CHAPTER 9

INFLUENCE OF ILLUMINATION INTENSITY ON THE PERFORMANCE OF PEC CELLS BASED ON MoS_xSe_{2-x} ELECTRODES

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9.1 Introduction

The efficiency and behaviour of most photoelectrodes in photoelectrochemical solar cells depend not only on the nature of the surface, nature of electrolyte, temperature of the electrolyte but also upon the intensity of the light with which the semiconductor-electrolyte junction is irradiated. The effect of electrolyte and its temperature on PEC behaviour has already been discussed in the earlier chapter. Since properties of PEC cells depend on the characteristics of incident light, the wavelength and intensity, author has described such studies on PEC cells based on molybdenum sulphoselenides in this chapter. Since performance of PEC cells depends heavily on the morphology of the semiconductor surface, a separate chapter 10 has been devoted to it.

9.2 Results and Discussions

The schematic diagram of experimental set up for studying the effect of intensity of illumination is shown in Fig. 6.2 (Chapter 6). Fresh iodide/iodine electrolyte having the same concentrations as used in the study of the effect of temperature, has been utilised in the present study. The incident light intensity was adjusted by changing the distance between PEC cell and light source.

The effects of intensity of illumination on the photocurrent density (J) - voltage (V) characteristics with molybdenum sulphoselenides electrodes (MoS_xSe_{2-x} , x = 0, 0.5, 1, 1.5, 2) are illustrated in Fig. 9.1 (a,b,c,d and e) respectively. These figures show that the photocurrent density-voltage curves shift outwards with the increasing light intensities. In order to study the nature of variation of short circuit current (I_{sc}), open circuit voltage (V_{oc}) with respect to incident intensity (I_L) and for evaluation of the ideality factor (n) of illuminated junctions, semiconductor electrodes with composition MoS_xSe_{2-x} (x = 0, 0.5, 1.0, 1.5, 2) were used. The results are shown in Fig. 9.2 (a, b, c, d and e). It is observed that plots of short circuit currents versus light intensity are linear upto a certain value after which they show the saturation trends for all compounds except MoSSe. However, the open circuit voltage (V_{oc}) are linear functions of logarithms of incident light intensity (Fig. 9.2 (a), (b), (c), (d), (e)) for all the compounds.

The non-linear dependence of I_{sc} demonstrates that the recombination of photogenerated carriers at the semiconductor-electrolyte interface is limiting the rate of overall charge transfer reaction over the range of light intensities employed. According to Kline et al[1] and Bicelli et al[2], the observed deviation from linearity of short circuit currents with respect to incident light intensity

Fig. 9.1 (a,b,c,d and e)

Photocurrent density (J) - voltage (V) characteristics at different intensities of illumination of PEC cells based on $MoSe_2$, $MoS_{0.5}Se_{1.5}$, MoSSe, $MoS_{1.5}Se_{0.5}$ and MoS_2 respectively.

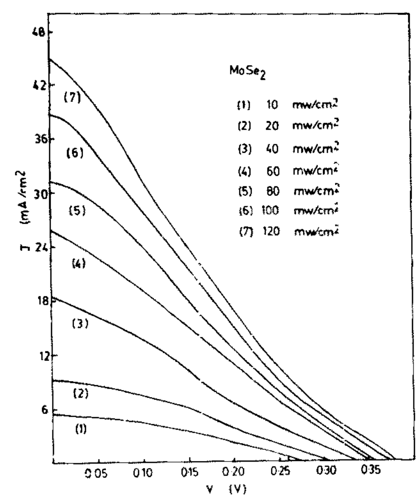

Fig. 9.1(a)

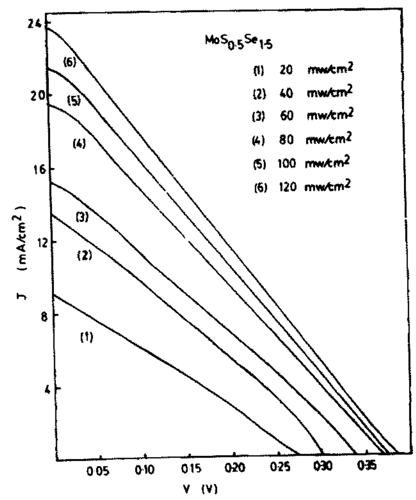

Fig. 9.1(b)

