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SOME EXPERIMENTAL ASPECTS OF THE CADMIUM-TELLURIUM, ELECTROCHEMICAL CODEPOSITION PROCESS

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SOME EXPERIMENTAL ASPECTS OF THE CADMIUM-TELLURIUM, ELECTROCHEMICAL CODEPOSITION PROCESS

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ABSTRACT

Steady-state and variable-frequency illumination is employed to examine the photovoltaic properties of electrodepositing Cd-Te thin films. The effect of illumination on the composition of Cd-Te deposits formed with a triangular-wave current source is demonstrated. It is shown by means of optical and electron microscopy that a rectangular-pulse current source significantly influences the surface morphology of Cd and Cd-Te electrodeposits .. The photoactivity of Cd-Tedeposits is found to depend on the pulse-current frequency.

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Introduction .

The unique physical properties of CdTe are reflected by the large number of devices constructed from this material. Numerous publications in the scientific literature are devoted to the study of CdTe fabrication processes and material characterization (see Reference 1, and references cited therein). Perhaps the most promising application of CdTe lies in the fabrication of photovoltaic devices. In 1956, Loferski {2} presented a theoretical treatment to aid in the selection of the optimum semiconductor for photovoltaic solar-energy conversion. The semiconductor yielding the highest efficiency, defined as the ratio of the maximum electrical power output to the solar-power flux incident to the semiconductor surface, was CdTe.

Thin films of CdTe have been prepared by chemical vapor deposition, vacuum evaporation, and electrodeposition processes. As is the case in the present study, most Cd-Te codeposition processes make use of an aqueous, cadmium sulfate, tellurium dioxide, sulfuric acid electrolyte {3-12}. Since the costs associated with thin-film electrodeposition processes are generally less than the previously mentioned fabrication techniques, this study is particularly relevant to the fabrication of large-area, CdTe solar cells.

In this study, we investigate the Cd-Te codeposition process by analyzing the photoresponse of a forming electrodeposit. The photoresponse of a forming Cd-Te electrodeposit is dependent on the electrodeposit composition; hence, collecting current-potential data while simultaneously illuminating the electrodeposit can provide valuable information regarding the Cd-Te codeposition process. We also investigate the effect of employing a pulse-current source, during the Cd-Te codeposition process {in the absence of light}, on the resulting deposit surface morphology and photovoltaic properties. As will be discussed below, a pulse-current source has been shown to improve the mechanical properties of cadmium electrodeposits: because of this, we are motivated to study the influence of a pulse-current source on the codeposition of Cd and Te. Coherent films of pure Te, however, cannot be electrodeposited from aqueous, sulfuric acid electrolytes and are not addressed in this study.

Experimental

The interfacial and homogeneous reactions relevant to this study are listed in Table 1. The Cd-Te codeposition process usually takes place with nearly 100 percent current efficiency-reactions *iii* and v are listed only for completeness. In our deposition studies, $0.3-M-H₂SO₄$ was used as supporting electrolyte. The aqueous, sulfuric acid electrolytes were prepared from analytical-reagent-grade chemicals and distilled water that was passed through a Culligan water-purification unit

t Reaction *i* represents the reference-electrode reaction used in the experiments.

Table 1. Reactions

consisting of an organic trap, a deionizer; and a microfilter. The specific conductance of the treated water was 15 Mohm-cm. Nitrogen, first equilibrated with a similar electrolyte, was bubbled through the cell solution for 1 hour prior to experiments. A nitrogen atmosphere was maintained above the electrolyte during the experiments. The Cd^{2+} species was obtained by adding cadmium sulfate, and the $HTeO₂⁺$ species resulted from adding tellurium dioxide to the electrolyte (reaction vi of Table 1). HTeO₂ is only sparingly soluble in aqueous, acidic solutions (13-17). The bulk concentration used in the present experiment was 0.001 M $HTeO₂⁺$, just slightly below the maximum solubility in the electrolyte. The Cd^{2+} bulk concentration was maintained at 0.1 M. Polycrystalline, cadmium rotating-disk electrodes (RDE's) were used. Standard metallographic polishing techniques were employed to remove all projections greater than 1μ m in height. The electrodes were cleaned with a dilute nitric acid solution before each experiment. The potential of the working electrode was measured against a mercury-mercurous sulfate reference electrode. The morphology of the developing electrodeposit was investigated in situ by placing a microscope, equipped with a camera (which contained Polaroid High Speed Land Film, type 47) below the glass-bottom cell. The photoresponse of the electrodeposit was investigated with a chopped light source that was placed below the electrochemical cell, the with light beam incident normal to the working-electrode surface. A Princeton Applied Research model 173 potentiastat/galvanostat controlled the operation of the cell. An Interstate F77 function

