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Effects of heat treatment on the composition and semiconductivity of electrochemically deposited CdTe films

Makoto Takahashi, Kohei Uosaki,[a] and Hideaki Kita
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan
Yoshikazu Suzuki
Government Industrial Development Laboratory-Hokkaido, Sapporo 061-01, Japan

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Effects of heat treatments on crystalline diameter, composition, and semiconductivity of CdTe films deposited electrochemically at -0.35 V (vs Ag/AgCl) from an acidic solution containing 1-M $CdSO_4$ and 1-mM TeO_2 were studied. As-grown films contained free Te in addition to CdTe. The intensity of x-ray diffraction peaks due to CdTe became stronger by the heat treatment at higher temperatures but x-ray diffraction peak due to metallic Te disappeared at the films annealed above 350 °C in a He atmosphere. The intensity of Auger peaks due to Cd increased and that due to Te decreased by increasing the annealing temperature. The composition of the films annealed above 350 °C was close to that of pure CdTe. The similar effects were observed at the films annealed at 350 °C for various heat treatment periods in a He atmosphere. The change of semiconductivity of the films from p to n type was observed at the films annealed at enough high temperatures and for enough long time. The disappearance of free Te from the films was explained in terms of the temperature dependence of vapor pressure of Te_2 from CdTe and metallic Te.

I. INTRODUCTION

The properties of cadmium telluride (CdTe) have been investigated in many laboratories[1-4] because of its potential use for wide varieties of application, e.g., solar energy conversion devices, and substrate for γ-ray, x-ray, and IR detectors.[5] Since its band-gap energy is 1.44 eV at room temperature,[6] CdTe-based solar cells are expected to have a high-solar-power conversion efficiency[7] and the application of CdTe for various types of solar cells such as Schottky barrier,[8] *p-n* junction,[9] and photoelectrochemical[10-13] cells has been reported. The direct mode of the main optical transition of CdTe results in a large absorption coefficient[14] which makes the thin-film solar cells possible. Various processes such as vacuum evaporation,[15] chemical transport,[16] molecular beam deposition,[17] and electrochemical deposition[18-25] have been employed to produce CdTe thin films as an active material for low-cast, large-area, high-efficiency solar cells. Among these, the electrochemical deposition is attractive because (a) both p- and n-type materials can be prepared just by changing the deposition potential, (b) films of desired thickness can be obtained by controlling the charge passed during the deposition, and (c) the method is a simple, low-temperature process.

We have thoroughly investigated the electrochemical deposition of CdTe films and reported the effect of the deposition conditions on composition, electronic properties, and photoelectrochemical characteristics of CdTe films.[26-28] The conversion efficiency at the electrochemically deposited CdTe films (as deposited) was low and we suggested the reasons for the low efficiency are (1) the crystalline diameter of the as-grown films is very low, and, correspondingly, many grain boundaries that act as recombination centers exist in the film, (2) excess free Te metal which acts as recombination center exist near surface, and (3) the hydrogen evolution rate on CdTe surface is low. Heat treatment increases the crystalline diameter in polycrystalline[29] and, accordingly, the solar energy conversion efficiency should be improved by the heat treatment.[30] The heat treatment may alter the composition and the semiconductivity of the films as well. The effects of heat treatment on the composition of CdTe films were studied by R. F. Brebrick[31] and by T. Yoshikawa *et al.*[32] According to R. F. Brebrick, when CdTe crystals were annealed in a temperature range of 780–939 °C in vacuum, the equal amount of Te and Cd element evaporated from the crystal surface. T. Yoshikawa *et al.* also studied the heat treatment of CdTe crystals in a temperature range of 100–900 °C in vacuum. While the evaporation of Cd from CdTe was observed at temperatures higher than 300 °C, Te evaporated only above 600 °C. At the temperatures above 700 °C, however, nearly equal amounts of Cd and Te evaporated. R. W. Bhattacharya *et al.* reported that the electrochemically deposited p-CdTe films became n type by the heat treatment at 600 °C for 50 min in an Ar gas flow.[33]

In this paper, we report the effects of heat treatment on crystalline diameter, composition, and semiconductivity of the electrochemically deposited p-CdTe films in detail studied by means of x-ray diffraction and Auger electron spectroscopy (AES) measurements.

