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Surface analyses of the $\text{CdSe}_{0.65}\text{Te}_{0.35}$ /aqueous polysulfide interface in relation to its photoelectrochemical properties

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The photocorrosion of *n*-Cd(Se,Te) electrodes, in potassium and cesium polysulfide solutions, is investigated by x-ray photoelectron spectroscopy and Auger electron spectrometry. It is shown that Se and Te are exchanged with sulfur from the solution during photocorrosion, possibly via two separate mechanisms: (a) preferential bleaching of tellurium from the crystal matrix, and (b) uniform photocorrosion of the crystal as a whole. Photocurrent spectrum measurements which are presented suggest that a graded band gap is formed when tellurium is preferentially bleached out of the original Cd(Se,Te) crystal. It is shown that cesium is present on the electrode surface which may explain the negative shift of the flat band potential, i.e., increased open circuit voltage of the photoelectrochemical cell. This suggests that the cesium treatment could be used to increase the open circuit voltage of photovoltaic cells.

I. INTRODUCTION

The output stability of Cd-chalcogenide aqueous polysulfide photoelectrochemical cells was investigated extensively in the past,¹⁻⁶ and strong evidence was brought forward that in order to explain its long lifetime in outdoor experiments (over one year in some cases) one must use kinetic arguments rather than thermodynamic ones.^{7,8} X-ray photoelectron spectroscopy¹ (XPS), photoluminescence,³ low-angle x-ray diffraction,⁴ and other techniques established that illumination of the semiconductor electrode leads to the onset of a surface exchange reaction in which chalcogen atoms belonging to the crystal are oxidized to their respective zero valency, dissolved off into the solution, and replaced by sulfur from the solution. This leads to the formation of a polycrystalline layer of CdS, or more likely of a mixed Cd-chalcogenide-sulfide layer which has a protective function and slows down the photocorrosion reaction.

Pseudoternary Cd(Se,Te) alloys were employed as thin films in polysulfide electrolytes and exhibited respectable conversion efficiencies.⁹ The output stability of these alloys was shown to depend on both their tellurium content and on the relative amount of the hexagonal structure in the film.¹⁰ A high-efficiency (12.7%) single-crystal $\text{CdSe}_{0.65}\text{Te}_{0.35}$ /cesium polysulfide was reported recently.¹¹ It has been further established¹² that cesium is preferable as a counterion in the polysulfide solution over all the other alkali metal ions. Both the open circuit voltage, the fill factor, and the output stability were improved by using cesium as a counterion. This was attributed to the higher conductivity and the larger activity coefficient of cesium polysulfide as compared to the other alkali metal polysulfide solutions.^{12(b)} Consequently, the charge transfer kinetics is ameliorated in the cesium solution which may account for the improved performance and out-

put stability of the cell. In addition the flat band potential of the electrodes is shifted cathodically in the cesium solution,^{12(b)} which can explain the higher open circuit voltage obtained with these cells. This observation could be related to the fact that top layers of cesium and oxides thereof reduce the electron affinity of semiconductors,¹³ a property that is being used in photocathodes and thermionic energy converters.¹⁴

It is expected that the mechanism of the photocorrosion reaction is more complicated for the ternary $\text{CdSe}_{0.65}\text{Te}_{0.35}$ alloy than for the binary Cd-chalcogenide analog. We have therefore used x-ray photoelectron spectroscopy and scanning Auger electron microprobe (SAM) and secondary ion mass spectrometry (SIMS) analyses in order to gain some understanding of the photocorrosion reaction of the ternary alloy in polysulfide electrolytes. In particular, the surface exchange between sulfur and selenium and tellurium was investigated in both potassium and cesium polysulfide solutions. Previously Polak used XPS and Auger parameters to investigate $\text{CdSe}_{0.65}\text{Te}_{0.35}$ thin films.¹⁵ It is shown that tellurium is predominantly exchanged during the photocorrosion reaction when potassium is used as a counterion and an almost stoichiometric exchange is observed in the cesium solution. The surface exchange which occurs in a CdSe/polysulfide cell, under illumination, results in an insulating polycrystalline CdS top layer and generally no photocurrent response ensues from that layer. The question which arises now is whether the Te-poor layer which is produced by the preferential bleaching of tellurium from Cd(Se,Te) is also electronically passivated. To answer that question we have carried out some photocurrent response measurements and we observed that under certain circumstances this intermediate layer, between the original Cd(Se,Te) and the top polycrystalline CdS layer, can be photoactive so that

we have produced a graded band-gap material of the form CdSe_{0.65}Te_{0.35}/CdSe_{0.65+y}Te_{0.35-y}/pc-CdS/electrolyte (pc stands for polycrystalline). Applications of this approach are briefly discussed.

