Studies of sub-bandgap response on surface-modified n-CdSe photoelectrodes

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Sub-bandgap response measurements have been shown to be a powerful and sensitive technique for determining the nature of the surfaces of n-CdSe photoelectrodes. The effect of Zn-modification of n-CdSe in Se^{2-}/Se_2^{2-} redox electrolyte has been shown to diminish sub-bandgap response considerably but on heat treatment it is enhanced. It is further shown that surface dissolution in $[Fe(CN)_6]^{4-/3-}$ redox electrolyte leads to enhanced sub-bandgap response. The results are correlated with the increase in flat-band potential due to its modification as demonstrated by capacitance–voltage measurements and also with significant changes in the spectral response.

1. Introduction

Surface modification of semiconductors has been shown to be a powerful technique for the improvement of the properties of photoelectrochemical (PEC) solar cells [1–9]. It has also been pointed out that the efficiency and PEC performances of most photoelectrodes depend significantly on the nature of the surfaces of the semiconductor [10–12]. In particular, mechanical damage and anodic dissolution of various semiconducting photoelectrodes used in the electrolyte system were found to have a detrimental effect on PEC performance. However, they were also found to enhance sub-bandgap response [13, 14] which can thus be used as a powerful tool for the evaluation of the surface properties of semiconductors. We have investigated the surface properties of thin-film n-CdSe electrodes, after different surface treatments, using broad-band sub-bandgap measurements. The Se^{2-}/Se_2^{2-} redox electrolyte was used in which stable operation of n-CdSe has been reported [15]. Heat treatment of n-CdSe samples produces a remarkable increase in sub-bandgap response. The spectral response of a n-CdSe PEC cell determined before and after modification indicated substantial reduction of surface states within the bandgap causing removal of fermi-level pinning. This agrees well with the observed increase in flat-band potential measured by capacitance–voltage (C–V) measurements.

2. Experimental procedure

Thin films of n-CdSe were deposited on titanium substrates from a chemical bath containing an aqueous solution 10 ml 1M cadmium acetate, 5 ml 7.40M triethanolamine, 10 ml 13.4M NH_3, and 15 ml 0.45M Na_2SeSO_3, as reported by Mandal *et al.* [16]. During deposition the solution was stirred continuously and maintained at 82 ± 2 °C. The films had a thickness of 4.2 μm obtained by three successive depositions in fresh deposition baths. They were annealed for 1 h at 500 °C in nitrogen, etched in 4:1 H_2O: aqua regia for 5–10 s and dried under argon. This treatment showed the optimal PEC performances as reported previously [17]. The measured resistivity was 2.8 Ωcm and the Hall effect measurements indicated majority carrier concentrations and mobilities of 1.23×10^{16} cm^{-3} and $182\ cm^2\ V^{-1}\ s^{-1}$, respectively. Prior to modification, samples of approximately 6 cm^2 in area were further etched in 50% HCl for 30 s to obtain a black matt surface. They were then immersed in 0.1 M $ZnCl_2$, H_2O in 0.1M HCl solution for 1 min to accomplish surface modification. This was followed by gentle washing in triply distilled water.

The electrochemical cell was a three-electrode system with a large area Pt-mesh as a counter electrode and a saturated calomel reference electrode. The light source was a 1.5 kW tungsten halogen lamp adjusted to produce AM1 illumination at the photoelectrode. High-purity argon was bubbled through the redox solutions initially and during experiments. Detailed spectral response of the photoelectrodes with and without Zn-modification was carried out between 1.0 and 0.4 μm, using a Bausch and Lomb high-intensity monochromator. The steady-state currents were measured using a Keithley 510B DMM multimeter. Monochromatic radiation was incident on the sample, the source intensity being calibrated using a Si p-i-n diode. Subsequently, the sub-bandgap response was studied using single-crystal CdSe ($N_d = 3.2 \times 10^{16}$ cm^{-3}, 0.031 cm thick), CdTe ($N_d = 2.8 \times 10^{16}\ cm^{-3}$, 0.026 cm thick), and GaAs ($N_d = 8.6 \times 10^{16}\ cm^{-3}$, 0.019 cm thick) as filters with a tungsten halogen source. The full AM1 intensity from the source was chopped by a PAR 125A chopper at 120 Hz and was

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incident on the specimen through one of the above filters. The output current from the cell was measured across a 10 kΩ load resistance for maximum response and was fed to a PAR Model 5202 lock-in-amplifier. The detection sensitivity was ± 0.01 μV. The CdSe, CdTe and GaAs semiconductor crystals acted as optical filters with high-energy cut off at 1.67, 1.48, and 1.39 eV, respectively, as estimated from their absorption spectra. The use of semiconductors as filters is very critical because the observed sub-bandgap response may be orders of magnitude smaller than the above bandgap response [10, 18], and a small amount of stray light could give an erroneous response.

