The study of photoelectrochemical behavior of germanium sulphoselenide crystals on enhancement of sulpher content

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Abstract *This paper represents the investigation on growth of single crystals of Germanium Sulpho Selenide using Direct Vapour Transport Technique. The stoichiometries of the grown crystals have been analyzed using EDAX which shows that the grown crystals possess nearly stoichiometric proportion of starting material. The orthorhombic semiconducting compound* $GeS_{0.25}Se_{0.75}$, $GeS_{0.5}Se_{0.5}$ *and* $GeS_{0.75}Se_{0.25}$ *having various interesting electrical, optical and photoelectric properties. Using UV-VIS-NIR spectrophotometer optical absorption spectra of the crystals to obtain direct and indirect band gap of the material. Author has attempted to fabricate Photo Electro Chemical solar cell with grown mixed Germanium Sulphoselenide single crystals. Mott-Schottky plots have been used to study the energy band location and redox analysis of the material. This study justifies the appropriate choice of electrolyte for PEC work. The solar cell parameters e.g. the fill factor (FF), open circuit voltage (Voc), short circuit current (Isc) and efficiency (η) for all the cells have been calculated. All the results have been studied and implications have been discussed in the paper.*

Keywords — *PEC, DVT, EDAX, Mott-Schottky, Electrolyte.*

I. INTRODUCTION

Stabilization of the light harvesting semiconducting electrode is a key factor in the design of a photoelctrochemical (PEC) system for solar energy conversion. PEC methods of converting sunlight into electricity and chemicals have been a fertile area of research in recent years. In science and technology of PEC system there are many advances reported [1-5]. Metal chalcogenides have attracted considerable interest among the many semiconducting materials because they have energy band gaps well suited for solar energy conversion [6]. A high absorption coefficient in the visible range and they show extremely good stability when in contact with various aqueous and non aqueous electrolyte. Perspective semiconductor materials for possible PEC solar cell fabrication include the metal chalcogenide and dichalcoginides, which incidentally satisfy most of the requirements for efficient solar energy to electrical energy conversion. Among these metal chalcogenide layered materials such as MoX_2 or WX_2 (X=S, Se) are known to be stable against corrosion [7-8] in the presence of suitable electrolytes and are very efficient in PEC solar cells. Within a layer of chalcogen-metal-chalcogen a strong covalent bond exists where as the layers are held together by much weaker Van der walls interactions. In this direction less explored material like Zirconium Sulphoselenide , Germanium Sulphoselenide etc. were focused due to reason that Germanium is relatively abundant metal, Germanium Sulphoselenide posses a layered type structure with a band gap lying between 1.2 to 1.7 eV and this type of material are potentially suitable in the combined conversion and storage of solar energy. Authors have carried out systematic study on the photoelectrochemical behavior of sulpher enhanced single crystals of Germanium sulphoselenide. The effect of increasing the concentration of sulpher in GeSxSe1-x on the photo response of solar cell fabricated using these crystals as electrodes has been studied and implication pointed out.

II. MATERIAL AND METHODS

A. Sample preparation

Single crystals of GeS_xSe_{1-x}(x=0.25, 0.5, 0.75) required for the present work were grown by Direct Vapour Transport technique [9].The two zone horizontal furnace with required dimensions was used for precise setting of the temperature gradients between the two zones. All the grown crystals were examined by EDAX for chemical composition analysis and using the transmission electron microscope single crystalline nature of the grown crystals has been confirmed. Electrical characterization showed that all crystals posses p-type semiconducting nature. Crystals with nearly plane faces were chosen after the examination of the sample under Epignost optical microscope.