II. EXPERIMENT

p-CdTe thin films were deposited cathodically at -0.35 V vs Ag/AgCl on Ti sheets from an aqueous sulfuric acid solution of pH = 1.4, containing 1-M $CdSO_4$ and 1-mM TeO_2. The details of the pretreatment of Ti sheets, preparation of the electrolyte, and the deposition method are already reported elsewhere.[26-28,30] The type of semiconductivity of the deposited films was determined by measuring the potential difference between a hot and a cold contact. X-ray dif-

[a] Author to whom correspondence should be addressed.

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fraction and AES measurements were carried out by using a Toshiba XC-40 x-ray diffractometer and JEOL JAMP system (10-keV electrons), respectively. Sputter etching for depth profiling by AES was carried out in an argon atmosphere at a pressure of 8×10^{-3} Pa with a 3-kV ion beam using an ion current density of approximately 140 $\mu A/cm^2$. The films were heat treated in a quartz tube under a He gas flow at various temperatures. Temperature was measured with a chromel-alumel thermocouple and controlled by using a thermocontroller (Model E560, Chino Works, Ltd.) with an accuracy of $\pm$ 5 °C. Temperature was raised to a preset value with a rate of 100 °C/h.

III. RESULTS

A. Effect of annealing temperature

X-ray diffraction patterns of the as-grown CdTe film and of the films annealed at 200, 350, and 500 °C for 4 h in a He gas are shown in Fig. 1. In addition to the diffraction peaks at $2\theta = 23.8$, 39.3, and 46.4°,[34] which correspond to (111), (220), and (311) face of CdTe,[35] respectively, a peak at $2\theta = 27.8°$ due to metallic Te (Ref. 35) is observed at the as-grown film [Fig. 1(a)], suggesting that excess metallic Te coexists with CdTe in the as-grown film. The crystalline diameter of the metallic Te is estimated to be 10–20 nm by using the Scherrer equation[36] with the value of the full width at half maximum (FWHM) of the diffraction peak at $2\theta = 27.8°$. The intensity of x-ray diffraction peaks due to CdTe increased and FWHM of these peaks decreased by the heat treatment [Figs. 1(b)–1(d)]. The intensity of the peaks became stronger by the heat treatment at higher temperature but it became weaker by the treatment about 500 °C. The diffraction peak due to metallic Te was also observed at the

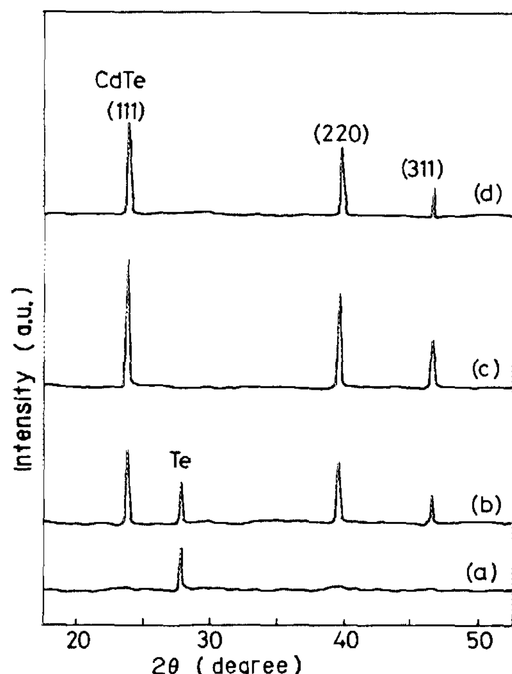


FIG. 1. X-ray diffraction patterns of the CdTe films deposited at −0.35 V (vs Ag/AgCl). (a) As grown. Other films were annealed in a He atmosphere for 4 h at (b) 200 °C, (c) 350 °C, and (d) 500 °C.