generator was used with the potentiostat/galvanostat. The data were stored on a Nicolet 1090A digital oscilloscope and later transferred to an HP9825A computer.

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The Periodic Electrodeposition of Cadmium

In this section, the effect of a rectangular-pulse-current source on the cadmium electrodeposit morphology is reported. Pulse-current electrodeposits of Cd have been observed to exhibit superior mechanical properties relative to deposits formed with a direct-current source (18,19). Figure 1 illustrates the pronounced effect of a rectangular-pulse-current source on deposit morphology. The photographs, obtained *in situ*, of the 1μ m-thick deposits were taken of the disk center. The maximum current density during the pulse on-time was one half the steady-state, Cd^{2+} -limiting-current density. The on-time was equal to the off-time; no current was passed during the off-time. Because of these conditions, the ratio of the Cd^{2+} surface concentration to the Cd^{2+} bulk concentration oscillated between 0.5 and 1.0. The resistance to Cd^{2+} mass transport was not significant in these experiments. For the direct-current electrodeposition process, the cell current was one-fourth the steady-state, Cd^{2+} limiting current. Thus, the average current for the pulse-current and direct-current experiments was identical. A series of photographs of Cd deposits, obtained at various pulse-current frequencies, is presented in reference 20. It was found that for these conditions, a 100.-Hz rectangular-pulsecurrent source formed the smoothest and most-coherent metallic film.

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Since the Cd-electrodeposit morphology is strongly influenced by the frequency of the cell-current source, we were motivated to study the effect of a pulse-current source on the Cd-Te-electrodeposit characteristics.

The Periodic Electrodeposition and Characterization of Cd- Te Thin Films

In this section, we address the atomic composition, phase structure, surface morphology, and photoresponse of Cd-Te electrodeposits. An x-ray analyzer was used to evaluate atomic compositions, and an x-ray diffractometer was employed to elucidate deposit phase structure. Scanning-electron microscopy provided information on the surface morphology. The photovoltaic properties of the Cd-Te deposits were investigated by means of steady-state and transient photoresponse experiments. _

To study the codeposition process, the experiments outlined in Fig. 2 were implemented. A low-frequency triangular current source with a minimum cathodic current density of 0 and a maximum cathodic current density of 5.1 mA/ $\rm cm^2$ is shown in the upper plot of Fig. 2. In the lower illustration of Fig. 2, the potential

response is given for varying illumination intensities. The deposits were illuminated with a 150 watt, tungsten-halogen, fiber-optic light source (Dolan-Jenner Industries, Inc., Model 510 Fiber-Lite). The potential response labeled "DARK" was obtained for no illumination of the deposit during the electrodeposition process. The two other potential response curves correspond to low- and high-illumination intensity, respectively, incident to the forming electrodeposit. At the beginning of the current ramp, the deposit is mostly Te. As the cell-current density approaches 1.5 times $i_{HTeO_4^+,lim}$, the diffusion-limited current density of the HTeO₂⁺ species, the deposit composition nears 1:1 mole ratio of Cd to Te (1:1 CdTe), and a photoresponse is seen.² The light, which generates minority carriers (electrons) in the p-semiconductor, displaces the electrode potential to more-positive values around the peak cathodic current density. Near zero current, the deposit surface is mostly metallic Te and no longer a semiconductor. It is apparent from Fig. 2, however, that the open-circuit potential (at 300, 600, and 900 s) is a function of the illumination intensity. This is due to the different deposit compositions, which have been altered by the incident light source during the deposition process. For higher illumination intensities, more Cd is incorporated into the electrodeposit, and a more cathodic potential is observed at zero current.

