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Electrochemical Deposition, Optical Properties, and Photoelectrochemical Behavior of CdTe Films

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ABSTRACT

Electrochemical deposition of cadmium telluride from acidic solutions containing CdSO_4 and TeO_2 is studied and the current-potential expression for this reaction is presented. The electrochemically deposited CdTe films are photoactive, and the maximum cathodic photocurrent due to hydrogen evolution is observed at CdTe films deposited at -0.40V . The photocurrents of the as-grown CdTe films are relatively small compared with those of CdTe single crystals. The major reason for this low efficiency is the effective recombination of hole-electron pairs at grain boundaries and at the surface. The photocurrents are increased significantly by the increase of crystallite diameter by the heat-treatment in a He atmosphere and by the removal of surface Te, which acts as a recombination center, by the etching treatment.

Since cadmium telluride (CdTe) is a direct gap semiconductor with a room temperature energy gap of 1.44 eV (1) and can readily be prepared in both n- and p-type form (2), it is considered to be a promising material for low cost thin film photovoltaic and photoelectrochemical cells. A variety of methods, such as liquid-phase epitaxial growth (3), vacuum evaporation (4), chemical transport (5), and direct combination method (6), have been employed to form CdTe thin films on foreign substrates. CdTe can also be deposited electrochemically from a solution containing CdSO_4 and TeO_2 (7). The electrochemical deposition has the following advantages. The thickness of the film can be controlled by the charge passed during the deposition, both n-type and p-type material can be formed by just changing the deposition potential, and the doping is performed easily by adding the foreign species other than CdSO_4 and TeO_2 in the solution.

Several papers on the photoelectrochemical behavior of CdTe single crystals (8-12) and CdTe thin films (13-16) have been published. Although one of us reported that p-CdTe is a stable photocathode for photoelectrochemical generation of hydrogen (8, 9), most of the work was on n-CdTe in solution containing redox couples as stabilizing agents. Photoelectrochemical studies on electrochemically deposited CdTe films published so far are all on n-CdTe (15, 16), except one, which we published recently as a preliminary note of this work (17).

In this paper, we investigate the electrochemical deposition of CdTe films and report the photoelectrochemical characteristics of the CdTe films deposited at several potentials ($-0.2 \sim -0.6\text{V}$ vs. Ag/AgCl) and the effect of annealing and etching treatment on the optical and photoelectrochemical properties of the electrochemically deposited CdTe films.

Experimental

The CdTe films were deposited from aqueous solutions of pH 1.4 containing CdSO_4 and TeO_2 on Ti or Ni (The Japan Lamp Industrial Company, Limited) sheets which were degreased by chloroform and ethanol vapor and washed in purified water before use. The reagent-grade H_2SO_4 , NaOH, CdSO_4 (purity 99.5%), and TeO_2 (purity 99%) were used without further purification. Water was purified by Milli Q water purification system (Millipore Corporation). The usual three electrode cells were used both for the preparation of CdTe films and for the photoelectrochemical measurements. A platinum sheet and a Ag/AgCl electrode were used as a counter and a reference electrode, respectively. A Hokuto Denko HA-301 potentiostat with a Hokuto Denko HB-105 programmable function generator or a Wenking Model 68 FRO.5 potentiostat was used for the potentiostatic deposition of CdTe films and photoelectrochemical measurements. Photoelectrochemical measurements were carried

out in 1M NaOH. A 300 or 500W Xe lamp (Usio Denki Company, Limited) with an IR absorbing filter (Toshiba, IRA-20) was used as a light source. A monochromator (Ritsu Oyo Kogaku Company, Limited) was used to obtain photocurrent action spectra. In all the measurements, currents were recorded on a Rika Denki RW-11T X-Y-t recorder. The electrochemical deposition and photoelectrochemical measurements of the films were carried out at room temperature after the electrolyte solutions were deaerated by passing purified He gas for about 20 min. The heat-treatments of the films were carried out in a quartz tube under a He gas flow. The etching treatment of the films was carried out in a solution containing 0.6M $\text{Na}_2\text{S}_2\text{O}_4$ and 2.5M NaOH at 80°C (18).

The type of semiconductivity of the CdTe films was determined by measuring the potential difference between a hot and a cold contact. The thickness of the films was determined by using a Surfcom 300B surface roughness measuring instrument (Tokyo Seimitsu Company, Limited). The reflection spectra of the films were recorded by a Beckman DK-2 reflectometer. X-ray diffraction measurements were carried out by using a Toshiba XC-40 x-ray diffractometer.