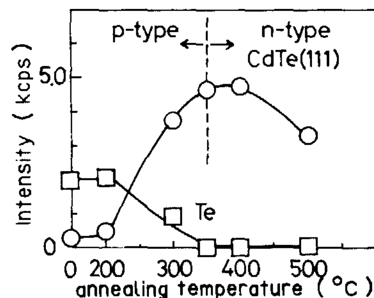


FIG. 2. Annealing temperature dependence of the intensity of x-ray diffraction peaks due to CdTe (111) face (○) and free Te (□) in the films used for the experiments presented in Fig. 1.

film annealed at 200 °C and the intensity and the FWHM are as same as those of the as-grown film [Fig. 1(b)]. The diffraction peak due to metallic Te, however, disappeared at the films annealed above 350 °C [Figs. 1(c) and 1(d)]. These results suggest that metallic Te evaporated from the surface of CdTe film by the heat treatment above 350 °C. The above results are summarized with the semiconductivity of the films in Fig. 2. The semiconductivity of the films changed from *p*-type to *n*-type around 350 °C.

AES spectra of the same films that are used to obtain results shown in Fig. 1 are shown in Fig. 3. Auger peaks due to Cd (375 and 382 eV),[37] Te (483 and 493 eV),[37] C (273 eV),[37] and O (516 eV)[37] were observed. In the case of the as-grown film and the film annealed at 200 °C [Figs. 3(a) and 3(b)], the intensity of Auger peaks of Te are several times larger than

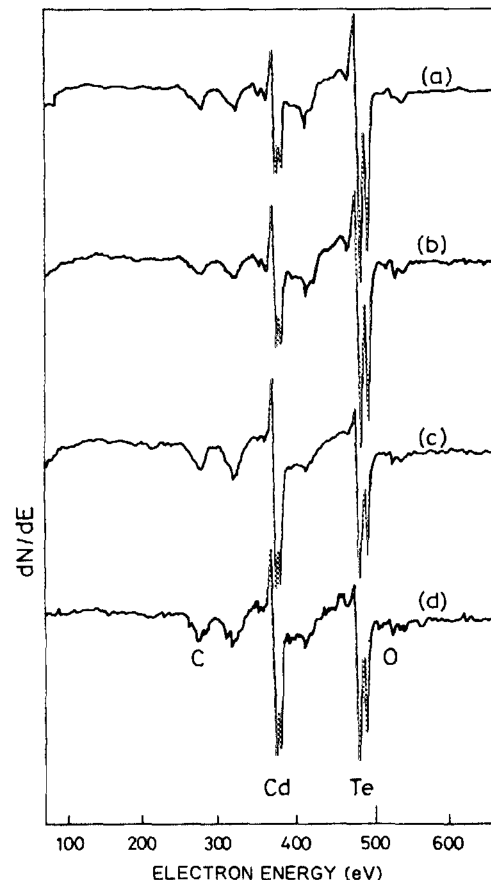


FIG. 3. Auger spectra of the CdTe films deposited at −0.35 V (vs Ag/AgCl). Spectra (a)–(d) correspond to the films cited in Fig. 1.

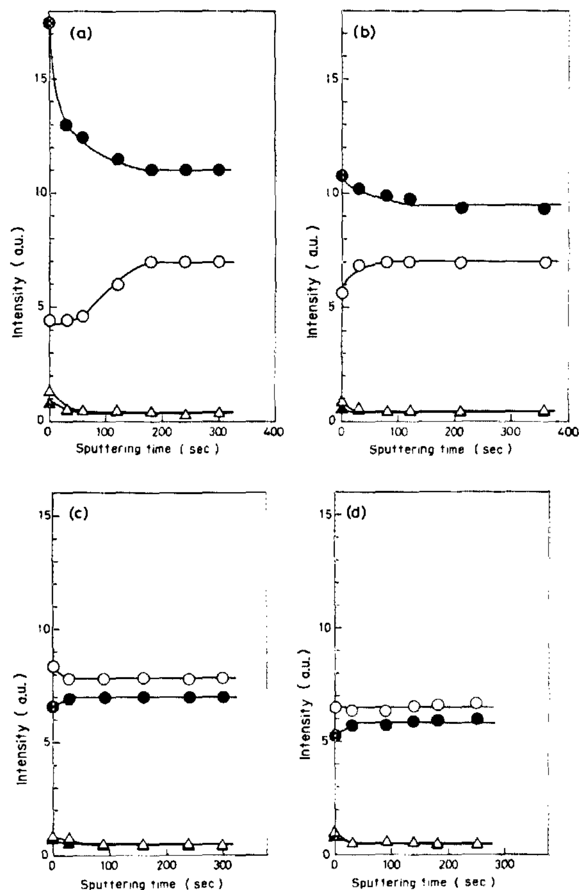


FIG. 4. Depth profiles of the CdTe films obtained with 3-kV Ar ions. (a) As grown. (b) Annealed at 200 °C. (c) Annealed at 350 °C. (d) Annealed at 500 °C. O: Cd, ●: Te, △: C, ▲: O.

