losses in product isolation and/or derivatization were avoided.

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Semiconductor Electrodes XV. Photoelectrochemical Cells with Mixed Polycrystalline n-Type CdS-CdSe Electrodes

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ABSTRACT

Solid solutions of CdS and CdSe of different compositions were prepared by sintering pressed pellets and vacuum evaporation. The bandgap of the mixtures varied monotonically with percent composition between that of CdS and CdSe. Studies of the photoassisted oxidation of sulfide with these electrodes with a $1M$ Na_2S, $0.1M$ NaOH electrolyte showed that the flatband potentials (V_{fb}) of the mixtures were shifted toward negative potentials with respect to pure CdS and CdSe. Solar cells using these electrodes formulated as (x)n-CdS $(1 - x)$CdSe/$1M$ Na_2S, $0.2M$ S, $0.1M$ NaOH/Pt are described. When $x = 0.9$, for a sintered pellet electrode, a power efficiency of 9% at a cell voltage of 202 mV (irradiation with 577 nm light of 1 mW/cm^2 intensity) was obtained.

There has been much recent interest in the application of n-type cadmium chalcogenide (CdX, where X = S, Se, or Te) electrodes to the construction of photoelectrochemical cells for the conversion of solar to electrical energy (1-14). These materials have bandgap energies (E_g) which are small enough (≤ 2.4 eV) to capture a reasonable fraction of the solar spectrum and can be operated for long time periods with little or no decomposition of the semiconductor electrode in suitable electrolytes (*e.g.*, S^{2-}/S_x^{2-}). Cells with solar energy power conversion efficiencies ($\eta_{p,s}$) of 7-8% (9) and monochromatic light efficiencies ($\eta_{p,m}$) of 9-10% (4) using single crystal CdX electrodes have been reported.

The maximum efficiency of a photoelectrochemical cell utilizing a redox couple with an equilibrium potential, V_{redox}, for conversion of light to electrical energy with no over-all change in electrolyte composition depends upon the flatband potential of the semiconductor, V_{fb}. For a cell with an n-type semiconductor photoanode, the more negative the value of V_{fb}, the greater the possible output voltage (which has a maximum value $V_{redox} - V_{fb}$) and the larger the maximum efficiency. Thus optimization of the semiconductor-electrolyte characteristics involves variation of E_g for optimum match with the solar energy spectrum (15) and V_{fb}. Other semiconductor characteristics of importance include the doping level, which

governs the material resistivity and the thickness of the space charge region at a given bias, the minority carrier lifetime in the bulk and at the surface, and the location and properties of intermediate levels within the gap region. We report here studies of electrodes produced by forming solid solutions of CdS and CdSe of different compositions prepared from sintered, pressed pellets or by vacuum evaporation and used as photoanodes in S^{2-}/S_x^{2-} electrolytes. The effect of composition and sample preparation on V_{fb}, E_g, efficiency and stability were of particular interest.

Experimental

The pellet semiconductor electrodes used in this study were prepared from high purity, reagent grade polycrystalline CdS and CdSe powder (Ventron, Beverly, Massachusetts). Mixtures of the two compounds, which are known to form solid solutions after sintering (16), were milled in acetone for 30 min prior to use. The 0.5 mm thick pellets were pressed at 5000 psi, sintered in a nitrogen atmosphere at 450°C for 12 hr, and then heated in a hydrogen atmosphere for 5 min. The densities of the pellets were about 87-89% of single crystal densities. An ohmic contact was made to the rear of each pellet with gallium-indium alloy. The resistance between the two faces of the pellet after sintering was generally less than 100Ω.

Electrodes were also prepared in a vacuum evaporation apparatus by vacuum deposition of the pure compounds and their mixtures on Pt and SnO$_2$-

coated glass substrates (donated by Texas Instruments, Dallas, Texas). Before the deposition, the Pt substrates were boiled in concentrated nitric acid for 5 min followed by several rinsings with water and then with ethyl alcohol. The SnO_2-coated glass substrates were soaked in alcoholic KOH for 1 hr and rinsed several times with distilled water, followed by baking in an oven at 200°C for 2 hr. The semiconductor films, which were about 1.5 μm thick as determined by weighing the electrode before and after deposition, were annealed first in a nitrogen atmosphere at 400°C for 2 hr and then in a hydrogen atmosphere at 400°C for 5 min. The resistance between the film surface and conducting substrate was less than 1Ω.

