Photoelectrochemical Generation of Hydrogen at Electrochemically Deposited p-\(\text{CdTe}\) Films: Effect of Heat -Treatment, Surface Modification by Platinum and Surface Oxide Layer on Conversion Efficiency

Makoto Takahashi, Kohei Uosaki and Hideaki Kita

doi: 10.1149/1.2108560

Receive free email alerts when new articles cite this article - sign up in the box at the top right corner of the article or [click here](http://jes.ecsdl.org/subscriptions)

To subscribe to *Journal of The Electrochemical Society* go to: [http://jes.ecsdl.org/subscriptions](http://hes.ecsdl.org/subscriptions)

© 1986 ECS - The Electrochemical Society
Photoelectrochemical Generation of Hydrogen at Electrochemically Deposited p-CdTe Films: Effect of Heat-Treatment, Surface Modification by Platinum and Surface Oxide Layer on Conversion Efficiency

Makoto Takahashi, Kohei Uosaki,* and Hideaki Kita

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

ABSTRACT

The effects of heat-treatment, Pt modification of the surface and surface oxide layer on the efficiency for the photoelectrochemical generation of hydrogen were investigated at p-CdTe films deposited electrochemically at ~0.35V (vs. Ag/AgCl) from an aqueous sulfuric acid solution of pH = 1.4 containing 1M CdSO4 and 1 mM TeO2. By heat-treatment in a He atmosphere, the crystalline diameter increased and, thus, the number of grain boundaries at which effective electron-hole recombination takes place decreased. Free metallic Te existing near the surface, which acts as a recombination center, was removed by the treatment at the temperatures above 350°C. The cathodic photocurrent was increased by the heat-treatment due to these two effects. The cathodic photocurrent was decreased and even the anodic photocurrent was observed at the films treated at too high a temperature and for too long a time. The films were converted to n-type by these treatments because the recombination rates of empty CdTe crystal lattice were reduced. Pt modification of the films by either vacuum deposition or codeposition, improved the efficiency, but the photocurrent is small, suggesting that the major reason for the low efficiency is still the bulk recombination. The oxide layer was easily formed on the CdTe films by exposure to air, but dissolved by contacting with solution and had no effect on the photoelectrochemical properties of the film.

Recently strong attention has been paid to photoelectrolysis of water by using semiconductor electrodes as one of the useful means to convert solar energy into chemical energy, hydrogen (1). To make this process practical, it is essential to find an economical method for the production of polycrystalline semiconductors which have appropriate photoelectrochemical characteristics (2).

Cadmium telluride (CdTe) has the following attractive properties for solar energy conversion devices. The bandgap energy is 1.45 eV (3) from which one expects a high solar energy conversion efficiency (4). The direct optical transition (5) results in a large absorption coefficient which makes the use of thin film solar cells possible. Both p- and n-type forms can be prepared (6).

Thus, the application of CdTe to solid-state solar cells (7) is possible. Both p- and n-type forms can be prepared (6). The production of polycrystalline semiconductors which have appropriate photoelectrochemical properties for solar energy conversion devices (2).

The electrochemical deposition has been studied extensively as a useful method for preparing large area, polycrystalline Cd-chalcogenide thin films which have also been reported to affect the photoelectrochemical properties of CdTe thin films. Recently strong attention has been paid to photoelectrolysis of water by using semiconductor electrodes as one of the useful means to convert solar energy into chemical energy, hydrogen (1). To make this process practical, it is essential to find an economical method for the production of polycrystalline semiconductors which have appropriate photoelectrochemical characteristics (2).

Cadmium telluride (CdTe) has the following attractive properties for solar energy conversion devices. The bandgap energy is 1.45 eV (3) from which one expects a high solar energy conversion efficiency (4). The direct optical transition (5) results in a large absorption coefficient which makes the use of thin film solar cells possible. Both p- and n-type forms can be prepared (6).

Thus, the application of CdTe to solid-state solar cells (7) is possible. Both p- and n-type forms can be prepared (6). The production of polycrystalline semiconductors which have appropriate photoelectrochemical properties for solar energy conversion devices (2).

The electrochemical deposition has been studied extensively as a useful method for preparing large area, polycrystalline Cd-chalcogenide thin films which have also been reported to affect the photoelectrochemical properties of CdTe thin films. Recently strong attention has been paid to photoelectrolysis of water by using semiconductor electrodes as one of the useful means to convert solar energy into chemical energy, hydrogen (1). To make this process practical, it is essential to find an economical method for the production of polycrystalline semiconductors which have appropriate photoelectrochemical characteristics (2).