II. EXPERIMENT

A detailed account of the synthesis, characterization, and electronic properties of the single-crystal CdSe_{0.65}Te_{0.35} ternary alloy was given before¹⁶ and will be repeated here in short only. Crystals were grown by the vertical Bridgman technique under controlled selenium pressure¹⁷ and cut in the orientations (0001) and (11 $\bar{2}$ 0). Their crystallographic parameters were determined by x-ray diffractometry. Their composition was determined by electron microprobe analyses and from their photoluminescence spectrum.⁶ To prepare electrodes a Ga-In eutectic was rubbed on the back surface of the crystal. The front surface of the electrode was polished and then etched for 20 s in aqua-regia (1:4 HNO₃:HCl mixture). The etched electrode was then immersed in a 10% (by weight) KCN solution for 10 min after which it was introduced into the photoelectrochemical cell. Polysulfide solutions were synthesized according to a previously published procedure.¹² A weighed amount of KOH was dissolved in deionized water and then hydrogen sulfide was bubbled through this solution until the reaction ceased. An equivalent quantity of KOH was added now to neutralize the hydrosulfide and finally an appropriate amount of sulfur was added. Cesium hydroxide was available as a 50% (wt./wt. %) solution. Following the irradiation, in the polysulfide electrolyte, electrodes were thoroughly rinsed with deionized water to dissolve any physisorbed species. To dissolve the chemisorbed polysulfide ion the electrodes were soaked for 10 min in a 10% (by weight) KCN solution and then transferred rapidly to a glove box with inert atmosphere which is connected directly to the XPS spectrometer.

For the Auger experiments electrodes were enclosed in a sealed bottle, which was flushed in Ar gas, and were transferred rapidly to the introduction chamber of the spectrometer.

XPS experiments were performed with an AEI 200B spectrometer provided with a MgK α (1253.6 eV) radiation source, with ~ 0.7 eV linewidth. Both wide scans (1–1000 eV binding energy) and narrow scans (20–40 eV) were made. An Ar ion gun was employed for the sputter etching. A reference surface was prepared by 15 min Ar-ion sputtering of a previously polished crystal. SIMS analyses were carried out on a Cameca IMC 3F secondary ion mass spectrometer with Cs as a primary beam. A Physical Electronics model 590A scanning Auger microprobe was used for the Auger analysis.

III. RESULTS

Figures 1 and 2 show the I - V curves and the output stability curves for two systems: (a) CdSe_{0.65}Te_{0.35} (0001) in a (1;1;1) potassium polysulfide solution (containing one mole of each KOH, K₂S, and S). (b) CdSe_{0.65}Te_{0.35} (11 $\bar{2}$ 0) in a cesium polysulfide solution, 1M with respect to CsOH, Cs₂S,

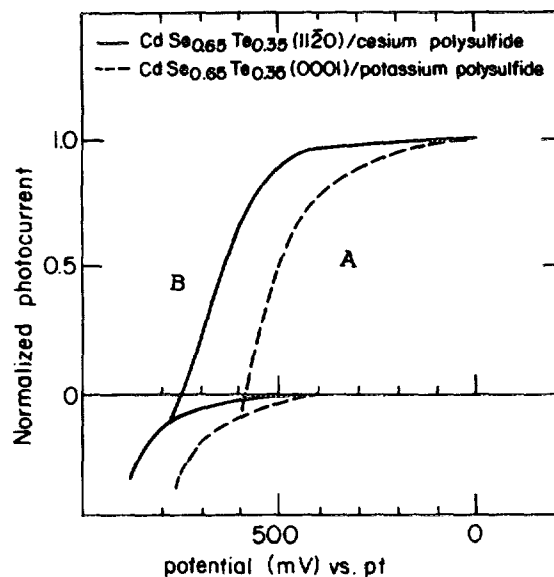


FIG. 1. I - V curves of CdSe_{0.65}Te_{0.35} in a polysulfide solution: (a) (0001) face in a (1;1;1) potassium polysulfide; (b) (11 $\bar{2}$ 0) face in a (1;1;1) cesium polysulfide solution (1M with respect to CsOH, Cs₂S, and S).

