Comparative study of ECPV characteristics of dye and without dye sensitized Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ mixed metal chalcogenide thin films

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ABSTRACT

We have synthesized dye sensitized Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ and without dye sensitized Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ thin films by APT on both regular and fluorine tin–oxide (FTO) coated glass substrate. These films were characterized by X-ray diffraction (XRD), optical absorption, SEM, EDAX, AFM, XPS and electro chemical photovoltaical (ECPV) techniques. XRD study revealed that the films were nanocrystalline in nature with rhobohedral phase. ECPV of Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ thin films without dye were measured. Further these films were loaded with Ru (II) dye and their ECPV properties were measured. The dye sensitized Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ / Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ without dye act as an working electrode, Platinum coated FTO as a counter electrode and Iodide / triiodide as an electrolyte, with illumination intensity 28m/w/cm^2 were used. Our results revels that the performance of ECPV cell recorded for dye sensitized Bi$_2$ (Te$_{1-x}$ Se$_x$)$_3$ thin films was found to be maximum as compared to Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ thin films without dye, due to maximum light absorption by dye sensitized photo electrodes

Keywords: APT, Metal Chalcogenides, X-ray diffraction, PEC, ECPV. Dye sensitized cell, FTO.

INTRODUCTION

The search for new semiconducting material for solar energy conversion has been the subject of intensive research. When the photosensitive n-type solar cell electrode is immersed in an electrolyte solution containing a suitable redox system where the Fermi level of the solar cell is more negative than that of the redox electrolyte (the chemical potential of electrons in the solar cell and electrolyte is given by the Fermi level and the redox potential, respectively), the equilibration of two chemical potentials occurs by the transfer of electrons from the solar cell to the electrolyte and it leads to a positive space charge layer in the semiconductor i.e. electrons in n-type semiconductors. As a result, the conduction and valence band edges are bent upwards in n-type semiconductors, forming a potential barrier against further electron transfer to the electrolyte. This process set up a counter field under open circuit conductions. The counter field is at its maximum and is the open circuit voltage; Voc is given by the equation-

$$V_{OC} = (nKT/e)\log[I_{SC} + 1/I_O] \qquad (1)$$

On the other hand, the counter electrode is being in the same electrolyte, the photo voltage acts as a driving force for the electrons to move under the short- circuit conditions from the semiconductor electrode to the counter electrode and a regenerative cell is formed .The short- circuit current is given by the equation-

$$I_{SC} = I_O[\exp(eV_{OC}/nKT)^{-1}] \qquad (2)$$

The electrons promoted to the conduction band drift towards the interior, while the holes, the minority carriers, come to the surface of the semiconductor. Here they encounter the reduced form of the redox couple in the solution. The component is oxidized by the holes, transported to the counter electrode and therefore gets reduced. This reduction is driven by the external connection from the semiconductor.

MATERIALS AND METHODS

In the construction of a practical Electro-Chemical Photo-Voltaic (ECPV) cell for the conversion of sunlight into electricity (or chemical energy), the most important fact is the long-term stability of cells that show reasonable conversion efficiencies. Thus, an increasing number of studies on photoelectrodes are concerned with their stability. Here ECPV cell consists of a semiconductor photoelectrode, a redox electrolyte and a counter electrode. All parts play an important role in the ECPV cell. The distance between photoelectrode and counter electrode is 0.4 cm. The counter electrode is of graphite for ECPV cell and it is pre-treated by etching with dilute HCl. The pre-treatment to graphite electrode is required to activate it.

The fabrication of ECPV cells has the following configuration

FTO │Bi2(Te1-xSex)3 │0 .1 M (Na2Sx -NaOH) │Cathode

The water filter was interposed between the lamp and the cell to avoid the heating of the cell. The photo anode area exposed to light was 1 cm2. The area of the semiconducting thin film other than that in contact with electrolyte was covered by insulating tape.

