Photo induced optical changes in Sb/As$_2$S$_3$ multilayered film and (As$_2$S$_3$)$_{0.93}$Sb$_{0.07}$ film of equal thickness

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ABSTRACT

The increase in optical band gap (photo bleaching) due to light illumination was studied at room temperature as well as at low (4.2 K) temperature for Sb/As$_2$S$_3$ multilayered film of 640 nm thickness by Fourier Transform Infrared Technique. The interdiffusion of Sb into As$_2$S$_3$ matrix results the formation of Sb–As$_2$S$_3$ ternary solid solutions which is explained by the change in optical band gap (E_g), absorption coefficient (α), Tauc parameter ($B^{1/2}$), Urbach edge (E_e). At the same time, photo darkening phenomena was observed in (As$_2$S$_3$)$_{0.93}$Sb$_{0.07}$ film of same thickness both at low and room temperatures. From our X-ray Photoelectron Spectroscopy measurements, we are able to show that some of the As–As, S–S and Sb–Sb bonds are converted into As–S and S–Sb bonds in case of multilayers. We found that the energetically favoured heteropolar bond formation take place by a phonon-assisted mechanism using the lone pair π electrons of S$_2{}^0$. But in case of (As$_2$S$_3$)$_{0.93}$Sb$_{0.07}$ film, the homopolar bonds are playing a major role.

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1. Introduction

A growing interest in the research of chalcogenide glasses can be currently witnessed, which is, to much extent, caused by newly opened fields of applications for these materials. Applications in the field of micro- and opto-electronics, xerography and lithography, acousto-optic and memory switching devices and detectors for medical imaging seem to be most remarkable [1]. Accordingly, photo induced phenomena in chalcogenide glasses are attracting much interest. These phenomena can be found both in uniform thin films as well as multilayered films. Among amorphous multilayers (AMLs), chalcogenide multilayers are attractive because of the potentials for tailoring the optical properties [2]. For example, photo induced diffusion in short period multilayer system is important because of its potential applications in holographic recording and fabrication of phase gratings. In spite of its practical usefulness, the mechanism of photoinduced diffusion is not properly understood.

Silver metal photo induced diffusion in chalcogenide glasses is well known for many decades [3]. By comparison, photo induced diffusion has been observed only recently in amorphous Se/As$_2$S$_3$ and similar multilayers [4,5]. This is an indication that the illumination can enhance the atomic mobility. Among these Sb/As$_2$S$_3$ nanomultilayered films are attractive because of its prominent

application in efficient amplitude phase modulated optical relief holograms [6] like Ag/As$_{30}$S$_{70}$ multilayers [7]. Moreover, the diffusion mechanism of Sb into As$_2$S$_3$ is completely unknown. The diffusion intermixing affects several parameters of the multilayer structure, such as optical absorption edge, layer thickness, photoluminescence intensity, electrical conductivity and photoconductivity [8]. The changes in these properties are explained based on the formation of ternary solid solution due to interdiffusion. However, the process by which Sb diffuses into As$_2$S$_3$ is still unclear. Our present studies revealed that the band gap and Tauc parameter increase after photo induced diffusion. We have done the optical absorption measurement in room and low temperature to ensure the photo bleaching effect. In order to understand the diffusion mechanism of Sb into As$_2$S$_3$ matrix, we mainly used the Tauc parameter ($B^{1/2}$) and Urbach energy. The main reason for using the above parameter is that they give information about the distribution of electronic states in the absorption region.

At the same time, the bulk characteristic plays a significant role in various applications also. Arsenic sulphide (As$_2$S$_3$) is the most studied chalcogenide glass and has applications in infrared optics and optical coatings because of its excellent IR transmission, large glass forming tendency, and resistance to moisture and chemicals [9]. A graded refractive index, which is required in some applications, may be produced in the arsenic sulphide glass of both bulk and thin film forms by gradually replacing the arsenic component with chemically similar antimony atoms [10]. Studies on thin films of Sb$_2$S$_3$ are attracting wide attention, for its special applications as a target material for television cameras, microwave devices,