Cadmium telluride (CdTe) has the following attractive properties for solar energy conversion devices. The bandgap energy is 1.45 eV (3) from which one expects a high solar energy conversion efficiency (4). The direct optical transition (5) results in a large absorption coefficient which makes the use of thin film solar cells possible. Both p- and n-type forms can be prepared (6).

Thus, the application of CdTe to solid-state solar cells (7) is possible. Both p- and n-type forms can be prepared (6). The production of polycrystalline semiconductors which have appropriate photoelectrochemical properties for solar energy conversion devices (2).

The electrochemical deposition has been studied extensively as a useful method for preparing large area, polycrystalline Cd-chalcogenide thin films which have also been reported to affect the photoelectrochemical properties of CdTe thin films. Recently strong attention has been paid to photoelectrolysis of water by using semiconductor electrodes as one of the useful means to convert solar energy into chemical energy, hydrogen (1). To make this process practical, it is essential to find an economical method for the production of polycrystalline semiconductors which have appropriate photoelectrochemical characteristics (2).

Cadmium telluride (CdTe) has the following attractive properties for solar energy conversion devices. The bandgap energy is 1.45 eV (3) from which one expects a high solar energy conversion efficiency (4). The direct optical transition (5) results in a large absorption coefficient which makes the use of thin film solar cells possible. Both p- and n-type forms can be prepared (6).

Thus, the application of CdTe to solid-state solar cells (7) is possible. Both p- and n-type forms can be prepared (6). The production of polycrystalline semiconductors which have appropriate photoelectrochemical properties for solar energy conversion devices (2).

The electrochemical deposition has been studied extensively as a useful method for preparing large area, polycrystalline Cd-chalcogenide thin films which have also been reported to affect the photoelectrochemical properties of CdTe thin films.

Recently strong attention has been paid to photoelectrolysis of water by using semiconductor electrodes as one of the useful means to convert solar energy into chemical energy, hydrogen (1). To make this process practical, it is essential to find an economical method for the production of polycrystalline semiconductors which have appropriate photoelectrochemical characteristics (2).

Cadmium telluride (CdTe) has the following attractive properties for solar energy conversion devices. The bandgap energy is 1.45 eV (3) from which one expects a high solar energy conversion efficiency (4). The direct optical transition (5) results in a large absorption coefficient which makes the use of thin film solar cells possible. Both p- and n-type forms can be prepared (6).

Thus, the application of CdTe to solid-state solar cells (7) is possible. Both p- and n-type forms can be prepared (6). The production of polycrystalline semiconductors which have appropriate photoelectrochemical properties for solar energy conversion devices (2).

The electrochemical deposition has been studied extensively as a useful method for preparing large area, polycrystalline Cd-chalcogenide thin films which have also been reported to affect the photoelectrochemical properties of CdTe thin films.

*Electrochemical Society Active Member.
that without Pt addition. Heat-treatment was carried out as for the films without modification. In the other method, Pt was vacuum deposited on the films by using Ulvac, EBH-6. In this case, the thickness of Pt was measured by using an interference microscope (Mizojiri Optical Company Limited, Model 2).

The type of semiconductivity of the CdTe films were determined by measuring the potential difference between a hot and a cold contact. X-ray diffraction patterns and reflection spectra were obtained by using Toshiba XC-40 x-ray diffractometer and a Beckman DK-2 reflectometer, respectively. X-ray photoelectron spectroscopy (XPS) measurements were carried out by using a V.G. Scientific, Limited, ESCA3.

Fig. 1. Photocurrent-potential relations of p-CdTe films deposited on Ti sheet at $-0.35$V (vs. Ag/AgCl) from an aqueous sulfuric acid solution of pH = 1.4 containing 1 M CdSO$_4$ and 1 mM TeO$_2$. The measurements were carried out in 1 M NaOH with 500 W Xe lamp illumination. O: As-grown. Other films were annealed in a He atmosphere for 4h at 200°C ($\oplus$), 350°C ($\bigcirc$), 400°C ($\triangle$), and 500°C ($\blacksquare$).

Fig. 2. X-ray diffraction patterns of the CdTe films used for the experiments presented in Fig. 1. (a) As grown, (b) annealed at 200°C, (c) annealed at 350°C, and (d) annealed at 500°C.

