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Chemically deposited n-CdSe thin film photo-electrochemical cells: effects of Zn^{2+}-modification

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The photoelectrochemical solar cell properties of chemically deposited n-CdSe films were studied before and after Zn^{2+} surface modification. It was shown that the surface properties underwent conceivable changes after Zn^{2+} treatment. The current–voltage characteristics in the dark showed a significant decrease in reverse saturation current density, J_0, from 5.4×10^{-7} to 1.2×10^{-9} A cm^{-2} and in ideality factor, n, from 2.46 to 1.27. Under AM1 illumination, other parameters have been found to be considerably enchanced, e.g. the open-circuit photovoltage, V_{oc}, increased from 0.53 to 0.85 V with respect to SCE; the short-circuit photocurrent density, J_{sc}, from 2.62 to 8.35 mA cm^{-2}; fill factor from 0.38 to 0.62 and the minority carrier diffusion length, L_p, from 0.16 to 0.22 μm. X-ray photoelectron spectroscopic data on the Zn^{2+}-modified CdSe showed the formation of metallic Zn islets and a thin layer of SeO_2 on the surface. All these important improvements of the CdSe PEC properties may be attributed to the redistribution of active interface states within the band gap due to strong interaction of the electrodepositive Zn^{2+} ions. Support for these observations were obtained by sub-band gap response studies, contact potential difference measurements in N_2 ambient and the estimation of the surface recombination velocities before and after modification.

1. Introduction

Surface modification of semiconductors has been shown to be an interesting technique for the improvement of the surface properties, thereby enhancing the efficiency and stability of photoelectrochemical (PEC) solar cell. While the initial investigations were carried out on GaAs and InP [1–6], the studies were later extended to the II–VI, CdSe and CdTe [7–17] which are of technological interest for thin film solar cell and other opto-electronic devices. An increase of V_{oc} and a significant decrease in J_0 of CdSe electrodes has been observed after dipping in a solution of $ZnCl_2$ [11–17] or in an aqueous solution of K_2CrO_4 [18, 19]. Dipping these electrodes in an aqueous solution of $CdCl_2$ has no significant effect on V_{oc}. It has been suggested that ZnS overlayer was formed by dipping the CdSe in $ZnCl_2$ solution and then reimmersing in S_n^{2-} solution [14, 15]. The improvement of the PEC solar cell performances with time was also observed on electrodes etched in dilute *aqua regia* and treated with 2 M $ZnCl_2$ solution. The efficiency was found to be 10% in aqueous polysulphide solution. This paper deals with a systematic study of the influence of the electrode surface treatment with $ZnCl_2$ on the PEC solar cell performance of CdSe in Se^{2-}/Se_2^{2-} solution. How this treatment affects the photoelectrode characteristics was determined using different measurements: broad-band sub-band gap, hole diffusion length and contact potential difference (CPD) with the Kelvin probe technique. On the other hand, the determination of the surface recombination velocity before and after $ZnCl_2$ treatment was used to explain the change of the interface state densities involving the improvement of the PEC solar cell performance.

2. Experimental procedure

Chemically deposited n-CdSe thin films were used as electrodes in the present studies. The deposition of the films was carried out on a titanium substrate from a chemical bath containing an aqueous solution of 10 ml of 1 M cadmium acetate, 5 ml of 7.40 M triethanolamine, 10 ml of 25% NH_3 and 15 ml of 0.45 M Na_2SeSO_3 as reported earlier [16, 17]. During the deposition, the solution was continuously magnetically stirred and maintained at 82 ± 2 °C. The film with a thickness of 4.2 μm was obtained after three successive depositions from fresh deposition baths. They were annealed for 1 h at 500 °C in air, etched in 10:1 H_2O:*aqua regia* for 10 s and dried under purified

