SYNTHESIS, STRUCTURAL AND PHOTO ELECTROCHEMICAL BEHAVIOUR OF $SnSe_{0.5}Te_{0.5}$ SINGLE CRYSTALS

G. K. SOLANKI, K. D. PATEL, RAHUL B. PATEL,
SANDIP UNADKAT[a], DIPIKA B. PATEL, N. N. GOSAI
Department of Physics, Sardar Patel University, Vallabh vidyanagar, Gujarat, India.
[a]BVM Engineering College, Vallabh Vidyanagar, Gujarat, India

This paper report the synthesis of $SnSe_{0.5}Te_{0.5}$ by direct vapour transport technique. These crystals having layered type structure and are therefore highly anisotropic. Increase interest in these materials have also been shown particular in the photoelectric properties, as it has been suggested that the material could be used successful as photosensitive film in TV camera tube. This single crystals obtained have been characterized by X-ray diffraction. Single crystalline nature of crystal has been verified through transmission electron microscopy. Optical absorption spectra of this crystal at ambient pressure and temperature were obtained in the range 200 nm to 2200 nm using UV-Visible near IR spectrophotometer. The spectra were analyzed in the absorption range to obtain direct and indirect band gap of as grown material. Authors have also fabricate photoelectrochemical solar cell using $SnSe_{0.5}Te_{0.5}$ single crystals to determine fill factor (F. F), open circuit voltage (V_{oc}), short circuit current (I_{sc}) and efficiency (η) different intensity of illuminations at room temperature. The electrode was prepared from crystals showing absolutely plane faces obtained through the act of cleavage with help of adhesive tape. All results have been carefully studied and their implications have been thoroughly discussed

(Received July 5, 2010; accepted July 15, 2010)

Keywords: Single crystal, Direct vapour transport technique, PEC Solar cell

1. Introduction

Semiconductor materials are always being the focus in material science and engineering due to their outstanding electronic and optical properties and extensively potential in various devices including light emitting diodes [1], single electron transistors [2] and field effect thin film transistors [3].

One of the efficient solar to electrical conversion devices is the photoelectrochemical (PEC) solar cell. Advantages of PEC solar cells over conventional solid state cells have well known now days. Perspective semiconductor materials for possible PEC solar cell fabrication include the metal chalcogenide and dichalcogenides, which incidentally satisfy most of the requirements for efficient solar to electrical energy conversion.

With growing global demand, the need for non- conventional energy resources is considered to be a potential driving force for the power requirement for the 21st century. The harnessing of one of the most abundant inexhaustible source of energy, namely solar energy for electrical energy conversion, still leaves much to be achieved. It is this that has attracted researchers to investigate potential materials for device fabrication in solar cell to electrical energy conversion systems, thus the science of photovoltaic has gained momentum in recent years.

Among these metal chalcogenide layered materials such as MoX_2 or WX_2 (X = S, Se) are known to be stable against corrosion in the presence of suitable electrolytes and are efficient in PEC solar cells. Thin films of metal dichalcogenide compounds with a layered structure, such as MoS_2 (or WSe_2) have been prepared for desired applications in [4].

A survey of chalcogenides of the cheaply available of the low band gap semiconductors found a little attention of on chalcogenides of the fourth group metals germanium and tin (i.e. GeS, GeSe, SnS, SnSe) for their use in the conversion of solar energy of solar energy to electrical energy or chemical energy via photoelectrochemical (PEC) cells. Photo activity of poly crystalline samples of SnS polycrystalline thin films had been fabricated for evaluating PEC technique and solar efficiency was found to be 0.5 % [5].

2. Experimental

Growth

In the present investigations $SnSe_{0.5}Te_{0.5}$ crystals have been grown by direct vapor transport (DVT) technique. Two zone horizontal furnace having required dimensions has been used which is shown in Figure 1. The furnace was constructed by a special sillimanite threaded tube closed at one end, 450 mm in length, 70 mm outer diameter, 56 mm inner diameter with threaded pitch of 3 mm, imported form from Koppers Fabriken Feuerfester, Germany. High quality quartz ampoules were used for growth experiment having dimensions of 24 cm length, 2.4 cm outer diameter and 2.2 cm inner diameter.