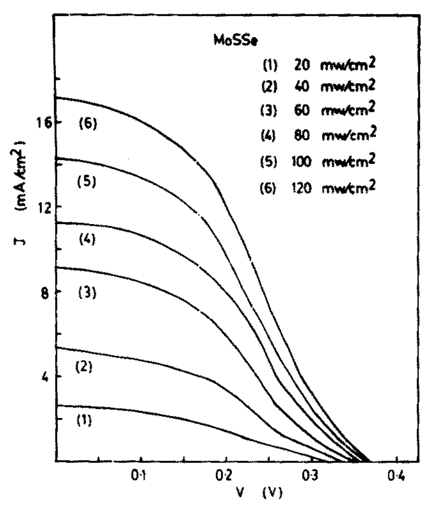

Fig.9.1(c)

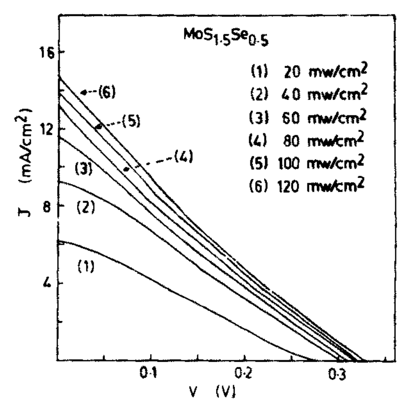

Fig. 9.1(d)

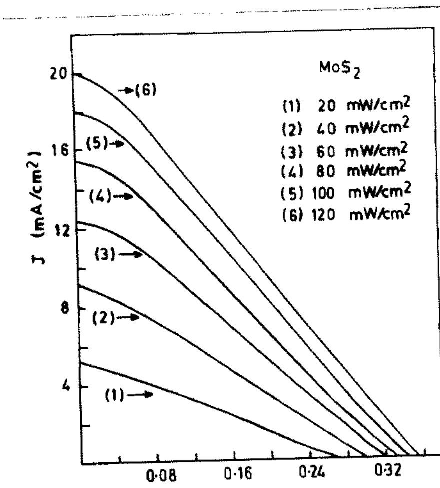

Fig. 9.1(e)

could mainly be attributed to the existence of numerous recombination centers. The recombination centers associated with samples having surface steps result in a lower quantum yield[3-5] at low intensity and limit the photocurrent at higher intensity. Bulk and space charge layer recombinations are also mechanisms which account for deviation from linearity.[1] The flattening of bands (conduction and valence) as a result of high intensity of illumination reduces the space charge and efficiency of charge carrier separation. Insufficient separation of charges increases the recombination of photo-generated carriers. According to Tributsch et al[6], reduction of photocurrent at intense illumination can be explained as follows :

The iodide is depleted near the electrode surface which limits the dissolution of iodine product in the form of I_3^- and the formation of iodine layer from photo-oxidation of iodide drastically reduces the photocurrent. The reduction in photocurrent is due to the combination of effects including (i) light scattering by layer, (ii) absorption of iodine near the electrode and (iii) passivation due to lower conductivity of the layer.

The junction ideality factors for the molybdenum sulphoselenides have been determined from the plots of open circuit voltage (V_{oc}) versus log I_L from

Fig. 9.2 (a, b, c, d, e) and compared with the reported values in Table 9.1. The lowest junction ideality factor (1.24) is found for $MoS_{1.5}Se_{0.5}$ samples. The possible reasons for higher values of ideality factor have already been discussed in Chapter 6.

The effect of light intensity on the light to electrical conversion efficiency and fill factor for molybdenum sulphoselenides (MoS_xSe_{2-x}, x = 0, 0.5, 1, 1.5, 2) are given in Fig. 9.3. The decrease in efficiencies of all compounds at higher light intensities can be attributed to the loss of fill factor and short circuit currents. According to Russak et al[8] the reduction in fill factor with increasing light intensity can be due to recombination at grain boundaries or defect sites in the space charge layer which becomes more pronounced with higher photon flux near the maximum power point. MoSSe cell shows a little abnormal variation of efficiency and fill factor with increasing illumination intensity.

Monochromatic efficiency measurements

For carrying out monochromatic efficiency measurements, radiations from a He-Ne laser (632.8 nm) were used. The monochromatic beam was expanded by using an optical lens to illuminate the entire area of the electrode.

