Materials Research Express

RECEIVED
14 February 2019

REVISED
15 March 2019

ACCEPTED FOR PUBLICATION
28 March 2019

PUBLISHED
10 April 2019

PAPER

Optoelectronic properties of In_2S_3 thin films measured using surface photovoltage spectroscopy

S Rasool[1], K Saritha[1], K T Ramakrishna Reddy[1], L Bychto[2], A Patryn[2], M Maliński[2], M S Tivanov[3] and V F Gremenok[4]

[1] Sri Venkateswara University, Tirupati—517 502, Andhra Pradesh, India
[2] Koszalin University of Technology, Koszalin, 75-453, Poland
[3] Belarusian State University, Nezavisimosti 4 av., 220030 Minsk, Belarus
[4] Scientific and Practical Materials Research Centre, National Academy of Sciences, 220072 Minsk, Belarus

E-mail: ktrkreddy@gmail.com

Keywords: solar energy materials, In_2S_3, thin films, SPV, band gap energy, diffusion length

Abstract

In recent years, In_2S_3 thin films were widely used as buffer/window layer in thin film solar cells as an alternative to toxic CdS. In the present work, we demonstrate the potential of surface photovoltage spectroscopy for estimation of minority carrier diffusion length, band gap energy and refractive index of thermally evaporated In_2S_3 thin films. The estimated minority carrier diffusion length of In_2S_3 thin films from SPV measurements were 0.112 μm and 0.052 μm for films annealed at 250 and 300 °C respectively.

1. Introduction

Indium sulfide (In_2S_3) is a III-VI semiconductor compound which is a promising material for various optoelectronic applications. It is an n-type semiconductor with band gap energy range from 2.0 to 3.3 eV and it is appearing to be suitable for use in thin film solar cells as a buffer layer [1]. Recently, Spiering *et al* [2] reported 18.2% conversion efficiency achieved by using a In_2S_3 buffer layer in Cu(In, Ga)Se_2 thin film solar cells that is close to the value in case when CdS buffer layer is used [3].

One of the factors that limit the performance of a photovoltaic device is the recombination of free charge carriers that take place at bulk, interface or surface regions. This may lead to lower diffusion length and lifetime of photo-generated charge carriers, which can influence the performance of the device. Therefore, determination of the minority carrier diffusion length and carrier lifetime of the semiconductors acting as active layers in the device is essential. In this context, surface photovoltage (SPV) spectroscopy is widely used to determine the minority carrier diffusion length in semiconductors. Based on the obtained SPV signal, the type of conductivity of the material can be determined [4, 5].

There were a small number of reports on SPV studies of In_2S_3 films [6–10]. However, to the best of our knowledge, the use of the SPV is to find the minority carrier diffusion length of polycrystalline In_2S_3 thin films was not performed previously. The experimental, structural, morphological and optical properties of as-deposited and annealed In_2S_3 films were reported elsewhere [11].

2. Experimental

In_2S_3 thin films with thickness of ~0.5 μm were deposited on soda lime glass substrates using the thermal evaporation technique at a constant substrate temperature of 300 °C and the as-deposited films were annealed at different temperatures (200 °C–300 °C) in sulfur atmosphere about 1 h.

The SPV measurements were performed in non-contact mode of metal-insulator-semiconductor (MIS) configuration according to the scheme presented in figure 1(a). The glass spacer was used to ensure an equal distance between sample's surface and each electrode. The experimental setup used for the SPV measurement is

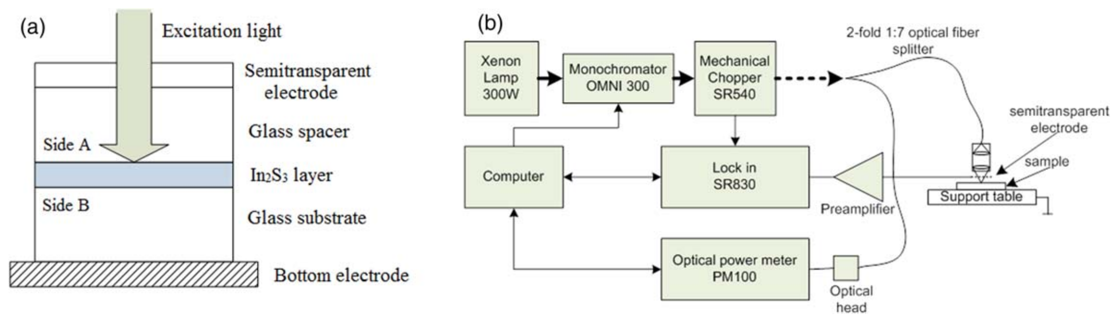

Figure 1. (a) Schematic representation of MIS configuration and (b) experimental setup of surface photovoltage spectroscopy measurement.

