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Electric field-effect-assisted persistent photoconductivity in CZTS

Nadarajah Muhunthan[1], Om P. Singh[1], Vidya N. Singh[1,2*], Kedar N. Sood[2], Rashmi[3]

[1]*Compound Semiconductor Solar Cell, Physics of Energy Harvesting Division,*
[2]*Electron and Ion Microscopy Section, Sophisticated and Analytical Instruments Division,*
[3]*X-ray Analysis Section, Sophisticated and Analytical Instruments Division,*
CSIR-National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi 110012, India

[*]Corresponding author. Tel: (+91) 1145608562; E-mail: singhvn@nplindia.org

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ABSTRACT

CZTS thin film was deposited by co-sputtering metal targets and post deposition sulfurization in H_2S. Temperature dependent electrical conductivity and photo conductivity effects in CZTS are studied. The low temperature electrical conductivity measurement shows acceptor level energy value as 36.85 meV. A large decay time of 108 s at 300K, 99 s at 200K and 94 s at 100K after switching off the light source was observed. The decay behavior of this persistent photoconductivity (PPC) in CZTS follows the double exponential function. The results show that defects are responsible for the observed PPC in CZTS. The combined measurements of low temperature electrical conductivity and photoconductivity give account of the defect level. Control of these defects can improve the quality of material and thus the resulting device. Copyright © 2015 VBRI press.

Keywords: Sputtering; CZTS thin film; persistent photoconductivity; defects.

Nadarajah Muhunthan is a Senior Research Fellow at CSIR-National Physical Laboratory, New Delhi, India. He did B.Sc in Physics (Honors) from University of Jaffna, Sri Lanka, M.Sc in Physics, University of Jaffna, Sri Lanka and Ph.D. in Physics, CSIR-National Physical Laboratory, AcSIR, New Delhi (Ph.D thesis submitted), He has more than 4 years of research experience in the field of deposition and characterization of CZTS thin films for solar cell applications. He has published more than 9 research articles in reputed journals.

Om Pal Singh is a Senior Research Fellow at CSIR-National Physical Laboratory, New Delhi, India. He did M.Sc. in Applied Physics from M.J.P. Rohilkhand University, Bareilly, India. Currently he is pursuing Ph.D in Physical Science at AcSIR National Physical Laboratory, New Delhi, India. His main research interest include synthesis of CZTS/CIGS thin film semiconductors and characterization for thin film solar cell application.

Vidya Nand Singh is a Scientist at CSIR-National Physical Laboratory, New Delhi, India. He earned his MSc degree (solid state physics, 1998) from Banaras Hindu University at Varanasi, India, M. Tech degree (solid state materials, 1999) and PhD (physics, 2005) from Indian Institute of Technology Delhi (IITD), New Delhi, India. He has nearly 15 years of research experience in the synthesis and applications of nanomaterials for gas sensing applications. Presently he is working on CIGS, CZTS and CdTe based thin film solar cells. He has published more than 100 research articles in reputed journals and have authored of two contributory chapters in international books.

Introduction

Copper zinc tin sulfide (CZTS) is an emerging solar photovoltaic absorber material which is composed of earth abundant, non-toxic and cheaper materials. It is a good substitute to copper indium gallium diselenide (CIGS), which is composed of rare, costly and relatively toxic materials. Although, CZTS with an absorption coefficient over 10^4 cm^{-1} and a band gap of ~ 1.5 eV stands out as an alternative for obtaining high efficiency thin film solar cells **[1-5].** The highest reported efficiency for CZTS solar cell is about 9.2 % **[6].** The main reason for low efficiency of CZTS solar cell is the presence of defects in CZTS. According to one previous theoretical report, the dominant defect in CZTS is p-type Cu_{Zn} antisite with acceptor level deeper than Cu vacancy, resulting in the formation of various polytype structures **[7]**. Therefore, a systematic study of the efficiency limiting factors, such as; Cu_{Zn} anti-site defects, etc is necessary. For studying defect states in the material, low temperature carrier transport and photoconductivity measurements are important. Low temperature transport measurement gives information about the location of the defects and photoconductivity measurements about the behavior of defects in the presence of light. Due to the presence of defects, the photoconductivity persists for longer time as reported by Gonzalez et al. **[8].** The low temperature transport and photoconductivity measurements combined together can give information about the defects. Controlling these defects shall help in improving the quality of the material and thus the performance of the device.

Experimental

Materials

In the present work, CZTS thin film was obtained by co-sputtering Cu, Zn and Sn metal targets on soda-lime glass (SLG) substrate and post deposition sulfurization in H_2S atmosphere at 550°C. The location of charge carrier defect states have been determined by the low temperature electrical measurements and the low temperature electric field effect assisted persistent photoconductivity (PPC) have also been observed in CZTS thin films. It has been shown that deep level defects are responsible for the PPC effect in CZTS. The PPC decay behavior has been analyzed in detail.