- **Selection of suitable electrolyte**
A suitable electrolyte was selected by determining λmax of various electrolytes e.g. Ferricynide/Ferrocynide (Fe^{3+}/Fe^{2+})couple, iodide and polyiodide couple as well as sulphide and polysulphide (S^{-}/S^{2-}) solution. The λmax of polysulphide solution was found to be suitable and it shows maximum absorption in visible (~390 nm) range of spectra.

The formal redox potentials of the various electrolyte were studied and with reference to that the suitability of the electrolytes was checked and the sulphide /polysulphide couple with formal redox potential -0.71 V vs SCE ±0.005 V was found suitable for constructing a ECPV cell of material under investigations.

- **Measurements of properties of ECPV cell**
An ECPV is the liquid junction analogue of a solid state Schottky cell. In its simplest configuration, a semiconductor with ohmic contact is dipped in an electrolyte and connected via a load to a graphite second counter electrode. When light is incident on the semiconductor creates electron/hole pairs that are separated by the electric field formed by the contact between the semiconductor and the electrolyte. Hole or electron is injected in to the electrolyte. The hole oxidizes some electrolyte species, while the electrons are extracted through the ohmic contact and flow through an external circuit to the counter electrode, where reduction occurs. If the same species is both oxidized (at the semiconductor electrode) and reduced (at the counter electrode), no net change occurs in the electrolyte and electrical energy is generated in the external circuit [1-4].

The performances of ECPV cell can be improved by desirable properties of the semiconductors are a photoelectrode that has high surface area to increase the interfacial reaction sites. An optically thicker and efficient photoelectrode to enable total absorption of solar light, morphological features (shape, size, interconnection of particles, grain boundary) that define energetics and kinetics at the electrode interface, and hence influence the ECPV efficiency of the solar cell and an electrode comprising densely packed array of grains can enhance ECPV performance by virtue of the improvement in carrier transport mechanism and minimizing surface trap states. The unique structure combining high crystalline and high surface area leads to higher ECPV efficiencies [5-8].

In dark and under illumination current-voltage (I–V) characteristics of "Glass/FTO/ $Bi_2(Te_{1-x}Se_x)_3$ mixed metal chalcogenide /SCE" cells were measured. The fill factor (FF) was calculated by equation ,

$$FF = \frac{I_{max}V_{max}}{I_{sc}V_{oc}} \qquad (3)$$

where, Isc is the short circuit current density, Voc is open circuit voltage, Imax is the maximum current density and V max is the maximum voltage across the junction. The power conversion efficiency (η) of solar cells was calculated using equation,

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$$\eta = \frac{I_{sc} V_{oc}}{P_{in}} \times FF \times 100 \qquad\qquad (4)$$