B. Preparation of semiconductor electrodes

By the act of cleavage step free crystals were selected for preparation of electrode. Semiconductor electrode of GeS_xSe_{1-x}(x=0.25, 0.5, 0.75) has been fabricated in the described manner [10]. A glass rod of 0.5 cm in diameter and 10 to 12 cm in length with a narrow bore of diameter 0.05 cm was used to prepare the electrode. One end of this narrow bore glass rod was flattened by hot gas blow. The flat portion was used as a platform for resting the crystal. The narrow bore was used as a passage for traversing a good conducting copper wire. The copper wire was flattened at one end for getting a contact with the crystal. In the present work, a semiconductor electrode was fabricated in such a way that the contacting material (adhesive silver paste) provided good ohmic contact between the copper wire and the backside of the crystal. The whole assembly was then kept in an oven for few hours at 100 ºC for baking. After proper setting of the crystal on the copper wire terminal, the semiconductor was covered with an epoxy resin (araldite) leaving a light exposed an area of 2-5 mm2 for exposure to light source. In present investigations, copper grid has been used in place of platinum as the counter electrode.

The schematic diagram showing the PEC cell with the electrodes immersed in an appropriate electrolyte and a copper grid as a counter electrode in Figure 1. The cell was illuminated with light from a Zenon flash lamp. Changing the distance of light source from the electrode the photo response for various intensities was examined. The intensity of illumination was measured using the intensity measuring instrument 'Suryamapi' manufactured by Central Electronics Limited, India. Photocurrent and photovoltage were recorded for different intensities using digital millimeter. The ideal characteristics of a solar cell are as given in Fig. 2.

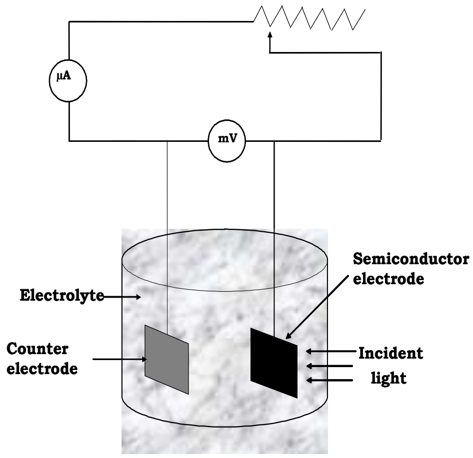

Fig. 1 The schematic diagram of PEC solar cell

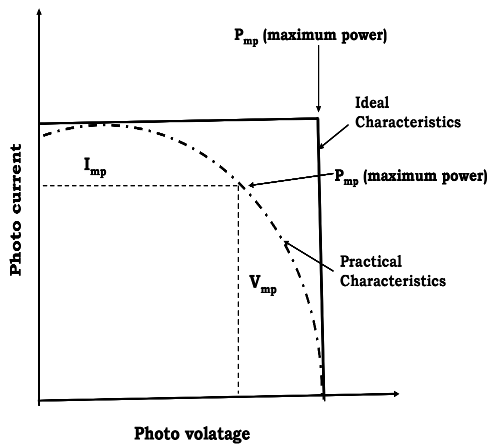

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Fig. 2 Ideal characteristics of Solar cell used to measure V-I characteristic

III.RESULTS AND DISCUSSION

A. Out put power measurements

Photoelectrochemical measurements were performed under potentiostatic conditions. Among all possible

Table I. Growth parameters of GeS_xSe1_{-x}(X = 0.25, 0.5, 0.75) single crystals.

Crystal	Temperature distribution		Growth Period (Days)	Dimension (cm^2)
	Reaction Zone (K)	Growth Zone (K)		
$GeS_{0.25}Se_{0.75}$	913	863	7	1.1 X 0.56
$GeS_{0.5}Se_{0.5}$	923	873	7	1.2 X 0.65
$GeS_{0.75}Se_{0.25}$	933	883	7	1.2 X 0.6

