Semiconductor Electrodes

XIX. An Investigation of S/Se Substitution in Single Crystal CdSe and CdS Photoelectrodes by Electron Spectroscopy

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ABSTRACT

Photoelectron spectroscopy studies verify the occurrence of S/Se substitution in single crystal CdSe and CdS photoanodes when used in photoelectrochemical cells containing S2- or Se2- solutions. A possible mechanism of the S/Se exchange is discussed as well as its consequences on the electrode stability and the output parameters of the photoelectrochemical cells.

A number of studies have shown that cadmium chalcogenide photoelectrodes can be stabilized in aqueous solutions by the addition of sulfide, selenide, or telluride ions (1-3). This stabilization is attributed to the favorable redox potential of the X/X2- couple (X = S, Se, Te) (4, 5) compared to the potential where electrode oxidation can occur or the preferential absorption of sulfide ions for the case of CdS. Recently (6), the behavior of mixed CdS/CdSe solid solution photoelectrodes in polysulfide solutions was described, where changes in the flatband potential and bandgap with variation in the S/Te ratio were observed.

Although CdS and CdSe show quite stable operation in sulfide and selenide electrolytes, changes in the photocurrent with time are observed and indeed one would expect from thermodynamic reasoning that exchange of solution chalcogenide ions with semiconductor lattice ions would occur. Recent reports (7-9) have provided evidence for such substitution. Thus Cohen et al. (7) showed x-ray photoelectron spectroscopy (XPS or ESCA) that sulfide substitution occurs on polycrystalline CdS. Similarly, beller et al. (8) found evidence of Se substitution in CdS by Auger electron spectroscopy (AES) and electron beam luminescence. Gerischer and Gebruch (9) also proposed that changes occur in the surface of CdS and CdSe single crystals under illumination in sulfide electrolytes, based on changes in the photo-current spectra and Hint-Schothwitz plots with operation time.

We report here detailed AES and XPS studies of the surface changes which occur in single crystal CdS and CdSe photoanodes when used in electrochemical cells (PEC). The results show that Se substitution occurs in the CdS/Se2- system and S substitution occurs in the CdS/Se2- system and provide information about the mechanism of substitution and its effect on the output parameters of the PEC.

Experimental

The electrochemical cells, light sources, method of electrode preparation, and instrumentation were the same as those previously described (6). Both single crystals (Cleveland Crystals, Cleveland, Ohio) and the polycrystalline powder (Ventron, Beverly, Massachusetts) were of high purity (99.999% S). We showed that the CdSe was Se-free and the CdS was S-free, as specified by the manufacturers, by AES and XPS analysis. Surface treatment carried out prior to use involved polishing of the single crystals with 6 μm alumina to a mirror finish followed by a chemical etch. The CdS crystals were etched in 6M HCl for 30 sec followed by rinsing with deionized water, while the CdSe crystals were etched for 30 sec in concentrated HNO3 followed by rinsing with a 0.1M KCN solution to dissolve any Se formed during etching, then followed by rinsing with deionized water. Na2S and Na2Se solutions were prepared from analytical grade reagents. The Na2Se solutions were obtained by bubbling HSe into a 1M NaOH solution under nitrogen. The Na2S solution was filtered twice then deoxygenated and stored under nitrogen. All experiments were performed under positive nitrogen pressure. Stirring was accomplished with a magnetic stirrer. After performing the photoelectrochemical experiments, the electrodes were rinsed with 1M NaCl solution followed by copious amounts of deionized water.