Fig. 9.2 (a, b, c)

Plots of open circuit voltage (V_{OC}) and short circuit current (I_{SC}) as a function of light intensity (I_L) and plots of open circuit voltage (V_{OC}) as a function of logarithms of light intensity ($\log I_L$) for PEC cells based on $MoSe_2$, $MoS_{0.5}Se_{1.5}$ and MoSSe.

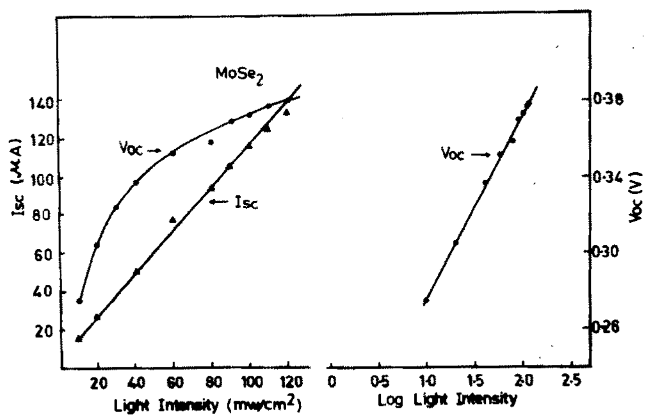

Fig. 9.2(a)

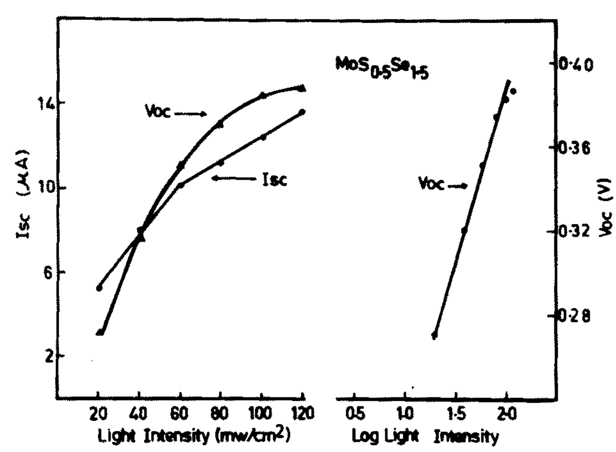

Fig. 9.2(b)

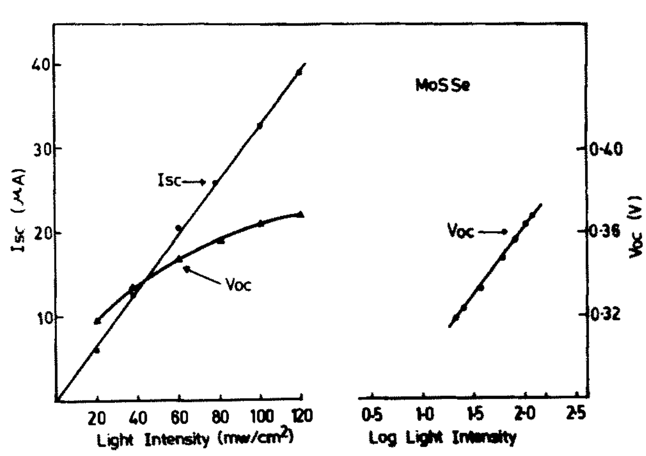

Fig. 9.2(c)

Fig. 9.2 (d and e)

Plots of open circuit voltage (V_{OC}) and short circuit current (I_{SC}) as a function of light intensity (I_L) and plots of open circuit voltage (V_{OC}) as a function of logarithms of light intensity ($\log I_L$) for PEC cells based on $MoS_{1.5}Se_{0.5}$ and MoS_2.