Method

The detailed deposition parameters and characterization of CZTS thin films have been reported earlier **[9-11].** For studying the temperature dependent carrier transport properties, sample was loaded in the cryostat chamber fitted with closed cycle helium refrigerator. The change in conductivity values with respect to temperature (77K-300K) were measured in four probe configuration using Keithley current source (model 6221) and nano voltmeter (model 2182). For photoconductivity measurements, sample was mounted in a closed-cycle helium cryostat and measurements were taken at different temperatures (300 K, 200 K and 100 K) with a constant bias voltage of 100 mV. The photocurrent response of CZTS thin film was recorded at different laser beam intensity (100, 80, 50, 20, and 10%) of He-Cd laser (441 nm wavelength, power density 470 $mWcm^{-2}$).

The photocurrent response of CZTS film was studied using the configuration shown in **Fig. 1**. Four gold stripes of width a mm coated on CZTS thin films deposited on SLG glass The gap between the strips was 0.5 mm. The photocurrent response of CZTS film was investigated under different laser beam intensity (100, 80, 50, 20, and 10%) of He-Cd laser, 441 nm wavelength (power density 470 $mWcm\text{-}^{2}$).

Results and discussion

When the sample was illuminated by a 441 nm (corresponding to 2.8 eV) laser light, the photoconductivity was observed and the results are shown in **Fig. 2 (a-c).** As the photon energy of the laser is larger than the band gap of CZTS (1.5 eV), a significant enhancement in the photo conductance was observed.

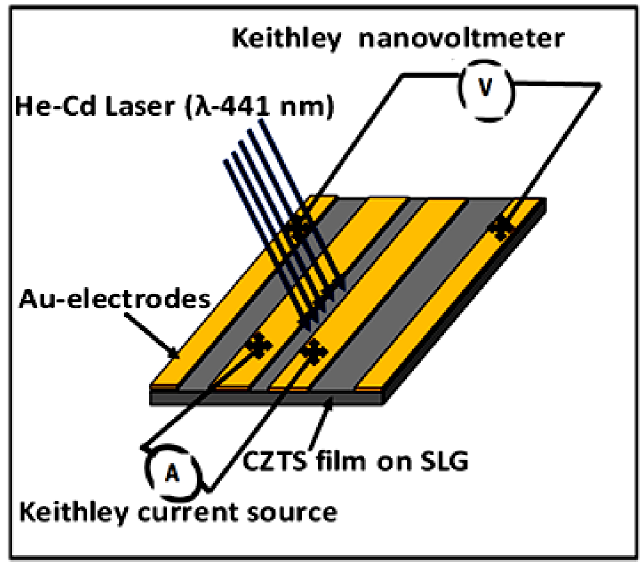

Fig. 1. Configuration used for studying the photoconductivity of CZTS thin film.

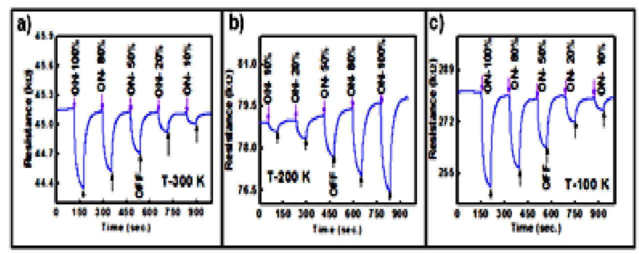

Fig. 2. Persistent photoconductivity at different substrate temperatures; (a) 300 K, (b) 200 K, and (c) 100 K, under He-Cd laser of (100, 80, 50, 20 and 10 %) intensity at constant bias voltage of 100 mV.

Fig. 2 (a-c) shows the photoconductivity response of CZTS thin film at 300 K, 200 K and 100 K, respectively. Due to laser light, many carriers get excited and the current increases. Long lasting photoconductivity was observed in the CZTS thin film even after switching off the light source. The observed effect is believed to be due to the presence of intrinsic defect levels in the forbidden band **[12].** The photo excited carriers get trapped, which suppresses the recombination.

A large decay time (τ) of 108 s at 300K, 99 s at 200K and 94 s at 100K after switching off the light source was observed as shown in **Fig. 3 (a-c).**

The PPC was lower at lower temperature. With increase in temperature, the thermal release rate of trapped holes from a shallow acceptor state to the valance band increases. The photo-induced decay current can be derived from the simplified continuity equation (1);

$$\frac{\partial I_c}{\partial t} = G - \frac{I_c - I_0}{\tau_m} \tag{1}$$

The concentration of photo charge carriers is equal to the generation rate G minus the recombination rate. In the above equation, I_c is the current due to charge carrier, I_o is the offset current, τ_m is the life time of the carrier, t is the time **[13].** The solution of above equation gives the decay in photocurrent which follows a double-exponential decay function:

$$I(t) = I_{fm} \exp\left(\frac{-t}{\tau_{fm}}\right) + I_{sm} \exp\left(\frac{-t}{\tau_{sm}}\right) + I_0 \quad (2)$$

Where, t is time; τ_{fm} and τ_{sm} are the life times of the fast recombination and slow recombination carriers; I_{fm} and I_{sm}, are fast and slow recombination photo carriers current.