switching devices and various opto-electronic devices. Even though As and Sb belongs to the same group of the periodic table, As_2S_3 and Sb_2S_3 do not display the same glass forming tendency. Glassy Sb_2S_3 is very difficult to form and its preparation requires high cooling rates [11]. However, addition of As_2S_3 to Sb_2S_3 enhances greatly the glass forming ability of the later and glasses in the mixed As–Sb–S system can be formed. The structure of glasses in the mixed system As_2S_3–Sb_2S_3 remains controversial. Some authors interpreted the EXAFS, IR and Mossbauer spectroscopy data on the atom Sb in the frame of a model with random substitution of arsenic atoms by antimony atoms with the formation of As–S–Sb bridges [12–14]. The glass structure is independent of As_2S_3 and Sb_2S_3 regions and joined by As–S–Sb linkages. The optical study done by Tichy et al. suggests the linear change of optical parameters with the Sb_2S_3 content [15]. It was therefore suggested that the structure of such glasses can be considered as a nearly ideal solution of non-interacting As_2S_3 and Sb_2S_3 micro-phases. Recent studies proposed that a random substitution of $AsS_{3/2}$ by $SbS_{3/2}$ pyramids takes place and leads to a homogeneous glass structure, instead of the formation of two different micro-phases [12,14,16]. So, it is clear from the above that As–Sb–S glass system is nothing but a mixture of As_2S_3 and Sb_2S_3. Recently, we prepared the ternary As–S–Sb chalcogenide glass composition $(As_2S_3)_{0.93}Sb_{0.07}$. The purpose of the work is two fold; first to study the local glass structure with Sb addition to As_2S_3 and second to explore the photo induced phenomena occurring in the bulk film. The structural changes in these materials are related to the change in their optical properties. The new bonds formation due to interdiffusion at room temperature is studied by X-ray Photoelectron Spectroscopy (XPS).

2. Experimental

The multilayer film of total thickness 640 nm with sub-layer thickness of Sb and As_2S_3 as 2–3 nm and 3–4 nm, respectively, were prepared by cyclic thermal evaporation method. The deposition rate was 1–2 nm/s in a vacuum of 5×10^{-4} Torr. Bulk glass of $(As_2S_3)_{0.93}Sb_{0.07}$ was prepared from stoichiometric mixture of high pure (99.999%) As, S and Sb. The mixture was placed in the quartz ampoule which was evacuated at a vacuum of 10^{-5} Torr and sealed. Melting was performed at 950 °C for 36 h inside a rotating furnace in order to ensure homogeneity of the melt. Glasses were then obtained by quenching the ampoule in liquid nitrogen. The elemental compositions of these glasses were 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 cm² size at 2.2×10^{-4} Pa pressure and the estimated average precision was about 1% in atomic fraction in each element. The amorphous state of the materials was checked by X-ray (Philips, $Cu_{K\alpha}$, $\lambda = 1.54 Å$) Diffractometer (XRD). The absence of crystalline peaks confirms glassy state of the prepared samples. Thin films were prepared by thermal evaporation method from the prepared bulk glasses onto the glass substrates (microscope slides). The films were coated in a coating unit attached with thickness monitor at a vacuum pressure of 2×10^{-5} Torr. During the deposition process (at normal incidence), the substrates were suitably rotated in order to obtain the films of uniform thickness. The thicknesses of the films were around 640 nm. The amorphous nature was again confirmed by taking XRD. The film composition was determined by EDAX. The optical absorption spectra were taken by using the Fourier Transform Infrared (FTIR) spectrometer (Bruker Optics (IFS66 v/S) in the visible wavelength range 400–1200 nm at room temperature. The films were illuminated by a diode pumped solid state laser (DPSS) of wavelength 532 nm with a power of 35 mW for 1 h and the spectra were taken after illumination. For low temperature measurement, we kept the sample inside an optical cryostat, and the temperature was brought down to liquid helium temperature (4.2 K). The transmission spectra were recorded after stabilizing the temperature at 4.2 K (~30 min). Then the sample was illuminated by DPSS laser for 2 h and the spectra were taken after illumination.

