CHIN. PHYS. LETT. Vol. 34, No. 7 (2017) 077802

X-Ray Radiation Sensing Properties of ZnS Thin Film: A Study on the Effect of Annealing

M. P. Sarma[1], J. M. Kalita[1,2**], G. Wary[1]

[1]*Department of Physics, Cotton College, Guwahati 781001, India*

[2]*Department of Physics and Electronics, Rhodes University, Grahamstown 6140, South Africa*

(Received 8 March 2017)

Chemically synthesized ZnS thin film is found to be a good x-ray radiation sensor. We report the effect of annealing on the x-ray radiation detection sensitivity of a ZnS thin film synthesized by a chemical bath deposition technique. The chemically synthesized ZnS films are annealed at 333, 363 and 393 K for 1 h. Structural analyses show that the lattice defects in the films decrease with annealing. Further, the band gap is also found to decrease from 3.38 to 3.21 eV after annealing at 393 K. Current-voltage characteristics of the films are studied under dark and x-ray irradiation conditions. Due to the decrease of lattice defects and band gap, the conductivity under dark conditions is found to increase from 2.06×10^{-6} *to* 1.69×10^{-5} *S/cm, while that under x-ray irradiation increases from* 4.13×10^{-5} *to* 5.28×10^{-5} *S/cm. On the other hand, the x-ray radiation detection sensitivity of the films is found to decrease with annealing. This decrease of detection sensitivity is attributed to the decrease of the band gap as well as some structural and surface morphological changes occurring after annealing.*

PACS: 78.66.−w, 07.85.Fv, 61.80.Cb, 73.61.At, 61.72.Cc DOI: 10.1088/0256-307X/34/7/077802

Wide band gap semiconductors have gathered considerable attention due to their technological applications. Zinc sulphide (ZnS) is such a material having a direct band gap of ∼3.65 eV.[1] Due to its unique optical and electrical properties, it has been used to fabricate many optoelectronic devices, for example, light emitting diodes, photo-detectors, modulators, solar cells, and electroluminescent devices. Moreover, nanostructured ZnS is also found to be a very promising material for ultraviolet (UV) sensors,[2] gas sensors[3] and pH sensors.[4] Most recently, Sarma *et al.*[5] for the first time, showed that a chemically synthesized ZnS film could be used to detect x-ray radiation by simply applying a suitable bias-voltage across the film. Indeed, the results show that the film under certain conditions could be used to detect x-ray more effectively than UV radiation.

For a material to be used as a radiation detector, it will be advantageous from the practical point of view if the material can sustain high temperature. In this regard, the literature shows that annealing changes various properties of ZnS films including crystallite size, grain size, surface roughness, and band gap, etc. For example, Vidal *et al.*[6] studied the annealing effect of ZnS films and observed that the band gap of the films decreases with annealing, which increases the conductivity of the films. Arenas *et al.*[7] and Roy *et al.*[8] showed that the crystallinity and surface smoothness of chemically deposited ZnS films increase due to annealing, which enhance the photoconductivity of the films. Further, Chen *et al.*[9] studied the effect of annealing on the photocatalytic activity of chemical bath deposited ZnS films. It was observed that the crystallite size and grain size increase with annealing temperature and heating rate. The increase of crystallite size and grain size improve the absorption in the visible region, which enhances the photocatalytic activity. Recently, Sarma *et al.*[5] found that the ZnS films could be used as a good x-ray sensor. Therefore, in this Letter, we study the effect of annealing on the x-ray radiation sensing properties of ZnS films.

To deposit ZnS thin films on glass substrates, a chemical bath deposition (CBD) method was used in our experiment. The detail synthesis process was reported by Sarma *et al.*[5] In the previous study,[5] it was noted that the films synthesized at 0.2 M can show the best lattice quality as well as high electrical conductivity. Therefore, in this study, we used only the 0.2 M films. To prepare 0.2 M films, 30 ml of 0.2 M zinc acetate solution was mixed with the 30 ml of equimolar thiourea solution. The reaction bath temperature was increased and maintained at 343 K. The pH of the solution was also maintained between 8 and 9 by adding NH_3. Afterwards, some chemically cleaned glass substrates were immersed into the solution. Maintaining the bath temperature up to 40 min, the reaction beaker was kept undisturbed at room temperature. After 24 h of deposition, the glass substrates, covered by white layers of the film, were taken out, washed with distilled water and then dried in air. The presence of Zn and S were confirmed by an x-ray fluorescence spectroscopic analysis.[5] The films were annealed in air at three different temperatures, namely at 333, 363 and 393 K for 1 h using a muffle furnace attached with an electronic temperature controller.