and S (1;1;1); and the I - V curve and output stability of CdSe_{0.65}Te_{0.35} with different faces exposed to the solution were similar in the potassium solution. The output stability of Cd(Se,Te) electrodes depends also on the freshness of the polysulfide solution; aging of the polysulfide solutions in the dark was discussed before.¹⁸ In fresh potassium polysulfide solutions one must use stronger light intensities ($> 2\text{AM}1$) to get the typical fast decay of the photocurrent as shown in Fig. 2. It was previously found for CdSe (Refs. 18,19) that the (11 $\bar{2}$ 0) face is more stable against photocorrosion than the (0001) face in a polysulfide solution which is cesium free. It was also shown¹² that CdSe is more stable in cesium than in potassium polysulfide. The main difference in stability between the two photoelectrochemical cells shown in Fig. 2 can be attributed to the counterion. Preliminary SIMS experiments used in the depth profiling mode of CdSe and CdSe_{0.65}Te_{0.35}, which were partially deactivated under illumination in polysulfide solution, were carried out. Surface exchange, with the sulfide from the solution could be evidenced from these measurements. Figure 3 shows the 3p

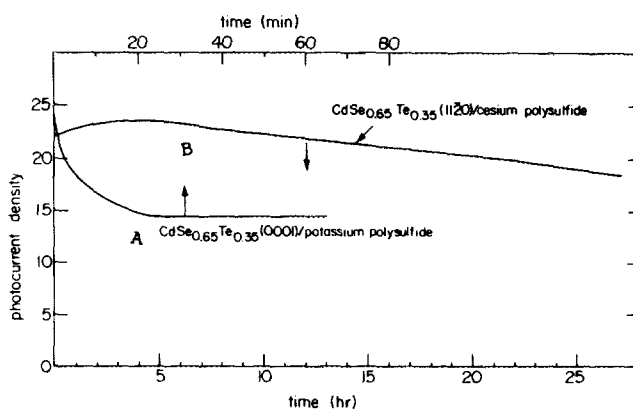


FIG. 2. Output stabilities for the two cells shown in Fig. 1.

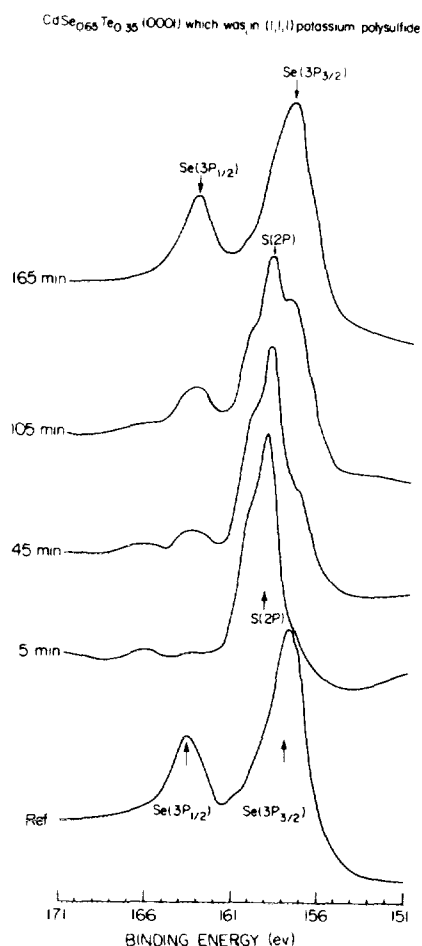


FIG. 3. XPS spectrum (p lines of S and Se) of sample A.