We used XPS to study the atomic movements as well as to analyze the new bonds formed between the components due to interdiffusion. It is a useful surface analytical technique to study the chemical state and local environment of an atom [17,18]. The chemical bonding is often realized through correlation with chemical shifts in XPS binding energies of the corresponding elements. Since XPS is a surface analytical technique, most of the signals will come from the top 70 to 100 Å layer. To study the atomic movement, we irradiated the sample inside the XPS chamber and measured the spectra. Since the time required to record a highly resolved XPS spectrum of any particular element for example As, or Sb, is much longer than the characteristic diffusion times, we irradiated the sample for a definite time and the measurements were carried out. Therefore, we irradiated the sample for a desired time inside the XPS chamber and the XPS spectra were recorded after switching
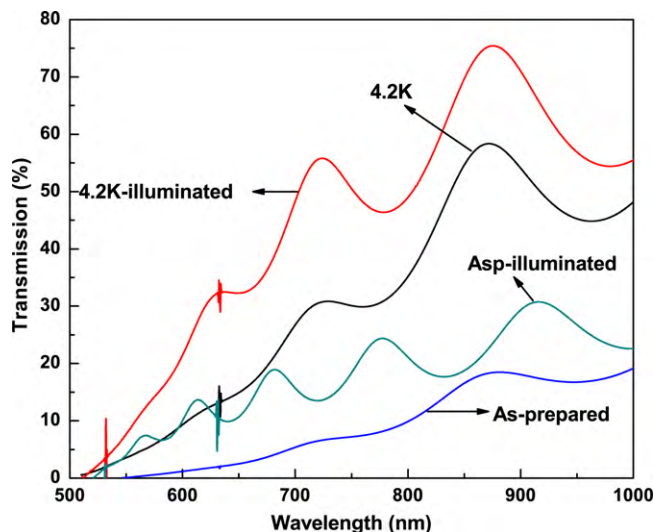

Fig. 1. Transmission spectra of the Sb/As_2S_3 multilayered film at room and low temperatures.

off the laser. The disadvantage of this method is that the transient effects are not visible, nevertheless gives an idea of the atomic movements which are permanent ones. XPS measurements were first made on the as-prepared samples. Thereafter, samples were then irradiated inside the XPS chamber with DPSS laser of 532 nm for a particular time (about 40 min) at the same spot where the XPS measurements were done. After irradiation, XPS spectra were again recorded at the irradiated area. This will allow us to make a clear correlation between the XPS data of as-prepared and irradiated state of the sample. The laser used for irradiation has the wavelength 532 nm. Since the intensity values are low, the change in temperature by illumination is not more than a 5 °C [19]. The XPS core level and valence band spectra were obtained with monochromatic Al K_{α} X-rays (1486.6 eV) at a vacuum of 10^{-9} Torr in Multilab 2000 Thermo Scientific UK instrument. The XPS data consisted of survey scans over the entire binding energy (BE) and selected scans over the core level peaks of interest. An energy increment of 1 eV was used for recording the survey spectra and 0.05 eV for the case of core level spectra. The core level peaks were recorded by sweeping the retarding field and using the constant pass energy of 30 eV. The data were averaged over three scans. The reproducibility of the measurements was checked on different regions of the investigated surfaces. For insulators such as glasses, the charging effect can change the BE of the electrons from sample to sample. Hence, the measurement of the absolute BE of electrons from a specified energy level is not reliable. The C 1s line from either adventitious carbon or intentionally added graphite powder on the surface has been widely used for charge referencing [20,21]. For this study, the adventitious carbon was used as a reference and the BE of the reference C 1s line was set as 284.6 eV. For each sample, a calibration factor was calculated from the difference between the measured C 1s BE and the reference value 284.6 eV [22]. The original BE data were corrected according to the calibration factor.

3. Results and discussion

The optical transmission spectra of the as-prepared and illuminated Sb/As_2S_3 multilayered film at room and low temperature are shown in Fig. 1. A noteworthy blue shift is observed for the illuminated spectra than the as-prepared film in the absorption edge region for the multilayered film. In the opposite side, red shift is found in the case of $(As_2S_3)_{0.93}Sb_{0.07}$ film at both the temperatures which is shown in Fig. 2. The absorption coefficient (α) of the thin films can be calculated using the well known equation:

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

where d is the thickness of the film and T is the transmission of the film. The optical band gap has been estimated according to generally accepted non-direct transition model for amorphous semiconductor by using the Tauc relation [23]
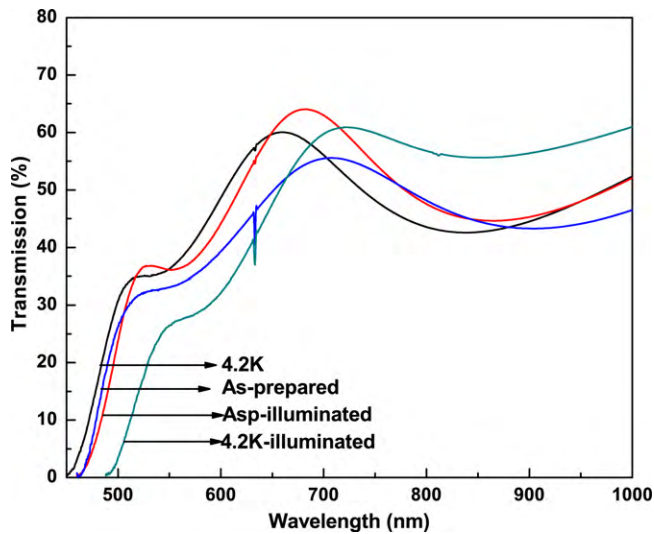
$$(\alpha h \nu)^{1/2} = B^{1/2}(h\nu - E_g) \tag{2}$$

Fig. 2. Transmission spectra of $(As_2S_3)_{0.93}Sb_{0.07}$ film at room and low temperatures.

Fig. 4. $(\alpha h\nu)^{1/2}$ vs $(h\nu)$ plots for the $(As_2S_3)_{0.93}Sb_{0.07}$ film.

where B is the Tauc parameter that depends upon the transition probability and E_g is the optical band gap of the film. The region with high absorption is characterised with interband transitions between valence band and conduction bands. By plotting $(\alpha h\nu)^{1/2}$ vs $h\nu$, the slope of the straight line fitting will give the value of B and the intercept of the line to $h\nu$ axis gives the value of optical band gap (E_g) which is shown in Fig. 3 for the multilayers and in Fig. 4 for the thin films. In the low absorption region ($\alpha < 10^4$ cm^{-1}), the absorption coefficient α shows an exponential dependence on photon energy $h\nu$, and obeys the Urbach relation [24]

$$\alpha(h\nu) = \alpha_0 \exp\left(\frac{h\nu}{E_e}\right) \qquad (3)$$

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 [25]. 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.

Photo induced interdiffusion was observed with above band gap light (2.34 eV) at both room and low temperature for the multi-
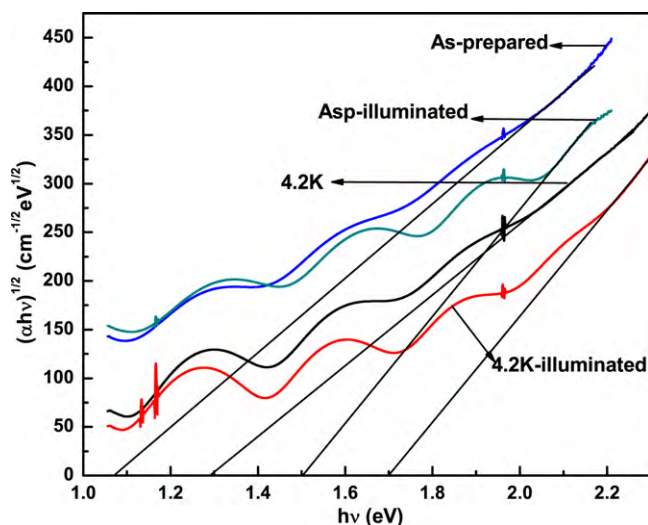