The effect of annealing on the structural proper-

**Corresponding author. Email: jitukalita09@gmail.com

© 2017 Chinese Physical Society and IOP Publishing Ltd

ties of the films was studied from the x-ray diffraction (XRD) patterns recorded by an x-ray diffractometer (Rigaku-TTRAX Ⅲ, Japan, $\lambda = 1.5406$ Å for Cu $K\alpha$ radiation, $V = 50$ kV, $I = 180$ mA). The XRD patterns were recorded within 20°–70° at a resolution of 0.05° (in 2θ scale). Figure 1 shows XRD patterns of the ZnS films once annealed at 333, 363 and 393 K. The XRD patterns of the un-annealed film synthesized in the same batch, which were the subject of our previous study,[5] are also shown for comparison. The XRD patterns show that the films are polycrystalline in nature. The peaks are indexed by comparing the JCPDS data file 05-0566. Apart from the indexed peaks, some additional peaks are found after annealing. These peaks may be due to ZnO, which is inherently present with ZnS when the ZnS films are synthesized under ambient conditions. Moreover, the additional peaks are also due to some structural defects, which are changed with annealing. For example, the structural and interstitial defects in ZnO are changed with annealing.[10]

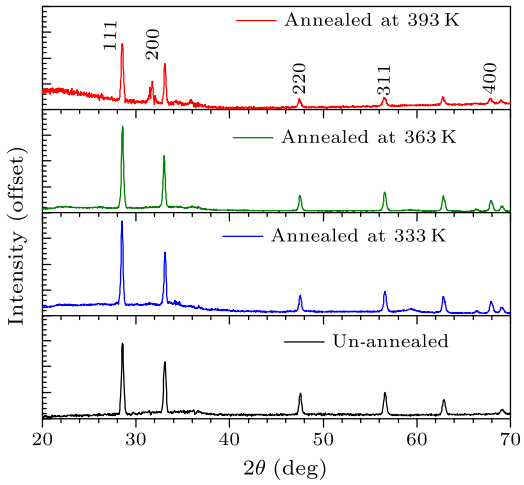

Fig. 1. XRD patterns of un-annealed and 333, 363 and 393 K annealed ZnS films.

The average crystallite size is estimated using Scherrer's equation.[11] For the films annealed at 333, 363 and 393 K, the sizes are 31.7, 34.2 and 35.5 nm, respectively. In comparison, the crystallite size of the un-annealed film is 26.3 nm.[5] This analysis shows that the crystallite size increases with the annealing temperature.

The Williamson–Hall (W-H) analysis[12] was carried out to study possible microstrain appearing in the films. According to the theory, the full width at half maxima β of a multiple ordered diffraction peak can be expressed as $\beta = (\lambda/D\cos\theta) + 4\varepsilon\tan\theta$, where λ is the wavelength of x-ray, θ is the diffraction angle, ε is the microstrain presenting in the crystal lattice, and D is the average crystallite size.[12] Thus a plot of $(\beta\ \cos\ \theta)/\lambda$ against $(2\sin\theta)/\lambda$ is linear with slope 2ε and intercept is equal to $1/D$. From the slope, the microstrains (ε) in the 333, 363 and 393 K annealed films are found to be 1.35×10^{-4}, 1.24×10^{-4} and 1.19×10^{-4}. On the other hand, the average crystallite sizes of the corresponding films as calculated from the intercept are 35.9, 37.3 and 38.4 nm respectively. In comparison, the microstrain in the un-annealed film was 1.36×10^{-4} whereas the crystallite size was 29.1 nm.[5] The small difference between the values of average crystallite size as calculated from Scherrer's equation and W-H analysis is due to the effect of strain.[12]

The minimum dislocation density, which is equal to $1/D^2$, is calculated from the average crystallite size.[13] For the 333, 363 and 393 K annealed films, they are found as 9.95×10^{14}, 8.55×10^{14} and 7.93×10^{14} line/m^2, respectively. For the un-annealed sample, the minimum dislocation density is 1.44×10^{15} line/m^2[5].