A copper wire was attached to the electrodes with conducting silver epoxy cement (Allied Chemicals, New Haven, Connecticut). The back and sides of the electrodes were insulated with epoxy resin cement (Devcon Corporation, Danvers, Massachusetts). The exposed areas of the electrodes were 0.25-1.0 cm². The electrodes were etched in 6M HCl prior to use. The etching times for the sintered and film electrodes were about 15 and 5 sec, respectively. Both polycrystalline CdS and CdSe electrodes show a comparable increase in photocurrent after a similar etching step.

The semiconductors were used as the working electrode in a conventional three-electrode cell with a platinum foil counterelectrode and an aqueous saturated calomel reference electrode (SCE). The semiconductor electrodes were irradiated through an optically flat Pyrex window. The two-electrode, single compartment solar cell contained a platinum foil counterelectrode (about 10 cm²) which was spaced about 0.5 cm from the semiconductor electrode. With this cell the current was measured as a function of load resistance under irradiation with no external power source.

The electrolyte solution (1M Na_2S, 0.2M S, and 0.1M NaOH) was yellow in color and a correction for absorption of the incident radiation by the solution was performed when calculating efficiencies.

For voltammetric measurements, a PAR (Princeton Applied Research, Princeton, New Jersey) Model 173 potentiostat and Model 175 universal programmer were employed. The current-voltage (i-V) curves were recorded using IR compensation on a Houston Instruments (Austin, Texas) Model 2000 X-Y recorder for scan rates less than 1 V/sec. Current-voltage curves at greater than 1 V/sec, obtained for capacitance measurements, were recorded on a Nicolet (Madison, Wisconsin) digital oscilloscope. An Oriel Corporation (Stamford, Connecticut) 450W xenon lamp and Model 7240 grating monochrometer were used to illuminate the electrodes. The radiant power was measured with a Model 550-1 Radiometer/Photometer (E.G. & G., Salem, Massachusetts).

ESCA and Auger electron analysis of the electrodes were carried out with a Physical Electronics Model 548 (Eden Prairie, Minnesota) instrument. The relative amounts of S and Se were determined from the area of the Se $3d_{5/2}$ peak at 54.18 eV as the amount of S increased in the mixture. Small amounts of carbon impurities were detected in the mixtures by Auger electron analysis. The x-ray diffraction spectrum (obtained with a Norelco x-ray diffractometer) of the mixed compound electrodes gave no lines characteristic of either of the pure components, indicating the mixtures were substitutional solid solutions.

Results

Electrode composition.—The composition of the electrodes prepared by sintering was known from the relative quantities of CdS and CdSe employed. The composition of the vacuum-deposited material was known approximately from the amounts of CdS and CdSe used as the source material and the known relative evaporation rates (16); the CdS content of

Table I. Properties of mixtures of CdS and CdSe[a]

Composition		E_g (eV)	$-V_{fb}$ (V vs. SCE)	V_{oc} (V)
% CdS	% CdSe			
Sintered pellets				
0	100	1.70	1.34	0.60
36	64	1.81	1.40	0.66
58	42	1.90	1.45	0.70
67	33	2.05	1.48	0.75
77	23	2.11	1.55	0.91
90	10	2.18	1.65	0.96
95	5	2.25	1.60	0.79
99	1	2.30	1.50	0.75
100	0	2.38	1.42	0.77
Vacuum-deposited films				
0	100	1.75	1.30	—
40	60	1.82	1.40	
63	37	2.00	1.50	
83	17	2.12	1.58	
100	0	2.40	1.40	

[a] For solution of 1.0M Na_2S and 0.1M NaOH under irradiation with white light.

the films was always higher than its relative amount in the source material. These films were analyzed by ESCA and x-ray diffraction, and the results, reported in Table I, are probably accurate to within 5% of the values listed. In general, the electrochemical behavior of sintered and vacuum-evaporated film electrodes of about the same composition was very similar, except where noted.