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nitrogen. The electrical parameters were determined by the four point probe resistivity and Hall effect measurements. A resistivity of 2.8 Ωcm, a carrier density of 1.2×10^{16} cm^{-3} and a carrier mobility of 182 cm^2 V^{-1} s^{-1} were obtained. The PEC measurements were carried out in a double compartment quartz cell with a standard three electrode configuration. A large area Pt gauze was used as the counter electrode and the reference electrode was a saturated calomel. The working electrolyte was 5 M NaOH with 0.05 M Se^{2-}/Se$_2^{2-}$ as redox in which stable operations of the electrode have been reported [20]. The electrolyte was thoroughly degassed with pure nitrogen and kept under a positive N_2 pressure during the experiments. Prior to $ZnCl_2$ treatment, samples of area approximately 0.8×0.5 cm^2 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 0.1 M HCl solution for 1 min to accomplish surface modification. This was followed by gentle washing in triply distilled water. It has also been verified that the treatment of the electrodes with 0.1 M HCl without $ZnCl_2$ has negligible effect on their PEC characteristics. The spectral response of the photoelectrodes with and without $ZnCl_2$ treatment was carried out between 1.0 and 0.4 μm, using a Bausch & Lomb high intensity monochromator. The steady-state currents were measured using a Keithly 510B DMM. Monochromatic radiation was incident on the sample, the source intensity being calibrated using a Si p-i-n diode. Subsequently, the sub-band gap 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 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 CPD measurements were carried out using the Kelvin vibrating probe technique. Experiments were conducted in a nitrogen ambient using a platinum reference electrode vibrated at 120 Hz. The 5202 lock-in-amplifer was used for signal detection while the voltage null was measured with a Keithley 510B DMM. Measurements of several specimens were reproducible within ± 5 mV. The details of the measurements have been described earlier [16]. XPS investigations were carried out using a Vacuum Generator ESCALAB MK II ESCA/Auger Spectrophotometer with MgK_α source (E = 1253.6 eV). Emission energies of electrons from the Se (3d$_{5/2}$ and 3d$_{3/2}$), Cd (3d$_{5/2}$ and 3d$_{3/2}$), Zn (2p$_{3/2}$ and 2p$_{1/2}$), O (1s), and C (1s) levels were examined and intensities recorded directly. The Zn^{2+} modified CdSe surfaces were studied before and after argon ion etching for a few minutes.

3. Results and discussion

The n-CdSe film photoelectrode exhibited good rectification in the dark. From the forward J–V characteristic, the ideality factor, n, was found to be 2.46 and the saturation current density, J_o, 5.4×10^{-7} A cm^{-2}. Plot of $1/C^2$ versus V measured at 10 kHz were straight lines in the large potential range (from 0 to + 1.5 V versus SCE). Thus the Schottky–Mott (SM) model is verified for these interfaces. The carrier concentration was estimated from the slope and found to be 1.6×10^{16} cm^{-3} and extrapolation of the intercept in the voltage axis gave the flat band potential, V_{fb}, to be − 0.86 ± 0.10 V versus SCE. With AM1 illumination, the PEC solar cell J–V plot shown in Fig. 1 showed a short-circuit photocurrent density, J_{sc}, of 2.62 mA cm^{-2} with an open-circuit voltage, V_{oc}, of 0.53 V versus SCE and a fill factor (FF) of 0.38.

After $ZnCl_2$ treatment a significant increase of the photoelectrochemical performances was observed. The forward J–V characteristics showed a decrease in J_o to 1.2×10^{-9} A cm^{-2} and in ideality factor to 1.27. The $1/C^2$ versus V plot after modification showed linear behaviour in the same range of potential as above and a flat band potential, V_{fb}, of − 1.08 ± 0.10 V versus SCE and $N_d = 1.3 \times 10^{16}$ cm^{-3} were deduced. The dark voltage increased from 22 to 38 mV. This may be attributed to the deposition of metallic Zn islets on the CdSe surface and would be shown later from XPS studies (to be discussed later). Macroscopic metal–electrolyte junction may cause slight increase in the dark voltage. A significant improvement of the PEC solar cell characteristic was observed (Fig. 1) after $ZnCl_2$ treatment, the values of V_{oc}, J_{sc} and FF were 0.85 V versus SCE; 8.35 mA cm^{-2} and 0.62, respectively. The stability experiments were conducted both in the dark and under AM1 illumination on the modified photoelectrodes and showed no significant weight loss over 460 h and the dark as well as photocurrent remained constant over these periods. The extremely low dark current and voltage were further indications of the electrode stability. Moreover, the solution in the cell was analysed for Cd content before and after illumination by using atomic absorption spectroscopy. No change in the Cd content of the solution ($< 4 \times 10^{-6}$ M) was observed.