The preceding structural analyses show that the microstrain in the films is decreased whereas the average crystallite size increases with annealing. Further, the minimum dislocation density is decreased with annealing. The decrease of microstrain as well as the dislocation density implies that the lattice defects among the grains decrease with annealing.

A field-emission scanning electron microscopic (FE-SEM) (ZEISS SIGMA VP, Germany) analysis is carried out on the annealed samples. Figure 2 shows the FE-SEM images of the un-annealed and 393 K annealed samples. The grains have a hexagonal rod-like structure. The boundaries of the hexagonal rods are found to disappear after annealing. During film growth, a large number of oxygen ions are chemisorbed and incorporated in the grain boundary as well as on the surface of the film. Due to annealing, those oxygen ions dissociate, which results in the decrease of grain boundaries.

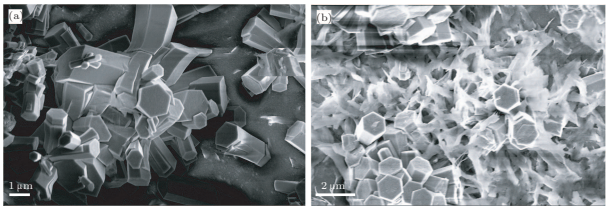

Fig. 2. FE-SEM images of (a) un-annealed and (b) 393 K annealed ZnS films.

To study the effect of annealing on the band gap, optical absorption spectra of the annealed films are recorded within 250–800 nm using the CARY-300 (Varian, Australia) UV-vis absorption spectrometer. Figure 3 shows the absorption spectra of the 333, 363 and 393 K annealed films. For all the films, a sharp absorption edge is found at ∼330 nm. Using Tauc's equation,[14] the band gaps of the 333, 363 and 393 K annealed films are found as ∼3.33, 3.26 and 3.21 eV,

respectively. The corresponding Tauc's plots for the films are shown as an inset in Fig. 3. The band gap of the un-annealed film is ∼3.38 eV[5] and it is found to decrease with annealing. The decrease of the band gap with annealing can be attributed to the increase of crystallite size, decrease of strain and dislocation density.[15]

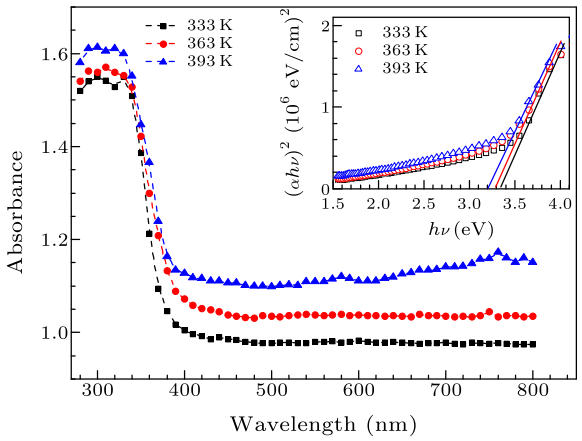

Fig. 3. Absorption spectra of the 333, 363 and 393 K annealed films. The inset shows Tauc's plot corresponding to the annealed films.

The electrical conductivity of the annealed films is calculated from the current-voltage (I–V) characteristics. To study the I–V characteristics, a bias-voltage across the film is applied through two aluminium electrodes by a variable dc power supply. The corresponding current passing through the film is recorded by a digital electrometer (Keithley, 6517B, United States). Due to the smaller work function of aluminium (4.17 eV[16]) than ZnS (7.00 eV[17]), the contact was ohmic.[16] To study the conductivity under x-ray radiation, the I–V characteristics were recorded by inducing x-ray on the films. The experimental setup used in this measurement is similar to the one reported by Sarma *et al.*[5] Unless otherwise stated, the x-ray source is operated at potential 35 kV and 15 mA filament current. The source emits the x-ray of wavelength 1.5406 Å.