PEC experiments were run with the electrodes po
tentialized at -1.5V vs. SCE using a large Pt counter-electrode (-10 cm2). The photocurrents produced under illumination with white light (intensities of 20-150 mW/cm2) were measured by a high impedance electrometer (Steen Model 250 Thickness Monitor, Santa Barbara, California). The PEC cells were used to simulate the pottlering of CdS and CdSe by the xenon ion beam in the electron spectroscopy analysis. AES and XPS analyses were performed with a Physical Electronics Model 548 Spectrometer (Eden Prairie,
Minnesota). A 5 kV, 10-15 μA, focused electron beam was used to sputter the substrate during AES measurements. While depth profiling, the voltage ramp was multiplied such that the S(LMM) (132 eV), C(LLL) (272 eV), Cd(MNN) (376 eV), and Se(LMM) (1315 eV) transitions could be sequentially scanned in less than 1 min. The argon ion beam used for sputter etching was operated at 3 kV and 30 mA emission yielding a uniform beam, with a current density of 3.65 × 10⁻⁶ A/cm². The cross-sectional area of the circular sputtered crater was approximately 0.13 cm². XPS measurements were taken utilizing both Al Kα and Mg Kα anodes. The data were collected digitally with zero counting and signal averaging techniques. Both broad scan 0-1000 eV binding energy (resolution < 1.6 eV FWHM) and high-resolution (0.8 eV FWHM) XPS analysis were carried out on the samples as a function of sputter time. Decreasing the sputtering process the ion pump was turned off and the vacuum chamber backfilled to 1 × 10⁻⁷ Torr in Ar. While taking XPS measurements the background pressure was maintained in the 5 × 10⁻⁶-5 × 10⁻⁵ Torr range. Finally, gas analysis showed the major contaminants to be H₂O and CO at these pressures. The intensities of XPS transitions are proportional to the peak area and can be expressed as

\[ I = I_0 \text{exp}(-\alpha D(x)) \]

where \( I_0 \) = x-ray flux, \( n \) = atomic density, \( \alpha \) = cross section for ionization, \( I(x) \) = mean free path of the escaping electron, and \( D(x) \) = the detector efficiency. The ratio of intensities for two elements can then be expressed (10) as

\[ \frac{I_A}{I_B} = \frac{n_A \alpha_A D_A}{n_B \alpha_B D_B} = \frac{n_A}{n_B} (Y) \]

The expression in parenthesis remains constant to a first approximation for a given matrix and thus can be determined empirically from standard samples. Both high purity pressed powders and clean single crystals were used to determine Y. Ratios of atomic densities could then be derived from intensity ratios. Using the same standards, relative Auger sensitivities were determined from peak-to-peak height ratios.

Sputtering rates were calibrated by depth profiling CdS and CdSe films of known thickness. The Cd (376 eV), S (132 eV), and Pt (297 eV) peaks were monitored while sputtering; the sputtering process was judged complete when the Cd and S signals were reduced to the noise level. Two profiles were run on each film, the craters being well isolated on opposite sides of the film as judged visually by the bright, shiny platinum at the crater bottom. By this method, sputtering rates for Cd and S of 16 ± 3 and 19 ± 3 Å/min, respectively, were found. This corresponds to a sputtering efficiency of 2.4 molecules/ion for CdS and 3.8 molecules/ion for CdSe. A constant Cd/Se Auger peak-to-peak ratio during the sputtering process indicated that Cd and Se were removed from the surface region at the same rate. Overlap of a platinum transition with the S (132 eV) peak precluded any such determination on CdS. The fact that the CdS and CdSe sputtering rates are the same within experimental error indicates that preferential sputtering is not significant.

Results

CdS single crystals. Three CdS single crystals were examined by electron spectroscopy after various pretreatments. One crystal was soaked in 1M NaOH, 1M Na₂S, 1M S solution for 30 min at open circuit under illumination; the other two crystals were used as photoanodes in a PEC with a total charge passed of 2.5 and 12.0 C/cm² in a similar solution. Initial XPS and XPS analysis after immersion and transfer to the spectrometer showed large amounts of C with lesser amounts of O on all of the crystals. The open-circuit crystal showed a small amount of S on the surface which was completely removed with less than 1 min of Ar⁺ bombardment. The C signal was also reduced to its background level with this same amount of sputtering. Whether this S is substituted, as suggested by Heller et al. (9) or merely adsorbed on the surface cannot be ascertained from our data but it is evident that S is only present in the first few atomic layers. A large amount of S was found in the surface region on the crystal which had been anodized for 8.5 C/cm². The ratio of AES peak-to-peak heights for Cd/Se, S/Se, and Se/S as a function of sputter depth given in Fig. 1, suggest that sulfur is substituted to a depth of 40 Å which corresponds to about 13 atomic layers. The high resolution XPS spectra of the S (2p)–Se (3p) and S (2p)–Se (3p) regions after 0.5 and 8 min of sputtering are given in Fig. 2 and 3. Contributions from both Se and S are evident after 0.5 min of sputtering but the S signal is completely gone after 8 min. The C signal on this sample was reduced to its background level by less than 1 min of sputtering. The CdSe crystal which was anodized for 12 C/cm² showed S substitution to a depth of about 60 Å or 20 atomic layers as shown by the atomic ratios of S/Cd, Cd/Se, and Se/S vs. sputter depth for this crystal (Fig. 4). The solid lines are from AES peak-to-peak height ratios corrected for elemental sensitivity as determined from the standard samples. In addition to the crystal which was anodized for 12