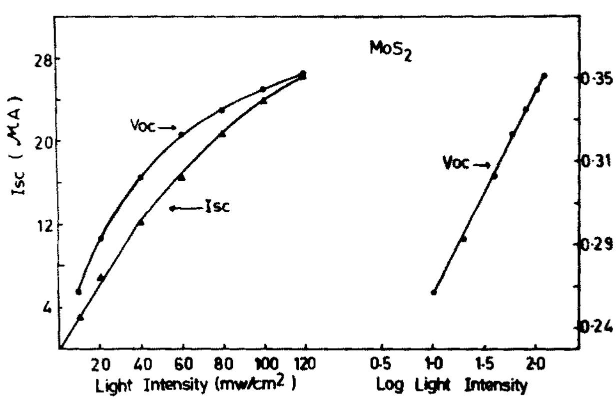

Fig. 9.2(d)

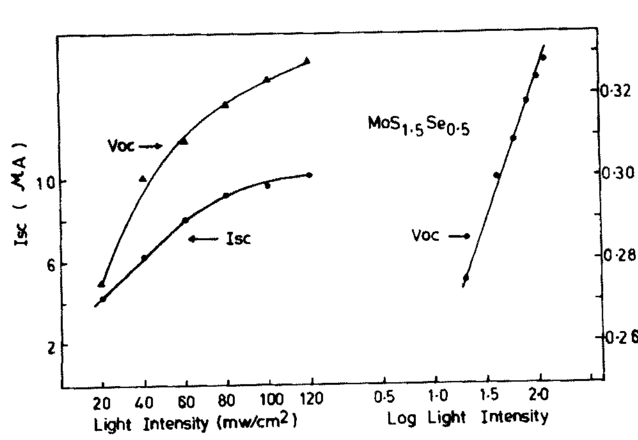

Fig.9.2(e)

Table 9.1

Junction ideality factors for illuminated molybdenum sulphoselenide-electrolyte interface

Compound	Ideality factor calculated 'n'	Ideality factor reported
$MoSe_2$	1.684	2.8[7)]
$MoS_{0.5}Se_{1.5}$	2.605	
MoSSe	1.535	
$MoS_{1.5}Se_{0.5}$	1.241	
MoS_2	1.670	

Table 9.2 contains a compilation of solar cell parameters for molybdenum sulphoselenides photoelectrodes under monochromatic illumination. Fig. 9.4 shows the photocurrent density (J) - Voltage (V) characteristics for these electrodes in I^-/I_2 redox system. The data in Table 9.2 indicates that the highest efficiency (12.64 %) has been observed for $MoSe_2$ while lowest efficiency of (5.61 %) has been obtained for $MoS_{1.5}Se_{0.5}$.

Solar measurements

The solar cell parameters for photoanodes of molybdenum sulphoselenides measured in sunlight have been summarized in Table 9.3, while photocurrent (J) - voltage (V) characteristics have been displayed in Fig. 9.5. The best MoS_2 sample has a solar conversion efficiency of 1.8 % which is considerably lower than the corresponding value for selenide i.e. ($MoSe_2$). The lower efficiency for sulphides may be due to the following reasons :

(1) direct and indirect bandgaps for sulphides at higher energy results in insufficient utilization of long wavelength radiation,

(2) lower fill factor is the result of poor electron transfer kinetics and

(3) the crystal perfection of sulphides is not as

Fig. 9.3 Plots of light to electrical conversion efficiency (η %) and fill factor as a function of light intensity for PEC cells based on $MoSe_2$, $MoS_{0.5}Se_{1.5}$, MoSSe, $MoS_{1.5}Se_{0.5}$ and MoS_2 electrodes respectively.

Fig. 9.4 Photocurrent density (J) - voltage (V) characteristics of PEC cells based on molybdenum sulphoselenides electrodes for monochromatic radiation of 632.8 nm, 7 mw/cm^2 in aqueous electrolyte of concentrations, 0.025 M I_2, 2 M NaI, 0.5 M Na_2SO_4 and 0.5 M H_2SO_4.

Fig. 9.5 Photocurrent density (J) - voltage (V) characteristics of PEC cells based on molybdenum sulphoselenides electrodes for the solar radiation (intensity indicated in Table 9.3) in aqueous electrolyte of concentrations, 0.025 M I_2, 2 M NaI, 0.5 M Na_2SO_4 and 0.5 M H_2SO_4.