where P is incident power

RESULTS AND DISCUSSION

**A) ECPV characteristics of dye sensitized $Bi_2(Te_{1-x}Se_x)_3$ thin films photoelectrode**
From experimental evidences Figure 1 shows the photocurrent-voltage (I-V) curves for $Bi_2(Te_{1-x}Se_x)_3$ for few samples in dark and under illumination (with intensity of 30mW/cm2). For all the films under visible illumination in terms of open circuit voltage (Voc), short circuit current density (Isc), fill factor (ff) and electron conversion efficiency are compared in Table 1
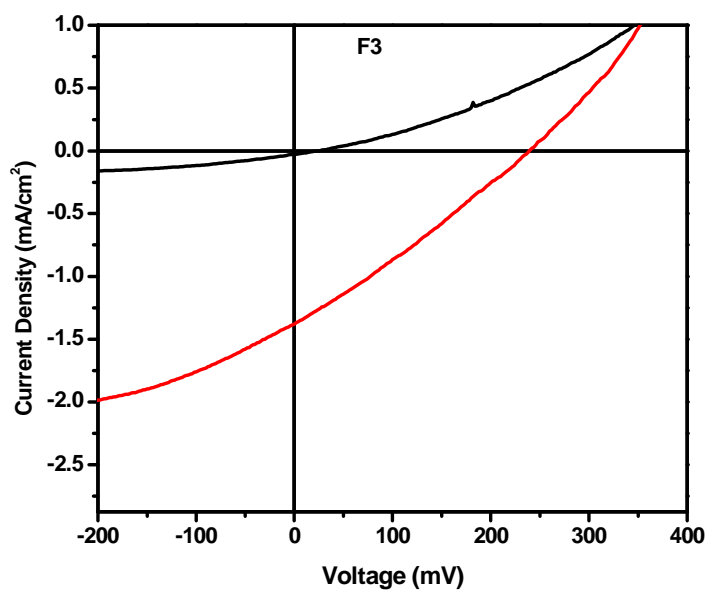
F₃
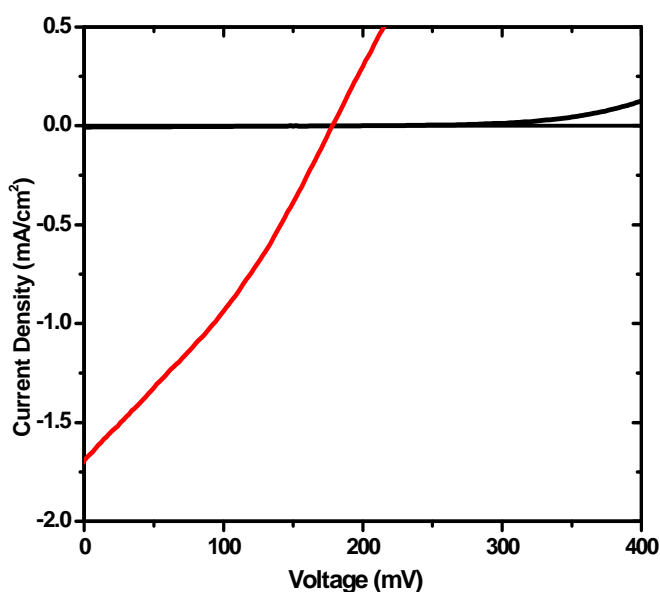
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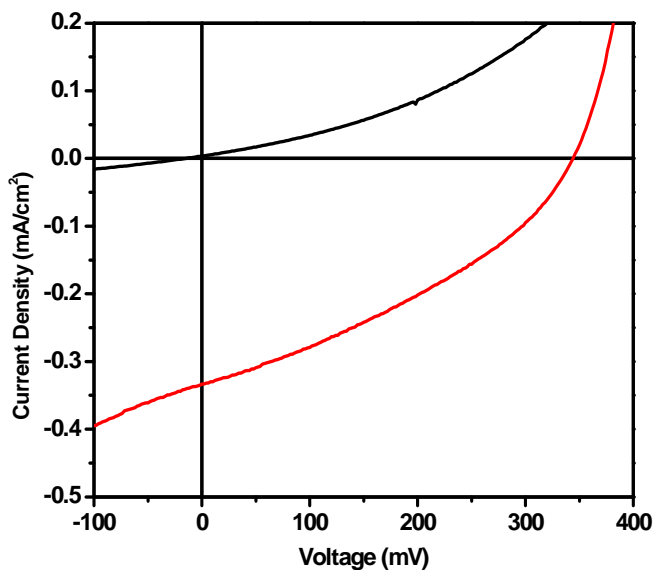
F_7

Figure 1. The photocurrent-voltage (I-V) curves for $Bi_2(Te_{1-x}Se_x)_3$ thin films

Table 1 Spectral properties of $Bi_2(Te_{1-x}Se_x)_3$ thin film photoelectrode

Composition Without dye	Grain Size in nm	Isc (mA/cm²)	Voc (mV)	I_{max} (mA/cm²)	V_{max} (mV)	Fill factor %	Conversion efficiency η %
F_1 : Bi_2Te_3	405	0.266	182	0.144	91	0.28	0.05
F_2 : $Bi_2(Te_{0.8}Se_{0.2})_3$	375	0.254	323	0.164	167	0.33	0.09
F_3: $Bi_2(Te_{0.6}Se_{0.4})_3$	341	1.36	238	0.386	115	0.20	0.215
F_4:$Bi_2(Te_{0.5}Se_{0.5})_3$	**325**	**1.65**	**178**	**0.948**	**101**	**0.33**	**0.32**
F_5: $Bi_2(Te_{0.4}Se_{0.6})_3$	390	0.934	330	0.432	149	0.20	0.22
F_6: $Bi_2(Te_{0.2}Se_{0.4})_3$	442	1.31	199	0.651	92	0.23	0.20
F_7: Bi_2Se_3	560	0.325	346	0.176	222	0.35	0.13