![Fig. 1. Atomic ratios of S/Se, Cd/Se, and S/Cd from AES peak-to-peak ratios as a function of sputter depth for a CdSe single crystal electron photoemissed in a 1M NaOH, 1M Na₂S, 1M S solution (2.5 C/cm²).](image1)

![Fig. 2. High resolution XPS spectra of the S (2p)–Se (3p) region of the same CdSe electron in Fig. 1 as a function of sputter time.](image2)
C/cm in 1M NaNO_3, another CdSe crystal was anodized under the same conditions except the solution was also 0.05M in dissolved Se. This has been shown to decrease the rate of current decay of CdSe photoanodes in 1M NaNO_3 under extended electrolysis. A plot of the AES results for this anode in Fig. 3 (compared to Fig. 4) indicates substitution at a depth of 33A. Besides the usual contaminants of O and Cl, traces of Na and SiO_2 were initially present on the surface of this crystal. The Na probably arises from the NaNO_3 solution itself and the trace of SiO_2 could originate from the silicone rubber sealant used to isolate the rear portions of the crystal from the solution, or from attack of the alkaline solutions on the Pyrex cells.

CdSe—CdS single crystals were protected in a manner similar to the CdSe crystals. One was immersed at open circuit for 50 min in 1M NaOH, 0.03M Na_2SeO_3, 0.5M Se solution while two others were anodized in a similar solution for times equivalent to 0.5 and 6 C/cm^2. Again C and O were initially observed on the surface of all of these crystals. The small amount of Se initially present in the open-circuit sample again was removed in less than 1 min of sputtering indicating no Se substitution beyond the surface region. The crystal which had been anodized for 6 C/cm^2 showed a layer of pure Se 250A deep, followed by a region of Se substitution into the CdS about 240A in depth.

This Se overlayer was highly contaminated with C as seen from Fig. 6. The C was essentially reduced to its background level as the region of substitution was approached. We define the region of substitution in this crystal to begin where the C and B signals first appear. The B (2p)—Se (3p) and Se k—ray induced regions as a function of sputter time for the 6 C/cm^2 crystal are shown in Fig. 7. The Se x-ray induced Auger transition, which appears at a binding energy of 178 eV when an Al Kα anode is used for excitation, is also shown. Even after this sample was sputtered for a total of 5 min Se could still be detected, as shown in Fig. 7. This indicates that Se substitution occurs deep into the bulk, >water than 200A in this case. The results on both CdSe and CdS crystals are summarized in Table I.

Table I. Summary of the extent of Se substitution for the CdS and CdSe photoanodes under different operating conditions.

<table>
<thead>
<tr>
<th>CdSe:Se0 — C/cm^2</th>
<th>CdSe:Se5 — C/cm^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open circuit</td>
<td>Open circuit</td>
</tr>
<tr>
<td>2.5 C/cm^2</td>
<td>6.5 C/cm^2</td>
</tr>
<tr>
<td>&lt;15</td>
<td>&lt;15</td>
</tr>
<tr>
<td>60</td>
<td>240</td>
</tr>
<tr>
<td>67 (334 Se)</td>
<td>&gt;800</td>
</tr>
</tbody>
</table>
Discussion