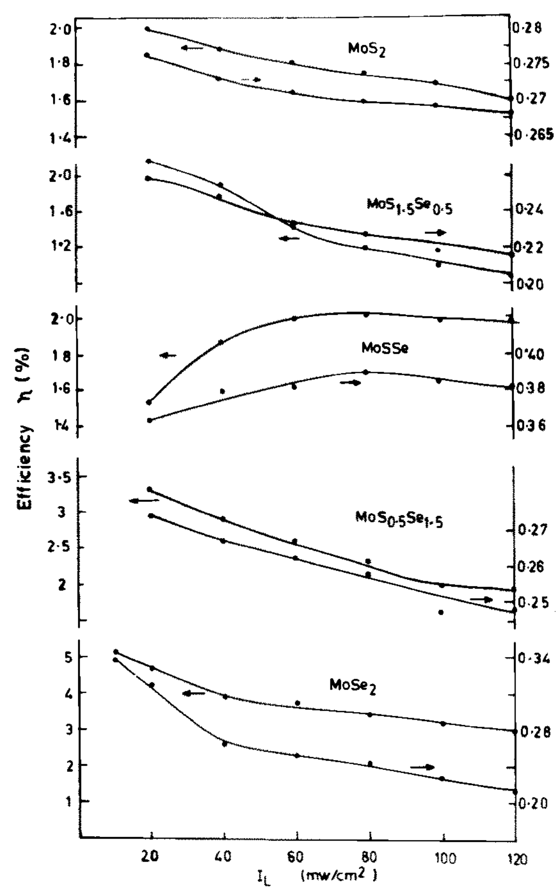

Fig. 9.3

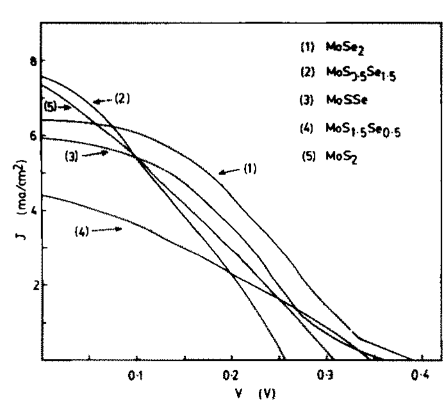

Fig. 9.4

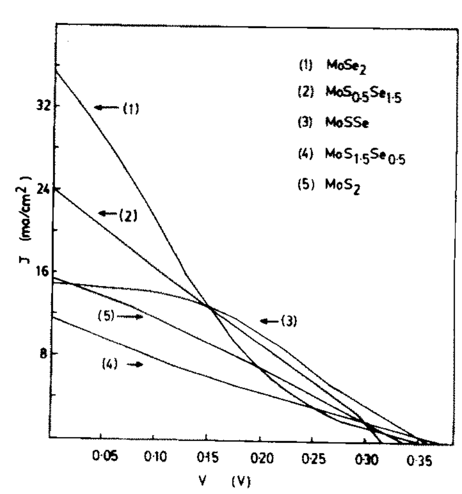

Fig. 9.5

Table 9.2

Monochromatic solar cell parameters for molybdenum sulphoselenides cells

Compound	Open circuit voltage V_{oc} (V)	Short circuit current density J_{sc} (mA/cm^2)	Fill factor ff	Efficiency η %
$MoSe_2$	0.389	6.409	0.3577	12.640
$MoS_{0.5}Se_{1.5}$	0.267	7.636	0.2825	8.228
MoSSe	0.359	6.000	0.34617	10.652
$MoS_{1.5}Se_{0.5}$	0.345	4.400	0.3061	5.612
MoS_2	0.308	7.424	0.2773	9.058

Table 9.3

Summary of solar conversion efficiencies

Compound	Open circuit voltage V_{oc} (V)	Short circuit current density J_{sc} (mA/cm^2)	Fill factor ff	Efficiency η (%)	Solar illumination I_L (mw/cm^2)
$MoSe_2$	0.350	35.66	0.1630	3.282	62
$MoS_{0.5}Se_{1.5}$	0.315	24.16	0.2512	2.73	70
MoSSe	0.358	14.85	0.3996	3.078	69
$MoS_{1.5}Se_{0.5}$	0.363	11.59	0.2194	1.154	80
MoS_2	0.337	15.38	0.2758	1.809	79

good as the diselenides, which results in variable short circuit densities due to an increased surface recombination.

During course of this investigation it is observed that nicely cleaned surfaces of crystals show a higher conversion efficiency.

9.3 Conclusions

1. The efficiency of light to electrical energy conversion for MoS_2 and mixed sulphoselenides of molybdenum is not as high as for $MoSe_2$.

2. The light to electrical conversion efficiency does not remain constant with increasing light intensity due to loss of fill factor at higher light intensities.

References

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