lines of Se and $2p$ line of S for the $\text{CdSe}_{0.65}\text{Te}_{0.35}$ (0001) electrode which was illuminated in potassium polysulfide as shown in Fig. 2. Thus, after relatively short illumination time a substantial exchange is apparent on the surface of the photoelectrode. After 165 min of argon-ion sputtering the original Cd(Se,Te), before photoelectrochemical operation, is almost restored. Although no direct correlation between sputtering time and depth was attempted, the (Se,Te) to S exchange occurred over few hundred angstroms as could be inferred from well-known standards. Figure 4 shows the Se($3d$) line for the same sample. Besides some broadening of the peak there is no obvious change in the line shape after PEC operation which suggests that the selenium atoms do not feel a very different chemical environment around it. A similar conclusion can be drawn for the Cd atoms. However, for the Te $3d$ peaks (Fig. 5) there are some clear changes in the spectrum, i.e., a shoulder appears on the higher energy side of the two main $3d$ peaks. These shoulders could arise from oxides that are produced during PEC operation as well as during excitation of the sample by the x-ray source which may then pick up oxygen from the chamber. They suggest that the tellurium atom is more prone to corrosion, than selenium atoms, in the lattice matrix. Table I contains a quantitative comparison between Cd, Se, and Te content in the analyzed crystal. This calculation was done on the basis

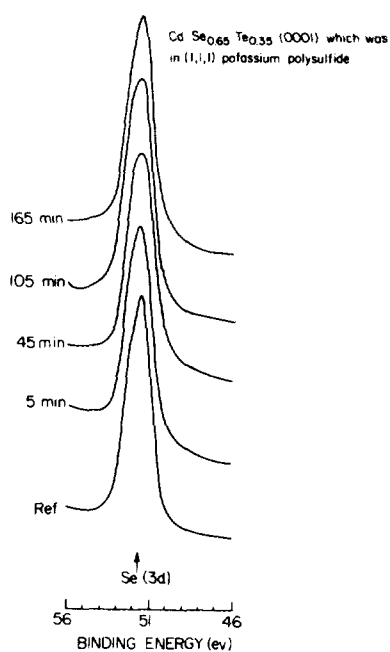


FIG. 4. Se $3d$ lines of sample A.

of the intensities of the $3d$ peaks, assuming the reference electrode had the appropriate composition, i.e., $\text{CdSe}_{0.65}\text{Te}_{0.35}$.

The main conclusion from Table I is that tellurium is preferentially attacked at the semiconductor surface during operation of the photoelectrochemical cell. This result is not unexpected in view of the better output stability of CdSe as compared to CdTe in polysulfide solutions.²⁰

Going now to the $\text{CdSe}_{0.65}\text{Te}_{0.35}$ (11 $\bar{2}$ 0) electrode which was operated for over 1 day in cesium polysulfide solution it was concluded that an extensive (Se,Te) to S exchange occurred on the electrode surface during the illumination peri-

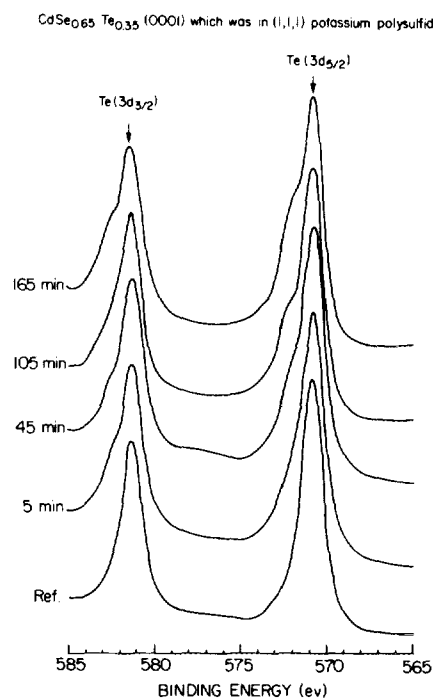


FIG. 5. Te $3d$ lines of sample A.

TABLE I. CdSe_{0.65}Te_{0.35} (0001) which was illuminated in a (1;1;1) potassium polysulfide.