E_g *and* V_{fb}.—The bandgap energy was determined by noting the longest wavelength (λ) which produced a photoanodic current with the electrode held at potentials 0.60-0.95V positive of V_{fb}. V_{fb} was estimated from the i-V curves and was taken as the potential for the onset of the photoanodic current. Typical i-V and i-λ curves for a film electrode are given in Fig. 1 and the rising portion of the photocurrent-V curves as a function of electrode composition is shown in Fig. 2. The shapes of the i-V curves were similar in solutions of 1M Na_2S and 0.1M NaOH, with and without dissolved sulfur. Values of E_g and V_{fb} for the
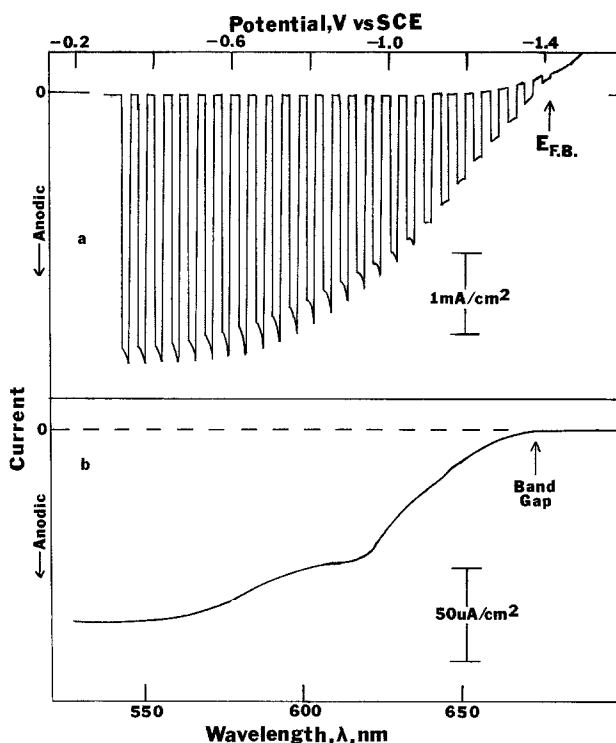