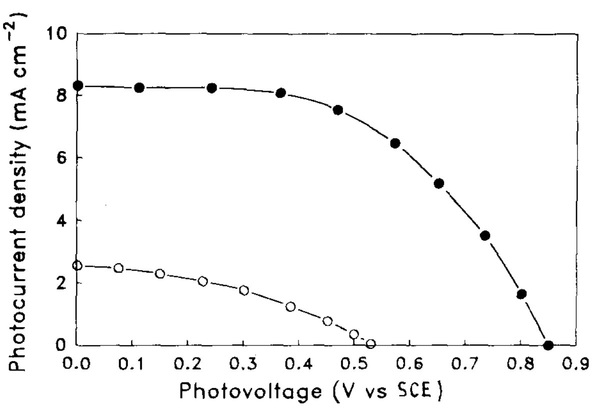

Figure 1 Solar cell characteristics under AM1 tungsten-halogen illumination: (○) unmodified surface; (●) Zn^{2+}-modified surface.

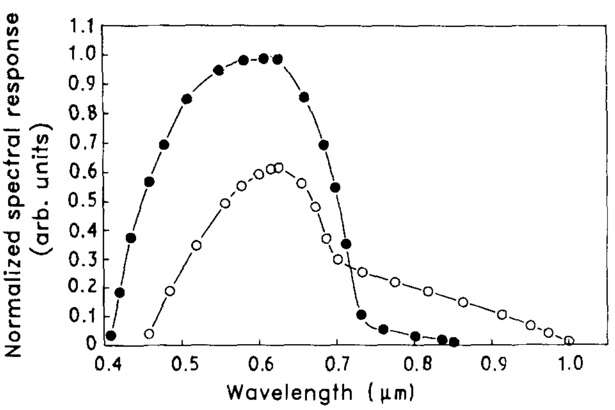

Figure 2 Normalized spectral response in the current mode of n-CdSe thin film photoelectrode in 5 M NaOH 0.05 M Se^{2-}/Se_2^{2-} redox: (○) before and (●) after Zn^{2+}-modification.

The spectral response of n-CdSe film PEC cell was determined before and after Zn^{2+} modification and is shown in Fig. 2. From the figure it is clear that a substantial reduction in photoresponse occurred after modification at energies below the band gap of 1.72 eV. The response at lower wavelengths is also considerably improved at the same time, thereby indicating a reduction of effective surface recombination velocity as discussed later.

The experimental evidence of the redistribution of interface states within the band gap was obtained by sub-band gap experiments using broad-band tungsten-halogen illumination with single crystalline CdSe, CdTe and GaAs as optical filters. Table I shows the response after different surface treatments. It is seen that there is an increase in response after matt etching followed by a substantial decrease after $ZnCl_2$ treatment. While the freshly etched surface appears to have a large response for photon energies near the band edge, the matt surface is characterized by large photoresponses below the absorption edge of the filters. These observations suggest that proper control of surface state engineering may significantly influence the charge transfer across the electrolyte interfaces. This is further discussed in connection with the CPD measurements.

The minority carrier diffusion length, L_p, was determined by measuring the quantum efficiency of carrier collection versus applied anodic bias under He–Ne laser illumination. The relation used is

$$\ln(1 - \eta) = \left(\frac{2\varepsilon\varepsilon_o}{qN_D}\right)^{1/2} (V - V_{fb})^{1/2} - \ln(1 + \alpha L_p) \qquad (1)$$

as described by Russak *et al.* [21], from a derivation of the Gartner equation [22] where α is the optical absorption coefficient, ε, the semiconductor dielectric constant and other terms have their usual significance. The optical absorption coefficient, α, of the specimen has been determined using the Beckman spectrophotometer in the range 0.60–0.90 μm. The obtained values are in good agreement with the literature [23]. The variation of $\ln(1 - \eta)$ versus $(V - V_{fb})^{1/2}$ is shown in Fig. 3. The values of N_D and L_p were calculated by using the value of α at 632.8 nm, i.e. $4.8 \times 10^4\ cm^{-1}$. The values of N_D thus determined are found to agree very well with those obtained from Schottky–Mott experiments. L_p is thus found to increase from 0.16 to 0.22 μm after the $ZnCl_2$ treatment. The change of the depletion layer width, W_d, due to the Zn^{2+}-modification is small. The calculated value of W_d is 0.118 μm for untreated electrode and 0.121 μm for treated electrode. Hence the change in L_p is not merely due to an increase of the band bending but also due to a decrease in surface recombination velocity. Support of this conclusion can be found through considerations of other published data [24, 25]. Jastrzebski *et al.* [25] have shown that, in the presence of surface recombinations, the effective diffusion length, L_{eff}, is reduced from the bulk value, L_o, according to the relation

$$L_{eff}^2 = L_o^2\left(1 - \frac{s}{s + 1}\right)\exp\left(-\frac{Z}{L_o}\right) \qquad (2)$$

where s is the reduced surface recombination velocity (SL_o/D), D the diffusion coefficient and Z the distance from the surface in the semiconductor bulk. Considering excitation at the surface, i.e., at $Z = 0$, it is found that for $L_o = 0.20$ μm, the observed increase in L_{eff}

