Chalcogenide Letters Vol. 9, No. 11, November 2012, p. 435 - 440

METAL BASED CHALCOGENIDE THIN FILMS FOR PHOTOVOLTAICS

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Thin films of $Sb_2Sn_5S_9$ have been prepared on soda lime glass substrate by using thermal evaporation techniques. These films were annealed in argon gas at 105°C, 150°C and 200°C in sealed glass ampoules. XRD of the films reveal that the films are poly crystalline with $Sb_2Sn_5S_9$ phase. The photoconductivity response of this new absorber layer has good response when annealed. The transmittance of the films is low and the transmittance decreases with the annealing temperature. The absorption coefficient of the films is above $10^5 cm^{-1}$. The band gap calculated by ellipsometry technique is in the range of 2.1-2.7eV. The films have n-type conductivity checked by hot point probe.

(Received October 10, 2012; Accepted October 30, 2012)

1. Introduction

The renewable energy resources are fossil fuels, renewable resources and nuclear resources [1]. These are resources of energy which can be used for energy production time and again often called alternative source of energy [2], e.g. wind, solar, biomass, geothermal etc. It is of highly concern that solar energy is one of the most abundant form of energy available in direct and indirect form. The earth intercepts 1.8×10^{14} KW power out of the total power of sun 3.8×10^{23}KW which has a vast scope of utilization in heating and cooking. Electrical energy is the backbone of all developmental efforts carrying out both in developing and non developing nations. The production of energy from fossil fuel involves the environmental impacts due to the consumption of fuel leading to the pollutants emission [3, 4].

The recent bang in photovoltaic modules demands has created a shortage in silicon supply, leads an opportunity for thin-film solar cell modules to enter the energy market replacing silicon. Thin films have revolutionized the cost structure of the solar cell modules as above 50% cost in silicon technology is that of module manufacturing.

This huge variation in price outstrips the demand of silicon supply, providing an opportunity for a number of thin film technologies. Categorically, they are

- Silicon; in crystalline, amorphous, nano-crystalline and polycrystalline phases
- Polycrystalline chalcogenide compounds
- Organo-metalic dyes and polymers

Silicon is the most widely used solar cell technology for production of electricity and is known as clean source of energy. The enhancement in the efficiency of solar cells, the quantity of material and system design, will reduce the requirement of energy and CO_2 emission [5]. We have proposed a new material “antimony tin sulphide” in the current research which has a potential to be commercialized in the near future [6].

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2. Experimental

SnSbS was deposited by thermal evaporator using co-evaporation techniques. SnS and Sb_2S_3 powder in the form of pallets were evaporated from two different crucibles inside vacuum coater simultaneously. Both materials were used of analytical grade. Tin sulphide powder was synthesized from analytical grade Sn and S powder. Both powders were mixed in a ratio Sn: S = 0.7873g: 0.2127g, crushed well and then annealed in argon gas at low pressure for 24hours at 600°C [11]. XRD of the powder confirmed SnS formation. Thin films were deposited on glass substrate retaining the pressure of the chamber at ~$2x10^{-4}$mbar with no substrate heating. The deposited films were annealed at 105°C, 150°C and 200°C in tube furnace in argon gas.

The elemental composition was confirmed by Energy dispersive X-ray spectroscopy (EDX) while the optical properties were measured by using J. A. Woollam variable angle spectroscopic Ellipsometry (VASE). For the photoconductivity measurement light of variable wavelength from 400nm to 1100nm is allowed to fall in dark on the film and the response of the photoconductivity is measured with the help of attached PC controlled with software. For the photoconductivity, molybdenum contacts were deposited 1 mm apart with the help of sputtering coater.

3. Results and analysis

Fig. 1 shows XRD spectra of the SnS ingot synthesized from Sn and S powder.