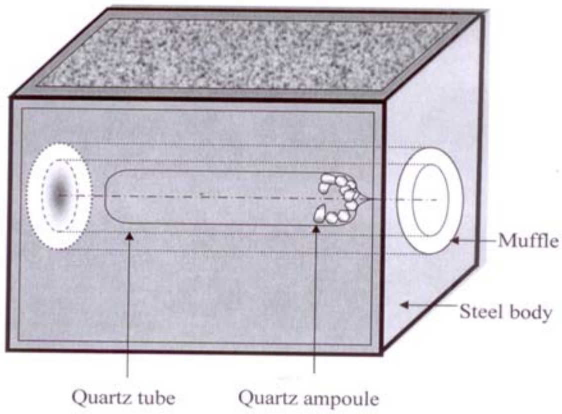

Fig. 1. The dual zone horizontal furnace with co-axially loaded ampoule.

For compound preparation the cleaned ampoule was filled with stoichiometric proportion of Sn (99.999%), Se (99.999%) and Te (99.999 %) pure of about 10 g for growth then ampoule was sealed under pressure of 10^{-5} Torr. The sealed ampoule was kept in two-zone horizontal furnace. The temperatures of both the zones were slowly but gradually raised upto desired temperature and maintained that temperature for 95 hours, after that furnace was cooled off at the room temperature. The ampoule was broken and shaken well with help of agate mortar to prepare fine powder of this compound.

Table 1. Growth conditions for $SnSe_{0.5}Te_{0.5}$ single crystals.

Crystal	Temp. range in furnace (T_1-T_2) (^{0}C)	Time for which ampoule was kept in temp. range (T_1-T_2) hours	Size of the crystals (cm × cm)	Thickness of the crystals (μm)
$SnSe_{0.5}Te_{0.5}$	45	95	1.5 x 0.65	35

Single crystallinity of the grown material i.e. single crystal is known by electron diffraction photography with the help of transmission electron microscopy as discussed later in this paper.

The optical absorption and transmission spectra of $SnSe_{0.5}Te_{0.5}$ single crystals were recorded over the wavelength range 400 to 2200 nm using a Perkin Elmer Model: Lamda- 19 spectrometer at room temperature and absorption coefficient 'α' were determined at every step of 250 nm with scanning speed of 240 nm/ min. Direct as well as indirect band gap was calculated here and found best agreement with reported one. As the crystals structure did not permit cutting and polishing, so measurements were not performed along the c- axis. The sample of $SnSe_{0.5}Te_{0.5}$ used in the present case was in the form of thin platelets, as grown crystals could be directly used for obtaining the absorption spectra.

Selection of materials

Single crystals of $SnSe_{0.5}Te_{0.5}$ have been taken to select the samples from the same batch. All the crystals when characterized by EDAX for their compositional analysis indicated that crystal growth without using the transporting agent and there are nearly stoichiometrically perfect.

Selection of appropriate electrolyte

The selection of electrolyte as well as selection of materials plays an important role in improving the solar conversion efficiency of PEC solar cell. To obtain workable photoconversion from PEC solar cell, the selection of suitable electrolyte is very important. The electrolyte decides the band bending in the semiconductor near the interface and hence the efficiency of photoconversion. For this PEC investigation author have used electrolyte with the composition 0.025M I_2 + 0.5 M NaI + 0.5 M Na_2SO_4 the light intensity was kept at 30mW/cm^2 and gave the minimum dark voltage (V_D) and dark current (I_D) and as well provides the maximum value of photocurrent (I_p) and photovoltage. In this case, a mixture of iodine (I_2), sodium iodide (NaI) and sodium sulphate (Na_2SO_4) was employed as an electrolyte. All the chemical products were reagent grade and the electrolyte solutions were prepared using triple distilled water. The solutions were not stirred during the measurement. Here photoelectrodes have been prepared using $SnSe_{0.5}Te_{0.5}$ single crystals having visibly smooth surfaces found as in the case of $GeS_{0.5}Se_{0.5}$ **[6].**

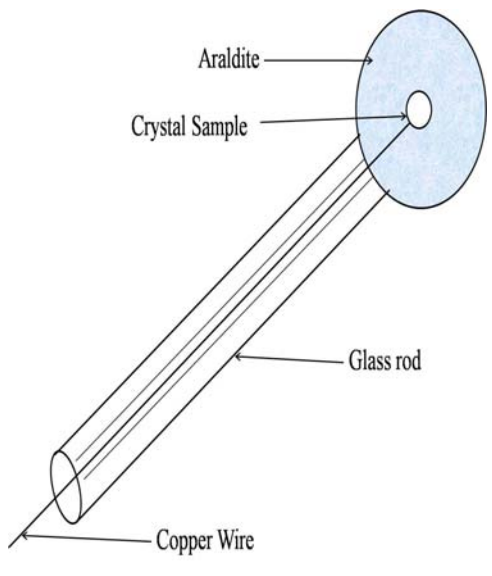

Fig. 2. The semiconductor electrode for PEC solar cell.