Sputtering time (min)	Relative No. of counts			Composition ^a	Se/Te
	Cd(3d _{3/2})	Se(3d)	Te(3d _{3/2})		
5	4578	749	1494	CdSe _{0.18} Te _{0.07} S _{0.75}	2.57
45	4679	1324	2871	CdSe _{0.32} Te _{0.13} S _{0.55}	2.46
105	4536	1830	4270	CdSe _{0.45} Te _{0.20} S _{0.45}	2.25
165	3473	1957	3602	CdSe _{0.63} Te _{0.23} S _{0.14}	2.74
Reference ^b	7057	4072	11,311	CdSe _{0.65} Te _{0.35}	1.86

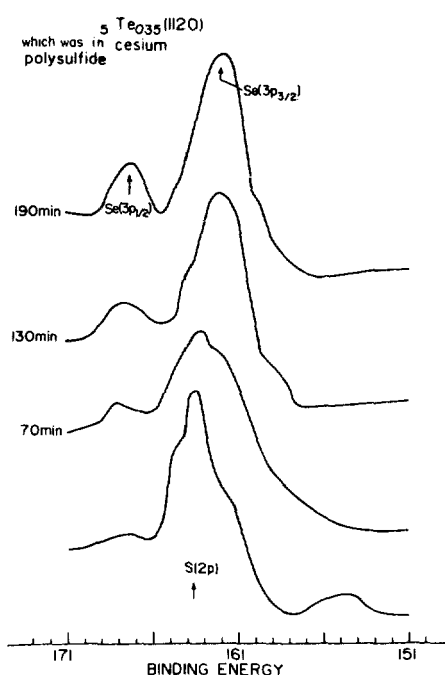
^a The sulfur content was not measured directly but it was calculated from the difference between the sum of anion fraction and one. The Se/Cd and Te/Cd ratio (and therefore the Se/Te ratio) was determined by comparing the number of counts of the CdSe_{0.65}Te_{0.35} reference electrode whose composition was known. The alloy CdSe_xTe_yS_{1-x-y} represents a mixture of Cd_{x+y}Se_xTe_y and (CdS)_{1-x-y} (see Sec. IV for further details).

^b Reference surface was prepared by polish followed by 15 min sputter etch in the preparation chamber of the XPS measurement.

od (see Fig. 6). A shift in the peak position of about 2 eV (to lower energies) was obtained for all elements. We have readjusted the peak positions in Fig. 6 so that they coincide with the expected values. It could be ascribed to some charging or contamination of the sample during the sputtering, or during analyses. Table II gives the calculation of the Se/Te ratio and the Cd(Se,Te) composition during sputtering. Unfortunately this table makes use of the Se(3p_{3/2}) line, since the 3d line was not available in this run.

Contrary to the results obtained in potassium polysulfide, no preferential bleaching of the tellurium atom is observed and the Te/Se ratio of ~2 was preserved throughout the depth profiling in cesium polysulfide (the results obtained for the 70 min sputtered electrode seem not to conform, probably due to an experimental inaccuracy).

In addition to that Te 3d peaks do not exhibit extensive broadening of their line shape upon sputtering. This can be compared to Fig. 5 where shoulders have developed on the high energy side of the two 3d peaks of tellurium.

FIG. 6. (a) *s* and (b) *p* lines of S and Se in sample B of Fig. 2.

Finally, analysis of the cesium 3d and 4d lines was made. The presence of cesium ions bound to the surface is confirmed (see Fig. 7). The cesium peak does not disappear even after prolonged sputtering time (190 min), the height of the peak though is reduced by a factor of 2.5. The existence of the cesium ions may lead to the reduction in the electron affinity of the semiconductor as discussed in Sec. I.

Complementary information was obtained from Auger analysis. Two samples of CdSe_{0.65}Te_{0.35} (0001) were used for this analysis. The time evolution of the photocurrent for both samples is shown in Fig. 8. Although the conditions are quite different from those presented in Fig. 2, and the differences between the cesium and potassium solutions are not as large, it is obvious that the electrode exhibits appreciably larger stability in the cesium polysulfide solution.