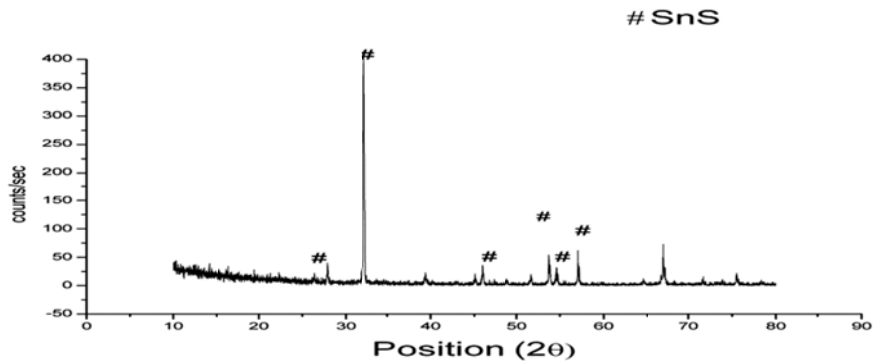

Fig. 1. SnS ingot XRD

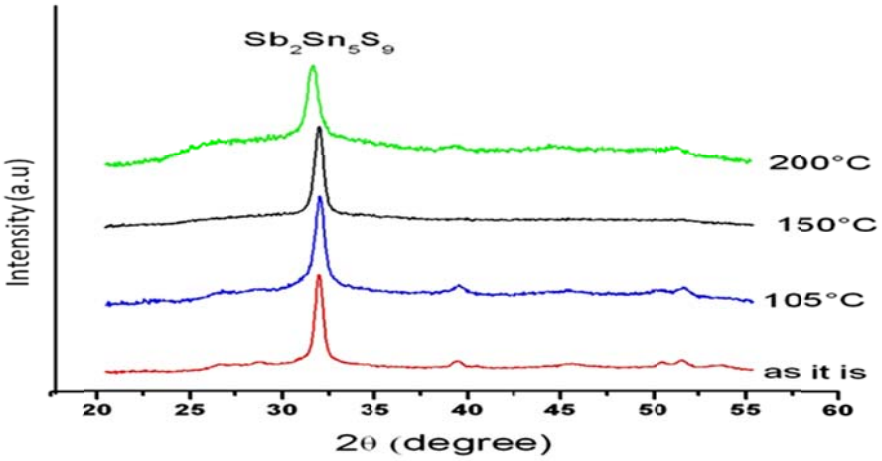

Fig. 2 XRD of tin antimony sulphide thin films as it as and annealed at different temperature.

It is obvious that the as it as and low temperature annealed (105°C and 150°C) Sn-Sb-S thin films have poly crystalline nature while high temperature annealed (150°C and above) thin films poly-crystallinity structure improves with high annealing temperature. . The peak of the XRD confirms the $Sb_2Sn_5S_9$ phase of the films.

The crystalline size was calculated by using Scherer's formula:

$$D=0.9\lambda/\beta\cos\theta$$

Where D is the average crystallite size, λ is the wavelength and β is the full-width at half maximum [7, 8]. The average grain size of our crystalline sample was 90-100Å.

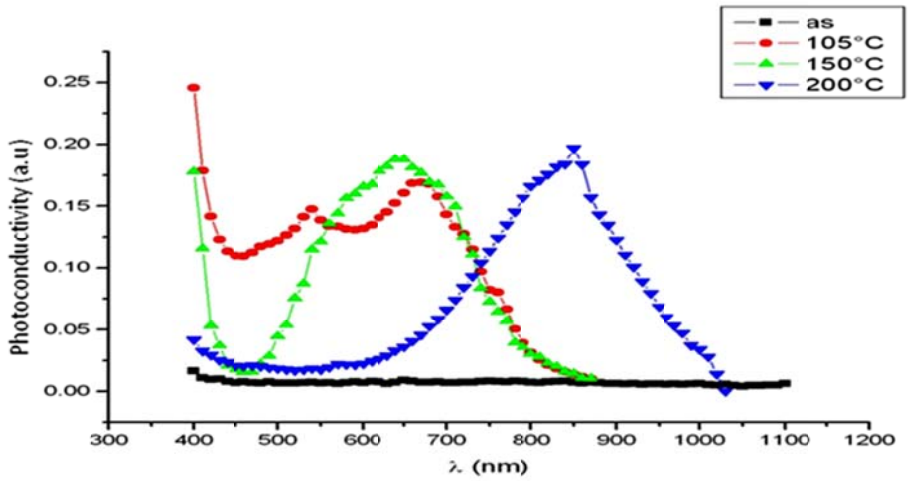

Fig. 3. Photoconductivity measurement

The photoconductivity result (figure-3) of the thin films shows that all films have different photoconductivity response at different annealing temperature. The blue and red shift is at different annealing temperature. The as-deposited film is not photoactive while the 105°C annealed film has good photo conductivity limited in the visible region only. The 150°C annealed films have very good photoconductivity response span from 500nm to 1050nm covering the visible and infrared part of the solar spectrum. The photoconductivity response of 200°C annealed film is in the range 600nm-1050nm and we see a red shift in its lower edge.