Figure 4 shows the I–V characteristics of the annealed films where Fig. 4(a) corresponds to the measurements made under dark conditions and Fig. 4(b) under the x-ray irradiation condition. For ease of comparison, the I–V characteristics of the un-annealed film are also shown in Fig. 4. Similar to the case of the un-annealed film,[5] the characteristics in the annealed films also follow Ohm's law, which means that the current increases linearly with the bias voltage. Under a dark condition, the current through the films increases with annealing (Fig. 4(a)). At room temperature (∼300 K), the conductivities of the 333, 363 and 393 K annealed films are found as 0.94×10^{-5}, 1.32×10^{-5} and 1.69×10^{-5} S/cm, respectively. In comparison, the conductivity of the un-annealed film is 2.06×10^{-6} S/cm.[5] The increase of conductivity with annealing can be attributed to several factors such as decrease of grain boundary and band gap.[18] Regarding the currents measured under the same bias-voltages but with simultaneous x-ray irradiation (Fig. 4(b)), the difference between the un-annealed and annealed films is not very significant. The conductivities of the 333, 363 and 393 K annealed films, in this case, are calculated to be 3.77×10^{-5}, 4.72×10^{-5} and 5.28×10^{-5} S/cm, respectively, whereas that of the un-annealed one is 4.13×10^{-5} S/cm.[5] The current and the conductivity of the films under x-ray irradiation are found to be significantly higher than that under dark conditions. The reason behind this is previously explained with the help of an energy band model.[5] According to the model, when a biased film is irradiated under x-ray, the current through the film is contributed by two types of electrons: (i) electrons excited by the potential and (ii) electrons excited by the radiation. However, the competition between these two excitation processes somewhat depends on the bias voltage, energy of the radiation and band gap of the material.[5]

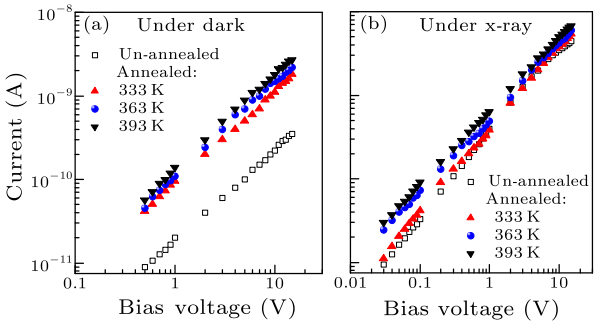

Fig. 4. The I–V characteristics of the 333, 363 and 393 K annealed and unannealed films recorded under dark conditions (a) and under x-ray irradiation conditions (b).

It was noted that the conductivities of the 333, 363 and 393 K annealed films during x-ray irradiation increased up to 301, 258 and 212 %, respectively. In comparison, the increase of conductivity in the un-annealed film is 1866%. The percentage increase in conductivity under x-ray irradiation gradually decreases with the annealing temperature. This decrease is somewhat related to the band gap of the material, which is found to decrease with annealing (see Fig. 3). When the band gap of the material is small, the majority of electrons excite to the conduction band due to the applied bias-voltage and only a few due to the x-ray radiation. As a result, the current contributed by the x-ray excited electrons become less significant.

For a particular energy of x-ray radiation, the detection sensitivity S of the films is calculated as a function of the bias-voltage (V) using the relation $S(V) = (I_r - I_d)/I_d$, where I_r is the current at a

bias-voltage V measured during x-ray irradiation (the x-ray is generated by the source at 35 kV and 15 mA filament current), and I_d is the dark current at the corresponding bias-voltage. Figure 5(a) shows the dependence of detection sensitivity of the annealed films on bias voltage (V). For comparison, the same feature of the un-annealed film[5] is also shown. The sensitivity of the films is found to be affected by annealing. For the un-annealed film, the sensitivity is constant within 0.5–6.0 V,[5] whereas that for the 333 K annealed film is constant within 1.0–7.0 V. On the other hand, the sensitivity for the 363 and 393 K annealed films is found to decrease with the bias voltage. This difference in the variation of sensitivity of the films is mostly due to the change of band gap as well as some structural and surface morphological changes as found in the annealed films.

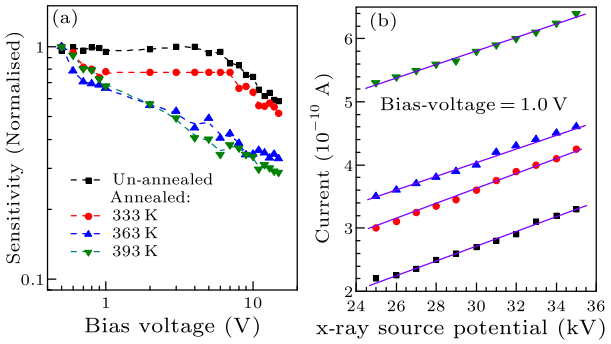

Fig. 5. (a) Dependence of x-ray detection sensitivity of the 333, 363 and 393 K annealed and un-annealed films on bias voltage. (b) For bias voltage $V = 1.0$ V, the variation of current with x-ray source potential. The symbols in (b) correspond to the same films as designated in (a).