3. Results and discussion

The photocurrent response obtained using a monochromatic beam on a n-CdSe specimen with and without Zn-modification in a Se^{2-}/Se_2^{2-} redox electrolyte is illustrated in Fig. 1. It is evident that the sub-bandgap response is diminished both in magnitude and spectral extent by the modification. The considerable improvement of the shorter wavelength response indicates the reduction in surface recombination velocity associated with removal of surface states as demonstrated by Nelson *et al.* [19].

Subsequent experiments were carried out alternately with white light followed by the use of CdSe, CdTe or GaAs filters. The ratio of response provided a method for rapid evaluation of surface properties as is evident from Table I. The response with white light illumination increased on Zn-modification while the sub-bandgap response decreased substantially. The effect of matt etching was an increase in sub-bandgap response. This may be due to the creation of states within the bandgap. After modification, the response remained unchanged after the electrode was kept in the dark for 24 h and subsequently illuminated at AM1 for 10 h. A further interesting feature that we noted is that the ratios of sub-bandgap with CdSe and CdTe filters and that with CdTe and GaAs filters are nearly the same. It was also found from the *C–V* measurements that Zn-modification increased V_{fb} (from − 0.86 to − 1.08 V versus SCE) in a Se^{2-}/Se_2^{2-} redox solution. This may account partly for the increased AM1 response. The shift in flat-band potential measured through Mott–Schottky plots can be attributed to additional surface charge which is computed to be $-3.6 \times 10^{15}\ cm^{-2}$ using the theory of Kingston and Neustadtar [20]. Our calculated value is supported by recent XPS measurements [21] which demonstrate a fairly high concentration of Zn atoms. A change in the surface stoichiometry (Cd : Se) ratio on modification and formation of a stable Se-rich oxide were also observed, the latter being expected to contain the additional surface charge [22].

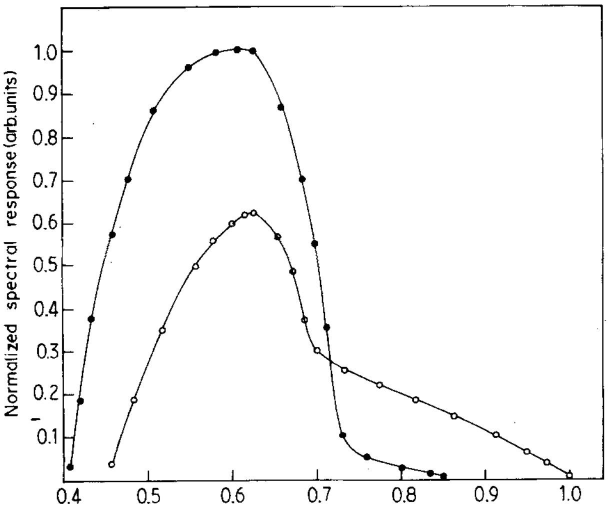

Figure 1 Normalized spectral response in the current mode of n-CdSe in 5M NaOH, 0.05M Se^{2-}/Se_2^{2-} redox electrolyte, (○) before and (●) after Zn-modification.

The effect of 0.1M HCl without $ZnCl_2$ was negligible as confirmed by control experiments. Moreover, modification by 0.1M $ZnCl_2$ without HCl showed the same magnitude of sub-bandgap response which confirmed the effect of the presence of Zn ions.