Sample preparation

Step free van der Waal (v d W) surfaces i.e. crystals with absolutely planes faces were procured after a careful examination of the samples under an epignost optical microscope. Such surfaces could be easily obtained by cleaving the as grown samples with an adhesive tape.

Solar cell fabrication

Semiconductor electrode, electrolyte and counter electrode are main three primary components for PEC solar cell. PEC solar cells with $SnSe_{0.5}Te_{0.5}$ photoelectrodes were fabricated in the same manner as described in [7]. The electrode was immersed in an appropriate contained in a corning glass beaker. A PEC cell may be consists of a photoactive semiconductor working electrode (either n- or p- type having suitable band gap) and counter electrode made of either metal (e.g. Pt) or semiconductors. But in the present case, platinum grid (3 cm x 3 cm) was used as the counter electrode. A schematic diagram showing the semiconductor electrode and PEC cell is given in Figure 2. and Figure 3. respectively. The cell was illuminated with light from an incandescent lamp from different intensities. The intensity of illumination was altered by changing the distance between the light source and the electrode and the intensity of illumination was measured each time by light measuring instrument 'Luxmeter' (TES electrical electronic corporation TES 1332A). Photocurrent and photovoltage were recorded using digital multimeters (Protek, 506 & RISH multimeter, 18S with accuracy of 0.1 mV/ µA). To vary the power point on V- I characteristics a series of variable resistance of different values has been used.

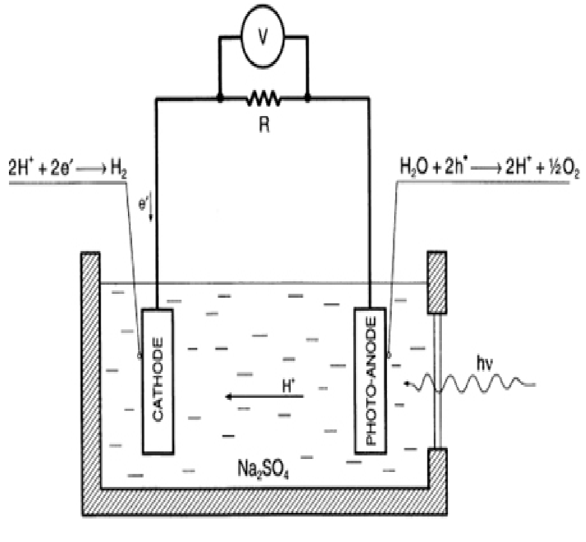

Fig. 3. Schematic diagram of PEC solar cell.

3. Results and discussion

X- ray diffraction

We grown successfully $SnSe_{0.5}Te_{0.5}$ single crystals using DVT technique and photograph of some grown crystals having maximum dimensions is shown in Fig. 4.