These (I-V) curves in dark indicate good junction rectification property. From the I-V measurements it is observed that the total conversion efficiency increases from 0.05% to 0.33 % for F1 to F4 $Bi_2(Te_{1-x}Se_x)_3$ thin films. And again it decreases up to F7. The improvement in the ECPV properties of the $Bi_2(Te_{1-x}Se_x)_3$ mixed metal chalcogenide thin films is due to morphological modifications that increases active surface area and quenching of the defect levels responsible for recombination losses [9-11]. Also the densely-packed spherical grains of $Bi_2(Te_{1-x}Se_x)_3$ of mixed

Metal chalcogenide thin films can absorb maximum light. This appreciable change into fill factor and conversion efficiency is due to increase in surface area to volume ratio with grain size. From above discussion we observed that the spherical grain morphology of films have for seeing impingement on the performance of the solar cells. The morphology of the films has less grain boundaries, which associate with traps or/and barriers for charge transport .So it gives faster conduction path and the electron transfer time from the point of carrier generation to the collection electrode is significantly reduced [12].

As deposited with varied metallo chalcogenide composition based ECPV cell shows good performance. The cell properties under illumination suggest that addition of selenium from F_1 to F_7 in $Bi_2(Te_{1-x}Se_x)_3$ thin films has been increasing cell performance for F_1 to F_4 compositions as compared to other thin film composition. This is might be due to decrease in grain size. A reduction in grain size provides large surface area of photoelectrode and maximizes optical absorption.

B) ECPV characteristics of dye sensitized $Bi_2(Te_{1-x}Se_x)_3$ thin films photoelectrode
Improvement in the cell performance and conversion efficiency has been studied by loading Ruthenium dye on all the samples (F_1 to F_7) for $Bi_2(Te_{1-x}Se_x)_3$ thin films for 12 h.

- **Optical properties of dye**

For dye sensitized ECPV cell a suitable redox electrolyte was selected by determining λmax of I-/I3- redox couple electrolytes. It has been the preferred redox couple since the beginning of DSC development and still yields the most stable and efficient DSCs. Overall, the iodide/triiodide couple has good solubility, does not absorb too much light, has a suitable redox potential and provides rapid dye regeneration. In solution, iodine will bind with iodide to form triiodide. If the iodine concentration is high, polyiodide species like I5-, I7-, and I9- may also be formed, but in practice only triiodide seems to be of importance in DSC electrolytes. The λmax of triiodide electrolytes solution was found suitable showing maximum absorption in visible range at 450 and 600 nm.

The formal redox potentials of 0.05 M lithium iodide in acetonitrile was found to be 0.335 (V) is suitable for constructing a dye sensitized ECPV cell of material under investigations that is mixed metal chalcogenide $Bi_2(Te_{1-x}Se_x)_3$ thin films photoanode.