Fig. 3. Reflection spectra of the CdTe films used for the experiments presented in Fig. 1. (a) As grown, (b) annealed at 200°C, (c) annealed at 350°C, and (d) annealed at 500°C.

Fig. 4. Photocurrent-potential relations of p-CdTe films. Experimental conditions for the deposition and the photoelectrochemical measurements were the same as those in Fig. 1. : As grown. Other films were annealed in a He atmosphere at 350°C for 2h ($\blacksquare$), 4h ($\bullet$), 6h ($\triangle$), 7h ($\bigcirc$), and 12h ($\oplus$).
heat-treatment. The higher the temperature, the stronger the intensity of the peaks. The intensity, however, became weaker by the treatment at 500°C. The crystalline diameter calculated by using Scherrer's equation (16) with the value of FWHM increased by annealing and are larger than 50 nm, which is the upper limit of the present arrangement, for the films treated above 350°C.

The reflection spectra of the above-mentioned samples are shown in Fig. 3. The reflectance was almost constant for the as-grown films but changed around 820-860 nm for the annealed films. The bandgap energy determined from the spectra is ca. 1.45 eV which is in good agreement with the value reported for CdTe single crystals (3).

Although the as-grown film was p-type, the semiconductivity of the annealed films differed depending upon the annealing temperature. The films treated below 350°C were p-type and those treated above 350°C were n-type. The semiconductivity of films treated around 350°C were difficult to determine by the method employed here.

Effect of the annealing time was also examined. Figure 6 shows the photocurrent-potential relations of the electrochemically deposited p-CdTe films annealed at 350°C for 0-12h. The cathodic photocurrent increased with the increase of annealing time up to 4h and then decreased. The anodic photocurrent was observed at the films treated for longer than 7h.

Table I. Effect of Pt modification on the photocurrents at the CdTe films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt modification</th>
<th>Annealing*</th>
<th>Photocurrent** at -0.8V/mA · cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>(as-grown)</td>
<td>-0.01</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Annealing only</td>
<td>-0.20</td>
</tr>
<tr>
<td>3</td>
<td>Codeposition</td>
<td>---</td>
<td>-0.07</td>
</tr>
<tr>
<td>4</td>
<td>Codeposition</td>
<td>---</td>
<td>-0.55</td>
</tr>
<tr>
<td>5</td>
<td>Electrodeposition</td>
<td>---</td>
<td>-0.28</td>
</tr>
<tr>
<td>6</td>
<td>Vacuum deposition</td>
<td>---</td>
<td>-0.06</td>
</tr>
<tr>
<td>7</td>
<td>Vacuum deposition</td>
<td>After Pt modification</td>
<td>-0.40</td>
</tr>
<tr>
<td>8</td>
<td>Vacuum deposition</td>
<td>Before Pt modification</td>
<td>-0.28</td>
</tr>
</tbody>
</table>

* Annealing treatments were carried out in a He atmosphere at 350°C for 4h.

** Photocurrents were measured in 1M NaOH under 500W Xe lamp illumination.
CdTe(111)

L

2O

PtTe2 Pt

AI

An, f

CdPt PtTe PtTe 2 PtTe

(b)

5O

I i I

30 40 28/degree

Fig. 7. X-ray diffraction patterns of the CdTe films used for the experiments presented in Fig. 6. (a) Annealing only (sample 2), (b) Pt codeposition followed by annealing, and (c) annealing followed by Pt vacuum deposition. Peaks corresponding to TiO2 which existed on substrate (Ti) were also observed. In Fig. 2 and Fig. 5, no peaks due to TiO2 can be seen because TiO2 portion was covered with epoxy resin when x-ray diffraction patterns were obtained.

X-ray diffraction patterns of the films used for the measurements shown in Fig. 6 are shown in Fig. 7. In addition to CdTe peaks (2θ = 23.8°, 39.3°, and 46.4°) (17), additional peaks at 2θ = 46.2° and 81.3° corresponding to Pt (17) were observed with sample 7 (Fig. 7c). Similar patterns were observed with sample 6. If the annealing was carried out after the Pt modifications, Pt reacted with CdTe and several Pt alloys were formed. Figure 7b shows the x-ray diffraction patterns of sample 4 and the diffraction peaks due to PtTe (2θ = 31.6°, 41.2°, and 45.8°) (17), PtTe2 (2θ = 30.7°, 43.5°, and 45.1°) (17), and CdPt (2θ = 38.8°, 43.5°, and 76.1°) (17) were also observed. Similar patterns were observed at sample 8.

