annealing temperature on the Urbach energy. Interestingly, the variation of α_0 with annealing temperature also shows similar features as observed in the case of E_0. By fitting the experimental points by trend lines, we find the slopes and intercepts of α_0 vs. T_A plots to be $-0.122\,cm^{-1}\ K^{-1}$ and $121.5\,cm^{-1}$, respectively, below a critical value of annealing temperature and $0.131\,cm^{-1}\ K^{-1}$ and $28.0\,cm^{-1}$, respectively, as the value of annealing temperature exceeds the critical value. Such dependencies of the parameters E_0 and α_0 on annealing temperature are strikingly different from those of thin cadmium sulphide films reported in our previous publication. We apprehend these features to have emerged as a consequence of structural phase transformation from monoclinic to body centered cubic, known to occur at around 180 °C.[22–25] As may be seen from Fig. 5, both the α_0 vs. T_A and E_0 vs. T_A plots indicate an existence of a critical annealing temperature somewhere between 100 and 200 °C. Thus, the above change in crystallographic phase change of the material due to annealing could possibly be a reason for the change of slope observed in the above plots of Urbach absorption parameters as a function of annealing temperature.

The above effect of phase transition on Urbach absorption parameters E_0 and α_0 is similar to the variation of the band gap energy with annealing temperature. The dependence of the band gap energy on annealing temperature is shown in Figure 7. The nature of variation of E_g clearly shows two linear segments (shown by dotted lines), one corresponds to the variation below the critical temperature of structural phase transition while the other corresponds to the case when the annealing temperature exceeds the critical value. By fitting these data linearly, we find the slopes of the two segments to be -1.056×10^{-3} eV K^{-1} and 6.98×10^{-4} eV K^{-1}, respectively. Different values of E_g for two crystallographic phases seem to have correlations with the Urbach absorption parameters as these parameters clearly shows two different slopes with respect to annealing temperature similar to the band gap energy.

The decrease in the absorption coefficient in the Urbach region may be related to the localized states at the grain boundaries which control the properties of polycrystalline semiconductor[26–28] in a manner similar to different other layered structures like, semiconductor heterojunctions[29] and metal-semiconductor devices.[30–32] Thus, considering the carrier trapping properties of these imperfections, one cannot possibly rule out their role on the optical absorption processes in the Urbach region. In such cases, the absorption coefficient is likely to be influenced as a result of grain boundary modification via possible changes in the density of localized states and interface width. The localized states have been attributed to be a cause for the sub-band gap optical transitions in the case of polycrystalline CdS films. However, in the present case of Ag_2S thin films, the observed change in the sub-band gap optical absorption with annealing temperature seem to have resulted as a consequence of combined effects of the structural phase transition and the modification of grain boundary localized states and/or interface width.

V. CONCLUSIONS

In conclusion, the optical absorption coefficient of thin silver sulphide films prepared by chemical conversion of cadmium sulphide films exhibit absorption tail, which has been found to be dependent on the annealing temperature. The analyses of the absorption tail reveal an exponential dependence on photon energy according to Urbach law, but with a steepness constant much different from that originally proposed by Urbach. The discrepancy has been attributed to polycrystalline nature of the sample. The experimental results further reveal distinct effects of annealing on the Urbach absorption parameters and band gap of the material through a possible structural phase transition and modification of grain boundary interface states. A similarity in the nature of variation of the absorption parameters in the Urbach region and the band gap of the material with annealing temperature indicate an interrelationship between the optical absorption parameters of the material.

[1]K. Hickman and W. Weyerts, Nature **132**, 134 (1933).
[2]S. Tajammul Hussain, S. Abu Bakar, B. Saima, and B. Muhammad, Appl. Surf. Sci. **258**, 9610 (2012).
[3]R. H. Zhang, X. T. Zhang, and S. M. Hu, Sens. Actuators B **177**, 163 (2013).
[4]T. Fu, Electrochim. Acta **121**, 168 (2014).
[5]C. Chen, Y. Xie, G. Ali, S. Hwa Yoo, and S. Oh Cho, Nanoscale Res. Lett. **6**, 462 (2011).
[6]H. Shen, X. Jiao, D. Oron, J. Li, and H. Lin, J. Power Sources **240**, 8 (2013).
[7]S. Shen, L. Guo, X. Chen, F. Ren, and S. S. Mao, Int. J. Hydrogen Energy **35**, 7110 (2010).
[8]A. Nayak, T. Tamura, T. Tsuruoka, K. Terabe, S. Hosaka, T. Hasegawa, and M. Aono, J. Phys. Chem. Lett. **1**, 604 (2010).
[9]Z. Xu, Y. Bando, W. Wang, X. Bai, and D. Golberg, ACS Nano **4**, 2515 (2010).
[10]M. Morales-Masis, S. J. van der Molen, W. T. Fu, M. B. Hesselberth, and J. M. van Ruitenbeek, Nanotechnology **20**, 095710 (2009).
[11]J. J. T. Wagenaar, M. Morales-Masis, and J. M. van Ruitenbeek, J. Appl. Phys. **111**, 014302 (2012).
[12]J.-L. Sun, J.-L. Zhu, X. Zhao, and Y. Bao, Nanotechnology **22**, 035202 (2011).
[13]S. Liu, X. Wang, W. Zhao, K. Wang, H. Sang, and Z. He, J. Alloys Compd. **568**, 84 (2013).
[14]F. L. Ezema, P. U. Asogwa, A. B. C. Ekwealor, P. E. Ugwuoke, and R. U. Osuji, J. Univ. Chem. Technol. Metall. **42**, 217 (2007).
[15]B. R. Sankapal, R. S. Mane, and C. D. Lokhande, Mater. Chem. Phys. **63**, 226 (2000).
[16]H. Metin and R. Esen, Semicond. Sci. Technol. **18**, 647 (2003).
[17]H. Metin and R. Esen, J. Cryst. Growth **258**, 141 (2003).
[18]F. Urbach, Phys. Rev. **92**, 1324 (1953).
[19]P. Chattopadhyay, B. Karim, and S. Guha Roy, J. Appl. Phys. **114**, 243506 (2013).
[20]P. Chattopadhyay and S. Guha Roy, Ind. J. Pure Appl. Phys. **51**, 98 (2013).
[21]S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (John Wiley & Sons., Inc., 1983), p. 40.
[22]M. Otfried, *Semiconductors: Data Handbook*, 3rd ed. (Springer-Verlag, 2004), p. 447.
[23]J. R. Ray and P. Vashista, J. Chem. Phys. **90**, 6580 (1989).
[24]D. Karashanova and N. Starbov, Appl. Surf. Sci. **252**, 3011 (2006).
[25]D. Zivkovic, V. Cosovic, Z. Zivkovic, N. Strbac, M. Sokic, N. Talijan, B. Boyanov, and A. Mitovski, Mater. Sci. Semicond. Process. **16**, 217 (2013).
[26]G. E. Pike and C. H. Seager, J. Appl. Phys. **50**, 3414 (1979).
[27]P. Chattopadhyay, J. Phys. Chem. Solids **56**, 189 (1995).
[28]P. Chattopadhyay, Semicond. Sci. Technol. **10**, 1099 (1995).
[29]P. Chattopadhyay and D. P. Halder, Appl. Surf. Sci. **143**, 287 (1999).
[30]P. Chattopadhyay and A. N. Daw, Solid-State Electron. **29**, 555 (1986).
[31]P. Chattopadhyay and B. Roychoudhuri, Solid-State Electron. **36**, 605 (1993).
[32]P. Chattopadhyay, J. Phys. D: Appl. Phys. **29**, 823 (1996).