Results

Electrochemical deposition of CdTe.—The current-potential (*i*-V) relation of a Ni sheet electrode in a solution containing 1M CdSO_4 , 1 mM TeO_2 , and 0.05M H_2SO_4 is shown in Fig. 1. Limiting current was observed at potentials between -0.30 and -0.65V vs. Ag/AgCl. The cathodic current increased significantly at potentials more negative than -0.65V . The *i*-V relations were affected by TeO_2 concentration very strongly, and a linear relation was observed between TeO_2 concentration and the limiting cur-

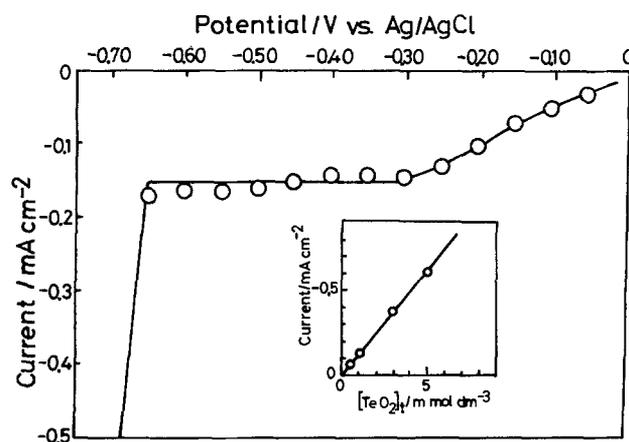


Fig. 1. Current-potential relation of Ni electrode in a sulfuric acid solution (pH 1.4) containing 1M CdSO_4 and 1 mM TeO_2 . Insert: TeO_2 concentration dependence of the current at -0.35V (vs. Ag/AgCl).

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rent, as shown in Fig. 1. However, CdSO_4 concentration affected the *i*-*V* relations little. The limiting current was larger when the solution was stirred. The thickness of the film and the charge passed during the deposition, Q_{dep} , are linearly correlated as shown in Fig. 2. The film thickness was found to be uniform throughout the film ($\pm 5\%$). As already reported, x-ray diffraction patterns of the deposited films confirmed the formation of CdTe (19). The x-ray diffraction peak due to Te was also observed in the films deposited at relatively positive potentials. The more positive the deposition potential, the stronger the diffraction peak due to Te (19). Cd deposition was not observed at the potential region employed in this study ($-0.20 \sim -0.60\text{V vs. Ag/AgCl}$). CdTe films deposited at relatively positive potentials were p-type, and those deposited at relatively negative potentials were n-type.

Optical properties and photoelectrochemical behavior of as-grown CdTe films.—A typical example of the diffuse reflection spectra of as-grown CdTe films is shown in Fig. 3. The wavelength dependence of the reflectivity was very small, and the energy gap was not able to be determined.

The photocurrent-potential relations of CdTe films deposited at various potentials are shown in Fig. 4. The most efficient cathodic photocurrent-potential relation was observed at the CdTe films deposited at -0.40V . The films deposited at the potentials at either more negative or more positive than -0.40V gave lower photocurrent, and no cathodic photocurrent was observed at CdTe films deposited either more positive than -0.20V or more negative than -0.55V . Even the highest cathodic photocurrent observed was relatively small compared with that at p-CdTe single crystals (9). The observed cathodic photocurrent at relatively positive potential seemed to be due to hydrogen evolution reaction, as suggested by bubble formation. The photocurrent increased significantly when the potential became more negative than -0.85V , and it seemed to be due to the cathodic decomposition of CdTe, as color of the solution near the electrode became purple, suggesting Te_2^{2-} formation.