Figure 2 gives the photo response of dye sensitized $Bi_2(Te_{1-x}Se_x)_3$ thin film electrodes prepared by APT method. It shows absorption spectrum of pure $(NCS)_2RuL_2$ dye in ethanol solution and semiconductor films with or without Ru dye .
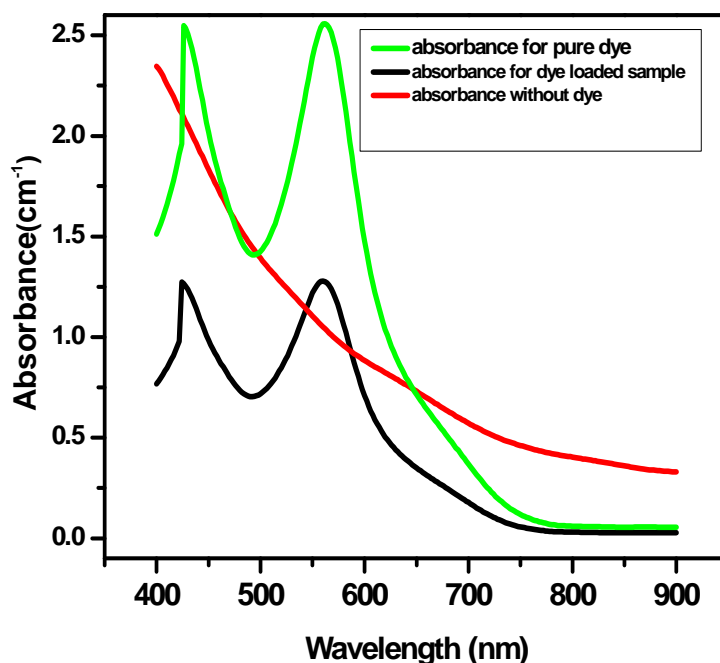

Figure 2. UV/Vis spectra of pure $(NCS)_2RuL_2$ dye in ethanol solution and of semiconductor films with or without Ru dye

Ruthenium-based dyes exhibit ligand-centered charge transfer (LCCT) transitions $(\pi - \pi^*)$ as well as metal-to-ligand charge transfer (MLCT) transitions (4d -)*) π^*). The absorption bands at lower energies represent the MLCT transitions ($\lambda 1$ and $\lambda 2$) whereas the more energetically demanding transitions ($\lambda 3$ and $\lambda 4$) correspond to LCCT transitions. Absorption spectrum shows broad and intense visible bands between 400 to 450 and 520 to 580 nm. The band at 422 nm is assigned to the $\pi-\pi^*$ transition of the ligand-centered transition due to dcbpy units. The absorption band at 560 nm corresponds to the MLCT caused by NCS ligands [13-14].

- **Mechanism in dye sensitized injection ECPV cells**

In dye-sensitized ECPV cells a photocurrent is generated when a photon excites a dye molecule, which then injects an electron into the mixed metal chalcogenide thin film. The oxidized dye molecule is subsequently recycled by electron transfer from a redox species in an electrolyte solution surrounding the sensitized metal chalcogenide thin film. In this ECPV cell, trapping of electrons in the metal chalcogenide thin film will be affect the charge transfer processes at the film/dye/electrolyte interface as well as the electron transport process through the nano structured network to the external circuit.

Mechanism of dye sensitized ECPV cell is as given. $Bi_2(Te_{1-x}Se_x)_3$ being used as negative polarity and platinised

platinum as the positive polarity end. In these devices, short-circuit conditions require the electron injection from the excited dye molecule into the conduction band of the chalcogenide semiconductor thin film and transfer of the hole to the platinum electrode. The excited state energy level of the dye should be located above the conduction band of the chalcogenide semiconductor thin film and the ground state must be below the upper edge of the valence band of the electrolyte material. This scenario is essential for electron transfer from the excited dye molecule to the conduction band of chalcogenide semiconductor thin film and hole transfer to the valence band of the electrolyte material. Thus for the cell all charge transfer processes are favored and current should be generated under illumination.

The I–V characteristics of the films were recorded using a semiconductor characterization system (SCS-4200 Keithley, Germany) with a two-electrode configuration under a under visible illumination for $Bi_2(Te_{1-x}Se_x)_3$ sample and halogen lamp (28 mW/cm2). The following cell configurations were used to record I–V plots:

Glass /FTO $\vert$ $Bi_2(Te_{1-x}Se_x)_3$ |Ru-dye $\vert$ iodide tri iodied electrolyte $\vert$ Pt-FTO

The $Bi_2(Te_{1-x}Se_x)_3$ mixed metal chalcogenide thin films (average area 1 cm2) deposited on FTO and platinum coated FTO were employed as the working and counter electrodes, respectively. An aqueous 0.05 M iodide triiodied (I-/I3-) solution was used as the redox electrolyte. Measurements for the power output characteristics and I–V plots were made at fixed intervals after waiting a sufficient amount of time for the system to reach equilibrium (both in the dark and under illumination). When both the electrodes are immersed in the redox electrolyte, the band bending of the semiconductor photoelectrode may occur. All the measurements were carried out at room temperature in air.