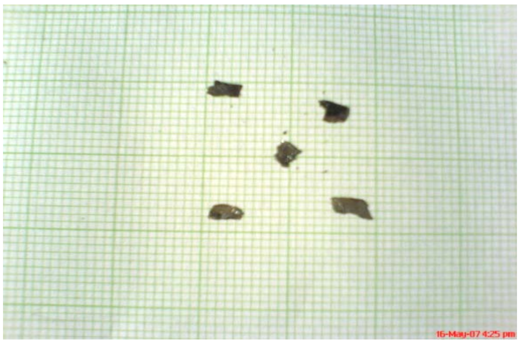

Fig. 4. Photograph of grown $SnSe_{0.5}Te_{0.5}$ *single crystals.*

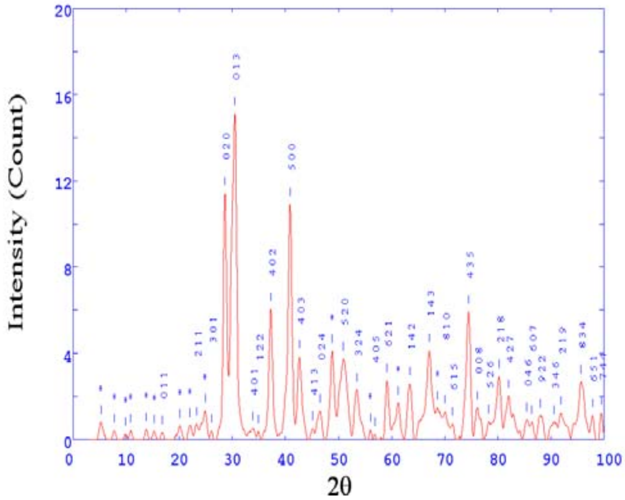

Fig. 5. X- ray diffractogram of $SnSe_{0.5}Te_{0.5}$ *crystal grown by direct vapour transport technique.*

The X- ray diffraction measurements were recorded by the means of X- ray diffractometer (Phillips, Model – X' PERT) using CuK_α radiation with wavelength of A^0. XRD pattern of $SnSe_{0.5}Te_{0.5}$ single crystal and its crystalline nature is shown in Figure 5. A well resolved X- ray peaks corresponding to the (013), (020) and (500) planes are observed. It proves that it has a strong preferred orientation and their crystallites are perpendicular to (013), (020) and (500) reflection plane. $SnSe_{0.5}Te_{0.5}$ layered compounds crystallizes in the D_{2h}^{16} space group of orthorhombic symmetry. The intensity of all other reflections is extremely weak compare to intensity of (013), (020) and (500) plane. The value of lattice parameters a, b, and c, unit cell volume and densities is listed in Table 2. by characterizing crystals by X- rays.

Table 2. Lattice parameters, unit cell volumes and X- ray densities for $SnSe_{0.5}Te_{0.5}$ *crystal.*

Crystal	a (A^0)	b (A^0)	c (A^0)	Unit cell volume (A^0)
$SnSe_{0.5}Te_{0.5}$	11	6.2	10	682

Here Figure. 6 shows the photograph of electron diffraction pattern of grown crystal was obtained by Transmission Electron Microscope (TEM, Philips, Model TECNAI) and it contains sharp white spot in a particular manner with the scale of 200 nm. This is the main evidence of single crystallinity of material.

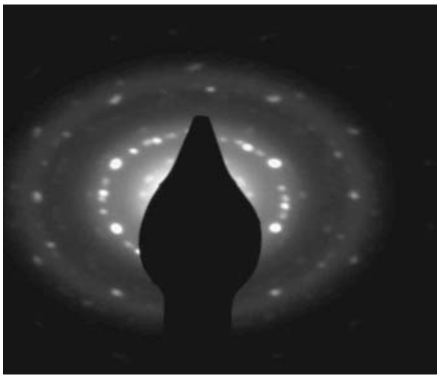

Fig. 6. Electron diffraction photograph of $SnSe_{0.5}Te_{0.5}$ single crystal.

The optical properties of a crystal such as IV- VI compound are governed by the interaction between the crystal and the electric field of the electromagnetic wave. Various types of transitions give rise to different wavelength dependencies of the absorption coefficient near the fundamental absorption edge.

The dependence of absorption coefficient 'α' in terms of direct and indirect transitions can be performed with the equation 1 and equation 2 for three dimensional crystals [8].

$$\alpha h\nu = A\left(h\nu - E_g\right)^r \tag{1}$$

$$\alpha h\nu = \sum_j B_j \left(h\nu - E'_g \pm E_{pj}\right)^r \tag{2}$$

where 'α' is the absorption coefficient, hν is the energy of the incident photon, E_g the energy of photon for the direct transition, E_g' the energy for indirect transition. A and B are parameters depending on the temperature [9]. Optical absorption study shows that wavelength within the range of 200 nm to 2200 nm were used.

A graph was plotted between $(\alpha h\nu)^2$ vs. hν for the determination of direct energy band gap of SnSe crystal as shown in Figure 7 and straight line was obtained. The extrapolation of the straight line gives the value of the direct band gap and indirect band gap of this sample shown in Figure 7 and Figure 8 and its value is 1.56 eV and 1.43 eV, respectively.