Figure 9 shows the wide scan Auger spectra of the two electrodes after they were irradiated as shown in Fig. 8. In the spectrum of the electrode which was irradiated in the potassium polysulfide solution, and which exhibited substantial photocorrosion, no selenium and tellurium signals are observed on the surface. An appreciable amount of oxygen is observed as well as potassium and sulfur. The appearance of oxygen after photocorrosion in polysulfide solution is quite unusual and was not observed with XPS analysis. It could be attributed to the relative long time lag between preparation and the surface analysis (1 day). Carbon, silicon, indium, and sodium are contaminant (the indium source originates from the ohmic contact, the way it leaked from the backsurface is not clear, however). With regards to the electrode which was irradiated in the cesium polysulfide the surface exchange reaction is appreciably slower. Selenium and tellurium peaks are clearly observed and oxygen uptake is much smaller here. Cesium is present on the surface as well as carbon and indium which can be regarded as contaminants. Figure 10 shows the depth profile of the two electrodes which were argon sputtered under similar conditions. It is clear that surface exchange is appreciably more extensive in the electrode which was irradiated in the potassium solution. In accordance with the XPS results it is observed that the relative proportions between Cd, Se, and Te are preserved at the CdSe_{0.65}Te_{0.35} electrode which was irradiated in cesium polysulfide solution.

Contrarily, in the electrode which was irradiated at the

TABLE II. Cd(S_xTe_{1-x}) (11 $\bar{2}$ 0) which was illuminated in (1;1;1) cesium polysulfide.

Sputtering time (min)	Relative No. of counts			Composition ^a	Se/Te
	Cd(3d _{5/2})	Se(3p _{3/2})	Te(3d _{5/2})		
10	2104	244	1571	CdSe _{0.32} Te _{0.16} S _{0.52}	2
70	1037	138	1372	CdSe _{0.37} Te _{0.28} S _{0.35}	1.32
190	1700	401	2581	CdSe _{0.65} Te _{0.33} S _{0.02}	1.97
Reference ^b	10 292	2422	16 731	CdSe _{0.65} Te _{0.35}	1.86

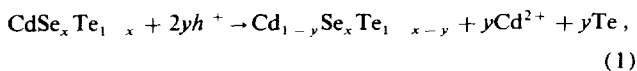
^a See comment on Table I.

^b Reference surface prepared as before.

potassium polysulfide solution this ratio is not preserved and hence the corrosion seems to occur through a different mechanism.

IV. DISCUSSION

The photocorrosion of CdSe_{0.65}Te_{0.35} in aqueous polysulfide may occur by two separate mechanisms, according to the above results. Photocorrosion may occur through preferential bleaching the Te from the solid matrix:



If such a mechanism is prevalent, the remaining Cd_{1-y}Se_xTe_{1-x-y} has a larger effective band gap and hence light absorption and photocurrent may drop quite fast as a function of time, as shown in Fig. 2. This mechanism prevails probably for the CdSe_{0.65}Te_{0.35} (0001) electrode which was illuminated in (1;1;1) potassium polysulfide (see Fig. 2).

If Cd_{1-y}Se_xTe_{1-x-y} is an "electronic grade" material, i.e., has low resistivity and a low density of recombination centers, then by using appropriate conditions for the photocorrosion we can obtain a graded band-gap interface:

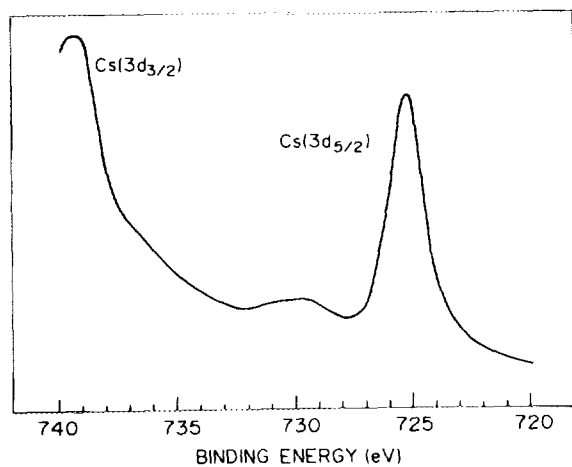
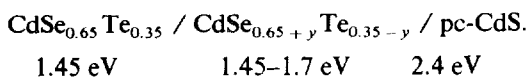


FIG. 7. Cs (3d) lines of sample B of Fig. 2.