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The preceding analysis is supported by the results displayed in Fig. 3. To obtain the data shown in the right-hand plot of Fig. 3, the experiment outlined in Fig. 2 was conducted with an additional variation: the fiber-optic light source was chopped to create a pulse-light source of low duty cycle; the on-time to offtime ratio was 0.1. Two key conclusions can be formulated from the analysis of Fig. 3. First, the pulse-light source of low duty cycle can be used to obtain *in situ* the photoresponse of the forming electrodeposit. During the off-time, a potential-response curve similar in form to the dark potential response in Fig. 2 was obtained. Since the total number of photons absorbed by the electrodeposit was very small throughout the deposition process, because of the pulse-light source being of low duty cycle, the composition was not substantially altered by the light source. During the on-time, a second potential-response curve was obtained, positive to the off-time data. The difference between the on-time and off-time traces represents the *in situ* photoresponse of the electrodepositing material. The second conclusion to be drawn in the analysis of Fig. 3 concerns the open-circuit behavior of the electrochemical system. Comparison of the potential response for the dark experiment with that of the pulse-illumination experiment shows that nearly iden-

²Since the concentration of HTeO₂ is much lower than that of Cd²⁺, and Te is more noble than Cd $(U_{Te/HTeO_2^+}^{\theta} = 0.55 \text{ V}$, and $\bar{U}_{Cd/Cd^2+}^{\theta} = -0.40 \text{ V}$, the HTeO₂⁺ species is diffusion limited when 1:1 CdTe is electrodeposited. As can be readily ascertained from Table 1, for 1:1 CdTe to be formed, i_{Cd} ₂+ = $i_{HT*O_2^+}/2$. The HTeO₂⁺ species, however, is diffusion limited, consequently $i_{\text{TOTAL}} = 1.5 \times i_{\text{HTeO}^+,\text{lim}}$

tical open-circuit potentials are obtained for these two experiments, in contrast to the values for the open-circuit potentials of the constant-light-source experiments displayed in Fig. 2. Because the integrated amount of light striking the deposit is small for the pulse-light source of low duty cycle, the electrodeposit composition is virtually unchanged by the light source, and the electrodeposit obtained from the dark experiment has the same composition as that of the deposit formed while illuminated with a pulse-light source. Near zero current, the electrodeposit surfaces are composed primarily of metallic Te and are no longer semiconducting or photovoltaic. Since the deposits are of identical composition, and the surfaces are not photovoltaic near zero current, identical open-circuit potentials are obtained.

The effect of a pulse-current source on the electrodeposit morphology is displayed in the scanning-electron micrographs of Fig. 4. The electrolyte composition and temperatures are listed in the figure caption. Deposit compositions were 47 \pm 2 atomic percent Cd, measured *ex situ* with a Kevax AMR 1000 x-ray analyzer. The deposit depicted in Fig. 4a was obtained with a direct-current source of $1.5 \times i_{\text{HTeO}} t_{\text{lim}}$. The rectangular-pulse-current source used to obtain the deposits shown in Figs. 4b and 4c had zero current during the off time, and an on-time cathodic current density of $1.7 \times i_{\text{HTeO}_2^+,lim}$. The factor 1.7 (instead of 1.5) placed more Cd in the deposit and compensated for some of the Cd dissolution during the off-times. In reference 21, the authors have presented a mathematical model, and complementary experimental results, which can be used to predict the composition of Cd-Te deposits for any specified cell-current source. Although there is a significant difference between the surface morphology for the direct-current deposit versus the pulse-current deposits, micrographs of the latter electrodeposits all displayed similar surface morphologies. The pulse-current sources produced deposits with amorphous, nodular structures. The direct-current source produced a smooth, coherent film covered with faceted crystals.