- **Measurements of efficiency of dye sensitized ECPV cells.**
The aim of this present study is to use the above thin film semiconductor electrodes in fabricating a dye sensitized ECPV cell with suitable power conversion efficiency paying attention to the role of dye as regards to its sensitization effect for improving maximum efficiency.

The power output characteristics of the dye sensitized ECPV cell were determined from the current-voltage (I - V) plot as shown in Figure 3. Dye loaded $Bi_2(Te_{1-x}Se_x)_3$ thin film electrodes in iodied triiodied redox electrolytes at an illumination intensity of 28 mW/cm^2. The dye sensitized $Bi_2(Te_{1-x}Se_x)_3$ thin film was found to have better optical to electrical conversion efficiency than found for $Bi_2(Te_{1-x}Se_x)_3$ thin films without dye. The efficiencies of the cell using $Bi_2(Te_{1-x}Se_x)_3$ have been increases from 0.08 to 0.42% for F_1 to F_4 sample and again decreases up to F_7.
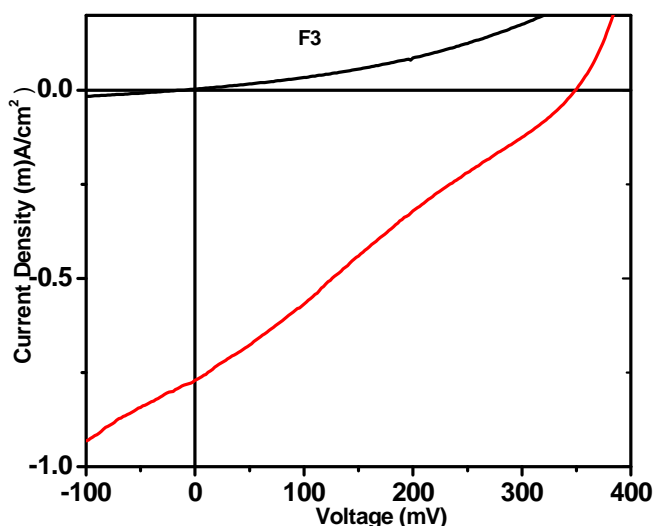
a) F_3
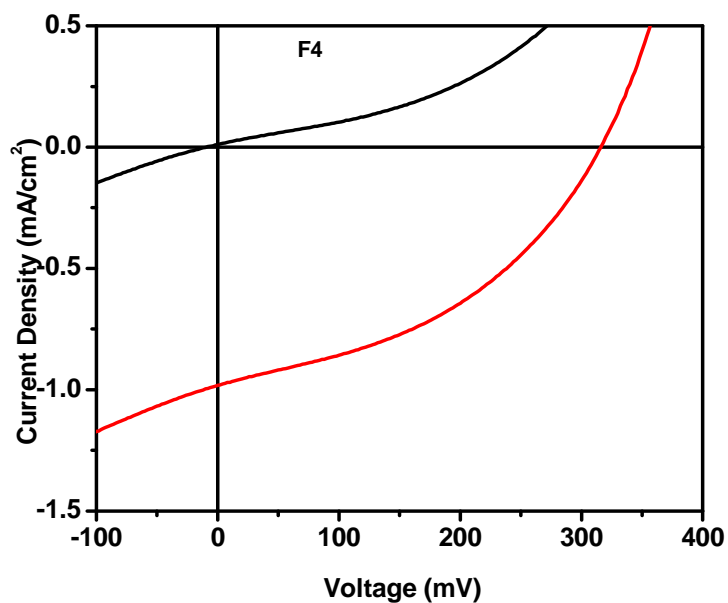
b) F_4
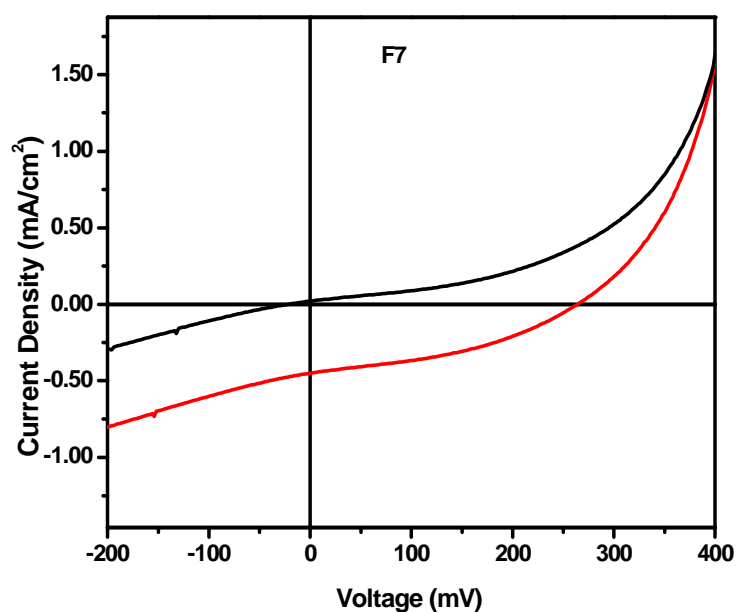
c) F_7