shown in figure 1(b). The setup uses a 300 Watt Xenon lamp and the emitted light was monochromatized through an OMNI-300 grating monochromator. This monochromated light beam was modulated by Standford Research SR 540 mechanical chopper along with a phase sensitive amplifier, which locks the modulating light frequency. Thus, the modulated light beam incident on the sample resulted in a variation of capacitance of MIS cell (figure 1(a)), which was detected by an SR 830 lock-in amplifier. The SPV signals were measured in the wavelength range of 400–700 nm at a constant frequency of modulation (226 Hz). The optical transmittance of the films was measured using Photon RT spectrophotometer.

The SPV is the illumination-induced variation of the surface potential. The surface potential is generally proportional to the concentration of generated carriers. During excitation of the sample with the light, the excess minority carriers are generated and due to diffusion and recombination processes, the minority carrier concentration distribution is changed. This causes a change in surface potential.

The surface photovoltage ΔV_A (ΔV_B) is the difference of surface potentials presented on the surface A (B) during 'light on' and 'light off'. Totally measured SPV signal is proportional to the difference between surface photovoltage of side A and side B.

$$U_{SPV} = \Delta V_A - \Delta V_B \tag{1}$$

Usually, the assumptions are made that both the light and diffusing carriers do not reach the bottom side ($\alpha \gg d^{-1}$) and ($L \ll d$) (α is absorption coefficient, d is thickness of the film and L is carrier's diffusion length). Then

$$U_{SPV} = \Delta V_A \tag{2}$$

3. Results and discussions

Figure 2 shows the SPV signal (U_{SPV} versus photon energy (hν) for as-deposited and annealed In_2S_3 films. All In_2S_3 films gave a positive SPV signal which indicates that they had n-type conductivity [12].

From figure 2, the generated surface photovoltage increases with annealing temperature. A very low surface voltage has been obtained for as-deposited and films annealed at $T_a = 200$ °C. It may be due to the recombination of the photo-generated carriers through available defect or surface states in the band gap region. On the other hand, the surface photovoltage is increased for films annealed at 250 and 300 °C. This may be due to these annealed layers having lower concentrations of bulk- and surface-defects, resulting in the increase of photo-induced carrier concentration near the surface region. This increase in carrier concentration causes an increase in surface voltage. At photon energies close to the band gap there is often a sharp change in slope of the SPV signal. The band gap energies of the films were determined more precisely from the intercepts of the SPV signals and were found to be 1.99, 2.12, 2.55 and 2.49 eV for as-deposited and those annealed at 200, 250 and 300 °C respectively (figure 2) [6, 9].

The refractive indices (n) of the In_2S_3 films were estimated from the Herve-Vandamme formula [13, 14], which provides small deviation for many semiconductors and chalcopyrites.

$$n = \left[1 + \left(\frac{A}{E_g + B}\right)^2\right]^{1/2} \tag{3}$$

where A and B are constants equal to 13.6 eV and 3.4 eV respectively. The obtained refractive index values are tabulated in table 1 and decrease with increasing annealing temperature. El-Nahass et al [15] also reported that

