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Preparation of Low Resistance Contact Electrode in Screen Printed CdS/CdTe Solar Cell

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Heating conditions of carbon electrodes for CdTe and the effect of impurities in the carbon paste on the characteristics of solar cells are investigated. The series resistance (R_s) and the conversion efficiency (η_i) of solar cells exhibit strong dependence on O_2 concentration in the heating atmosphere. Addition of Cu to the carbon paste causes R_s and diode factor (n) to decrease, resulting in a remarkable improvement in η_i. As a result of preparation of low resistance contact electrode for CdTe, a cell with 0.78 cm^2 active area which was made from 50 ppm Cu-added carbon paste showed $V_{oc}=0.754$ V, $I_{sc}=0.022$ A, $FF=0.606$ and $\eta_i=12.8\%$.

§1. Introduction

Low resistance contacts between electrode and semiconductor are essential for the production of high efficiency solar cells. It has, however, been very difficult to make a low-resistance and low-noise ohmic contact to p-type CdTe. The reason for this difficulty lies in the compensation mechanism common to all II-VI semiconductors. Through the years, several attempts[1–4] have been made to obtain good ohmic contacts to p-type CdTe. Such electrical contacts are usually attained by the evaporation of electroless plating of metal layer on the surface of CdTe followed by a thremal treatment. The contacts, however, often suffer from poor reproducibility and short lifetime.

For the screen printed thin film CdS/CdTe solar cell[5–9] developed in our laboratory, a carbon thin layer is formed on a p-type CdTe film as an electrode. The carbon electrode was heated in an atmosphere produced by a combination with N_2 gas flow into a belt-type furnace and ventilation from the furnace. This heat treatment led to a poor reproducibility in production of high efficient solar cell, which arises from the high series resistance (R_s). Oxygen in the furnace was thought to play an important role in formation of low resistance contact between CdTe and carbon electrode. Also it was suggested in provious papers[9,10] that the carbon layer played the role not only of a positive electrode of the solar cell but also as a source of impurities for CdTe; i.e., a trace of impurities, such as I and V group elements included in the carbon electrode, diffused into CdTe during heat treatment and served as an acceptor inside it. The impurity effect on the characteristics of the CdS/CdTe solar cell, however, has not yet been clarified.

In the present study, an optimum sintering condition of the carbon electrode is investigated since the contact resistivity between the electrode and CdTe strongly depends on heat treatment of the carbon electrode. The effect of impurities in the carbon electrode on characteristics of the solar cell is also investigated with the aim of providing a high efficiency solar cell.

§2. Experimental

The CdS paste, mixture of 91.9 wt% CdS powder, the balance $CdCl_2$ and an appropriate amount of propylene glycol, was screen printed on a 10×10 cm^2 borosilicate glass substrate and dried at 120°C for 60 min. in air. Subsequently, the CdS layer was sintered at 690°C for 90 min. in N_2 atmosphere. (Cd + Te) paste was then screen printed on the CdS sintered film and dried at 100°C for 30 min. The (Cd + Te) layer was sintered in N_2 atmosphere at 620°C for 60 min. During the sintering, Cd and Te react to form CdTe layer and CdS/CdTe heterojunction is obtained. A carbon electrode was formed on the CdTe film by screen printing and heat treatment. Ag and Ag + In electrodes were formed on the carbon electrode and the CdS film, respectively by screen printing and heat treatment. Thus the CdS/CdTe solar cell is fabricated entirely via successive screen printing and heat treatments. Details of cell preparation have previously been reported.[8,9]

The following experiments were carried out in order to find the optimum sintering conditions for the carbon electrode and also to study the effect of impurities on the characteristics of the solar cell. (1) A printed carbon electrode was heated at 380, 400, 450 and 500°C for 30 min in atmospheres including different amount of O_2. (2) An impurity, such as Cu, Ag, P, Sb, and Bi, was added to the carbon paste and the paste was screen printed on the CdTe sintered film to serve as an electrode. The screen printed carbon electrode was then subjected to an optimum heat treatment. The V/I characteristics of the solar cells were measured under simulated AM 1.5 sunlight (100 mW/cm^2).

§3. Results and Discussion

The carbon electrode screen printed on the CdTe film was heated in various atmospheres at 380, 400, 450 and 500°C for 30 min. Figure 1 shows series resistance and intrinsic conversion efficiency (η_i) of solar cells heated at 400°C vs oxygen concentration in the sintering atmospheres. The solar cell of highest efficiency was obtained by heating the carbon electrode in an atmosphere containing 1.0–1.5 mol% O_2 at 400°C for 30 min. Heat treatment at the same temperature in concentrations higher or lower O_2 than 1.0–1.5 mol% O_2 resulted in increase of R_S because of increase in contact resistivity between CdTe and the carbon electrode. The effects of oxygen in the heating atmosphere on efficiency of the solar cell is not clear. Two explanations,

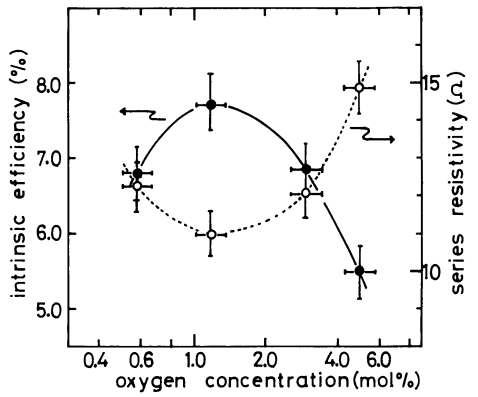

Fig. 1. Dependence of intrinsic efficiency and series resistivity on O_2 concentration in heating atmosphere for the cells heated at 400°C for 30 min.