Fig. 3. $(\alpha h\nu)^{1/2}$ vs $(h\nu)$ plots for the Sb/As$_2$S$_3$ multilayered film.
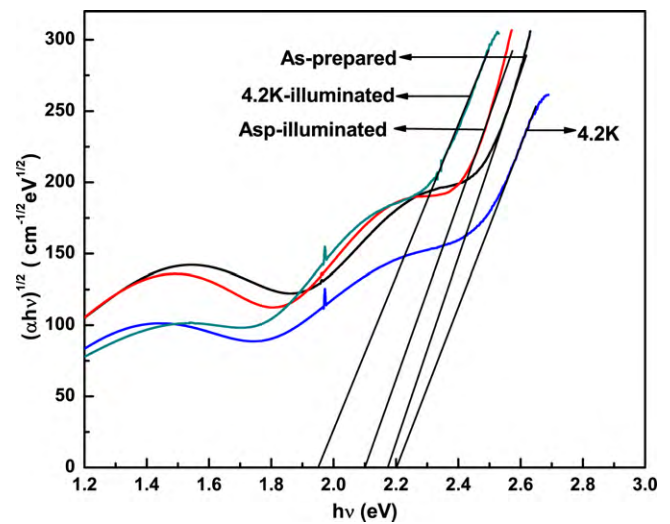
layers. The optical band gap of illuminated film (1.503 eV) clearly shows a blue shift (photo bleaching) compared to the as-prepared film (1.078 eV) at room temperature. The diffusion of unbounded Sb atoms of the top Sb layers into the As$_2$S$_3$ layers with laser light causes the creation of new bonds between the components due to interdiffusion and formation of ternary solid solution of Sb–As$_2$S$_3$ at the interface. This solid solution creates more no of heteropolar bonds by removing homopolar bonds which can be observed from the optical parameters. The band gap of the as-prepared film at 4.2 K is found to be 1.297 eV which is more than that of as-prepared film band gap at room temperature. This increase in bad gap can be attributed to the lowering of defect states due to low temperatures. But the optical band gap increases with illumination at 4.2 K refers to the photo diffusion process at low temperatures. The optical band gap was found to be 1.702 eV after illumination at low temperature. Explaining and understanding the observed effects is of major importance. At this point we assume that Sb will react with light excited atoms in the chalcogenide layer and produce diffusion. Earlier studies on unannealed films have shown that the evaporated As$_2$S$_3$ sub-layer contains a large number of species such as As, As$_4$, S$_2$, S$_8$, AsS$_3$, As$_4$S$_5$, As$_4$S$_4$, As$_2$ [26]. This means that even in a stoichiometric film such as As$_2$S$_3$, where the stoichiometry would only allow As–S bonds, a large number of so-called wrong bonds As–As, S–S are present. Spectroscopic studies on unannealed films have shown that irreversible band gap light-induced photostructural changes are mainly due to the photo induced As–As bond breaking (As–As being the weakest bond) followed by the phonon-assisted creation of As–S bonds [27].

$$2As_3^0 + S_2^0 + h\nu \leftrightarrow As_2^+ + As_2^- + S_2^0 + phonon \leftrightarrow As_3^0 + S_3^+ + As_2^-$$
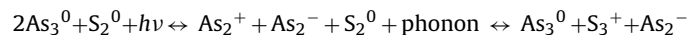
Here, the superscript indices designate the electric charge of atoms, and the subscript indices their coordination number. These reactions will take place far from the interface. However, at the interfaces, we conjecture that some of the S$_2^0$ states react with Sb atoms and form Sb–S bond and facilitate the photo induced diffusion. These energetically favoured heteropolar bond formation take place by a mechanism using the lone pair π electrons of S$_2^0$ similar to those observed in the case of Se/As$_2$S$_3$ [5]. Following the above model, it turns out that the photo induced structural rearrangements are producing the light-induced diffusional intermixing and there is no reason that they should vanish at low temperatures.

But at the same time, the reverse phenomena is observed in case of $(As_2S_3)_{0.93}Sb_{0.07}$ film at both room and low temperatures. The optical band gap of the as-prepared and illuminated film at room

temperature was found to be 2.174 and 2.108 eV. This decrease in band gap (photo darkening) observed in bulk film is due to the presence of Sb atoms which is chemically bonded with As_2S_3 matrix, is changing the absorption spectra towards the lower energy side. This may be due to the increase of some of the homopolar bonds due to illumination. The optical band gap for the as-prepared film at 4.2 K is 2.201 eV which is more than that of room temperature value. This increase of 0.027 eV value is due to the decrease of the band tails at low temperature. When we illuminated the film at low temperature, the band gap reduces to 1.95 eV. This reduction of 0.251 eV in optical band gap at low temperature illumination is attributed to the increase in homopolar bonds which are created during illumination. The films become more disorder after illumination which we can see from the $B^{1/2}$ values.

$B^{1/2}$ is a very useful parameter to determine the degree of disorder during photo induced diffusion (provided that the change in disorder during photo diffusion will change the valence and conduction band density of states). Based on the experiments in a–Ge–H, a–Si–H, a–SiN and a–GeN based alloys, Zanatta and Chambouleyron [23] showed that $B^{1/2}$ is sensitive to topological disorder only when electronic structural changes occur. The value of $B^{1/2}$ for as-prepared and illuminated Sb/As_2S_3 multilay-