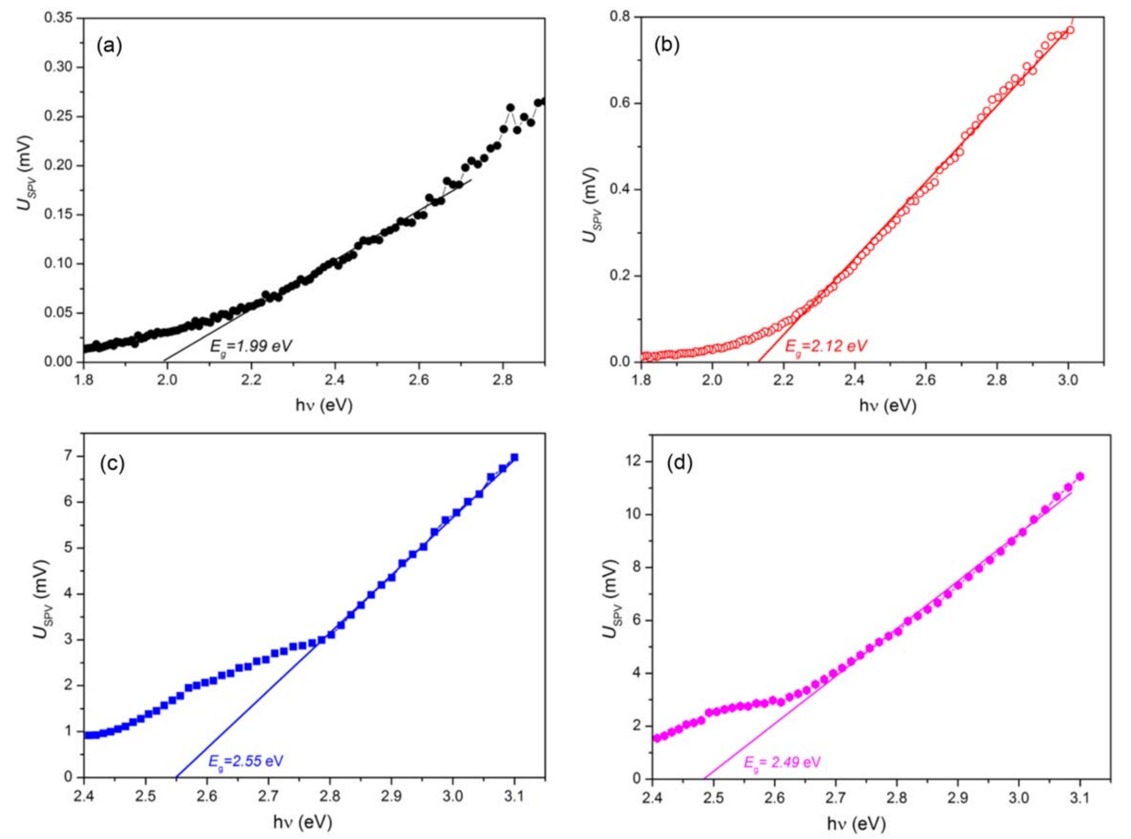

Figure 2. SPV signal versus photon energy of In_2S_3 films (a) as-deposited (b) $T_a = 200$ °C, (c) $T_a = 250$ °C and (d) $T_a = 300$ °C.

Table 1. Comparative table of minority carrier diffusion length of different semiconductors.

Semiconducting material	Type of conductivity	Thickness (μm)	Minority carrier diffusion length (μm)	References
CdS	n-type	3–8	0.2–0.46	[17]
CdSe	n-type	—	0.12	[20]
CdTe	n-type	4.0	0.8	[19]
		—	0.13–5.0	[20]
ZnSe	n-type	—	0.017–1.20	[18]
		—	0.45	[20]
SnS_2	n-type	—	0.17–0.23	[21]
In_2S_3	n-type	0.5	0.112	Present work

the refractive index decreased with increase of annealing temperature of In_2S_3 thin films deposited by the thermal evaporation technique.

Here, we also used the SPV method to determine the minority carrier diffusion length of the semiconductors. In the present work, the variation of SPV signal generated at different photon energies was measured and compared with the different absorption coefficient values corresponding to the photon energy values. In the constant flux method, for small excitation level, i.e. surface photovoltage ΔV_A (ΔV_B) is much smaller than kT/q, the SPV signal U_{SPV} is related to the absorption coefficient (α) by the relation (4) [16],

$$\frac{1}{U_{SPV}} = \frac{n_0(s_1 + D_h/L_h)}{(kT/q)(1 - R)\phi}\frac{(L_h + 1/\alpha)}{L_h} = C(L_h + 1/\alpha) \tag{4}$$

where C is a constant, L_h is the diffusion length of holes and the absorption coefficient (α) values were taken from the optical transmittance measurements using the following relation.

$$\alpha = -\frac{\ln T}{d} \tag{5}$$

where d is the thickness of the films and T is optical transmittance. The variation of α^{-1} with photon energy is as shown in figure 3.