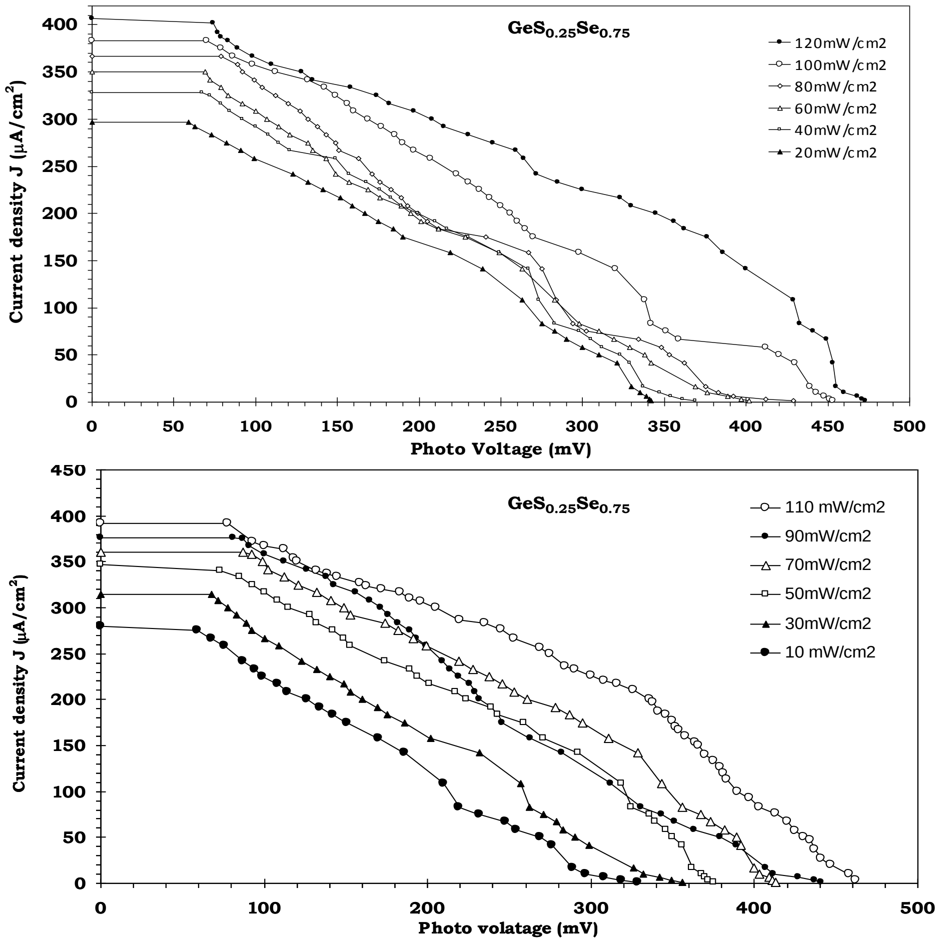


Fig. 3(a). Photovoltage (Vph) vs. current density (J) for $GeS_{0.25}Se_{0.75}$

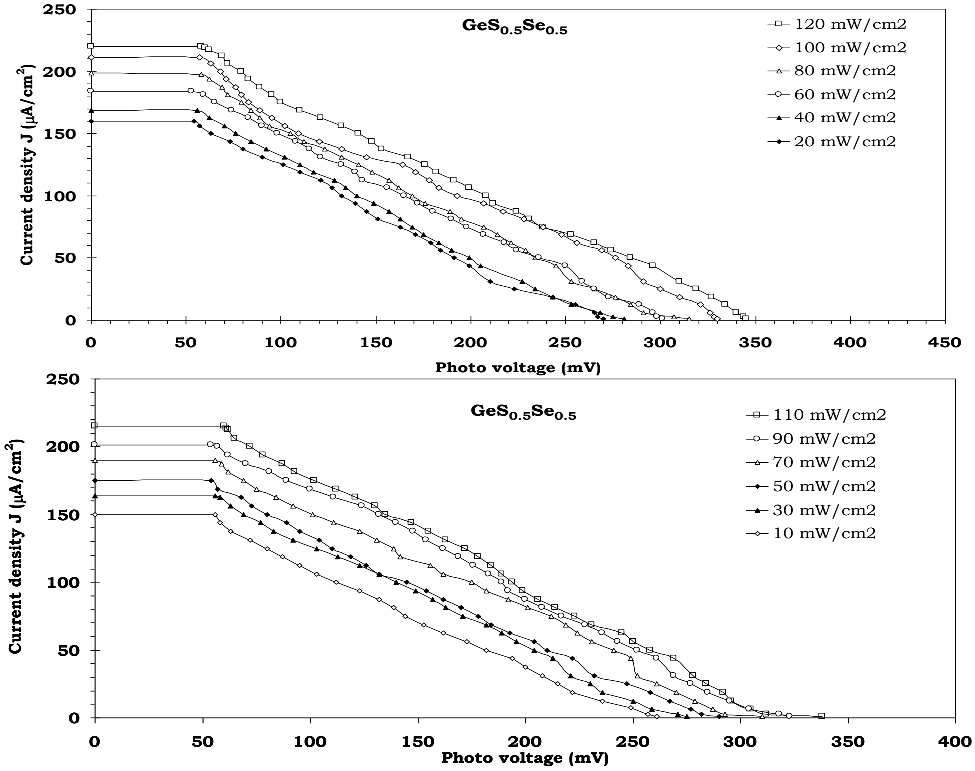
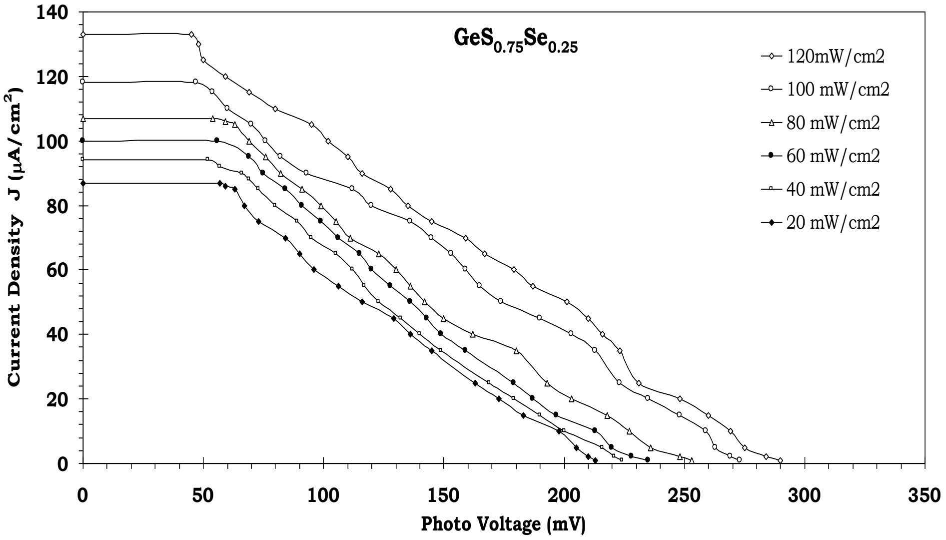


Fig. 3(b). Photovoltage (Vph) vs. current density (J) GeS0.5Se0.5 single crystals

Table II. PEC Solar cell parameters and band gap of all the samples

	Intensity of illuminations I_L = 10 (mW/cm^2)		
Parameters	$GeS_{0.25}Se_{0.75}$	$GeS_{0.5}Se_{0.5}$	$GeS_{0.75}Se_{0.25}$
Energy Band Gap (E_g) (eV)	1.445	1.466	1.570
I_{sc} (μA)	16.8	12	8.5
V_{oc}(mV)	330	261	208
Fill factor (F. F.)	0.291	0.295	0.294
Efficiency η %	0.269	0.116	0.052