that of the peaks of Cd. On the other hand, the intensity of the Auger peaks due to Te is similar to that of the peaks due to Cd in the case of the films annealed above 350 °C [Figs. 2(c) and 2(d)]. The AES spectra of pure CdTe (purity 99.999%) showed that the ratio of the intensity of the peaks due to Te to that of peaks due to Cd is about 1. Thus, these results suggest that an excess amount of Te compared with Cd exists in the surface region of the as-grown film and of the films annealed below 200 °C. The composition of the films annealed above 350 °C is close to that of pure CdTe.

AES depth profiles of the samples used to obtain the results shown in Fig. 3 are shown in Fig. 4. In all cases [Figs. 4(a)–4(d)], the intensities of peaks due to C and O were small and decreased with the increase of sputtering time. The intensities of peaks due to C and O became constant after 30-s sputtering. In the case of the as-grown film and the film annealed at 200 °C [Figs. 4(a) and 4(b)], the intensity of peak due to Te (483 eV) decreased and that due to Cd (375 eV) increased with the increase of sputtering time. The intensities of these peaks became constant after 80–160-s sputtering. However, when the films were annealed above 350 °C, the intensity of peak due to Te increased slightly with the increase of sputtering time [Figs. 4(c) and 4(d)], while the intensity of peak due to Cd decreased slightly [Fig. 4(c)] or was constant [Fig. 4(d)] with the increase of sputtering time. Thus, the excess amount of Te existed in the surface region of

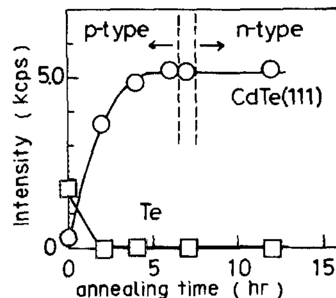


FIG. 5. The intensity of diffraction peaks due to CdTe (111) face (O) and free Te (□) as a function of annealing time. The films were annealed in a He atmosphere at 350 °C for a period shown in abscissa.

the as-grown film and was preferentially removed by the heat treatment, particularly at higher temperatures (> 350 °C). These results are in good agreement with the results of x-ray diffraction as presented above.

B. Effects of annealing time

The intensity of the x-ray diffraction peaks due to CdTe (111) and metallic Te and the semiconductivity of the CdTe films annealed at 350 °C are shown in Fig. 5 as a function of annealing time. The diffraction peak due to metallic Te disappeared when the film was annealed for longer than 2 h. The diffraction peaks of CdTe increased with the increase of the annealing time, suggesting the increase of crystallinity. When the films were annealed for longer than 7 h, the semiconductivity of the film changed from p to n type.

The intensities of AES peaks due to Cd and Te of the CdTe films annealed at 350 °C are shown in Fig. 6 as a function of annealing time. As already shown, Te peak was stronger than Cd peak at as-grown film. The intensity of Cd peak increased and Te peak decreased with the increase of annealing time to 4-h annealing and after that these intensities became constant with the intensity ratio of unity. Then the results of Figs. 5 and 6 showed that excess free metallic Te

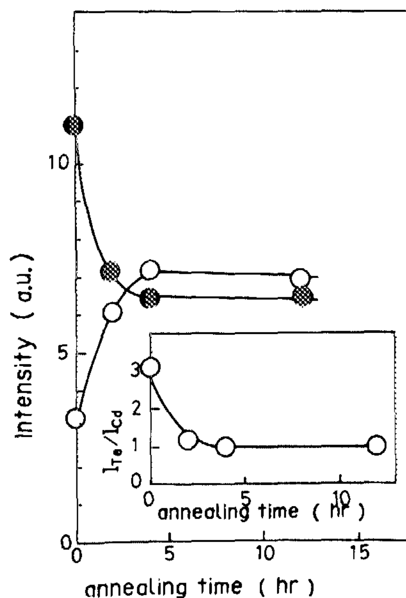


FIG. 6. The intensity of Auger peaks due to Cd (O) and Te (●) as a function of annealing time. The CdTe films were the same as those in Fig. 5. Inset: Annealing time dependence of the ratio of the intensity of Auger peak due to Te to that due to Cd.