Fig. 1. (a) Photocurrent-potential curve (light chopped at 0.23 Hz); (b) photocurrent *vs.* wavelength at —0.8V *vs.* SCE, for the 40% CdS-60% CdSe evaporated film electrode in 1M Na_2S, 0.1M NaOH.
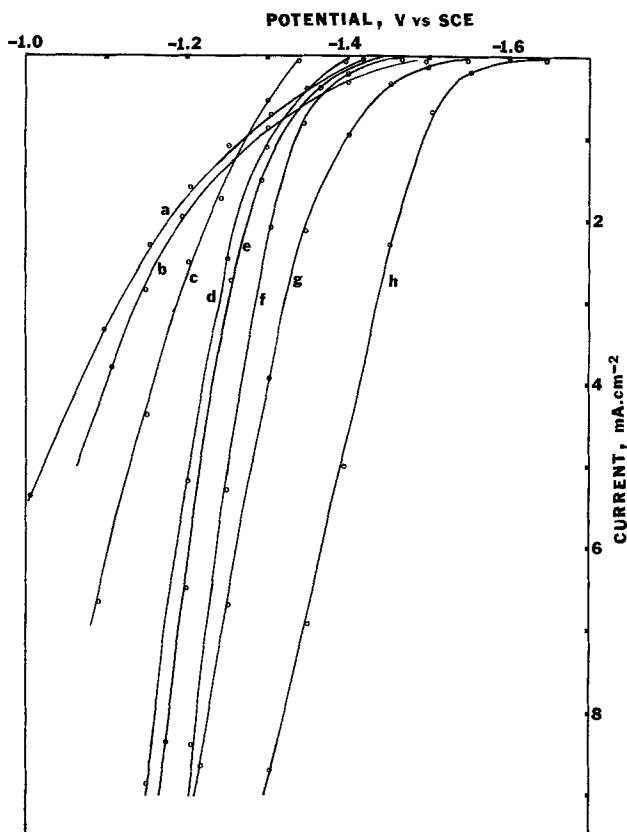
Fig. 2. Photocurrent-potential curves for pressed pellets of the following composition (illuminated with white in 1.0M Na₂S, 0.1M NaOH): (a) 100%CdS, 0%CdSe; (b) 99%CdS, 1%CdSe; (c) 0%CdS, 100%CdSe; (d) 36%CdS, 64%CdSe; (e) 58%CdS, 42%CdSe; (f) 67%CdS, 33%CdSe; (g) 77%CdS, 23%CdSe; (h) 90%CdS, 10%CdSe.
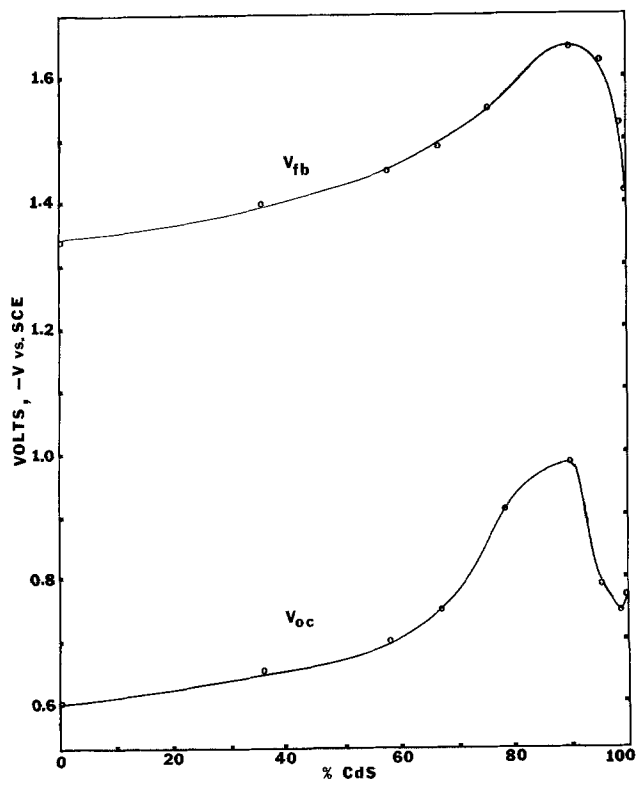

Fig. 3. Values of the flatband potential (V_{fb}) and open-circuit potential (V_{oc}) for pressed pellets containing different amounts of CdS and CdSe in a 1M Na₂S, 0.1M NaOH solution with Pt counter-electrode.

different electrodes are given in Table I; the variation of V_{fb} with electrode composition is shown in Fig. 3. Butler (17) has recommended that V_{fb} be determined not from the potential of onset of the photocurrent but from the extrapolated value of a plot of V vs. (photocurrent).[2] The trend in such extrapolated values with composition generally is the same as that in Fig. 3 but displaced to more positive values. Similar i-V behavior was observed in 0.1M NaOH alone, with the onset of photooxidation shifted in a positive direction by about 0.5V compared to the sulfide-containing solutions. In these solutions the electrodes underwent photodissolution to Cd^{2+}, S, and Se (with the appearance of a yellowish film in the case of CdS-containing electrodes and a gray film on the CdSe electrode) and the photocurrent decreased with time.

The dark anodic curent in 0.1M NaOH at the film electrodes appeared at potentials positive of 0V vs. SCE and bubbles were observed forming on the electrode surface. No dark anodic current was found at the sintered electrodes until potentials well positive of +1.0V vs. SCE. A cathodic current in 0.1M NaOH was observed at potentials just negative of V_{fb}, occurring at slightly more positive potentials at the film electrodes. Attempts to determine V_{fb} from Mott-Schottky plots (18), with the capacitance determined by cyclic voltammetry (19) over a potential range where no dark faradaic current was observed led to intercepts that were frequency dependent. The slopes of these plots showed doping levels between 10^{18} and 10^{20} cm^{-3}.

