Thickness dependent photoelectrochemical cells performance of CdSe and HgS thin films

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The search for new semiconducting material for solar energy conversion has been the subject of intensive research [1–2]. Number of binary semiconductors are deposited by chemical bath deposition (CBD) method and studied for their photoelectrochemical behavior [3–5]. However, few reports are available on the photoelectrochemical properties of nanocrystalline CdSe and HgS thin films deposited by CBD method. In earlier communications, the nanocrystalline films of CdSe [6] and HgS [7] have been synthesized by changing thickness and their structural, optical, and electrical properties are reported.

In the present investigation, we have deposited nanocrystalline CdSe and HgS thin films with different thicknesses by CBD method. These films are deposited onto fluorine doped tin oxide (FTO) coated glass and titanium substrates. Using these nanocrystalline films as a photoelectrode and carbon as a counter electrode, the photoelectrochemical (PEC) cells are formed. Their photoelectrochemical characterizations are carried out.

For photoelectrode formation, nanocrystalline CdSe and HgS films with different thicknesses are deposited onto titanium substrate (1×1 cm^2) by using following procedure. For the preparation of nanocrystalline CdSe films of different thickness, 0.1 M $CdSO_4$ solution was taken in a beaker and 0.05 M Na_2SeSO_3 solution was formed by dissolving Se in Na_2SO_3. Ammonia solution was added to bath to form the complex and the pH was raised between 9 and 10. The solution was stirred for a few seconds and then transferred to another beaker containing titanium substrates. In order to get films with different thickness, the bath solution was kept at different deposition temperatures for different time periods.

For the preparation of HgS films of different thicknesses, 0.05 M $HgCl_2$ solution was taken in a beaker and equal volume of 0.1 M $Na_2S_2O_3$ solution was added to it. The pH of the solution was between 2 and 3. The deposition temperature was varied between 273 and 358 K and deposition time was varied between 45 min and 75 hr. After film formation, both the films were taken out of the bath, washed with double distilled water, and preserved in airtight container. Thickness of both the films was measured by the Fizeau fringe method. The thickness of the film was found to be deposition temperature–dependent. The CdSe films deposited at 273 and 358 K showed thickness of 605 and 2390 Å, respectively and the HgS films deposited at 273 and 358 K showed thickness of 510 and 1815 Å, respectively.

The two-electrode system, consisting of nanocrystalline CdSe and HgS films on titanium substrate was used as a working electrode, graphite as a counter electrode. 0.1 M polysulphide and 0.1 M polyiodide electrolytes were used for CdSe and HgS, respectively. The current-voltage (I-V) characteristics are measured in dark and under illumination using tungsten filament lamp. A water filter was interposed between lamp and PEC cell to prevent heating of the PEC cell. Photovoltaic output characteristics of cells were studied under 42 mW/cm^2.

Dark, I-V characteristics of PEC cells based on CdSe and HgS photoelectrodes are shown in Figs 1 and 2, respectively. A dark voltage, V_d and dark current, I_d are observed. The polarity of $V^\wedge$ is negative towards CdSe electrode and positive towards graphite electrode. For HgS, V_d is positive towards FtgS and negative towards graphite electrode. The origin of the dark voltage is attributed to the difference between Fermi levels of the semiconductor electrode/electrolyte. The dark current observed may be due to deterioration of the photoelectrode in dark. The non-symmetric nature of I-V curve (Figs 1 and 2) in forward and reserve bias shows the rectification property of the semiconductor electrolyte junction. From I-V curve, the junction ideality factor in dark (n_d) and in light (n_l) are calculated at different film thickness and are listed in Table I. For all the film thickness 'n' is much greater than the ideal value, which indicates that CdSe and HgS thin films form non-ideal junction. The increase in 'n' under illumination may be due to increased charge transfer across semiconductor electrolyte interface with significant recombination contribution from the surface states and deep traps [8].

The effect of film thicknesses on I-V characteristics of CdSe and HgS PEC cells are studied, these curves exhibit diode behavior. Especially, relatively high magnitude of the photocurrent in saturation region is a notable observation. According to Hodes *et al.* [9] porosity of the nanocrystalline film allows an electrolyte to establish an intimate contact to individual crystallites and upon illumination, this situation leads to rapid removal of holes allowing electrons to transfer several

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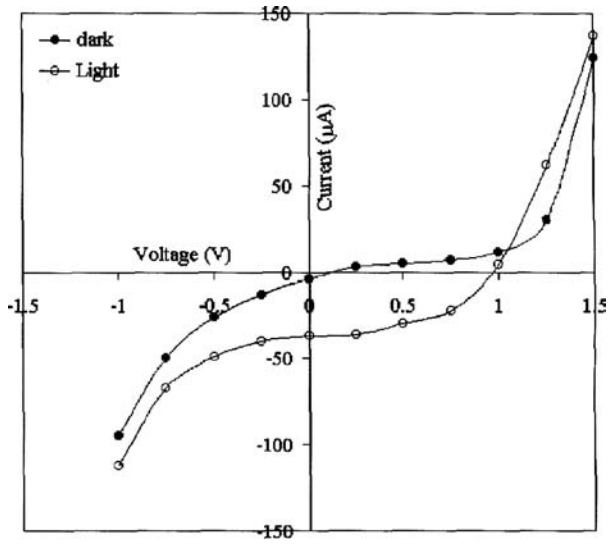

Figure 1 Current-Voltage (I-V) characteristics of PEC cell based on CdSe thin film with thickness 605 Å.