Effect of heat-treatment.—By the heat-treatment at 200°C in a He atmosphere, the x-ray diffraction peaks due

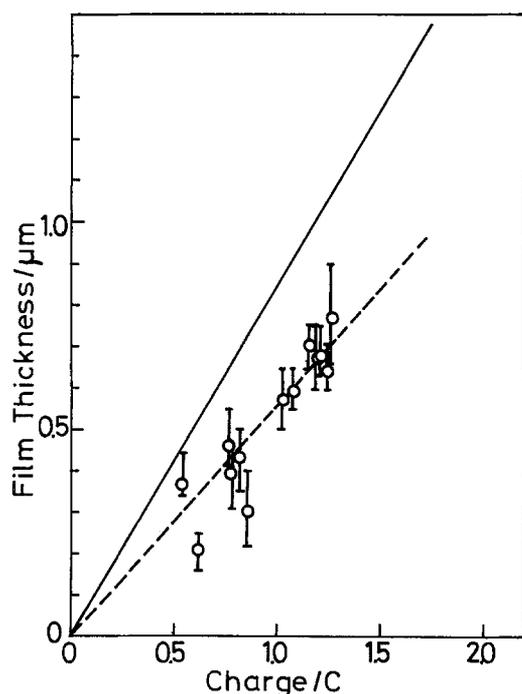


Fig. 2. The thickness of the electrochemically deposited films on Ni as a function of charge passed. The deposition was carried out at -0.35V (vs. Ag/AgCl) in a sulfuric acid solution (pH 1.4) containing 1M CdSO_4 and 1 mM TeO_2 . Solid line shows the theoretical value calculated by assuming six-electron process.

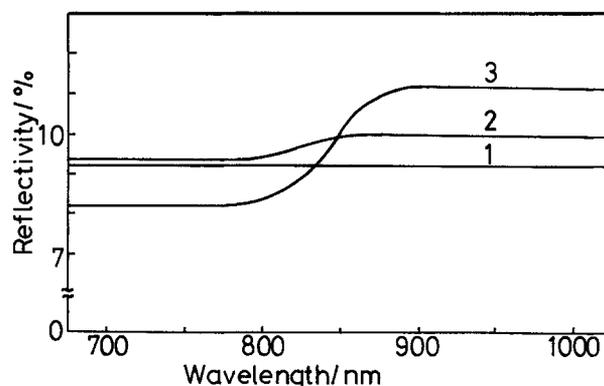


Fig. 3. Diffuse reflection spectra of the electrochemically deposited films ($3\ \mu\text{m}$ thick) on Ti substrate. The other deposition conditions are the same as those in Fig. 2. Curve 1: As grown. Curve 2: Heat-treated in a helium atmosphere at 200°C for 12h. Curve 3: Etched in a solution containing $0.6\text{M Na}_2\text{S}_2\text{O}_4$ and 2.5M NaOH at 80°C after heat-treatment in a He atmosphere at 200°C for 12h.

to CdTe became stronger and sharper by the increase of annealing time, but the peak due to Te was not affected by this treatment (17). The crystallite diameter calculated by using Scherrer equation (20) with the value of the full width at half maximum (FWHM) of x-ray diffraction peak due to (311) face of CdTe as well as the photocurrent increased with increase of annealing time, as shown in Fig. 5. By the heat-treatment, the reflection spectra of the CdTe films became clearer, as shown in Fig. 3. The band-edge energy determined from the reflection spectra is 1.45 eV and is in good agreement with the value reported for CdTe single crystal (1). The photocurrent-wavelength relation also showed the same energy gap (17).

Effect of etching treatment.—The effect of the etching treatment was studied at p-CdTe films which were deposited at -0.35V and annealed at 200°C in a He atmo-

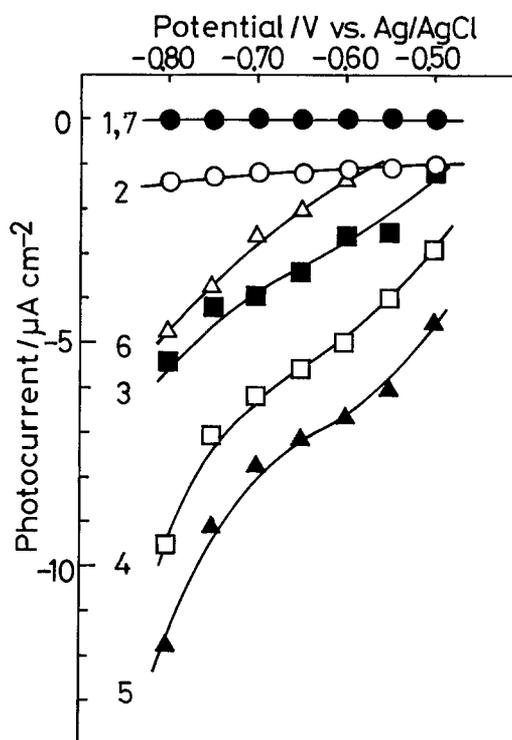


Fig. 4. Photocurrent-potential relations of the as-grown films deposited on Ti at several potentials, from a sulfuric acid solution (pH 1.4) containing 1M CdSO_4 and 1 mM TeO_2 . Curve 1: -0.20V . Curve 2: -0.25V . Curve 3: -0.30V . Curve 4: -0.35V . Curve 5: -0.40V . Curve 6: -0.50V . Curve 7: -0.55V . All vs. Ag/AgCl. Photoelectrochemical measurements were carried out in 1M NaOH solutions. A 300W Xe lamp with an IR absorbing filter was used as a light source.