Efficiency and solar cells.—The quantum efficiency for electron flow, Φ_e, defined as the number of electrons flowing in the external circuit divided by the number of photons impinging on the electrode, was $100 \pm 2\%$ for all electrodes maintained at -0.70V vs. SCE. The open-circuit voltages, V_{oc}, of the two-electrode solar cells (x)n-CdS $(1 - x)$CdSe/1M Na₂S, 0.2M S, 0.1M NaOH/Pt measured between the illuminated sintered semiconductor electrode and the platinum cathode are listed in Table I. The maximum value of V_{oc} is $V_{fb} - V_{redox}$, where V_{redox} is -0.7V vs. SCE (4, 20-23). The trend in V_{oc} with electrode composition followed very closely that of V_{fb} determined from the i-V curves, with a maximum with an electrode composition of about 90% CdS-10% CdSe (Fig. 3). The open-circuit photopotentials were dependent on light intensity. For example, in the case of the measurement made using the 67% CdS-33% CdSe, when white light from the 450W xenon lamp was reduced by 50%, the open-circuit potential, V_{oc}, decreased from 0.75 to 0.66V; at intensities reduced to 10 and 1%, V_{oc} was 0.58 and 0.45V, respectively. Similar dependence was observed when measuring the potential drop through a 1000Ω resistor. This dependence on light intensity was also evident when measuring solar cell efficiencies. The $\eta_{p,s}$ of the 90% CdS-10% CdSe sintered material electrode was measured to be about 1% for solar intensities of about 75 mW·cm^{-2} compared to 5.9% with an attenuated solar intensity (using neutral density filters) of 1.1 mW·cm^{-2}. A similar decrease of efficiency with increasing irradiation intensity was also observed by Wrighton et al. (3, 4) in CdS and CdSe cells. The monochromatic light power efficiency, $\eta_{p,m}$, of the photoelectrochemical cell, defined as the ratio of the output power across the external load resistor to the incident radiant power, was determined with 577 nm light (12 nm bandpass) with an intensity of 1 mW·cm^{-2}. For the 90% CdS-10% CdSe sintered pellet with a 1000Ω load resistor, the output voltage was 202 mV and the current was 0.45 mA·cm^{-2}, yielding $\eta_{p,m} = 9\%$. The maximum value of $\eta_{p,m}$ found with the film electrodes was with the 60% CdS-40% CdSe material on Pt substrate with a 800Ω load resistor, and incident power of 0.4 mW·cm^{-2}. $\eta_{p,m}$ was 7% with an output voltage of 157 mV. The measured $\eta_{p,m}$ and $\eta_{p,s}$ values were quite vari-

able from electrode to electrode; this can be attributed to the high and variable internal resistance of the sintered electrodes and the poor adhesion of the vacuum evaporated films to the substrates, particularly the SnO_2-coated glass. Separate experiments in which the sintered electrodes were used as photoanodes in stirred solutions containing $1M$ NaS, $0.2M$ S, and $0.1M$ NaOH for periods (about 14 hr) which would have been sufficient to dissolve all the electrode material by photooxidation of the lattice showed weight loss of about 1%. This small loss was attributed to surface erosion of the pressed pellets during the long periods of stirring and soaking of the electrode. The stability of the cell current was dependent on the sulfide-polysulfide concentration. For example, when the solution contained $1M$ S and the initial current density was 16 mA·cm^{-2} (100Ω load) the current dropped to about 55% of its initial value in 14 hr. With $0.2M$ S, the current dropped to 26% of its initial value after the same period of time. Furthermore, when illumination was interrupted for several minutes and then resumed the onset current would reach a value slightly smaller than its initial value. After a 10 sec etch in $6M$ HCl, the current would attain almost its initial value.