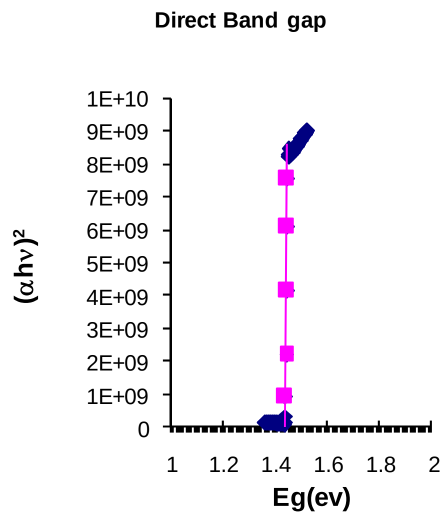

Fig. 7. $(\alpha h\nu)^2$ versus photon energy and

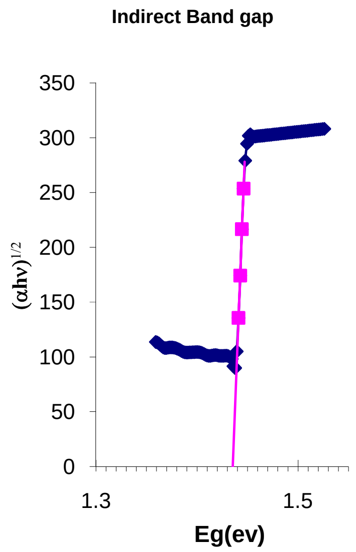

Fig. 8. $(\alpha h\nu)^{1/2}$ *versus photon energy for the DVT grown single crystal.*

In order to see the effect of using electrodes with $SnSe_{0.5}Te_{0.5}$ single crystals on photoresponse in the PEC solar cell, the surface of all the electrodes were taken after cleaving them with an adhesive tape. Data for photoresponse study of grown crystals used in PEC solar cell is given in Table 3. The Solar cell parameters e.g. I_{sc}, V_{oc}, the maximum power (P_{max}) the voltage at maximum power (V_{max}), the fill factor (F. F) and the efficiency (η) as determined as shown in Table 4. The photoresponse studies carried out in electrolytes of different compositions established that the electrolyte with the composition 0.025 M I_2 + 0.5 M NaI + 0.5 M Na_2SO_4 is the most suitable befitting electrolyte for the present work.

Table 3: Data for photoresponse study of grown crystals used in PEC solar cell.

Particulars	$SnSe_{0.5}Te_{0.5}$
Type	P type
Surface	Plane obtained after cleaving the as grown face
Contact	Silver Paste
Electrolyte	0.025 M I_2 + 0.5 NaI + 0.5 M Na_2SO_4
Area of the electrode surface exposed	3.14×10^{-6} m^2

The short circuit current depends upon many parameters like photogeneration of charge carriers within the semiconducting material and their effective separation, charge transfer process across the semiconductor electrolyte interface and the overall series resistance of solar cell. Among all these parameters, the series resistance will decide the magnitude of the short circuit current. Due to this reason we have evaluated short circuit current by by different methods at different intensity of illuminations of polychromatic light. Further the photogeneration of charge carriers and their contribution to the charge transfer mechanism decides the variation of short circuit current with illumination light.

The variation of the short circuit current I_{sc} of fabricated PEC solar cell with the incident intensity of polychromatic light show non linear type nature. We found that short circuit current increases with the increasing value of illumination or with the decreasing the distance between photoelectrode and incident light for $SnSe_{0.5}Te_{0.5}$ PEC solar cell.

The existence of numerous recombination centers is responsible for the non linearity nature of obtained graph. This recombination centers are associated for with samples having surface steps result in a lower quantum yield [9, 10, and 11] at low intensity and limit the photocurrent at higher intensities. Bulk and space charge layer recombinations are also mechanisms which may contribute in the deviation from linearity [13].

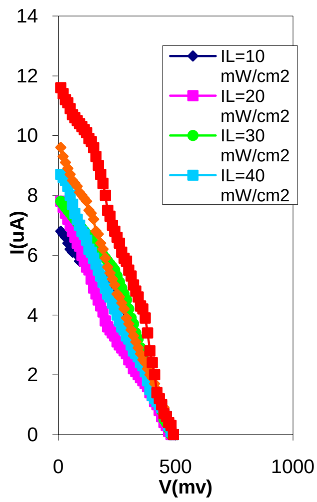

Fig. 9. Variation of photocurrent versus photovoltage for different illumination of light.