The top CdS layer is polycrystalline, with a low conductivity and a very short minority carrier lifetime, and can be either used as a passivating layer, or it can be easily dissolved with HCl. It does not contribute to the photocurrent response because it has a high density of recombination centers and a very short minority carriers lifetime (see Fig. 11), and therefore it cannot be considered as an "electronic grade" material. To check whether the intermediate CdSe_{0.65+y}Te_{0.35-y} layer is of "electronic grade," i.e., if electron-hole recombination is not prevalent there, we have performed some photocurrent response measurements. The light intensity for the photodeactivation experiment was chosen in such a manner that the photocurrent of the n-CdSe_{0.65}Te_{0.35}/potassium polysulfide dropped very fast, in accordance with the experiment shown in Fig. 2 (curve A). Figure 11 shows the spectral response of the crystal prior to and after the photodeactivation process. The appearance of a short wavelength response, in the partially photodeactivated crystal, is obvious especially under forward bias where sampling from a near surface layer occurs. This observation shows that fast photocorrosion of the CdSe_{0.65}Te_{0.35} electrode produces a higher band-gap material at the electrode surface which can be associated with the bleaching of the tellurium. If the crystal was photodeactivated under milder conditions, a gradual decay in the photocurrent occurred and the spectral response did not change appreciably.

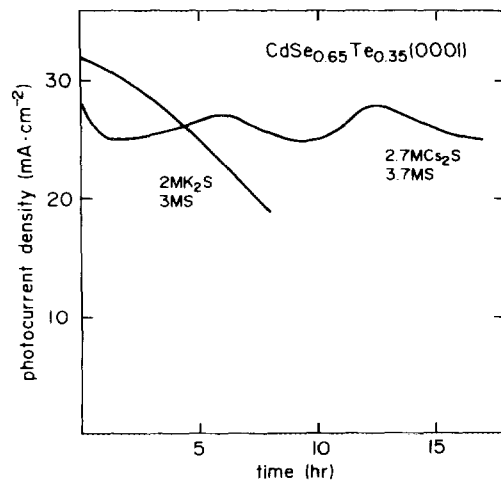


FIG. 8. Output stability of two CdSe_{0.65}Te_{0.35} (0001) electrodes used for the Auger analysis. Solution composition is marked for each curve.

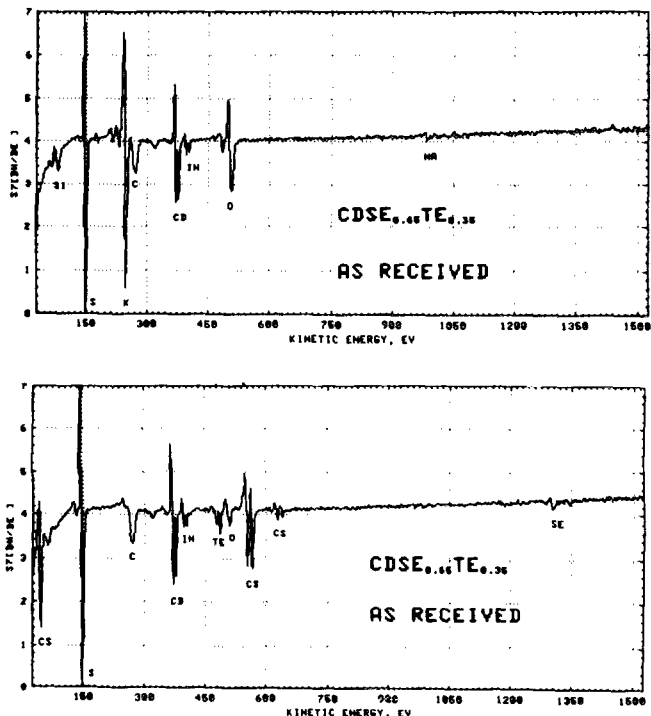
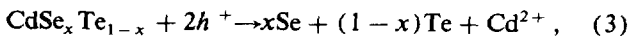


FIG. 9. Wide scan Auger spectrum of CdSe_{0.65}Te_{0.35} which was irradiated in potassium polysulfide (top) and in cesium polysulfide (bottom) solutions.