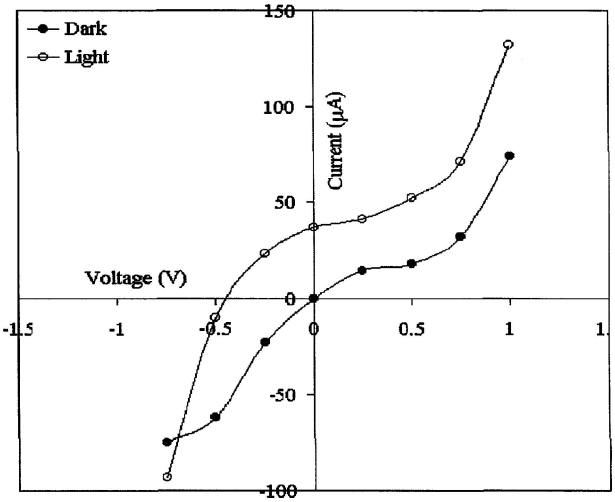

Figure 2 Current-Voltage (I-V) characteristics of PEC cell based on HgS thin film with thickness 510 Å.

crystallites with little chance of their recombination in the particulate film based PEC system.

Figs 3 and 4 show the photovoltaic power output characteristic of CdSe and HgS films with two different film thicknesses. Short circuit current, I_{sc} and open circuit voltage, V_{oc} increased with film thickness of CdSe and HgS films. Tables I and II shows that film thickness decreases as deposition temperature decreases. The low value of I_{sc} and V_{oc} can be attributed to the high series resistance (10^7–10^8 Ω-cm), of the film or nanocrystalline thin film. Efficiency decreases as film thickness

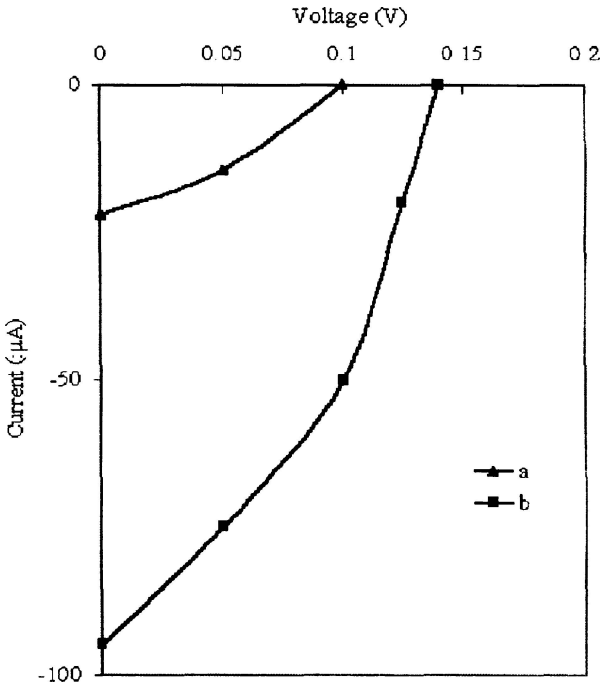

Figure 3 Photovoltaic output characteristics of PEC cells based on CdSe thin film with thickness (a) 605 and (b) 2390 Å.

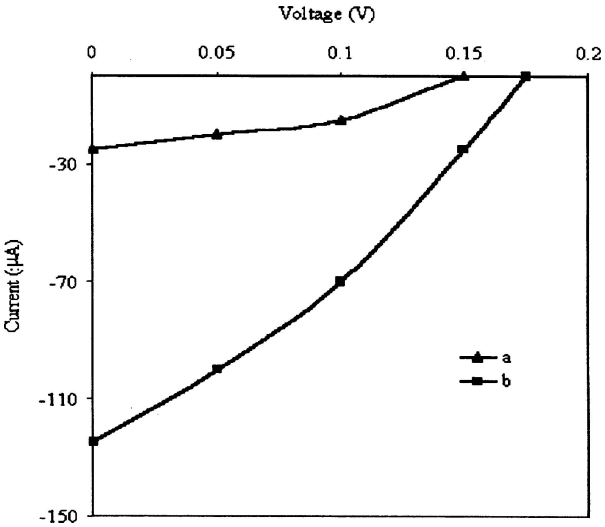

Figure 4 Photovoltaic output characteristics of PEC cells based on HgS thin film with thickness (a) 510 and (b) 1815 Å.

decreases, due to nanocrystalline nature of CdSe and HgS films [10].