Figure 4 shows a transmittance curve for the library. It is noted that the transmittance decreases with the annealing temperature. The as it is and 105°C annealed films have nearly same transmittance while the transmittance decreases with further annealing and at 150°C annealed film, the transmittance start at 700nm and we found a dramatic change in the transmittance at 200°C annealing. We found that there is no transmittance below 850nm confirms that tin antimony sulphide thin films have good optical properties. The maxima and minima of the transmitted spectrum an indication of the optical homogeneity of the films [10].

Fig. 5 represent the refractive index (n) variation with annealing temperature as well as with the wavelength. The refractive index of the material is in the range 2.5-4. The refractive index for 200°C annealed film is 2.5 with no enough variation with wavelength.

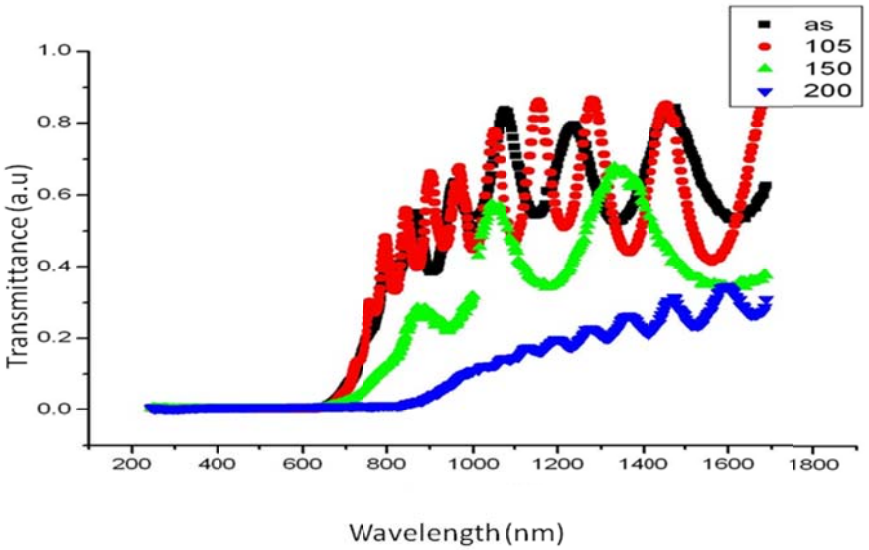

Fig. 4. Transmittance vs. wave length for SnSbS thin films

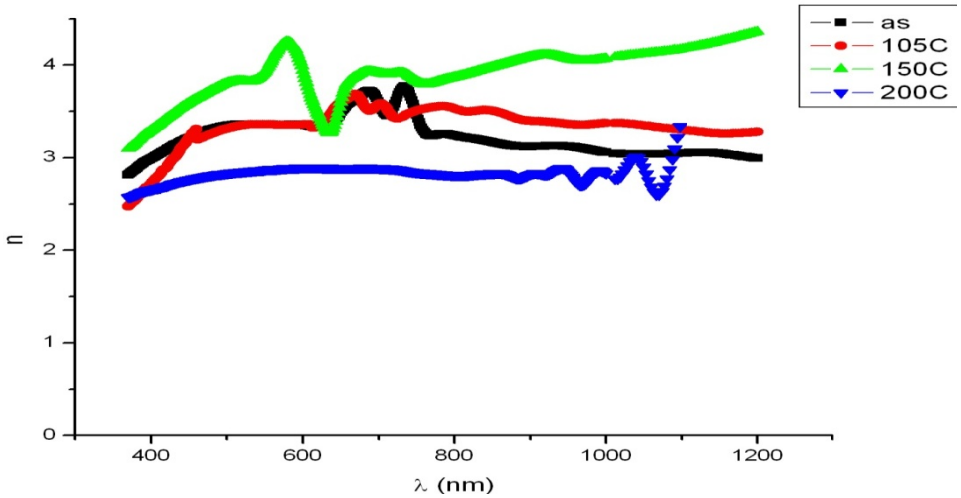

Fig. 5 Refractive index of tin antimony sulphide thin film

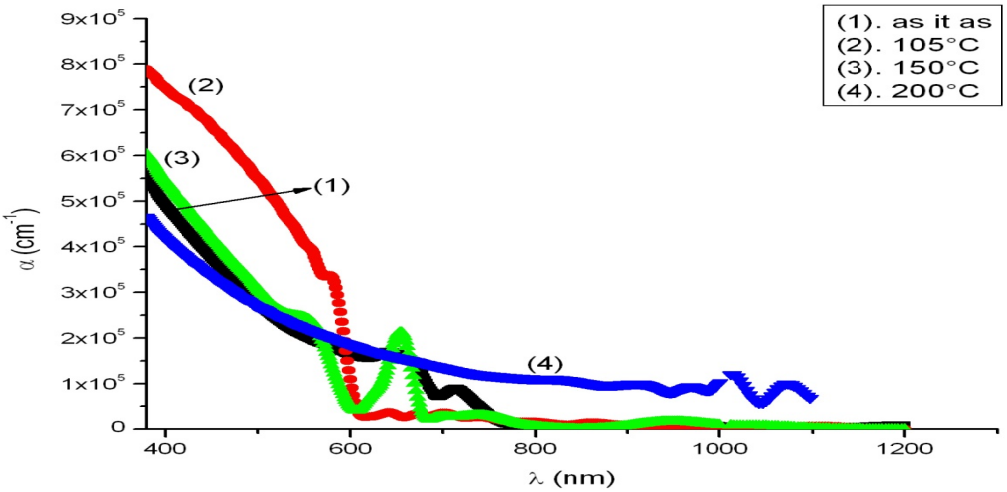

Fig. 6. Absorption coefficient of tin antimony sulphide thin film.

The graph of absorption coefficient (α) vs. wavelength (λ) is plotted for the as-deposited as well as the annealed films is shown in figure 6. The absorption coefficient can be calculated using by using the following relation

$$\alpha = 4\pi k/\lambda$$

Where k is the extinction coefficient of the material.

The figure shows that absorption coefficient decreases with the increase in wavelength. The maximum value lies in the visible region which is of the order of $8\times10^{6}cm^{-1}$. Thin films with this absorption coefficient are termed as good photovoltaic materials.