Discussion

The mixtures (x)CdS $(1 - x)$CdSe gave the expected monotonic variation of E_g as the composition was changed from pure CdS to pure CdSe (16, 24). It is particularly interesting that the variation of V_{fb} with x shows a maximum (Fig. 3) with the mixture where $x = 0.9$ having a V_{fb} ca. 0.2V more negative than either pure CdS or CdSe. To seek the reason for this behavior let us consider the factors that affect V_{fb}. These include the electron affinity of the semiconductor (EA), the potential drop through the Helmholtz layer (V_H), the potential drop across the diffuse double layer (V_d), and the difference between the Fermi level and the conduction band $(E_F - E_C)$; to put V_{fb} on a scale relative to a given reference electrode using the absolute EA (in eV), a constant term, E_{ref}, usually taken as ca. 4.75 eV for the SCE vs. the vacuum level (25) is used. The following equation, which is an extension of one given by Butler and Ginley (26), can then be written

$$V_{fb} = \frac{EA}{e} - \frac{E_{ref}}{e} - (V_H + V_d) + \frac{(E_F - E_c)}{e} \quad [1]$$

Taking $E_F - E_c$ as 0.10 eV, $E_{ref} \simeq 4.75$ eV, and assuming a negligible drop across the diffuse double layer $(V_d \sim 0)$ this can be written

$$V_{fb}(V) \simeq \frac{EA}{e} - 4.7 - V_H \quad [2]$$

The values of V_{fb} for CdS and CdSe in NaOH and in the presence of S^{2-} taken from various sources are shown in Table II. The V_{fb} values for CdS and CdSe in sulfate media are independent of pH (4, 27) and the relative values agree quite well with those pre-

dicted from E_g and the intrinsic Fermi level (E_F^i) calculated by Nethercot (28) from electronegativities. In the latter case E_F^i is calculated from the Pauling electronegativities for the atoms A and B (χ_A and χ_B) using the equation (28, 29)

$$E_F^i = 2.86(\chi_A\chi_B)^{1/2} \quad [3]$$

If one takes EA as the difference in energy between the conduction bandedge and vacuum (26), then

$$EA = E_F^i - E_g/2 \quad [4]$$

Calculated EA values are shown in Table II. When these values are used in Eq. [2], a V_H of about 0.9 (± 0.1)V is obtained for both CdS and CdSe in the NaOH medium. The addition of S^{2-} causes the V_{fb} values to shift toward negative values by about 0.5V for CdS and 0.7V for CdSe (4) presumably because specific adsorption of S^{2-} causes a change in the voltage drop across the Helmholtz layer (to about 1.4 and 1.6V for CdS and CdSe, respectively).

Thus the change in V_{fb} with composition could be ascribed to changes in the EA or specific adsorption (V_H). The fact that the same sort of maximum of V_{fb} with composition is observed for NaOH solutions in the absence of S^{2-} suggests that this variation can be attributed to changes in the EA and that the introduction of small amounts of CdSe into the CdS lattice yields a material with a significantly smaller EA. However it is also possible that the composition of the surface layer of these electrodes changes upon immersion or operation in the sulfide electrolyte medium. Under these conditions a junction potential could arise between the surface layer and the bulk semiconductor which would affect the observed V_{fb} values obtained under illumination. Investigations of the changes in the electrode surfaces by ESCA and Auger electron spectroscopy are currently underway in this laboratory.

It is of interest to consider in a general way how the efficiency of a photoelectrochemical solar cell varies with E_g and V_{fb}. For irradiation with light of energy equal to that of the bandgap the maximum efficiency, or the so-called open-circuit voltage efficiency (15), is

$$\eta_{p,m}(\text{max}) = \frac{(V_{redox} - V_{fb})e}{E_g} \quad [5]$$

Thus both the maximum output voltage and efficiency depend upon V_{fb}. When one considers the solar energy efficiency of a threshold semiconductor device the ultimate power efficiency, η_{ult}, depends upon the value of E_g [as given in Ref. (15), Eq. [2], and Fig. 3]. Thus, considering the variation of both V_{fb} and E_g, the maximum (open-circuit voltage) efficiency for solar irradiation is $\eta_{p,m}(\text{max}) \, \eta_{ult}$; typical curves showing the efficiency (for AM1 sunlight) are given in Fig. 4. With these curves and the V_{fb} and E_g values