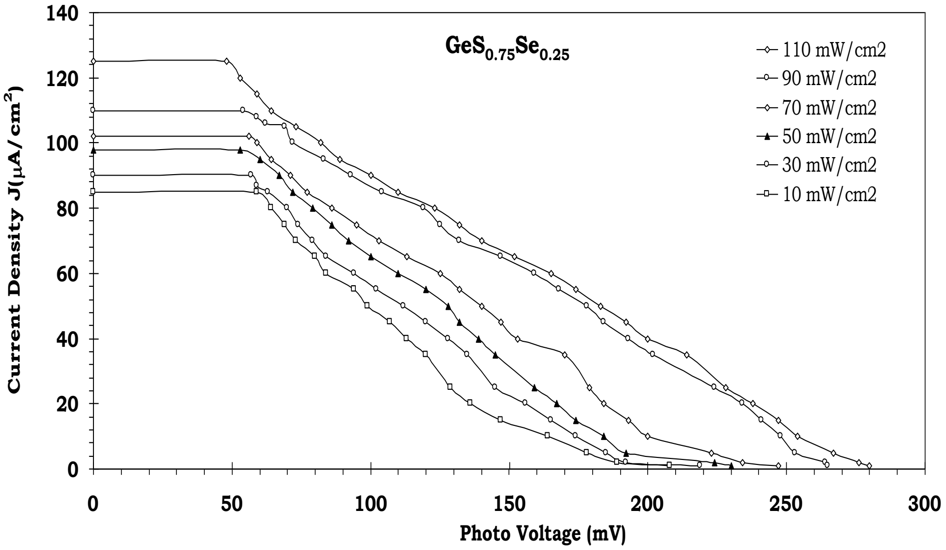


Figure 3(c). Photovoltage (Vph) vs. current density (J) for $GeS_{0.75}Se_{0.25}$

TABLE III. SUMMARY OF RESULTS OBTAINED FROM MOTT-SCHOTTKY PLOTS FOR GeS_XSe_{1-X} (X= 0.25, 0.5, 0.75) SINGLE CRYSTALS

Properties	$GeS_{0.25}Se_{0.75}$	$GeS_{0.5}Se_{0.5}$	$GeS_{0.75}Se_{0.25}$
Type	P	P	P
Band Gap (E_g)(eV)	1.445	1.466	1.570
Electrolyte used	$0.025MI_2 + 0.5$ M NaI + 0.5 M Na_2SO_4		
Flat band potential (eV)	1.41	1.16	1.27
Band bending (V_b) (eV)	0.605	0.237	0.462
Carrier concentration (n_A) (m^{-3})	3.53×10^{14}	1.74×10^{12}	1.17×10^{14}
Density of states in the valence band (m^{-3})	7.57×10^{22}	1.49×10^{22}	5.89×10^{22}
Depletion width (W) (m)	5.17×10^{-11}	7.17×10^{-9}	1.31×10^{-11}
Conduction band edge (E_c) (eV)	0.461	0.286	0.219
Valence band edge (E_v) (eV)	-1.906	-1.751	-1.780
Redox Fermi level of the electrolyte $E_{F, redox}$	-0.805	-0.900	-0.808