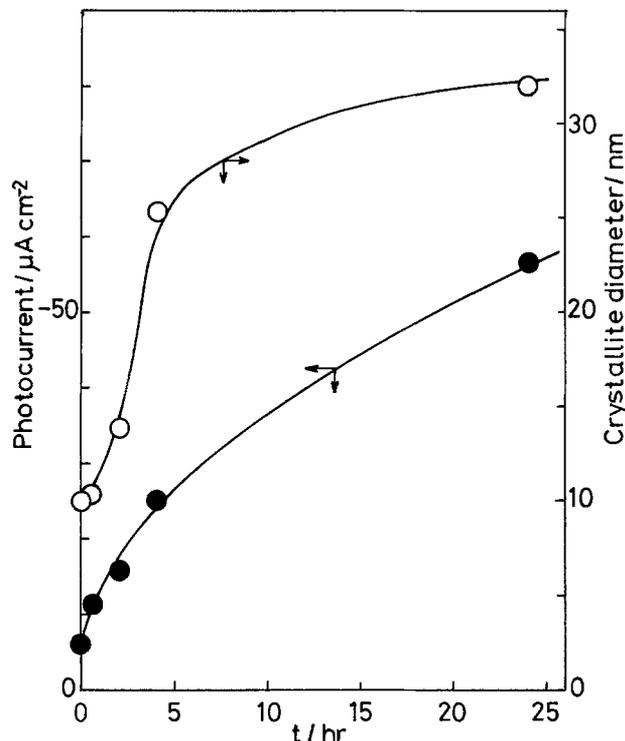


Fig. 5. Photocurrent at -0.65V (vs. Ag/AgCl) in 1M NaOH under illumination of 300W Xe lamp and crystallite diameter of the electrochemically deposited films ($3\ \mu\text{m}$ thick on Ti) as a function of annealing time. Deposition conditions are as same as those in Fig. 2.

sphere for 12h. As shown in Fig. 6, the intensity of x-ray diffraction peak due to Te decreased and that of x-ray diffraction peaks due to CdTe increased with the increase of the etching time. The FWHM of CdTe peaks was not affected by the treatment, suggesting the crystallite diame-

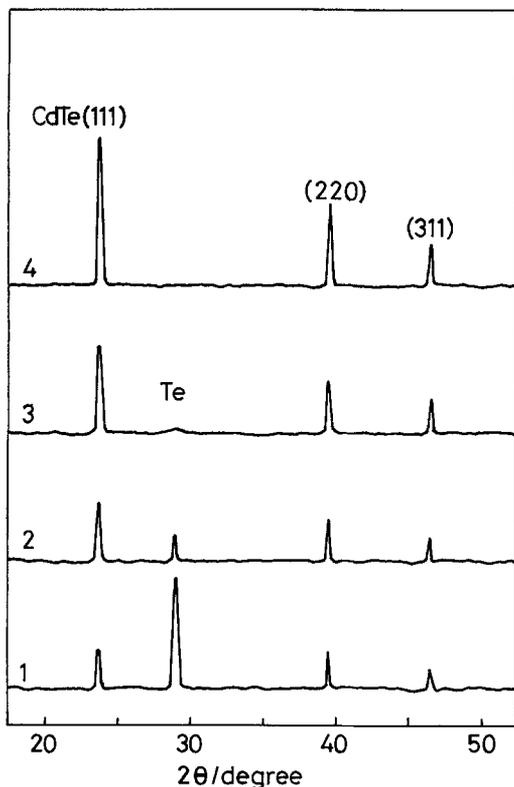
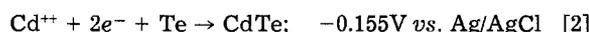
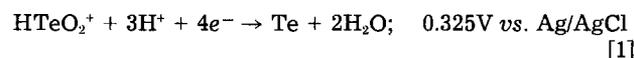