For the un-annealed and 333 K annealed films, the detection sensitivity corresponding to the particular energy of x-ray radiation is constant within the bias-voltage ∼1.0–6.0 V. Therefore, using a constant bias-voltage between 1.0 and 6.0 V across the films, the current flowing through the films is studied by changing the energy of the x-ray radiation. Although the sensitivities of the 363 and 393 K annealed films are not constant within any specific range of bias voltage, the similar analysis is also carried out for completeness. In this experiment, the energy of the x-ray is varied by changing the x-ray source potential between 25 and 35 kV while keeping the filament current constant at 15 mA. Figure 5(b) shows the current passing through the un-annealed and annealed films for bias-voltage $V = 1.0$ V. For all the films, the current is found to increase with the x-ray source potential. The magnitude of the slope of the current versus x-ray-source potential plot corresponding to the un-annealed film is found to be $(1.26\pm0.02)\times10^{-11}$ whereas those for the 333, 363 and 393 K annealed films are $(1.14\pm0.03)\times10^{-11}$, $(1.00\pm0.01)\times10^{-11}$ and $(1.00\pm0.02)\times10^{-11}$, respectively. This implies that the rate of increase of current per unit change of x-ray energy is maximum for the un-annealed film and decreases with annealing. The similar trend is also observed for bias-voltages $V = 2.0$, 3.0 and 5.0 V. This suggests that the un-annealed film which has the highest band gap is more sensitive than the annealed ones.

From this study, it can be concluded that the band gap of the ZnS film plays a crucial role in the detection sensitivity of x-ray. Due to a decrease in band gap as well as some structural and surface morphological changes, the detection sensitivity of the films is found to decrease with annealing. However, in spite of the decrease, the film annealed up to 393 K can still be used to detect x-ray.

We thank the Department of Physics of the Indian Institute of Technology (IIT) in Guwahati for providing the XRD facility, and the Institute of Advance Studies in Science and Technology (IASST) in Guwahati for the FESEM report.

References

[1] Gao X D, Li X M and Yu W D 2004 *Thin Solid Films* **468** 43
[2] Sou I K et al 2000 *J. Cryst. Growth* **214** 1125
[3] Shinde M S et al 2015 *J. Nanotechnol. Adv. Mater.* **3** 99
[4] Kumar P, Maikap S, Prakash A and Tien T C 2014 *Nanoscale Res. Lett.* **9** 179
[5] Sarma M P, Kalita J M and Wary G 2017 *Mater. Sci. Semicond. Process.* **61** 131
[6] Vidal J et al 1999 *Mater. Chem. Phys.* **61** 139
[7] Arenas O L, Nair M T S and Nair P K 1997 *Semicond. Sci. Technol.* **12** 1323
[8] Roy P, Ota J R and Srivastava S K 2006 *Thin Solid Films* **515** 1912
[9] Chen Y et al 2012 *Mater. Lett.* **75** 221
[10] Kalita J M and Wary G 2017 *J. Electron. Mater.* **46** 4287
[11] Cullity B D 1978 *Elements X-Ray Diffraction* (London: Addison-Wesley Publishing Co. Inc) chap 3 p 102
[12] Williamson G K and Hall W H 1953 *Acta Metall.* **1** 22
[13] Williamson G K and Smallman R E 1956 *Philos. Mag.* **1** 34
[14] Tauc J 1968 *Mater. Res. Bull.* **3** 37
[15] Ahn H and Um Y 2015 *J. Korean Phys. Soc.* **67** 1045
[16] Rhoderick E H 1978 *Metal Semiconductor Contacts* (Oxford: Clarendon Press) chap 2 pp 25, 54
[17] Fang X et al 2007 *Adv. Mater.* **19** 2593
[18] Luo W, Zhu L L and Zheng X J 2009 *Chin. Phys. Lett.* **26** 117502