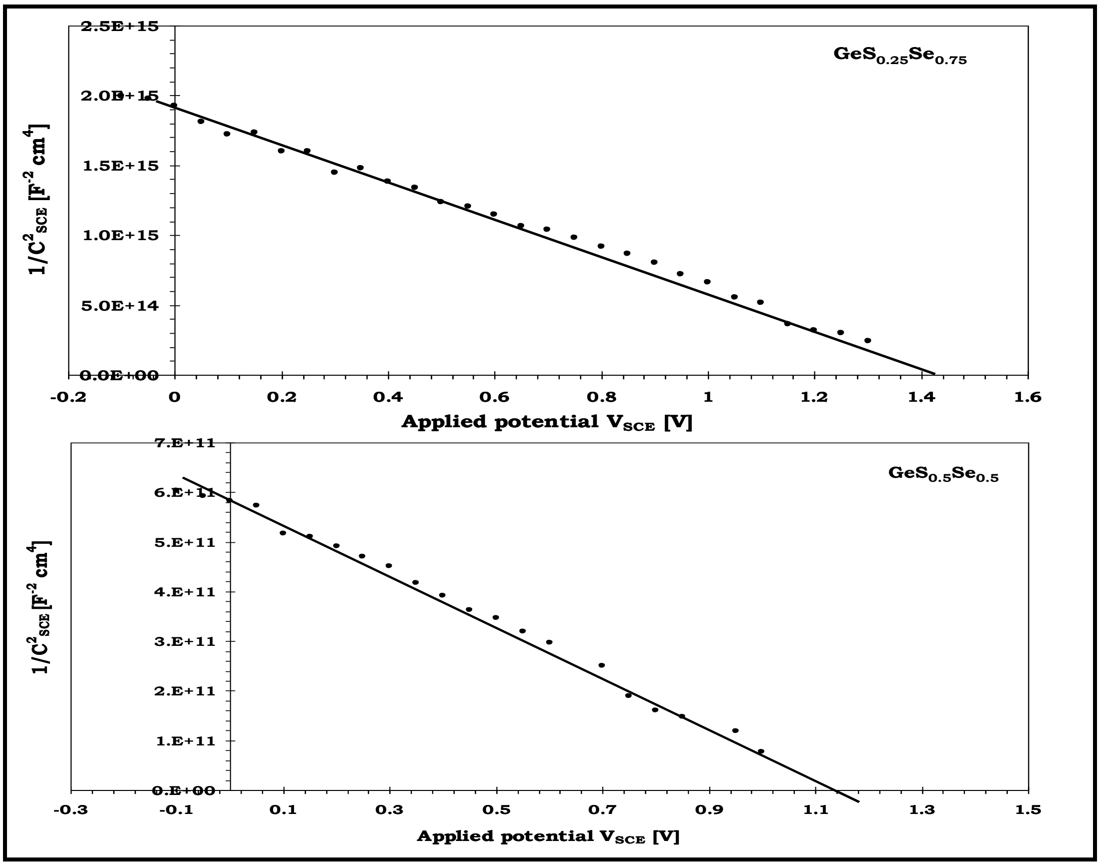


Fig. 4 (a) Mott-schottky plots of $GeS_{0.25}Se_{0.75}$ and $GeS_{0.5}Se_{0.5}$ single crystal