ered film at room temperature are 384, 550 $cm^{-1/2}$ $eV^{-1/2}$ and at 4.2 K are 361, 551 $cm^{-1/2}$ $eV^{-1/2}$, respectively. It shows that disorder decreases during photo diffusion at room temperature as well as at low temperatures. So during photo diffusion, the density of Sb–Sb, S–S and As–As homopolar bonds may decrease and changes in conduction and valence band states may occur. As a consequence, the absorption edge becomes steeper and the magnitude of $B^{1/2}$ increases. In the case of a–Si/a–Ge alloys a change in $B^{1/2}$ has been found with decrease in Ge–Ge/Si–Si bond density [28]. But in the case of $(As_2S_3)_{0.93}Sb_{0.07}$ film the values $B^{1/2}$ decreases which refers to the increase of disorder due to illumination. The value of $B^{1/2}$ for as-prepared and illuminated $(As_2S_3)_{0.93}Sb_{0.07}$ film at room temperature are 652, 627 $cm^{-1/2}$ $eV^{-1/2}$ and at 4.2 K are 566, 527 $cm^{-1/2}$ $eV^{-1/2}$, respectively.

It is known that the Urbach edge is a useful parameter to evaluate the degree of disorder. The values of the E_e of the as-prepared and illuminated films are 897 meV and 404 meV for Sb/As_2S_3 multilayered film at room temperature and 569, 388 meV at low temperature. The Urbach energy E_e of the illuminated sample is less than that of as-prepared sample which indicates the decrease in disorder after illumination. The higher values of $B^{1/2}$ and lower values of E_e of the irradiated samples over the corresponding as-
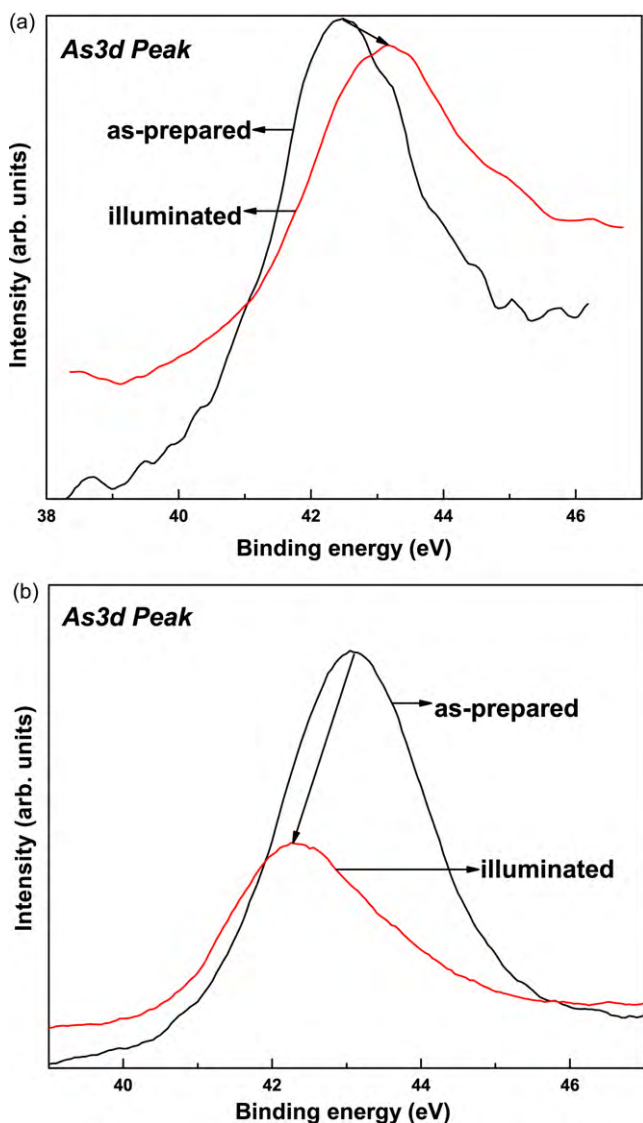

Fig. 5. (a) As 3d core level spectra of Sb/As_2S_3 multilayer thin film. (b) As 3d core level spectra of $(As_2S_3)_{0.93}Sb_{0.07}$ film.