XPS spectra of sample 4 and 7 show that platinum existed as metallic (Pt(0)).

The photocurrent-potential relations were not much affected at the thickness of Pt between 5 and 300 Å.

Growth of surface oxide layer and its effect on the photoelectrochemical behavior.—It has been reported by Werthen et al. that surface oxide layer grows on CdTe single crystal (18). XPS spectra of the CdTe films which were annealed at 300°C in a He atmosphere for 4h, then annealed at 500°C for 4h, show the peaks due to Te(IV) and Te(0). The peaks corresponding to Pt (4f7/2) and Pt (4f5/2) appeared only at 35.0 eV and 33.5 eV, respectively, which are known to be due to Pt(0).

Fig. 8. XPS spectra of p-CdTe films in the region of Te 3d2/3 and 3d5/2 peaks. The deposition conditions of the films were the same as those in Fig. 1. The films were annealed in a He atmosphere at 300°C for 4h then exposed to air for (a) 15 min, (b) 10 days, and (c) 80 days.

Fig. 9. The ratio of XPS peaks corresponding to Te(IV) and Te(0) as a function of air-exposed time.

Fig. 10. The photocurrent under illumination of 500W Xe lamp at -0.70V (vs. Ag/AgCl) in 1M Na2SO4 at the CdTe films as a function of air-exposed time. The films were deposited and annealed in the way shown in Fig. 8.
exposed to air for 15 min, 10 days, and 80 days are shown in Fig. 8 in the region of Te 3d_{5/2} and 3d_{3/2} peaks. The peaks at 572.5 and 583.0 eV correspond to Te(0) and those at 576.0 and 586.5 eV correspond to Te(IV) (18, 19). While only peaks due to Te(0) were observed at the films exposed to air for 15 min, peaks due to Te(IV) were also observed at the films exposed to air for longer time periods. The ratio of Te(IV)/Te(0) increased at the beginning with the increase of the time of exposure to air and reached a constant value as shown in Fig. 9. The shape and the intensity of the peaks which correspond to Cd 3d_{5/2} and 3d_{3/2} were not affected by the air exposure. These results suggest the formation of TeO₂ near the surface by air exposure as proposed by Werthen et al. (18). Air-exposure time did not affect the cathodic photocurrent as shown in Fig. 10. XPS spectra taken after the films were immersed in 1M NaOH showed no peaks due to Te(IV), suggesting that the surface oxide dissolved in the solution.

Discussion

As mentioned before, the major reasons for low efficiencies at as-grown films are the bulk recombination at grain boundaries, the surface recombination due to the existence of excess free Te metal, and the slow hydrogen evolution reaction. The annealing treatments were carried out primarily to increase the crystalline diameter so that the number of grain boundaries should be decreased.

4 Although White et al. showed the existence of Te⁺⁻ in CdTe (19), Werthen et al. suggested that Te existed as Te⁰ in CdTe. In our measurements, the position of Te peaks of sputtered CdTe films agreed with that of Te peaks of sputtered elemental Te within experimental error, suggesting that Te existed as Te⁰ in CdTe.

Crystalline diameter, intensity of x-ray diffraction peaks, and photocurrents are plotted as a function of the annealing temperature (Fig. 11) and of the annealing time (Fig. 12 at 350°C and Fig. 13 at 200°C). As shown in Fig. 13 the annealing at 200°C increased the crystalline diameter but did not affect the free Te concentration. In this case the increase of the photocurrent is solely due to the increase of crystalline diameter. The annealing above 300°C not only increased the crystalline diameter but also removed the free Te which existed near the surface and acted as the surface recombination center. Thus, the annealing improved the efficiency due to these two effects. The cathodic photocurrent, however, declined by the annealing at too high temperature or for too long time (Fig. 11, 12). The films were converted to n-type by these treatments and even anodic photocurrents were observed (Fig. 12). This is due to the removal of the lattice Te from CdTe crystal. The Te vacancy is known as a donor center (20). Although the details of the effect of the annealing on the composition and the electronic properties of the films will be reported elsewhere (21), it should be emphasized here that the effect of the annealing on the photocurrent is the result of the increase of the crystalline diameter, the decrease of free Te concentration and the change of the electronic properties.