Experiments with the $[Fe(CN)_6]^{4-/3-}$ redox electrolyte system given in Table I, showed that the sub-bandgap response was larger by an order of magnitude than in the Se^{2-}/Se_2^{2-} redox electrolyte system, indicating the creation of surface states within the bandgap. The AM1 response was also higher due to a more efficient hole transfer. The result in the $[Fe(CN)_6]^{4-/3-}$ system also showed a strong time dependence, i.e. a decrease in AM1 response by 20% and an increase in sub-bandgap response by 70%–80% compared with much smaller changes in the Se^{2-}/Se_2^{2-} redox system over a period of 10 h. Zn-treatment again diminished the sub-bandgap response. Owing to anodic dissolution with $[Fe(CN)_6]^{4-/3-}$ redox electrolyte system after 10 h illumination, the ratio of sub-bandgap response to that just after modification increased by a factor of two.

Heat treatment of n-CdSe thin films at 500–600 °C is normally necessary to obtain larger grain size and better electrical properties. However, it has been found that when the sample is annealed in N_2-ambient at 650 °C, it does not give an enhanced PEC effect, but rather a deleterious one. The drastic effect of heat treatments at different temperatures on n-CdSe sub-bandgap response are shown in Table II. The results show that even by heating for a short time at 650 or 750 °C in an argon atmosphere, there is a detrimental effect on the surface properties of n-CdSe which may be due to out-diffusion of selenium. Such heat treatments are commonly encountered in ohmic contact formation. The present method thus gives a quantitative estimation of surface evaluation by examining the sub-bandgap response in the Se^{2-}/Se_2^{2-} redox system. These results have the potential to illustrate the following important observations. Most interestingly, the white light AM1 response decreases 30% –50% approximately with the increase in heat treatment from 600–700 °C even for 1 min duration, while the sub-bandgap response increases at a faster rate under similar conditions. Moreover, it is noted that the magnitude of sub-bandgap response increases approximately 5 times and 2.5 times in succession for the

TABLE I Sub-bandgap response on n-CdSe in 5M NaOH

Surface treatments	White light AM1 response (10^{-3} V)	Sub-bandgap response (10^{-6} V)		
		CdSe filter ($E_g = 1.70$ eV)	CdTe filter ($E_g = 1.50$ eV)	GaAs filter ($E_g = 1.43$ eV)
Polished and etched	A[a]: 188	49	36	27
	B: 346	421	316	236
Matt surface	A: 93	92	68	48
	B: 172	827	618	462
Zn-modified	A: 272	17	12	9
	B: 508	112	84	61
10 h AM1 illumination	A: 268	16	12	8
	B: 407	201	155	113

[a]A = 0.05M Se^{2-}/Se_2^{2-}, B = 0.10M $[Fe(CN)_6]^{4-}$, 0.20M $[Fe(CN)_6]^{3-}$.

TABLE II Effect of heat treatment on sub-bandgap response: n-CdSe in 5M NaOH 0.05M Se^{2-}/Se_2^{2-} redox electrolyte

Heat treatment in argon atm		White light AM1 illumination (10^{-3} V)	Response with		
(°C)	(min)		CdSe filter (μV)	CdTe filter (μV)	GaAs filter (μV)
600	5	166	64	46	34
650	1	121	325	232	161
700	1	84	829	588	415

enhancement of every 50 °C heat treatment. Such a drastic increase in its magnitude indicates the creation of new states at the CdSe-electrolyte interface.

4. Conclusions

The experimental results presented in this paper indicate that the sub-bandgap response is due to optical excitation from states within the bandgap to either band. These states may be either in the bulk within the absorption depth or at the surface. The variation of sub-bandgap response with surface treatment favours the latter conclusion. The magnitude of response would depend on the density of states and also on the excitation mechanism. Direct excitation from surface states to either band is known to have a low probability. Hence, a two-step process involving excitation in the bulk followed by charge transfer to surface states within the bandgap, and finally hole transfer to the redox level is envisaged. The sub-bandgap response studies demonstrate a decrease in surface state density through Zn-treatment and an increase due to dissolution in the $[Fe(CN)_6]^{4-/3-}$ solution or heat treatment. The broad similarity of the behaviour with CdSe, CdTe or GaAs filters points out that the density of surface states increases sharply towards the band edges over an energy range 0.2–0.3 eV [4] within the band edges but decreasing away from the edges.

The increase in V_{fb} with Zn-modification indicates the removal of Fermi-level pinning due to surface states, while the change in spectral response asserts that these states remain inactive in carrier trapping at the surface by Zn-modification.

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