Open circuit voltage increases with the increasing value of illumination or with the decreasing the distance between photoelectrode or with the decreasing the distance between photoelectrode and incident light. This means that Voc as well as I_{sc} are changing in same pattern with changing intensity of illumination.

Table 4: Parameters of the investigated PEC solar cell.

	Intensity of illuminations I_L (mW/cm^2) 10	20	30	40	50	60
Parameters						
Isc (μA)	6.8	7.7	7.8	8.7	9.6	11.6
Voc (mV)	478	480	486	493	497	502
Efficiency (η %)	0.6605	0.214	0.2389	0.13	0.12	0.151
Fill Factor (F. F)	0.376	0.214	0.350	0.23	0.25	0.289

The photoconversion efficiency and fill factor are shown in Fig. for solar cell structure under different intensities of incident illuminations. In ideal case, $I_{mp}= I_{sc}$ and $V_{mp}= V_{oc}$, but practically in the present case Imp and V_{mp} deviate largely. As a result of this we have obtained lower fill factor. The overall photo conversion mechanism of PEC solar cell has so many factors [12- 15, 16, 17 and 18].

4. Conclusions

We have grown successfully single crystal semiconductor $SnSe_{0.5}Te_{0.5}$ and also prove its single crystalline nature. We have fabricated photoelecrochemical solar cell by using this crystal and represent that how all the solar cell parameters (i.e. open circuit voltage V_{oc}, short circuit current I_{sc}, fill factor and efficiency η) are dependent on the intensity of illumination of polychromatic light.

Acknowledgement

Authors are thankful to UGC, New Delhi, India for the sanction of a major research project to G.K. Solanki which provided the necessary financial help for carrying out this work.

References

[1] V. L. Colvin, M. C. Schlamp, A. P. Alivisatos, Nature **370**, 354 (1994)
[2] D. L. Kleim, R. Roth, A. K. L. Lim, A. P. Alivisatos, P. L. Mc Euen, Nature **389**, 699 (1997).
[3] B. A. Ridley, B. Nivi, J. M. Jacobson, Science **286**, 746 (1999).
[4] T. Tsirlina et al, Solar Energy Materials and Solar Cells Volume **44**(4), 457 (1996).
[5] Koteswara Reddy, N.; Ramakrishna Reddy, K.T. Photovoltaic Specialists Conference, 1997., Conference Record of the Twenty-Sixth IEEE,Volume,Issue, 29 Sep-3 Oct 1997. pp-515.
[6] T. R. Patel, M.Phil Dissertation, "PEC behaviour of GeS_xSe_{1-x} (I_2) (x =0, 0.5, 1) as grown single crystals", Sardar Patel University, Vallabh Vidyanagar, Gujarat, India (2009).
[7] Patel, R. G., Deshpande, M. P., Arora, S.K., Agarwal, M. K., 2001, *Bull. Elctrochemistry,* **17**(8), pp. 361-366.
[8] M. P. Deshpande, G. K. Solanki, M. K. Agarwal, Materials Letters **43**, 66- 72 (2000).
[9] J. A. Wilson, A. D. Yoffe, Adv. Phys.**18**. 193 (1969).
[10]. H J Lewerenz, H Tribusch, M. Spiesser J. Electronichem. Soc., **132**(3), 700 (1985).
[11] T E Fratak, D. Canceled, B. A. Parkinson, J. Appl. Phy, **51**, 1877 (1980)
[12] R Srivatsava, V M Pathak, Nat. Acad. Sci. Letters. 12 (1989).
[13] M Y A Rahman, M M Salleh, I A Talib, M Yahaya, A Ahmed, J. Current Appl. Phys. **7,** 446 (2007),
[14] N Mullen, D Cahan, Solar cells **9**, 229 (1983).
[15] M Skyallus Kazacos, F F Mc Cann, D Haneman, Solar Energy Mater. **4**, 215 (1981).
[16] B Bhatacharya, S K Tomar and jung Ki park Nanotechnology, **18**, 48571 (2007)
[17] Ana F Nogueria, Marco A De Paoli, Solar Energy Materials and Solar cells **61**, 135 (2000).
[18] Chen Fang. Chung, Quianfei xu, Yang Yang, Applied Physics Letters, ISSN 0003 – 6951 84 (2004) 31813.

*Corresponding author: solankigunvant@yahoo.co.in