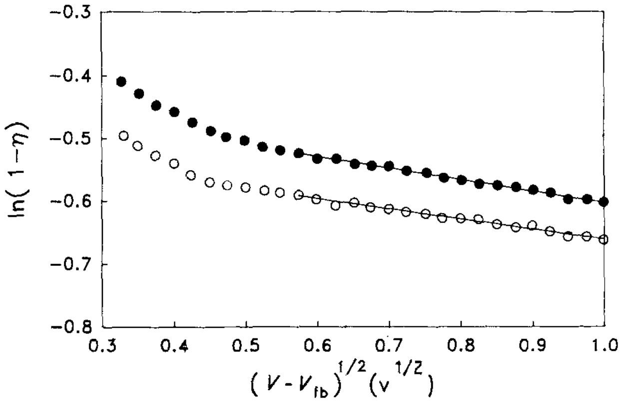

Figure 3 Quantum efficiency versus potential plot at $\lambda = 632.8$ nm: (●) unmodified surface and (○) Zn^{2+}-modified surface.

TABLE I Sub-band gap response on n-CdSe thin films in 0.05 M Se^{2-}/Se_2^{2-}, 5 M NaOH

Surface treatment	White light AM1 response ($\times 10^{-3}$ V)	Sub-band gap response ($\times 10^{-6}$ V)		
		CdSe filter ($E_g = 1.72$ eV)	CdTe filter ($E_g = 1.50$ eV)	GaAs filter ($E_g = 1.43$ eV)
Freshly etched	188	49	36	27
Matt	93	92	68	48
Zn^{2+}-modified	272	17	12	9
10 h AM1 illumination	268	16	12	8

TABLE II Effects of Zn^{2+}-modification on the properties of thin film n-CdSe–electrolyte interfaces

Surface conditions	J_o (A cm^{-2})	n	L_p (μm)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	s (cm s^{-1})
Before modification	5.4×10^{-7}	2.46	0.16	0.53	2.62	0.38	2.8×10^4
After modification	1.2×10^{-9}	1.27	0.22	0.85	8.35	0.62	3.4×10^3

corresponds to a decrease in s from 2.8×10^4 to 3.4×10^3 cm s^{-1}. The decrease of s by an order of magnitude appears to be the first observations for CdSe by using the simple chemical modification technique. For comparison, the improvement of the PEC results before and after modification are summarized in Table II.

To understand the surface modification mechanism which still remains intriguing in view of the suggestions of Aspnes [26] that an alternative explanation may lie in the shift of the surface Fermi level, the Kelvin CPD measurement technique was undertaken. The values of CPD before modification, after matt etching, and after modification are given in Table III. As may be seen, after matt etching the CPD value is more positive than that obtained on freshly etched sample. Consequently, the energy bands bend upward at the surface thereby indicating the creation of acceptor states at the surface. This is similar to usual observations on ground or damaged surfaces of elemental semiconductors [27]. Therefore, the effect of $ZnCl_2$ treatment changed CPD to more positive values corresponding to an increase of band bending in upward direction. Thus the depletion layer conditions were enhanced resulting in an increase of barrier height. The change in CPD was + 0.31 eV. The values of open-circuit voltage, V_{oc} under AM1 illumination with different electrode surfaces in PEC cells are also shown in Table III. It is seen that the increase in V_{oc} of 0.32 V versus SCE is in remarkably good agreement with the changes in V_{CPD} [1, 4]. The shift in surface Fermi level and an increase in V_{oc} on modification can be attributed to additional surface charges provided by the Zn^{2+} ions. From the observed changes in V_{oc}, using the theory of Kingston and Neustadtar [28] the density of surface charges was calculated to be -3.6×10^{15} cm^{-2}.