Spectral response study of the CdSe and HgS PEC cells were carried out. Figs 5 and 6 show the plot of

TABLE I Variation of ideality factor and efficiency with film thickness of CdSe thin film

Sr. no.	Deposition temperature (K)	Thickness (Å)	Ideality factor n_d	Ideality factor n_1	Fill factor (ff)	Efficiency (η)
1	273	605	3.8	11.6	0.18	0.003
2	301	1200	2.9	7	0.2	0.005
3	318	1675	3.4	5.2	0.22	0.009
4	338	2115	2.3	7.5	0.25	0.01
5	358	2390	4.3	6.9	0.35	0.02

TABLE II Variation of ideality factor and efficiency with film thickness of HgS thin film

Sr. no.	Deposition temperature (K)	Thickness (Å)	Ideality factor n_d	Ideality factor n_1	Fill factor (ff)	Efficiency (η)
1	273	510	3.6	3.8	0.22	0.009
2	301	690	4.3	5.8	0.25	0.0023
3	318	1365	4.7	7.0	0.28	0.0089
4	338	1585	6.9	9.9	0.27	0.010
5	358	1815	6.3	11.6	0.33	0.015

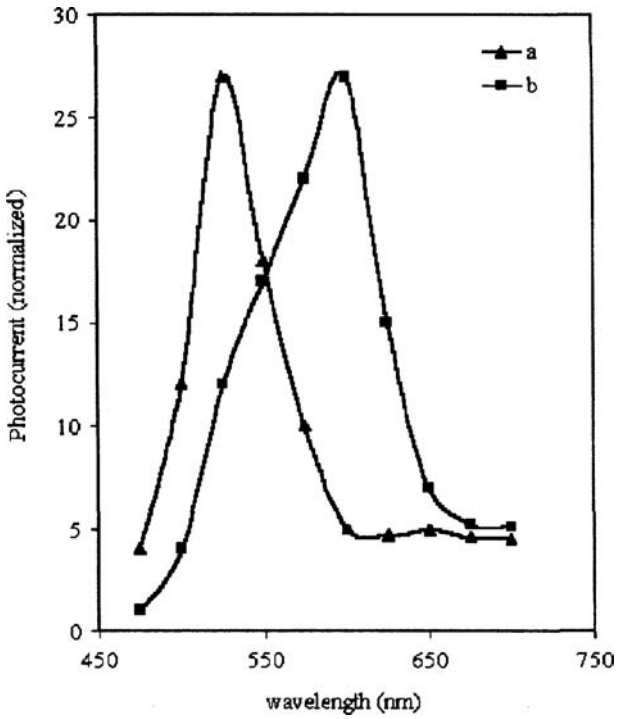

Figure 5 Spectral response of PEC cells based on CdSe thin film with thickness (a) 605 and (b) 2390 Å.

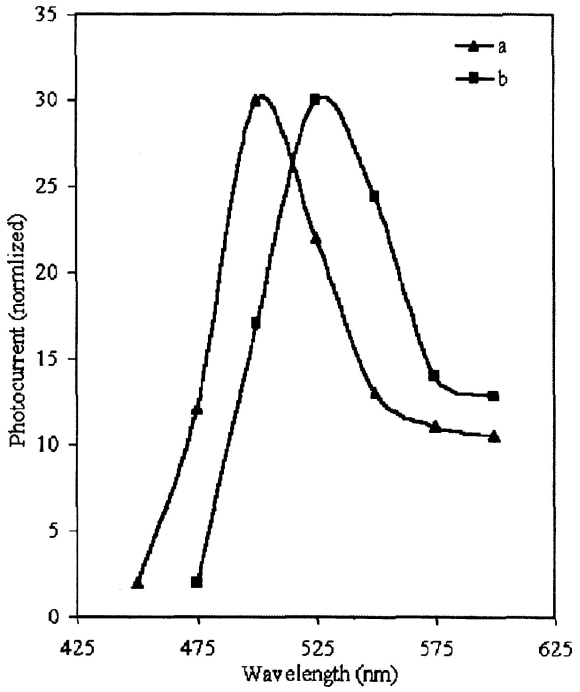

Figure 6 Spectral response of PEC cells based on HgS thin film with thickness (a) 510 and (b) 1815 Å.

I_{sc} as a function of wavelength (V) for CdSe and HgS, respectively. In both the cases, the photocurrent increases, attains the maximum value, and decreases with further increase in wavelength. The maximum values of I_{sc} were found to be at wavelength 6100 and 5300 Å for CdSe film with thickness 2390 and 605 Å, respectively. Similarly, for HgS thin film maximum values of I_{sc} at wavelength 5700 and 5100 Å for film thickness 1815 and 510 Å, respectively were observed. For both the films, shifting of peaks towards higher energy sides in spectral response as film thickness decreases, is attributed to the smaller film thickness and grain size of CdSe and HgS films [10].

In conclusion, it is found that CdSe and HgS nanocrystalline thin films are deposited from CBD method by varying film thickness. These films showed photoactivity in polysulphide and polyiodide electrolyte, respectively. The PEC performance of these films was found to be film thickness dependent. The 'Blue shift' was observed in spectral response of CdSe and HgS films with decrease in film thickness due to smaller grain size.

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