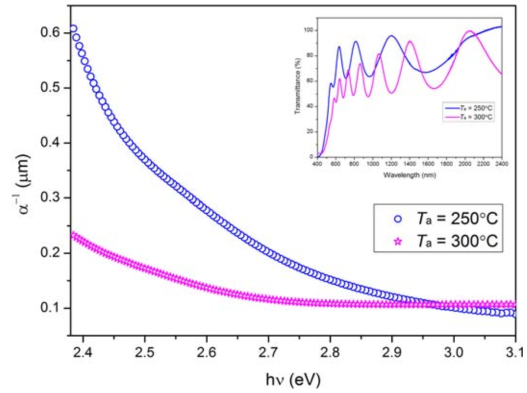

Figure 3. Variation of α^{-1} with photon energy hν.

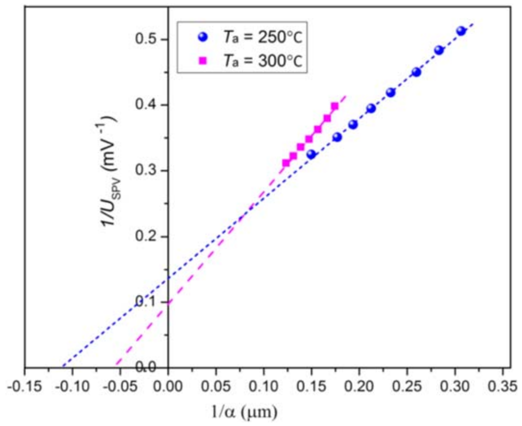

Figure 4. The plot of U_{SPV}^{-1} versus α^{-1} of In_2S_3 films annealed at $T_a = 250$ and 300 °C.

The linear fit of the plot $1/U_{SPV}$ against $1/\alpha$ (h$\nu > E_g$) yielded a straight line for which the intercept on the $1/\alpha$ axis when $1/U_{SPV} = 0$ directly gives the minority carrier diffusion length (L_h). This method was used earlier by researchers for diffusion length measurement of different binary semiconductors like CdS, CdSe, ZnSe and CdTe [17–19]. For the as-grown and the films annealed at 200 °C, the L_h values could not be determined as the films exhibited mixed phases with poor crystallinity and high density of impurity states present in the films which was already reported elsewhere [11]. Figure 4 shows the plot of U_{SPV}^{-1} (mV^{-1}) versus α^{-1} (μm) of In_2S_3 films annealed at 250 °C and 300 °C, through which the determined L_h values are 0.112 μm and 0.052 μm. It should be noted that generally the carrier diffusion length may change due to various factors (various impurities, point defects, clusters, grains and grain boundary parameters) which affect the recombination process, especially in such non-perfect materials.

Table 1 lists some of the reported values of minority carrier diffusion length of II-VI, III-V and IV–VI group semiconductors along with our results, which are mostly used as buffer/window layers in thin film solar cells.

Moreover, the mobility—lifetime product ($\mu_h \cdot \tau_h$) can be deduced from the diffusion length, $L_h = \sqrt{D_h \tau_h}$ and Einstein equation, $D_h = \mu_h \left(\frac{kT}{q}\right)$ [22, 23]

$$\mu_h \tau_h = \left(\frac{q}{kT}\right) L_h^2 = 38.65\ L_h^2 \tag{6}$$

where μ_h, τ_h and L_h are in cm^2/V·s, s and cm respectively and these values are tabulated in table 2. Robert *et al* [24] reported the mobility-lifetime product value as 6×10^{-7} cm^2 V^{-1} for In_2S_3 thin films prepared by ALD technique. Also, the $\mu\tau$ product can influence the drift length ($L_{drift} = \mu\tau \cdot E$) of the carriers and hence it defines the quality of the material.

Table 2. The optical and optoelectronic parameters of as-deposited and annealed In_2S_3 films.