Fig. 3 (a-c) is fitted using equation (2) and the value of decay current and saturation current were calculated for different temperature. The I_{fm} (fast recombination charge carriers current) decays to 36% at 300K, 29% at 200K and 26% at 100K in 100 ms, and I_{sm} (slow recombination charge carriers current) reaches nearly saturation current (dark current) within 30 s at 300K, 26 s at 200K and 19.4 s at 100K. The decay process of the experimental data and fitting from double-decay exponential function are shown in the **Fig. 3 (d-f**). A good match between the experimental values and fitted data is observed.

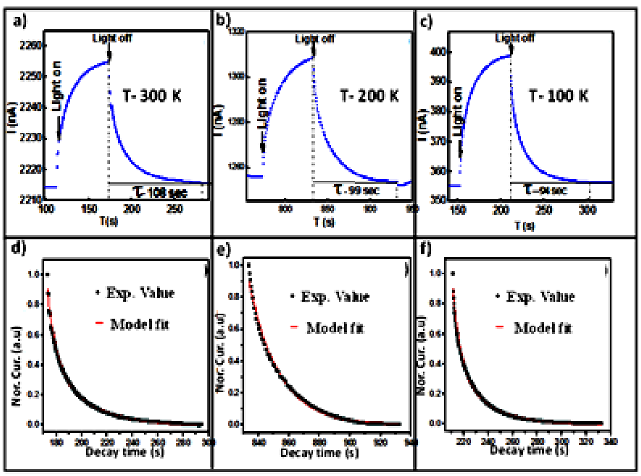

Fig. 3. Photo response current decay curve at different substrate temperatures; (a) 300 K, (b) 200 K, and (c) 100 K and the double exponential fitting of decay current; (d) 300 K, (e) 200 K and (f) 100 K, under the He-Cd laser of (100 %) intensity.

Fig. 4 (a) shows the plot of 1000/T versus logarithm of the conductivity of the CZTS thin films (measured in the temperature range of 77-300K). The activation energy (E_A) of a system which exhibits NNH transport is the energy required by a charge to hop from its current site to the next site. Value of activation energy (E_A) has been calculated using the very well-known equation (3) for thermally activated transport **[14],**

$$\sigma = \sigma_0 \, e^{-\left(\frac{E_A}{K_B T}\right)} \quad (3)$$

The tangent to this curve gives the value of activation energy. The estimated value of activation energy for the sample under investigation is 36.85 meV. This value is close to value of NNH activation energy (20-30 meV) reported by Kosyak et al **[15].** The conduction is due to the hopping of the charge carriers from filled state in one grain to an unfiled state in an adjacent grain. Reduction or eliminating of these hopping distances may improve carrier mobility (conductivity) and performance of solar cells **[14]. Fig. 4 (b)** shows the effect of light intensity (100% to 10%) on the normalized resistance of CZTS thin film at different measurement temperatures (300K, 200K and 100K). From the figure it can be seen that at room temperature (300 K), there is a very small decrease in the conductivity (~ 1 %) of the sample when light intensity is decreased from 100% to 10%. The decrease in conductivity was 3 % and 11 % (when light intensity was decreased from 100% to 10%) for measurements at lower temperatures of 200 K and 100 K, respectively. Thus, for low temperature measurements, the heating effect due to the incident laser light can't be ruled out. The conducting GB becomes more semiconducting with increasing in temperature which may reduce the charge generation near the interface. The intrinsic carrier concentration increases the dark saturation (recombination) current with increase in temperature **[16]**. Temperature dependent drift and diffusion current enhances phonon scattering which in turns destroy the photo-charge carriers. Space charges, copper vacancies, and trapped charges may also be responsible for the fast recombination at elevated temperature.

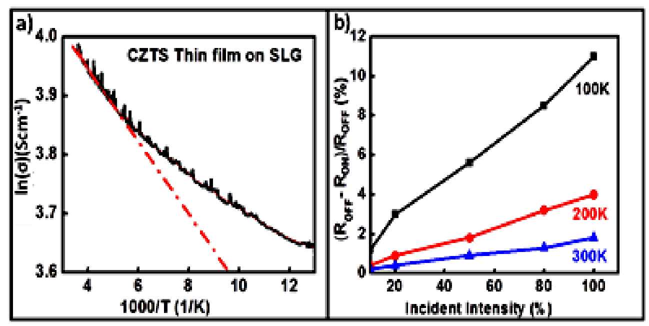

Fig. 4. (a) Temperature dependence of the electrical conductivity for CZTS thin film on SLG and (b) Change in normalized resistance with incident light intensity at different temperature (100K, 200K and 330K).

Conclusion

Temperature dependent electrical measurement showed that the charge conduction follows nearest neighbor hopping mechanism in CZTS thin film. The low temperature electrical conductivity measurement shows acceptor level energy value as 36.85 meV. A large decay time of 108 s at 300K, 99 s at 200K and 94 s at 100K after switching off the light source was observed. The decay behavior of this larger persistent photoconductivity (PPC) in CZTS follows the double exponential fast and slow recombination photocurrent function. In summary, through the study of low temperature electrical conductivity and photoconductivity measurements, the presence of defect states and effect of light on it can be clearly understood. Controlling the defects in material shall help in improving the performance of CZTS based thin film solar cell.

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