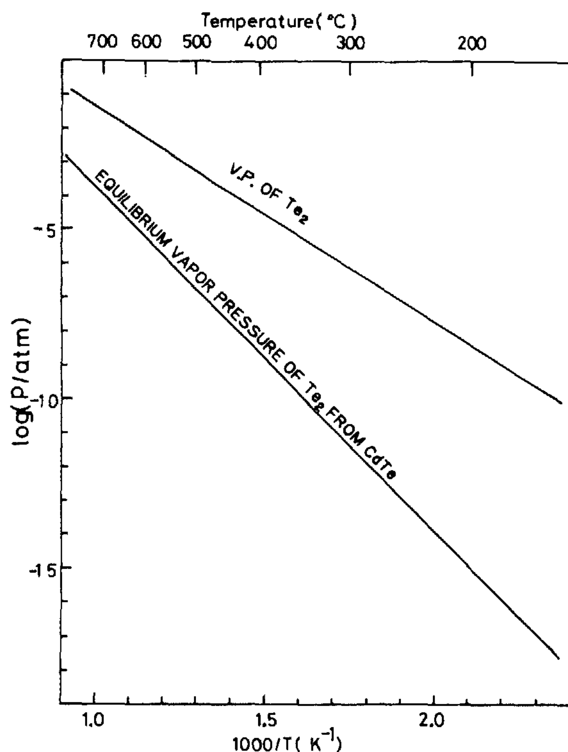


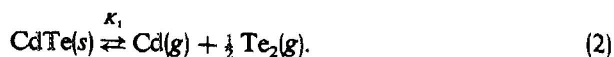
FIG. 7. The equilibrium vapor pressures of tellurium from cadmium telluride and from elemental tellurium in a temperature range of 150–750 °C.

which existed in the surface region of as-grown film was removed by the heat treatment at this temperature and after about 4-h treatment the composition of the film became as that of pure CdTe.

IV. DISCUSSION

Results summarized in Figs. 2 and 5 show that excess metallic Te which existed in the surface region of the as-grown film disappeared first when the films were annealed above 350 °C. Then the semiconductivities of the films changed from p to n type. The change of the semiconductivity which corresponds to the composition change from Te-rich to Cd-rich material means the evaporation of Te from CdTe lattice. Let us consider how the evaporation of free Te and of Te from CdTe lattice proceeds. The as-grown films are composed of CdTe and Te. The Te evaporation is assumed to occur through the following reactions[38]:

$$\mathrm{Te}(s) \overset{K_2}{\rightleftarrows} \tfrac{1}{2}\,\mathrm{Te}_2(g), \tag{1}$$



$$\mathrm{CdTe}(s) \overset{K_1}{\rightleftarrows} \mathrm{Cd}(g) + \tfrac{1}{2}\,\mathrm{Te}_2(g). \tag{2}$$

If the rate of gas flow is low, partial vapor pressures of Cd and Te reach values at an equilibrium. The equilibrium vapor pressures of Te_2 corresponding to the processes (1) and (2) are calculated as a function of temperature in a similar manner of Chu *et al.*[39] and are shown in Fig. 7. The thermodynamic data used for the calculation were taken from Ref. 38. P_{Te_2} due to reaction (1) is larger than that due to reaction (2). Thus, when the films in which the excess metallic Te exists are annealed, excess metallic Te evaporates first from the surface and the dissociation reaction of the CdTe should be suppressed. Thus the composition, i.e., the semiconductivity, of the films is not affected by the annealing until free metallic Te evaporates away as experimentally observed. The above argument, however, cannot explain why the semiconductivity changed from p to n type, i.e., the preferential evaporation of Te from CdTe lattice. This must be due to the fact that the state of $CdTe_{1-x}$ which is produced by the vaporization of Te from CdTe is more stable than the state of $Cd_{1-x}Te$ which is produced by the vaporization of Cd from CdTe but no thermodynamic data to prove this is available.

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