T_a (°C)	E_g (eV)	n	L_h (μm)	$\mu_h\tau_h$ (cm^2 V^{-1})
As-deposited	1.99	2.71	—	—
200	2.12	2.65	—	—
250	2.55	2.48	0.112	0.484×10^{-8}
300	2.49	2.50	0.052	0.100×10^{-8}

4. Conclusion

The SPV method was employed to study the optical and optoelectronic properties of the In_2S_3 films. The experiments have shown the real possibility of completely non-destructive measurement of the In_2S_3 thin-film structures using the quasi-non-contact SPV measurement method and determination of the parameters essential for materials that are promising for photovoltaic application. The measurements revealed that all the films had n-type conductivity and the surface photovoltage increases with annealing temperature. The present work revealed that In_2S_3 films annealed at 250 °C had wider band gap (2.55 eV) with lower refractive index and larger diffusion length (0.112 μm) compared to all other layers and hence such films are the most suitable as window/buffer layer in the development of hetero-junction thin film solar cells.

Acknowledgments

This work was supported by the Belarusian State Programme for Research ≪Physical Material Science, New Materials and Technologies.

One of the authors, S Rasool thanks the University Grants Commission (UGC), New Delhi for the financial assistance via the 'UGC-BSR fellowship'.

ORCID iDs

S Rasool https://orcid.org/0000-0002-0807-9951
K Saritha https://orcid.org/0000-0003-4345-4937

References

[1] Mughal M A, Engelken R and Sharma R 2015 *Sol. Energy* **120** 131
[2] Spiering S, Nowitzki A, Kessler F, Igalson M and Abdel Maksoud H 2016 *Sol. Eng. Mat & Sol. Cells* **144** 544
[3] Poncelet O, Kotipalli R, Vermang B, Macleod A, Francis L A and Flandre D 2017 *Sol. Energy* **146** 443
[4] Cavalcoli D and Cavallini A 2010 *Phys. Stat. Sol.* C **7** 1293
[5] Cavalcoli D, Fraboni B and Cavallini A 2008 *J. Applied Physics* **103** 4
[6] Gorji N E, Reggiani U and Sandrolini L 2015 *Int. J. Photoenergy* **2015** 5
[7] Wafula H, Juma A, Sakwa T, Musembi R and Simiyu J 2016 *Coatings* **6** 30
[8] Shi Y, Yang Y L, Fan R Q, Li L, Yu J and Li S 2014 *RSC Adv.* **4** 17245
[9] Pomaska M, Sáez-Araoz R, Steigert A, Fu Y P, Hergert F, Lauermann I, Dittrich T, Lux-Steiner M and Fischer C H 2015 *Sol. Eng. Mat & Sol. Cells* **132** 303
[10] Tapia C *et al* 2016 *J. Phys. Chem.* C **120** 28753
[11] Rasool S, Saritha K, Ramakrishna Reddy K T, Tivanov M S, Trofimova A V, Tikoto S E, Bychto L, Patryn A, Maliński M and Gremenok V F 2019 *Curr. Appl. Phys.* **19** 108
[12] Kronik L and Shapira Y 2001 *Surf. Interface Anal.* **31** 954
[13] Herevé P and Vandamme L K J 1994 *Infrared Phys. Technol.* **35** 609
[14] Nehra S P, Chander S, Sharma A and Dhaka M S 2015 *Mater. Sci. Semicond. Process.* **40** 26
[15] El-Nahass M M, Khalifa B A, Soliman H S and Seyam M A M 2006 *Thin Solid Films* **515** 1796
[16] Schroder D K 2001 *Meas. Sci. Technol.* **12** R16
[17] Mora S, Romeo N and Tarricone L 1980 *IlNuovo Cimento* B **60** 97
[18] Mora S, Romeo N and Tarricone L 1980 *Solid State Commun.* **33** 1147
[19] Tarricone L, Romeo N, Sberveglieri G and Mora S 1982 *Sol. Engy. Mat.* **7** 343
[20] Gautron J and Lemasson P 1982 *J. Crys. Grow.* **59** 332
[21] Fotouhi B and Katty A 1986 *Electrochimical Acta* **31** 795
[22] Higuchi H and Tamura H 1965 *Jpn. J. Appl. Phys.* **4** 316
[23] Marshak A H and Assaf D 1973 *Sol. State Elect.* **16** 675
[24] McCarthy R F, Schaller R D, Gosztola D J, Wiederrecht G P and Martinson A B F 2015 *J. Phys. Chem. Lett.* **6** 8