TABLE III Changes in V_{CPD} and V_{oc} on Zn^{2+} modification

Surface conditions	V_{CPD} (eV)	V_{oc} (V)
Freshly etched surface	− 0.12	0.53
After matte etching	+ 0.05	0.72
After Zn^{2+}-modification	+ 0.19	0.85

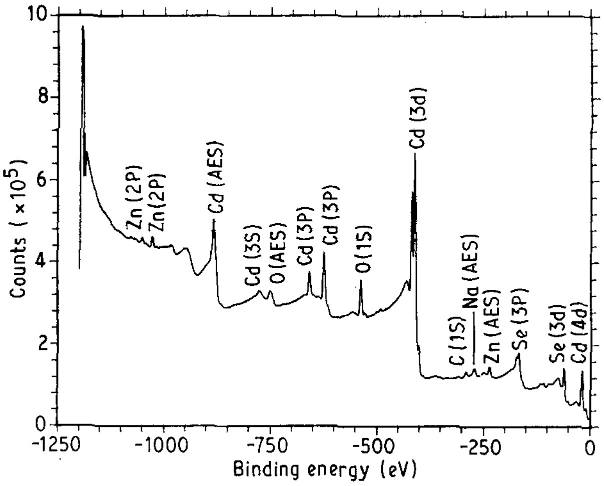

Figure 4 XPS survey scan for Zn^{2+}-modified CdSe surface.

The physical reasons for the improvement of the CdSe properties after modification were studied by X-ray photoelectron spectroscopy (XPS). Fig. 4 shows XPS survey spectrum along with the peak assignments of Zn^{2+}-modified CdSe sample. The peaks corresponding to Cd, Se, O and Zn are clearly seen. A trace amount of C and Na was detected and which may be due to surface contamination from air exposure and sample handling. Fig. 5a shows the binding energies of the Cd (3 $d_{5/2}$ and 3 $d_{3/2}$) levels before and after argon etching and its data are given in Table IV. Examination of the Cd spectra (Fig. 5a) shows that the nature of the spectra is unchanged by argon etching, the Cd peak binding energies at 405.3 and 412.2 eV are being characteristic of the Cd in CdSe. The Cd (LMM) Auger spectra were also taken and resembled that of Cd in CdSe with all the fine structures due to the d^8 final states. Fig. 5b shows the binding energies of the Se (3 $d_{5/2}$ and 3 $d_{3/2}$) levels on Zn^{2+}-modified n-CdSe surfaces. It is clearly seen from the spectra that the emission energy levels of Se (3 $d_{5/2}$ and 3 $d_{3/2}$) are shifted to higher binding energies (BE) as compared to the pure element [29]. The O (1 s) level is also shifted to lower BE. In general, these shifts are due to transfer of electrons from Se to O. This is further supported by the fact that O (3.5) is more electronegative [30] as compared to Se (~ 2.5). After a few minutes Ar-ion etching the higher energy peaks due to SeO_2 totally disappeared. The lower energy peak due to Se (3 $d_{5/2}$ and 3 $d_{3/2}$) appeared with considerably enhanced intensity. The chemically shifted higher energy peaks are due to Se^{4+}, present on the surface in the form of thin layer of SeO_2, while the lower energy peaks are due to Se in CdSe and agree very well with the reported literature [29, 31, 32]. Fig. 6 shows the spectra for Zn on modified CdSe. The Zn (2 $p_{1/2}$ and 2 $p_{3/2}$) levels are clearly observed with the binding energies 1044.5 and 1027.4 eV, respectively. The persistence of the Zn levels even after argon etching is possibly due to the rough nature of the surface after the matt etching step. Both of these energy levels observed for Zn (2 $p_{1/2}$ and 2 $p_{3/2}$) are characteristic of Zn metal and there is no indication of the presence of any chemically shifted level corresponding to Zn-related compounds [29].

Finally, the stability measurements were carried out and it is observed that the decrease in photocurrent density for n-CdSe after modification to be only 2.8% in 460 h compared with 78% over the same period for