Fig. 6. X-ray diffraction patterns of the films deposited at -0.35V (vs. Ag/AgCl), heat-treated at 200°C in a He atmosphere for 12h and etched in a solution containing $0.6\text{M Na}_2\text{S}_2\text{O}_8$ and 2.5M NaOH at 80°C for several time periods. Curve 1: No etching treatment. Curve 2: 2s. Curve 3: 10s. Curve 4: 40s.

ter did not change during the treatment. The etching treatment also increased the photocurrent. The etching time dependence of the intensity of x-ray diffraction peaks and the photocurrent at -0.70V are shown in Fig. 7. The effect of etching on the reflection spectra is shown in Fig. 3. The absorption edge became much clearer by this treatment. By the too-long treatment, however, the photocurrent as well as the intensity of x-ray diffraction peaks due to CdTe decreased, suggesting that, not only Te, but also CdTe dissolved during the etching treatment.

Discussion

Panicker *et al.* studied the cathodic deposition of CdTe mainly by galvanostatic method (7) and proposed that the following reactions were involved in the formation of CdTe



and that the diffusion of HTeO_2^+ preceding reaction [1] is the rate-determining step. The results of the present work also support this mechanism. The current due to reaction [1] at diffusion limited region, i_{Te} , is given by

$$i_{\text{Te}} = -\frac{4DFc_{\text{HTeO}_2^+}}{\delta} \quad [3]$$

where D and $c_{\text{HTeO}_2^+}$ are the diffusion coefficient and the bulk concentration of HTeO_2^+ , and δ is the diffusion layer thickness. The current due to reaction [2], i_{CdTe} , is given by

$$i_{\text{CdTe}} = -2Fk'c_{\text{Cd}^{2+}}\theta_{\text{Te}}e^{-\alpha F\Delta\phi/RT} \quad [4]$$

where k is the rate constant, $c_{\text{Cd}^{2+}}$ is the concentration of Cd^{2+} , θ_{Te} is the surface coverage of Te, α is the transfer coefficient and $\Delta\phi$ is the potential difference across the interface. By considering mass balance, θ_{Te} is given by

$$\theta_{\text{Te}} = k'f_{\text{Te}} = k' \frac{i_{\text{Te}}/4 - i_{\text{CdTe}}/2}{i_{\text{Te}}/4} \quad [5]$$

where f_{Te} is the fraction of Te at the surface of the films and k' is a proportional constant. From Eq. [3], [4], and [5]

$$\theta_{\text{Te}} = \frac{k'Dc_{\text{HTeO}_2^+}/\delta}{(Dc_{\text{HTeO}_2^+}/\delta) + kk'c_{\text{Cd}^{2+}}e^{-\alpha F\Delta\phi/RT}} \quad [6]$$

By using Eq. [3], [4], and [6], the total current, i , is given by

$$i = i_{\text{Te}} + i_{\text{CdTe}} = -\frac{DFc_{\text{HTeO}_2^+}}{\delta} \left(4 + \frac{2kk'c_{\text{Cd}^{2+}}e^{-\alpha F\Delta\phi/RT}}{(Dc_{\text{HTeO}_2^+}/\delta) + kk'c_{\text{Cd}^{2+}}e^{-\alpha F\Delta\phi/RT}} \right) \quad [7]$$

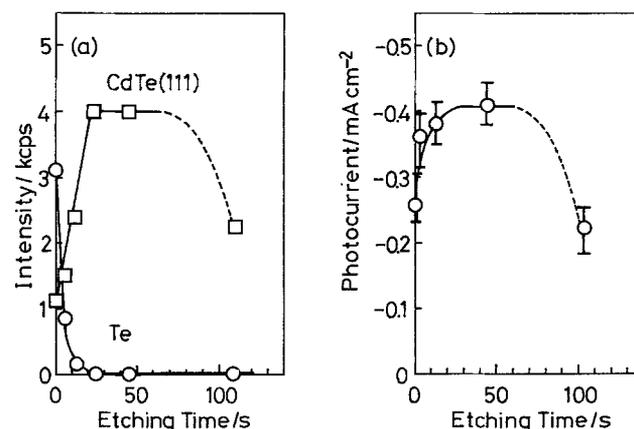


Fig. 7. Etching time dependence of (a) the intensity of x-ray diffraction peaks due to CdTe (111) face (\square) and Te (\circ) and (b) the photocurrent in 1M NaOH at -0.70V (vs. Ag/AgCl) under illumination of 500W Xe lamp with an IR absorbing filter. Experimental conditions are the same as those in Fig. 6.