Table II. Characteristic data for CdS and CdSe

	V_{fb} (0.1 M NaOH)	V_{fb} (1.0M Na$_2$S)	$E_F^{i\,d}$ (eV)	E_g^e (eV)	EA^f (eV)
	(V vs. SCE)				
CdS	−0.90[a] −0.80[b]	−1.4[a] −1.42[c]	5.90	2.46	4.67
CdSe	−0.70[a]	−1.45[a] −1.34[c]	5.78	1.68	4.94

[a] From Ref. (4).
[b] From Ref. (4) and (27).
[c] This work.
[d] From Ref. (28), calculated using the following Pauling electronegativities (χ_D): Cd, 1.7; S, 2.5; Se, 2.4.
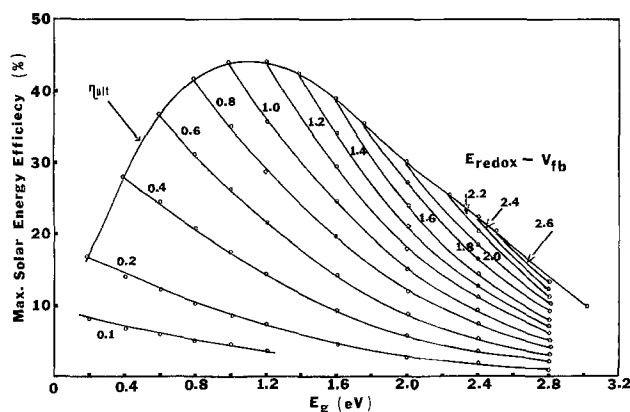[e] From Ref. (28)
[f] Calculated using Eq. [4].

Fig. 4. Maximum solar efficiency (AM1 sunlight) for various values of E_g and ($V_{redox} - V_{fb}$). Values of η_{ult} used in preparing this figure from (15).
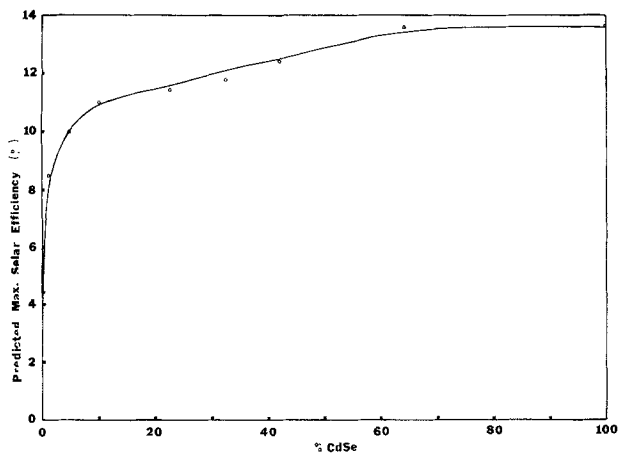
Fig. 5. Predicted maximum solar efficiency vs. composition for the (x)CdS $(1 - x)$CdSe system with S^{2-}, S_x^{2-} electrolyte.

of the various CdS-CdSe mixtures a plot of maximum solar efficiency as a function of composition can be derived (Fig. 5). The results suggest that the addition of only a small amount of CdSe greatly improves the maximum efficiency of a CdS electrode. Although the efficiency in this case is smaller than that of CdSe alone, this principle when applied to other systems could, by suitable manipulation of V_{fb} and E_g, yield higher efficiencies than the pure compounds.

Solid solutions such as (x)CdS $(1 - x)$CdSe may also be utilized in preparing a film electrode with a gradient composition, i.e., an increasing CdSe content with depth. This would allow one to take advantage of the negative shift in V_{fb} at the solution interface (with high CdS content), and to absorb a greater fraction of the visible spectrum further into the space charge region (with the higher CdSe content). Work is currently being carried out in our laboratory to improve the conductivity of the pellets and extend the concept of solid-state solutions to other semiconductor systems.

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