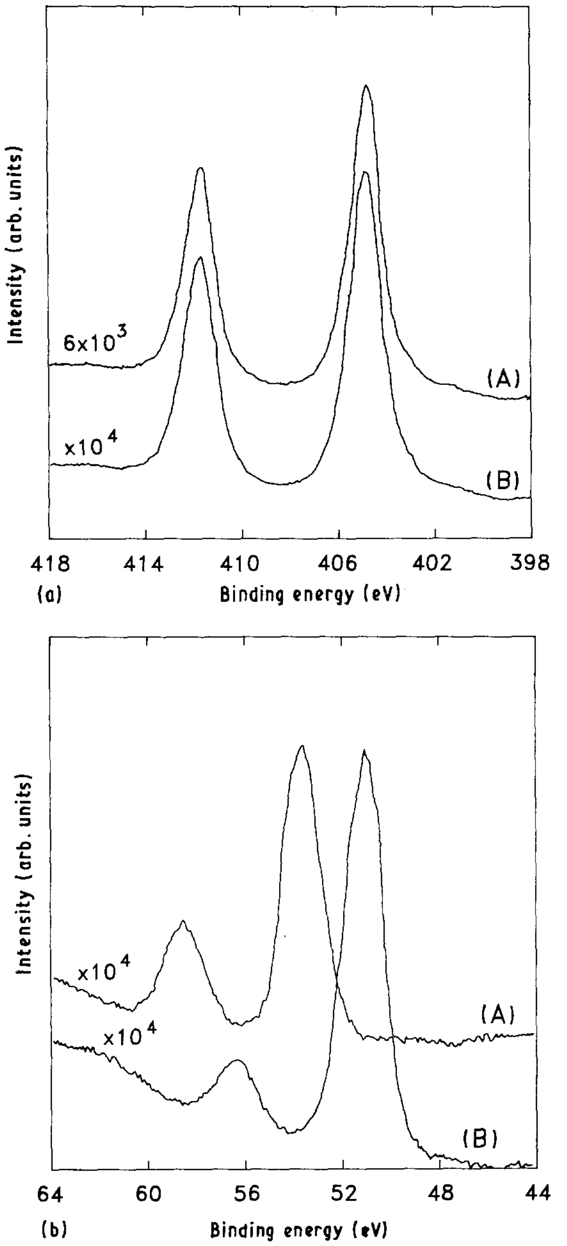

Figure 5 (a) Photoemission spectra of Cd (3 d) levels on Zn^{2+}-modified n-CdSe: (A) unetched and (B) after argon etching; (b) photoemission spectra of Se (3 d) levels on Zn^{2+}-modified n-CdSe: (A) unetched and (B) after argon ion etching.

TABLE IV Binding energies of Cd, Se, Zn, O, CdSe and SeO_2

Element and compound	Binding energy (eV)				
	$3\ d_{3/2}$	$3\ d_{5/2}$	$2\ p_{1/2}$	$2\ p_{3/2}$	1 s
Cd	412.0	405.0	–	–	–
Se	57.0	52.0	–	–	–
Zn	–	–	1045	1022	–
O	–	–	–	–	531
Cd in CdSe	412.2	405.3	–	–	–
Se in CdSe	57.3	51.1	–	–	–
Se in SeO_2	58.9	53.8	–	–	–
O in SeO_2	–	–	–	–	529.4

unmodified electrodes. These results indicate the high stability due to $ZnCl_2$ treatment.

4. Conclusion

The effects of $ZnCl_2$ treatment on n-CdSe thin films have been described. The results showed significant improvement of the PEC solar cell properties. It has also been shown that the electrode surface treated with $ZnCl_2$ induces excess surface charge along with a change in the surface Fermi level. The excess surface charge caused an increase in band bending thereby increasing the V_{oc} in PEC solar cells. Direct evidence of distribution of the active interface states within the band gap after modification has been demonstrated by sub-band gap and spectral response studies. The growth of metallic Zn islets and a thin SeO_2 as confirmed by XPS studies may be responsible for the reduction of the surface recombination velocity leading to an increase in effective diffusion length.

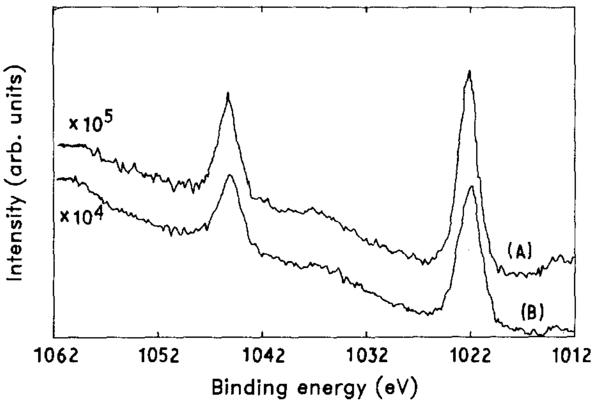

Figure 6 Photoemission spectra of Zn (2 p) level after Zn^{2+}-modification on n-CdSe: (A) unetched and (B) after argon etching.

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