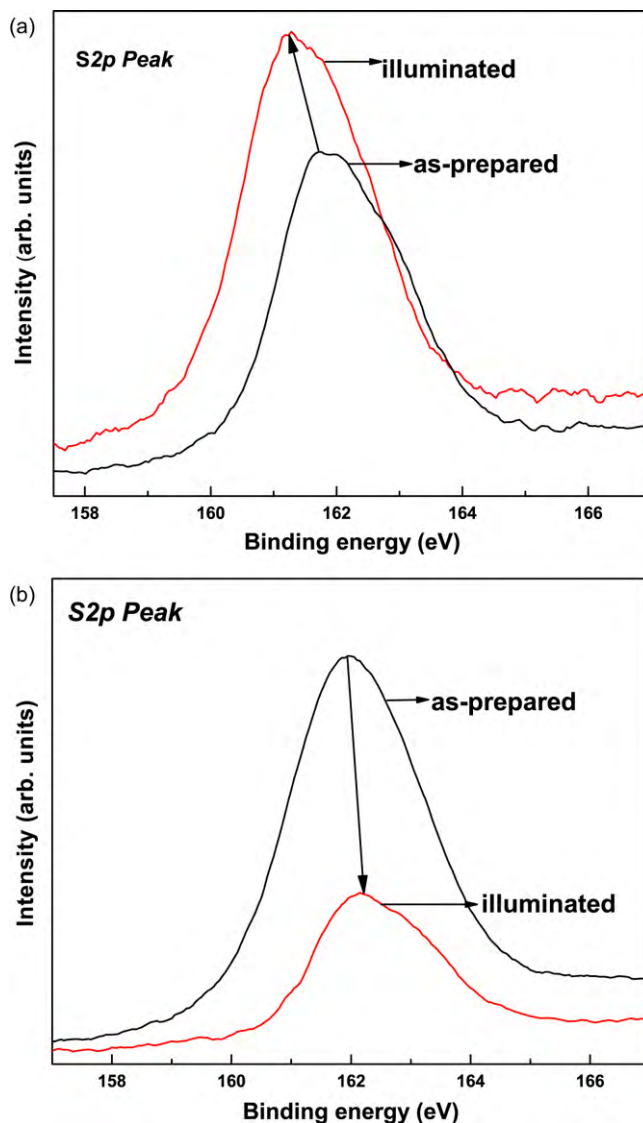**Fig. 6.** (a) S 2p core level spectra of Sb/As_2S_3 multilayer thin film. (b) S 2p core level spectra of $(As_2S_3)_{0.93}Sb_{0.07}$ film.

prepared samples clearly indicate that the illuminated samples are more ordered (chemically) than the as-prepared samples, i.e., the removal of homopolar bonds after photo diffusion. But the opposite trend was found in case of $(As_2S_3)_{0.93}Sb_{0.07}$ thin film. The value of E_e for as-prepared and illuminated $(As_2S_3)_{0.93}Sb_{0.07}$ film at room temperature are 277, 305 meV and at 4.2 K are 270, 393 meV, respectively. The Urbach energy E_e of the illuminated sample is more than that of as-prepared sample which indicates the increase in disorder after illumination. The lower values of $B^{1/2}$ and higher values of E_e of the irradiated samples over the corresponding as-prepared samples clearly indicate that the illuminated samples are more disordered (chemically) than the as-prepared samples, i.e., the creation of homopolar bonds after photo diffusion.

The XPS analysis provides more insight into the atomic movements during photo diffusion. The peak position of the As 3d spectrum (see Fig. 5a) for the as-prepared film is at BE 42.4 eV. But after irradiation of the as-prepared film, the peak position shifts to a BE value of 43.1 eV. This shifting of peak towards higher BE value indicates the formation of As–S bonds. During light irradiation, As–As bonds are broken and phonon-assisted As–S bond formation take place by using the lone pair π electrons of S_2^0 [27]. From the spectra of As 3d peak (see Fig. 5b), it is found that due to illumina-tion the peak is shifting towards the lower BE due to the formation of As–As homopolar bonds.

The BE of the S 2p peak (see Fig. 6a) shifts towards lower energy side upon light illumination. The BE of as-prepared S 2p peak is located at 161.7 eV. But after 1800 s of irradiation, it moves to 161.2 eV. Due to light illumination, we assume some of the S–S bonds converted into As–S and Sb–S bonds. As a result, ordering in the structure takes place and the $B^{1/2}$ values increases that we got from the optical transmission spectrum. On the other hand, the S 2p peak of the illuminated film shifts towards higher BE shows the formation of S–S bonds due to illumination (see Fig. 6b) in case of $(As_2S_3)_{0.93}Sb_{0.07}$ film.