It is clear from the results that S/Se substitution takes place in both systems, i.e. from a polyselenide solution into the CdSe photoanode and from the polysulfide solution into the CdS photoanode. The extent of substitution of Se into CdS is greater than S into CdSe, as indicated by the relative depth of penetration. The solubility product constants for CdS and CdSe are $5 \times 10^{-32}$ and $1 \times 10^{-31}$, respectively, as calculated from thermodynamic data (11). That the substitution of the anion is greatly enhanced on the passage of charge under illumination is clear from the data given in Table 1. The exchange could occur via some initial photo-oxidation of the CdS and CdSe electrodes in a manner suggested by several investigators (4, 12), followed by reprecipitation of the CdS-

$$\text{CdSe} + 2p^+ \rightarrow \text{CdS}^\equiv + \text{Se}$$

[1]

$$\text{Se} + \text{S}^2- \rightarrow \text{SSe}^2-$$

[2]

$$\text{Cd}^2+ + \text{S}^2- \rightarrow \text{CdS}$$

[3]

and

$$\text{CdS} + 2p^+ \rightarrow \text{CdS}^\equiv + \text{S}$$

[4]

$$\text{S} + \text{Se}^2- \rightarrow \text{SSe}^2-$$

[5]

$$\text{Cd}^2+ + \text{Se}^2- \rightarrow \text{CdSe}$$

[6]

Because of the high concentration of the anion in solution the CdS$^\equiv$ will precipitate very quickly as CdS or CdSe. The pure Se layer found in one of the CdS samples can probably be attributed to slow kinetics in [2], as also found by Ellis et al. (13). The newly formed material will probably possess a more polycrystalline character of different composition, as suggested by Geriander and Grobecht (9). A 900-magnification SEM picture (Fig. 8) clearly shows the change in the surface nature of a CdS electrode before and after anodization in a polyselenide solution. The increased roughness and graininess of the surface probably indicates a reconstituted one by the reprecipitation of CdSe to give a surface containing both anions and exhibiting a polycrystalline character with a different doping level, resistivity, adhesion characteristic toward the anions in solution, and electron affinity. We have recently described the behavior of CdSe-CdSe solid solution electrodes (6) and showed that the flatband potential and open-circuit voltage changed with electrode composition. We attributed this behavior to a change in the electron affinity with the change in composition of the anions. Just as the open-circuit voltage ($V_{oc}$) increased with the above solid-solution electrodes at the composition of one of the anions was increased, a similar change in the $V_{oc}$ was observed with the CdS and CdSe photoanodes as the anion substitution proceeded.

The short-circuit current of these electrodes has been shown by several groups (7, 8) and was confirmed in this laboratory, to decrease with operation time. The rate of the initial decrease was greater for higher intensities (initial currents of $5$ to $40$ mA/cm$^2$ corresponding to 50 to 165 mW/cm$^2$ white light intensities). Typical behavior of the photocurrent for a
CdSe operated in a polysulfide solution is shown in Fig. 9. This deactivation can be rationalized in terms of the energy level diagram one can establish for these substituted electrodes. If the operation of these electrodes is carried long enough so that a substituted layer is formed at the surface of the electrode, the energy level diagram for equilibrium condition will be as shown in Fig. 10 for a CdS layer on CdSe electrode and in Fig. 11 for CdSe on CdS. The relative position of the conduction bands for both materials was taken from the electron affinities. From Fig. 10 one sees that a layer of larger bandgap n-type semiconductor on a similar semiconductor of smaller bandgap will tend to inhibit the passage of holes in the surface and the flow of electrons into the bulk. In the opposite situation, i.e., a CdSe layer on a CdS electrode, the flow of holes to the surface is favorable, however, the flow of electrons into the bulk is inhibited as seen in Fig. 11. The magnitude of the barrier is progressively changing as z changes in the CdS...S and CdS...Se, with operation time, where z ≡ 0 means formation of a substituted layer. Other factors to be considered are a lattice mismatch between CdS and CdSe and the possibility of defects at the surface of the newly formed layer which creates traps and thus sites for carrier recombination.

Recently, Heller and co-workers (4) showed that the current blockade in a CdSe electrode can be reduced or eliminated by maintaining an adequate amount of dissolved selenium in the polysulfide solution which resulted in maintaining adequate selenium concentration in the surface film. In this work the results as shown in Fig. 5 indicate that substitution of S for Se into a CdSe electrode operated in a selenium-containing polysulfide solution is appreciably reduced.

In summary, we show in this work that although CdS and CdSe are stable against photodissolution in polysulfide and polyselenide solutions, the latter contribute, through main substitution, to the deterioration of the output parameters, with time of operation.

Acknowledgment

The support of this research by the National Science Foundation (to A.J.B.) and the Office of Naval Re-
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