Pt modification was carried out with the hope that the hydrogen evolution reaction is enhanced by Pt which is known as a good catalyst for this reaction (22). The results shown in Table I, Fig. 6, and Fig. 7 support that this expectation was correct. However, the increment by the treatment is not as large as those reported for p-type single-crystal electrodes, e.g., p-InP (23), and the photocurrent at RHE is still small. Thus, it can be concluded.
tra measurements, respectively. Vacuum deposition was the x-ray diffraction measurements and reflection spec-
Maekawa and to Professor Y. Matsunaga for the help in
are most grateful. Mr. Kiya is acknowledged for con-
carried out with the help of Dr. M. Taniwaki for which we
with the fact that there is no pH dependence of the
chemical hydrogen evolution reaction at p-InP (15). In the
recombination is still the major reason for
loss in the films after the Pt modification is
flatband potential (24), which also suggests no oxide
oxidized by exposing it to air, the oxide layer thus formed
of CdTe films. This result agrees
Annealing time / hr

Fig. 13. (a) The crystallite diameter as a function of annealing time,
(b) the intensity of x-ray diffraction peaks corresponding to CdTe (111)
face (⊂) and free Te (□), and (c) the photocurrent at −0.80V. The films
were annealed at 200° C. Other conditions were as same as those in Fig.
that the bulk recombination is still the major reason for
the low efficiency at these films. The role of Pt alloys
found in the films annealed after the Pt modification is
not clear.

According to Heller, surface oxide layer plays an impor-
tant role in determining the efficiency for photoelectro-
chemical hydrogen evolution reaction at p-InP (15). In the
present case, however, although the surface is very easily
oxidized by exposing it to air, the oxide layer thus formed
disappears just by immersing the film into 1M NaOH,
and, therefore, cannot play any role in the photoelectro-
chemical properties of CdTe films. This result agrees
with the fact that there is no pH dependence of the
flatband potential (24), which also suggests no oxide
layer at the surface in contact with solution.

Acknowledgments

Thanks are due to Professor T. Yokokawa and Dr. T.
Maekawa and to Professor Y. Matsunaga for the help in
the x-ray diffraction measurements and reflection spec-
tra measurements, respectively. Vacuum deposition was
carried out with the help of Dr. M. Taniwaki for which we
are most grateful. Mr. Kiya is acknowledged for con-
structing electrochemical cells. This work was partially
supported by a Grant-in-Aid for Scientific Research,

Manuscript submitted April 2, 1985; revised manuscript
received July 9, 1985.

Hokkaido University assisted in meeting the publication
costs of this article.

REFERENCES
1. (a) A. Fujishima and K. Honda, Nature, 238, 37 (1972); (b) A.
Heller, Acc. Chem. Res., 14, 154 (1981); (c) A. J. Bard,
2. (a) B. Miller and A. Heller, Nature, 262, 680 (1976); (b) W.
J. Danaher and L. E. Lyons, ibid., 271, 139 (1978);
(c) J. F. McCann and M. Skylas Kazacos, J.
(1976).
4. S. Wagner, in “Solid State Chemistry and Energy Con-
version and Storage,” J. B. Goodenough and M. S.
Whittingham, Editors, p. 109 Adv. in Chem. Ser. of
6. A.B. Ellis, S. W. Kaiser, J. M. Bolts, and M. S. Wrighton,
7. J. O’M. Bockris and K. Usoski, This Journal, 124, 1348
11. (a) J. H. Reeves and M. Cocivera, This Journal, 131, 2042
(1984); (b) G. J. Houston, J. F. McCann, and D.
Haneman, J. Electroanal. Chem., 134, 37 (1982); (c) G.
Hodes, J. Manassen, and D. Cohen, Nature, 261, 403
(1976); (d) M. Skylas Kazacos and B. Miller, This
Journal, 127, 869 (1980); (e) M. P. R.
Panicker, M. Knaster, and F. A. Kröger, ibid., 125, 508
(1976).
14. M. Takahashi, K. Usoski, and H. Kita, This Journal, 131,
18. J. G. Werthen, J-P. Haring, and R. H.
19. H. S. White, A. J. Ricco, and M. S. Wrighton,
4292 (1965).
22. J. F. Llopis and F. Colom, in “Encyclopedia of Electro-
chemistry of the Elements,” Chap. VI-4, A. J. Bard,
Editor, Marcel Dekker, Inc., New York and Basel
(1976).
Heller, and B. Miller, This Journal, 127, 90 (1980).
24. J. L. Sculfort, R. Triboulet, and P. Leniasson, ibid., 131,