Thus, the current should be proportional to the bulk concentration of H^+TeO_2^+ , i.e., TeO_2 , as observed experimentally. The more negative the potential is, the higher f_{CdTe} and the less free Te are expected from Eq. [6]. Experimental results also confirmed this expectation. When $D_{\text{H}^+\text{TeO}_2^+}/\delta \ll k'c_{\text{Cd}^{2+}}e^{-\alpha F\Delta\phi/RT}$, i.e., the potential is very negative and $\theta_{\text{Te}} \approx 0$, then Eq. [7] becomes

$$i = - \frac{6DFc_{\text{H}^+\text{TeO}_2^+}}{\delta} \quad [8]$$

By assuming that the film is mainly CdTe, that the density of CdTe is 6.2, and that the deposition of CdTe is a six-electron process, as Eq. [8] shows, the current efficiency is calculated as 75% from the data of Fig. 2. The other reaction involved may include the reduction of oxygen, which is left in small amount despite the deaeration before the experiment. The other supporting evidence for this mechanism is that only the films deposited electrochemically at the potentials more negative than -0.25V were photoactive while the standard redox potential of reaction [2] is calculated as -0.155V (vs. Ag/AgCl).

As far as the films deposited at the potentials more positive than -0.40V were concerned, the more negative the deposition potential, the higher the photocurrent. One reason for this seems to be that the amount of free Te left is smaller, and another is that the amount of CdTe is larger in the films deposited at more negative potentials. Free metal is known to act as an electron-hole recombination center and reduce the photoconversion efficiency (21). The higher concentration of CdTe naturally increases the photoresponse. The films deposited more negative than -0.45V are n-type (19), and the more negative the deposition potentials, the lower the cathodic photocurrent.¹

As mentioned before, the photocurrents of the as-grown CdTe films were much smaller than those of CdTe single crystals. Since the usual cause of small efficiency is the effective recombination of hole-electron pairs at grain boundaries and at the surface, the increase of grain size by heat-treatment and removal of surface recombination center by etching treatment are considered to improve the photoconversion efficiency. As shown in Fig. 5, the heat-treatment increases the crystallite diameter as well as the photocurrent. Due to the increase of the crystallite diameter, the number of grain boundaries decreases, and therefore the photoconversion efficiency should be increased. In this case, since the amount of free Te was not affected, only the crystallite diameter affected the photocurrent.

The fact that no diffraction peak due to Te was observed in the x-ray diffraction patterns after the etching treatment suggests that the free Te existed mainly near the surface.² The Te at CdTe surface would act as a surface recombination center which should decrease the photocurrent. As shown in Fig. 7, the photocurrent was increased by removing the surface Te and, thus, it is confirmed that the surface Te was also responsible for the small photocurrent. The fact that the x-ray diffraction peaks due to CdTe were increased and the reflection spectra became much clearer by the etching treatment is explained by the removal of the surface Te-rich layer. This was supported by the fact that FWHM of x-ray diffraction peaks due to CdTe was not changed by the etching treatment.

Conclusion

1. The current-potential expression for the electrochemical deposition of CdTe films is presented.

¹ The anodic photocurrents were observed at potentials more positive than ca. -0.40V .

² The effect of Ar⁺ sputtering on Auger spectra also support this result (19).

2. The electrochemically deposited CdTe films are photoactive, and the maximum cathodic photocurrent which is due to hydrogen evolution reaction is observed at CdTe films deposited at -0.40V (vs. Ag/AgCl). The photocurrents at CdTe films deposited at more positive potentials than -0.40V are smaller because the amount of free Te, which acts as a surface recombination center, is larger, and, accordingly, the amount of CdTe is smaller. The photocurrents at CdTe films deposited at potentials more negative than -0.40V are smaller because the CdTe films deposited at these potentials are n-type.

3. The photocurrents of the as-grown CdTe films are relatively small compared with those of CdTe single crystals. The major reasons for this low efficiency are the effective recombination of hole-electron pairs at grain boundaries and at the surface. The photocurrents are increased significantly by the increase of crystallite diameter by the heat-treatment in a He atmosphere and by the removal of surface Te, which acts as a recombination center, by the etching treatment.

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