If photocorrosion of the crystal is uniform, i.e., if Te and Se are oxidized at the same rate, then



In this case, the photocurrent may fall down more gradually since the effective band gap of the semiconductor electrode is

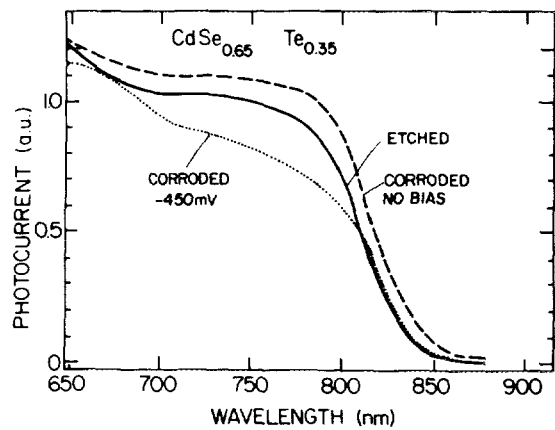


FIG. 11. Spectral response of CdSe_{0.65}Te_{0.35} (0001) in potassium polysulfide, before (without external bias) and after (with and without external bias) partial photodeactivation. Bias vs Pt electrode.

not expected to change appreciably with time (the absorption of the CdS can be neglected due to its high band gap). Further study is necessary to explore this point in more detail.

From the practical standpoint it would be interesting to explore the possibility to carry out the photocorrosion in the absence of sulfide ions in order to avoid the intermixing of the polycrystalline CdS layer with the rest of the crystal. Also it would be interesting to start from a Te-rich *p*-Cd(Se,Te) and to obtain a *p/n* heterostructure by bleaching the Te from the top surface.

The presence of Cs on the electrode surface after prolonged illumination of the Cd(Se,Te) electrode in cesium polysulfide is unexpected. This observation explains probably the cathodic shift in the flat band potential of Cd chalcogenides immersed in a cesium polysulfide solution. Thus, adsorption of cesium ions on the electrode surface may explain the negative shift in the flat band potential^{12(b)} and the higher open-circuit voltage of the photoelectrochemical cell which employs cesium as a counterion. It is tempting to try to use monolayers of cesium oxides for the improvement of other photovoltaic devices.

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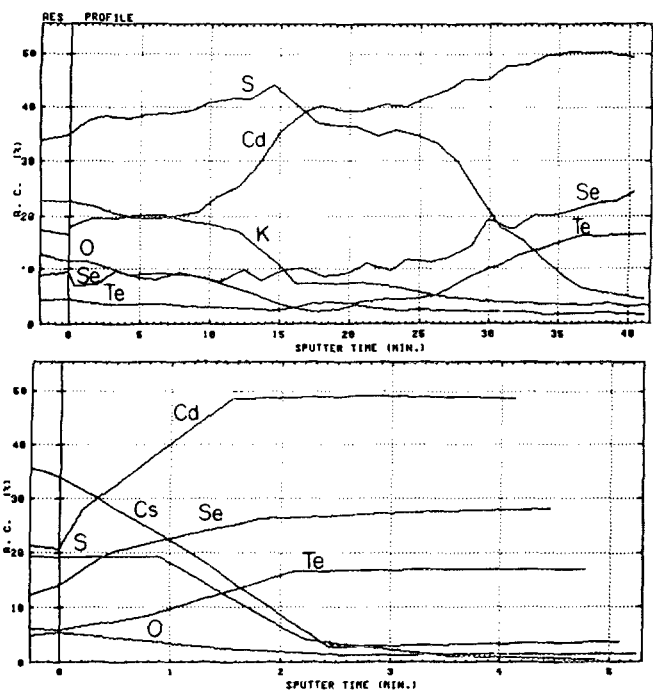


FIG. 10. Auger depth profile of the two electrodes shown in Fig. 9.

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