Figure 3. The photocurrent-voltage (I-V) curves for $Bi_2 (Te_{1-x}Se_x)_3$ (with dye) samples

Table 2 Spectral properties of dye sensitised $Bi_2(Te_{1-x}Se_x)_3$ thin film photoelectrode

Film Composition With Dye	Isc (mA/cm²)	Voc (mV)	I_{max} (mA/cm²)	V_{max} (mV)	FF	η (%)
$F_1 : Bi_2Te_3$	0.411	205	0.191	110	0.25	0.08
$F_2 : Bi_2(Te_{0.8}Se_{0.2})_3$	0.720	194	0.342	93	0.23	0.11
$F_3 : Bi_2(Te_{0.6}Se_{0.4})_3$	0.711	348	0.401	172	0.29	0.23
$F_4 : Bi_2(Te_{0.5}Se_{0.5})_3$	**0.972**	**314**	**0.708**	**175**	**0.41**	**0.42**
$F_6 : Bi_2(Te_{0.4}Se_{0.6})_3$	1.46	199	0.742	95	0.24	0.24
$F_6 : Bi_2(Te_{0.2}Se_{0.4})_3$	0.840	346	0.423	159	0.23	0.23
$F_7 : Bi_2Se_3$	0.440	266	0.306	163	0.43	0.17

Table 3 Comparison I-V measurements of thin films without dye loaded and dye loaded of $Bi_2(Te_{1-x} Se_x)_3$

Composition	Grain Size(nm)	Without Dye		With Dye	
		FF	η (%)	FF	η (%)
$F_1:Bi_2Te_3$	405	0.28	0.05	0.25	0.08
$F_2:Bi_2(Te_{0.8}Se_{0.2})_3$	375	0.33	0.09	0.23	0.11
$F_3:Bi_2(Te_{0.6}Se_{0.4})_3$	341	0.20	0.215	0.29	0.23
$F_4:Bi_2(Te_{0.5}Se_{0.5})_3$	**325**	**0.33**	**0.32**	**0.41**	**0.42**
$F_5:Bi_2(Te_{0.4}Se_{0.5})_3$	390	0.20	0.22	0.24	0.24
$F_6:Bi_2(Te_{0.2}Se_{0.4})_3$	442	0.23	0.20	0.23	0.23
$F_7:Bi_2Se_3$	560	0.35	0.13	0.43	0.17