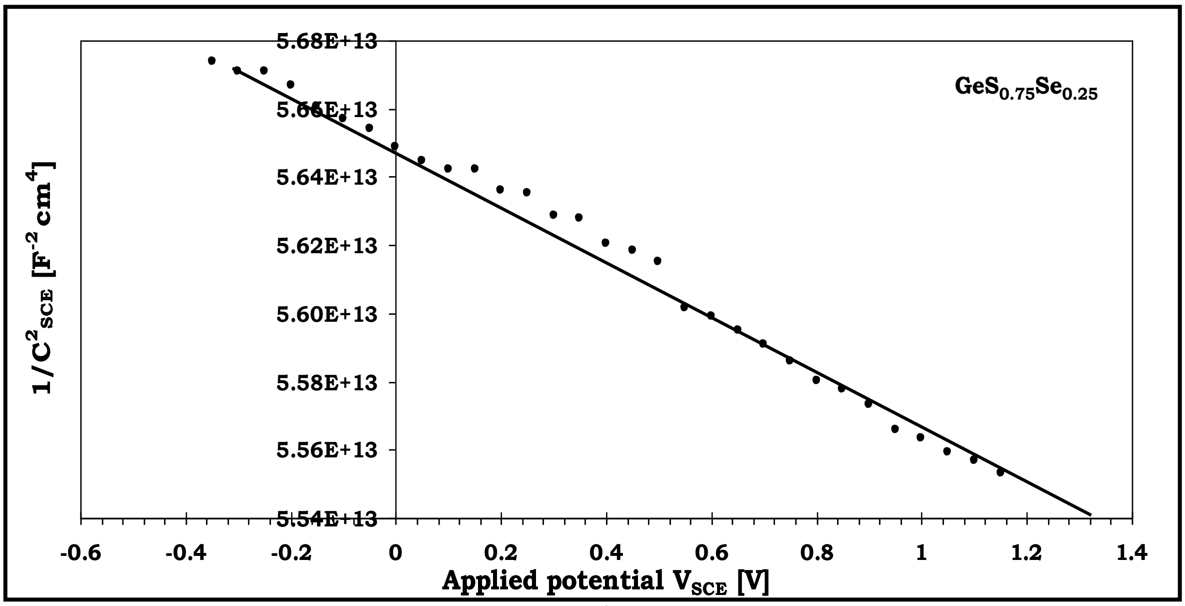


Fig. 4 (b) Mott-schottky plots of $GeS_{0.75}Se_{0.25}$ single crystal

electrolytes it was observed that electrolyte with the composition 0.025 MI2 + 0.5 MNaI+ 0.5 M Na2SO4 gave the minimum dark voltage 'VD' and dark current 'ID' and as well provided the maximum value of photocurrent (Iph) and photovoltage (Vph) for the electrodes which are used to fabricate PEC solar cell in present investigations.

Figure 3(a), 3(b) & 3(c) shows the diverging behaviour with increase intensity and this is quite obvious because the increase in intensity of incident illumination directly means that the number of quanta of photons incident on the semiconducting materials surface increases. $GeS_{0.25}Se_{0.75}$ has the highest short circuit current and gradually decreases with the increase in sulpher content. These observation are quite obvious because the short circuit always depends upon many parameters like photo generation of charge carriers within the semiconducting material and their effective separation, charge transfer process across the semiconductor electrolyte interface and the overall series resistance, also the photogeneration of charge carriers and their effective separation and contribution to the charge transfer mechanism decides the variation of short circuit current.

The PEC solar cell has been fabricated for all the samples. The results of the study have been shown in figure 3(a), 3(b) and 3(c) and data represented in table 2. Maximum efficiency depends upon the band bending and energy band gap [11]. In spite of lower band bending and depletion width the large value for efficiency could be due to lower optical band gap of $GeS_{0.25}Se_{0.75}$ the other two samples. Therefore increase photoconversion efficiency is contributed to the lower value of the band gap, lower value of bulk resistivity and higher value of carrier concentration in the sample.

However efficiency so obtained in the present work with GeSxSe1-x crystals is practically low but the aim of the present work is to study the effect of enhancement of sulpher content on the photoresponse. But to make viable PEC solar cell with high efficiency electrode modification, photo etching, electrolyte modification etc. have been described and discussed by Pandey et al [12] and Patel et al, [13].

B. Mott-Schottky evaluations

Capacitance measurements were undertaken with GeS_xSe_{1-x} (x= 0.25, 0.5, 0.75) electrodes at various potentials. Capacitance data from these electrodes were carried out to construct the Mott Schottky plots ($1/C^2SC$ versus V). Figure 4 (a) and 4 (c) present such plots for GeSxSe1-x (x= 0.25, 0.5, 0.75) single crystal electrodes respectively using the electrolyte (0.025MI2 + 0.5M Na I + 0.5 M Na2SO4).

In the graphs of $1/C^2_{SCE}$ versus V_{SCE} the voltage axis intercepts give the flat band potentials Vfb which in present case the obtained value is shown in table 4. The acceptor concentration nA, dielectric constants, carrier concentration, valence band edge, conduction band edge parameters have been calculated for GeS_xSe_{1-x} (x= 0.25, 0.5, 0.75) from the slopes of the straight line portions of the Mott-Schottky plots using the standard formulas.

IV. CONCLUSIONS

We have successfully grown single crystals of GeSxSe1-x(x=0.25, 0.5, 0.75) using Direct Vapour Transport technique. From the XRD it is confirmed that these crystals having orthorhombic crystals structure. After the almost twenty five electrolyte it is found that 0.025 MI2 + 0.5 MNaI+ 0.5 M Na2SO4 this composition gives high photo response. Using Hall effect and Mott Schottky plots it is concluded that the crystals are P-type in nature. From Mott-schottky plots various parameters have been calculated. The Fermi energy level is close to the top of the valence band which again confirm that GeSxSe1-x (x= 0, 0.25, 0.5, 0.75, 1) single crystals having p-type semiconducting nature. As the sulpher content increased the band gap of the material also increased and so the value of photocurrent and efficiency of the solar cell decreases. These parameters also depend on the intensity of light.

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