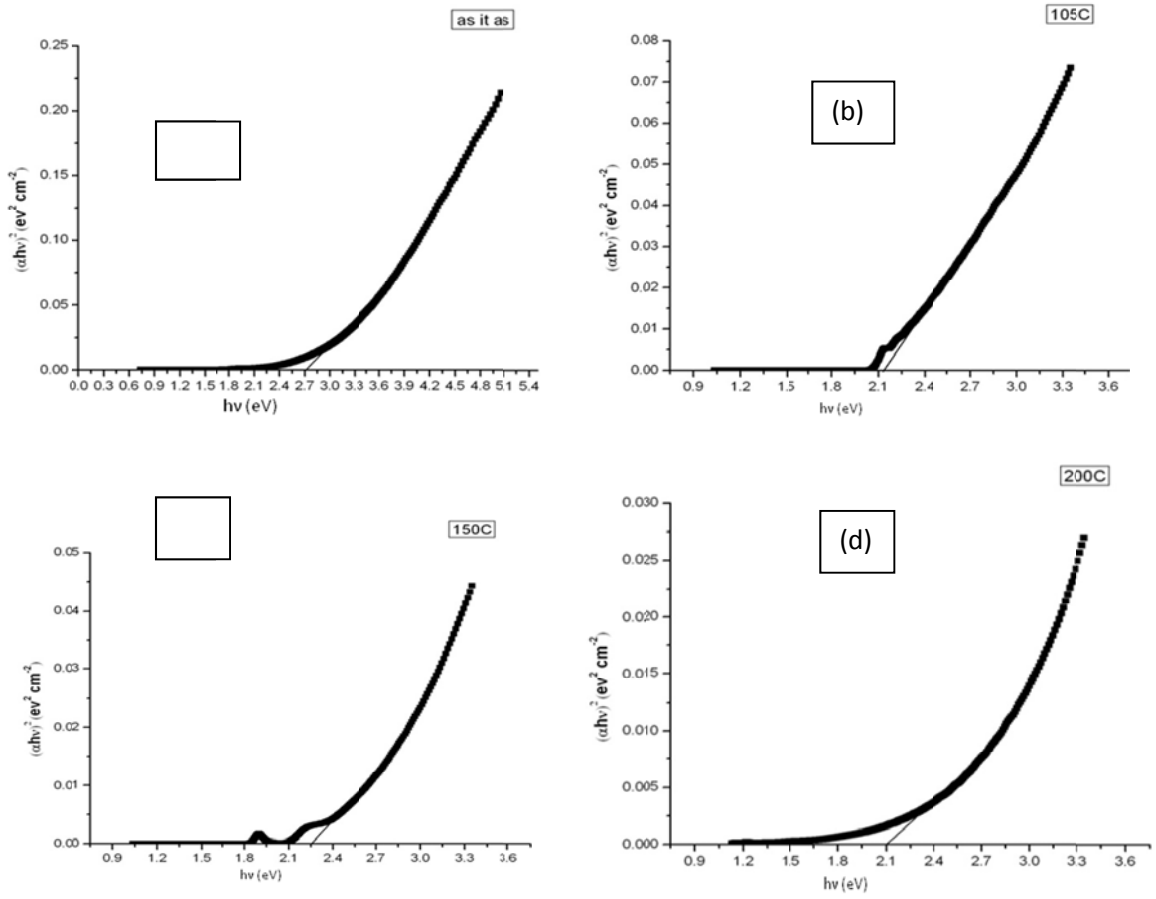

Fig. 7. Band gap of the films (a) as it as (b) 105°C (c) 150°C (d) 200°C.

The band gap of the film is calculated by extrapolating the straight section of the $(\alpha h\nu)^{2}$ vs. hν curve to the horizontal energy axis [9] by using the following equation [9]

$$\alpha h\nu = A\,(h\nu - E_g)^{n}$$

Where h is Plank constant, A is a constant and n is equal to ½ for a direct band gap and 2 for indirect band gap semiconductors. The band gap for the as deposited tin antimony sulphide thin film as in figure 7 (a) is 2.7eV which decreases with the increase in annealing temperature. The band gap is 2.11eV for 105°C, 2.25 for 150°C and 2.10 for 200°C annealing temperature. The decrease in the band gap is because of the increase in the grain size with the annealing temperature [11].

Hot point probe method was used for the checking of the conductivity type of tin antimony sulphide thin films. We found n-type conductivity for the current material by already calibrated hot point probe instrument [12]. This is shown in figure 8.