If we compare the Sb 4d BE (see Fig. 7a) of the as-prepared and irradiated sample, it is clear that, the BE of Sb 4d is shifting towards higher energy side during photo diffusion. The as-prepared Sb 4d peak was at 33.89 eV whereas after 1800 s of irradiation, it shifts to 34.57 eV. During photo induced diffusion, some of the Sb–Sb bonds are converted into Sb–S bonds. We assume that the Sb–S bond for-mation takes place by the reaction between S_2^0 and Sb. From the spectra of Sb 4d peak (see Fig. 7b), it is found that due to illumina-tion, the peak is shifting towards the lower BE due to the formation of Sb–Sb homopolar bonds.
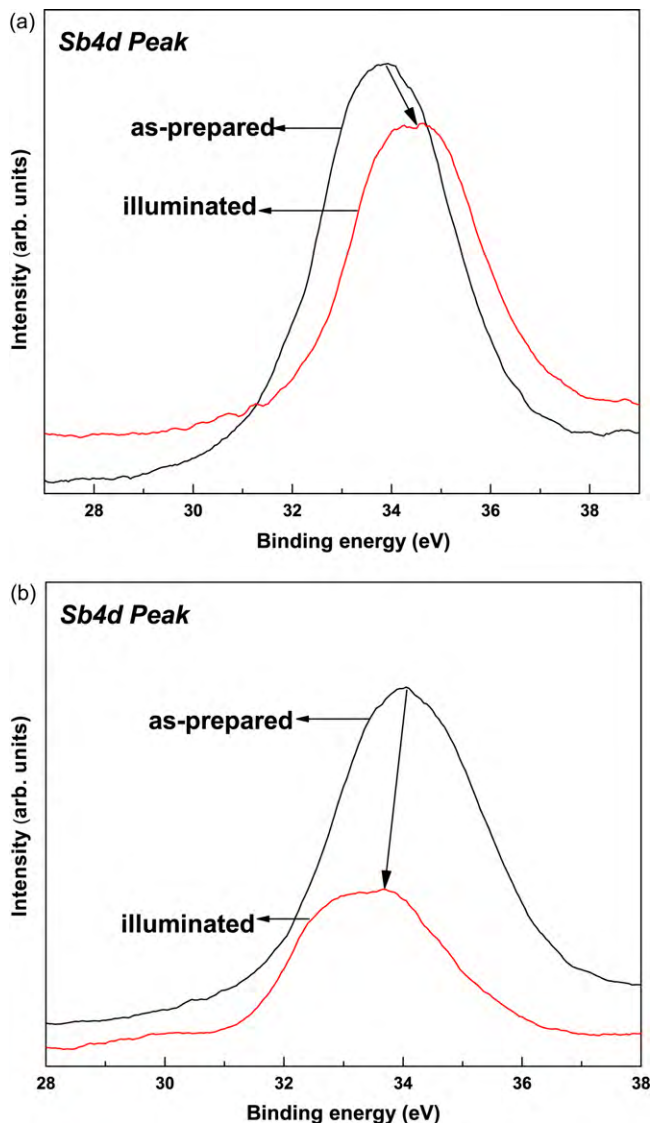
4. Conclusions

The optical absorption measurements reveal that the photo bleaching (increase in band gap) occurs in amorphous nanolay-ered Sb/As_2S_3 film at room and low temperature due to photo induced diffusion. The diffusion of unbounded Sb atoms of the top Sb layers into the As_2S_3 layers with laser light causes the creation of new bonds between the components due to interdif-fusion and formation of ternary solid solution of $Sb-As_2S_3$ at the interface. This solid solution creates a larger number of heteropo-lar bonds by removing homopolar bonds which can be observed from the optical parameters and XPS analysis. We assume that the energetically favoured heteropolar bond formation take place by a phonon-assisted mechanism using the lone pair π electrons of S_2^0. On the other hand, photo darkening (decrease in band gap) is hap-pening in case of $(As_2S_3)_{0.93}Sb_{0.07}$ film of same thickness at low and room temperatures. This is due to the presence of Sb atoms which is chemically bonded with As_2S_3 matrix, is changing the absorption spectra towards the lower energy side. On illumination, polymer-destructive changes occur, leading to the weakening of some bonds and to strengthening of others. The existence of structural changes in such chalcogenide films on illumination is supported by changes studied through XPS.

Acknowledgments

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Fig. 7. (a) Sb 4d core level spectra of Sb/As_2S_3 multilayer thin film. (b) Sb 4d core level spectra of $(As_2S_3)_{0.93}Sb_{0.07}$ film.

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