Solar-cell-grade CdTe is usually deposited from aqueous, sulfuric acid electrolytes at higher temperatures to promote large-grain growth in the electrodeposit. The electrolyte temperature used in the deposition of the sample shown in Fig. 4c was 85 \pm 0.5°C. High-temperature data for $i_{\text{HTeO}^{\pm},lim}$ (20) were used as a guideline for the production of nearly 1:1 CdTe. A spectrum of cell-current frequencies were employed in the high-temperature experiments; the compositions of the resultin"g deposits are given in Table 2. In general, the electron micrographs for the pulse-plated electrodeposits were similar to those obtained for the 25°C electrolyte. The diameters of the spherical nodules, however, were larger in the high-temperature experiments, as can be seen by the comparison of Figs. 4b and 4c. The larger diameters of the spherical nodules may be due to the fact that approximately 3 times as much material was deposited in the 85°C experiments relative to the 25°C experiments. The spheres are more developed and separate in

Sample	Frequency of	Atomic % Cd	Atomic % Cd
Number	Current Source (Hz)	(disk center)	(disk edge)
	0.10	47.5	48.5
2	1.00	45.5	45.8
3	10.0	47.0	47.3
	100.	46.0	46.0
5	1000	46.7	48.8
Mean Composition:		46.5	47.3

Table 2. Compositions of pulse-plated, CdTe electrodeposits.

the 85° C experiments than in the 25° C experiments—this is probably attributable to the etching process completed for the electrodeposits formed at 85°C. (The deposits formed at 25°C were not etched.) As predicted by potential theory, and shown in Table 2, more Cd deposits at the outer edge of the RDE. The $HTeO₂⁺$ species encounters much greater mass-transport resistance, diminishing the effect of the electric field on its reaction distribution, which is nearly uniform.

The electrodeposits had slightly more Te than Cd; consequently, these deposits were p-semiconductors. Trace amounts of lead, plutonium, thallium, and uranium were also detected in some of the electrodeposits. To evaluate the photoresponse of the different high-temperature electrodeposits, the following experiment, illustrated in Fig. 5, was completed for each deposit. After approximately a 3μ m-thick Cd-Te film had been formed, the deposit was etched in a 50° C, 10-M-NaOH solution for 1 min. During the etching process, the disk-rotation rate was maintained at 2000 rpm. The NaOH etch solution has been found to be effective in previous studies of p-CdTe (22). Immediately afterwards, the disk electrode was placed in a 1.O-M-NaOH solution at 25°C and kept stationary. A O.l-Hz (on-time equal off-time), rectangular-square-pulse light source was then employed, along with the low-frequency, triangular current-sweep shown in Fig. 5. During the photoresponse analysis, the following electrode reaction took place:

$$
2H_2O + 2e^- \rightleftharpoons 2OH^- + H_2.
$$

For all of the electrodeposits tested, the maximum photoresponse was observed during the first 20 seconds, during which time $|i|$ < 3.0 mA/cm². In Fig. 6, the effect of the etching process on a lOO.-Hz electrodeposit is portrayed. In the upper plot, no etching of the 100.-Hz electrodeposit was completed prior to the photoresponse experiment; consequently, no significant photoresponse resulted. In the lower plot, after I minute of the NaOH etching process previously described,

the resulting potential response was obtained. The etch process is an important aspect of semiconductor-electrode pretreatment and has been investigated by a number of authors for CdTe photovoltaic materials. Takahashi *et* al. (12) noted a similar relationship between the etching process and the photoresponse for CdTe electrodes. Gaugash and Milnes (23) tested ten different etch solutions for CdTe electrodes. Their results indicated that a Te-rich surface layer often resulted. This might be explained by the more noble character of Te relative to Cd.

As can be seen in Fig. 6, no significant photoresponse results after 20 seconds. In Fig. 7, the low current density photoresponse, corresponding to short times in Fig. 6, is presented. Again, the light source depicted in Fig. 5 was used. The current was swept linearly from 0 at a rate of $-60 \mu A/cm^2 - min$. The periodic potential response shown in Fig. 1 indicated that no significant electrodeposit corrosion occurred: the surface remained unaltered after the experiment was duplicated 25 times. The authors have recently presented (24) a mathematical model that can be used to describe the transient and periodic illumination of a semiconductor-electrolyte interface, provided that all of the physicochemical parameters of the system are known. In an effort to compare the photoresponse of the different electrodeposits listed in Table 2, the potential response for the experiment outlined in Fig. 5 was obtained for each electrodeposit. The amplitude of the periodic potential response for each deposit is plotted in Fig. 8 for each electrodeposit listed in Table 2. The deposit created with the lOO.-Hz cell-current source yielded the largest photoresponse.