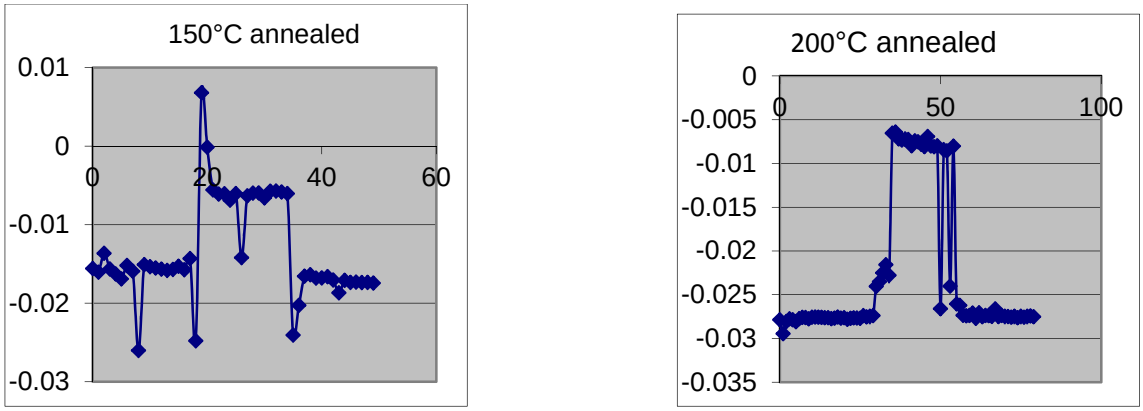

Fig. 8. Hot point probe measurement.

4. Conclusion

Smooth antimony tin sulfide ($Sb_2Sn_5S_9$) thin films were synthesized by thermal evaporation. The annealing effect on the films was studied in argon gas. It can be concluded that the properties of the thin films are improved due to annealing. The as deposited and annealed films showed better optical properties in the visible and IR region. The films have the absorption coefficient above $10^5 cm^{-1}$ which is a property of absorber layer. Our material showed a direct band gap of 2.1eV -2.7 eV for the as deposited and the annealed films with n-type conductivity.

Acknowledgement

The authors are thankful for the financial support of HEC Pakistan which provides funds for carrying out this research work.

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