Study of injection of dye sensitized electro-chemical photo-voltaic (DS ECPV) cell of $Bi_2(Te_{1-x}Se_x)_3$ thin films are carried out. The power output characteristics of the dye sensitized ECPV cell were determined from the current-voltage (I - V) plot as shown in Figure 3. The dye sensitized $Bi_2(Te_{1-x}Se_x)_3$ thin film was found to have better optical to electrical conversion efficiency than dye unloaded thin films. The efficiencies of the cell using dye sensitized $Bi_2(Te_{1-x}Se_x)_3$ thin films have been increases from 0.08 to 0.42% for F_1 to F_4 sample and again decreases up to F_7 due to decrease in grain size as shown in Table 2. It is concluded that $Bi_2(Te_{1-x}Se_x)_3$ thin films are suitable for fabrication of ECPV cell.[15-19]

CONCLUSION

It is concluded that comparison of I-V measurements of thin films without dye loaded and dye loaded of $Bi_2(Te_{1-x}Se_x)$ shows that the total conversion efficiency increases for dye loaded thin film have high efficiency as compared to without dye loaded thin film. For example sample F_4 (without dye) is 0.33 % and F4 (with dye) is 0.42 %. The results show that, the overall solar to electric energy conversion efficiency (η) was found to be high and it is suitable for solar cell applications. This is attributed to the fact that the density of charge carriers increased due to maximum light absorption by dye sensitized photoelectrodes.

REFERENCES

[1]P. T. Landsberg, *Solid-State Electro*, **1975**, 18, 1043-1052.
[2]R. Memming, *Electrochimica Acta*, **1980**, 25, 77-88.
[3] I. Balberg ,*Vacuum*, **1983**, 33, 579-583.
[4] L. Peraldo Bicelli, *Surface Tech.*, **1983**,20, 357-381.
[5]P. N. Bhosale, Ph.D. Thesis, Shivaji University, (Kolhapur, M. S. India **1985**).
[6]A. A. Yadav, M. A. Barote, E. U. Masumdar, *Chalcogenide Letters* , **2009**,6 ,149-153.
[7]S. Sampath, K. V. Ramanaiah, *Bull. Mater. Sci*, **1985**, 7, 63-69.
[8]S. H. Pawar, L. P. Deshmukh, *Bull. Mater. Sci*, **1985**, 7, 127-130.
[9]H. Tributsch, H. Gerischer: Ber. Bunsenges. *Phys. Chem.*, **1969,** 73, 850-854.
[10]W. Kautek, J. Gobrecht , H. Gerischer: Ber. Bunsenges,*Phys.Chem.*,**1980**, 84,1034-1040.
[11] C. D. Lokhande ,S. H. Pawar, *Mater. Chem. Phys*, **1984**, 11, 201-209.
[12] S. H. Pawar, S. P. Tamhankar, C. D. Lokhande , *Mater.Chem. Phy*, **1984** ,11, 401-412.
[13]H. Desilvestro , Y. H. Dyesol Ltd., Dominion Place, Queanbeyan NSW 2620 Australia.
[14]H. M. Nguyen, D. N. Nguyen, N. Kim, *Adv. Nat. Sci. Nanosci. Nanotechnol*. **2011**, 2, 023002(13pp).
[15]M. Grätzel, *Nature*, **2001**,414, 338-344.
[16]T. Daeneke, *Nature Chem*. **2011**, 3, 211-215.
[17]M. A. Sangamesha, K. Pushpalatha, G. L. Shekar, S. Shamsundar, *ISRN Nanomaterials*, **2013**, 2013 Article ID 829430, (8 pp)
[18]F. Liu, J. Zhu, Y. Xu, L. Zhou, Y. Li, L. Hu, J. Yaob , S. Dai, *Chem. Commun.*, **2015**,51, 8108-8111.
[19] S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, F. Basile   E. Curchod, Negar Ashari Astani, I. Tavernelli, U. Rothlisberger, Md. Khaja Nazeeruddin &Michael Grätzel *Nature Chem.*, **2014**, 6, 242-247.