Although it is clear that a pulse-current source influences the morphology of both Cd and CdTe thin films, it cannot be said without further evidence that this explains the data of Fig. 8. As shown in Table 2., the are significant variations . in deposit compositions, and it is well known that the photovoltaic properties of semiconducting materials are usually sensitive to even slight changes in composition. Although the results of Fig. 8 cannot be used to draw sharp conclusions, they do point to interesting possibilities with regard to the use of a pulse-current source for fabrication processes of semiconductor devices.

X-ray diffraction patterns indicated that the deposits were polycrystalline, containing little long-range order. Lower pulse-current frequencies and higher electrolyte temperatures yielded sharper x-ray diffraction patterns, indicating more long-range order. Because of the polycrystalline, disordered nature of the electrodeposits, quantitative information regarding the amount of each phase present could not be obtained from the x-ray diffraction patterns.

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Conclusions

The codeposition of Cd and Te represents an intriguing process problem with unique. chemistry. Photoresponse results are presented for the *in situ* investiga-

tion of the Cd-Te codeposition process. A pulse-light source of low duty cycle, in conjunction with a triangular current source, was employed to resolve anomalous open-circuit potentials of the illuminated Cd-Te-CdTe/electrolyte interface. The effect of a pulse-current source on the Cd-deposit morphology was analyzed *in situ* and in the absence of significant mass-transport resistance. Photoresponse measurements and scanning-electron micrographs were used to illustrate the influence of a pulse-current source on the photoresponse and surface morphology of Cd-Te electrodeposits. Knowledge of the material properties resulting from the electrodeposition conditions should prove helpful in the electrochemical fabrication of Cd Te devices.

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FIGURE 2.

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FIGURE 3.

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FIGURE CAPTIONS

Figure 1. Cadmium electrodeposits. A direct-current source was used to form the electrodeposit shown in the left-hand photo, and a 100-Hz pulse-current source was used to form the deposit shown in the right-hand photo. The photos represent the disk center. The width of each photo corresponds to 30μ m. A 25° C, 0.3-molal- $H₂SO₄$, 0.1-molal-CdSO₄, aqueous solution was used.

Figure 2. Photoresponse of electrodepositing cadmium-tellurium material. Upper plot: cell-current density. Lower plot: potential response for varying illumination intensities. The illumination intensities (DARK, LOW, HIGH) are indicated for each curve.

Figure 3. Potential response for the current source given in Fig. 2. Lefthand curve: no illumination. Righthand curve: a low intensity, pulse-light source with a duty cycle of 0.1 illuminated the electrodepositing cadmium-tellurium material.

Figure 4. Scanning-electron micrographs of Cd-Te electrodeposits. The width of each micrograph corresponds to 7μ m. A 0.3-molal-H₂SO₄, 0.001-molal-HTeO₂⁺, 0.1 -molal-Cd²⁺, aqueous electrolyte was used. The leftmost and middle photos show deposits formed at 25° C. The deposit shown in the rightmost photo was formed at 85°C. A direct-current source was used to form the deposit shown in the leftmost photo; the other two deposits were formed with a 100.-Hz rectangularpulse-current source.

Figure S. Pulse-light source and triangular current-sweep function for electrodeposit characterization.

Figure 6. Effect of etching process on electrodeposit photoresponse. Upper curve: no etch. Lower curve: I-min etch in a SO°C, 10-molal-NaOH solution. During the etching process, the RDE rotated at 2000 rpm. For the photoresponse experiment, a 25° C, 1.0-molal-NaOH solution was used.

Figure 7. Low current-density photoresponse of 100-Hz electrodeposit. The pulse-light source is shown in Fig. 5. The current was ramped from 0 at -60 μ A/cm² - min. A 25°C, 1.0-molal-NaOH solution was used.

Figure 8. Amplitude of periodic-potential response of the deposits listed in Table 2. The experimental conditions are identical to those described in Fig. 7.

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Figure 1.

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A B C XBB 872-1098

Figure **4.**

FIGURE 6.

FIGURE 7.

PHOTORESPONSE, millivolts

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