however, might be possible. In the first, Tyan and Perez-Albuerne[11] reported a small amount of oxygen introduced during deposition of the CdS and CdTe layers enhanced the p-type character of the CdTe film and ensured the shallow-junction behavior of the device. An appropriate amount of oxygen in the heating atmosphere probably is essential in order to obtain the highest efficiency CdS/CdTe solar cell. Oxygen, however, is not known to be a p-type dopant to CdTe. The second, a decomposition of resign in carbon electrode may be associated with oxygen concentration in the furnace. The sheet resistance of carbon electrodes heated at 400°C for 30 min in different atmospheres between 1.0 mol% and 2.5 mol% O_2 showed nearly the same value of about 9/Ω□. The heat treatment at the same temperature in atmospheres with 0.1 mol% O_2 and 6 mol% O_2 gave the sheet resistivity of about 10 and 12 Ω/□, respectively. Adhesion between carbon electrode and CdTe layer may also be dependent on the amount of residual resin in carbon elecreode. The carbon electrode heated in the 6 mol% O_2 atmosphere resulted in a poor adhesion to CdTe layer and high R_S. Carbon electrode which has low sheet resistivity and gives good contact to CdTe is essential in the fabrication of the high efficiency solar cells. Figure 2 shows lower efficiency solar cells which were obtained by heating at 380, 450 and 500°C. Heat treatments at lower and higher temperature than 400°C lowered the open circuit voltage (V_{OC}) and the short circuit current (I_{SC}). Heat treatment at 380°C for 30 min was probably not high enough to induce impurities, such as Cu in the carbon electrode, into CdTe. Many defects which result from donor impurities for CdTe, such as Al in carbon electrode and residual Cl in CdS film, are probably induced into CdTe during the heat treatment at higher temperature causing the junction to deteriorate (Spectrochemical analysis showed the carbon paste included about 50 ppm Al).

In order to investigate an impurity's effect on CdS/CdTe solar cells, impurities of I and V group elements in carbon paste before bing added were measured by spectrochemical analysis. Approximately 10 ppm Cu and less than 2 ppm Ag were detected. Au, P, Sb or Bi could not be detected.

Carbon paste with 50, 100, 200, 300 and 500 ppm Cu added were screen printed on a CdTe film and heated at 400°C for 30 min in 1.0–1.5 mol% O_2 atmosphere. The addition of Cu improved η_i, i.e., η_i of the cells made from carbon paste with 50 and 100 ppm Cu added was increased by approximately 13 or 14% beyond that of cells made from carbon paste with no impurity added, as shown in Fig. 3. This increase resulted from increases in V_{OC} and fill factor (FF) and decreases in R_S and diode factor (n). The increase of V_{OC} and the decreases of R_S and n lead to the increase in FF. Reverse saturation current density (J_O) was reduced from $\sim 10^{-7}$ A · cm^{-2} to $\sim 10^{-8}$ A · cm^{-2} by the addition of Cu. R_S and n were decreased from 10∼12 Ω · cm^{-2} to ∼10 Ω · cm^{-2} and 2.8∼3.3 to 2.0∼2.4 respectively, with the addition of Cu up to approximately 100 ppm. Further addition only served to make n and R_S large. Since the noble metals Au, Ag and Cu primarily substitue for Cd, act as acceptors and secondarily fill interstitial positions, and act as donors,[12] large additions of Cu resulted in the increase in the contact resistance

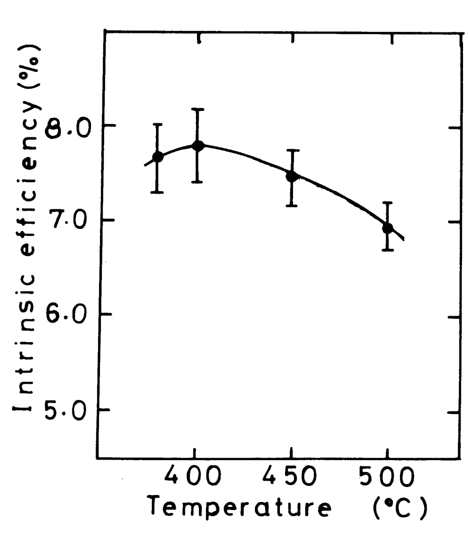

Fig. 2. Intrinsic efficiency of solar cell heated in optimum atmosphere as a function of sintering temperature of carbon electrode.

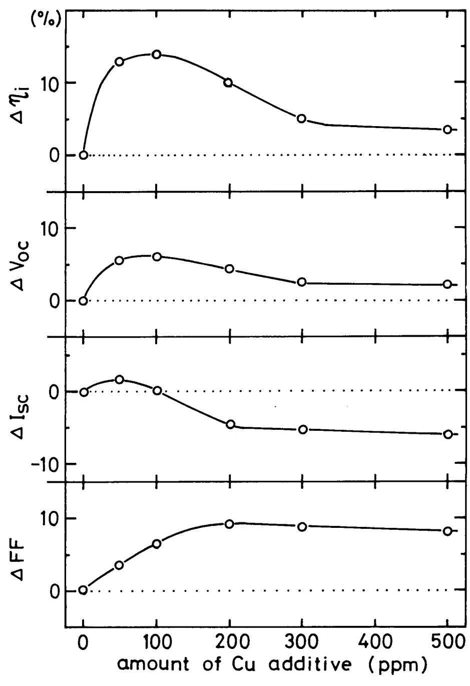

Fig. 3. Effects of Cu addition on characteristics of solar cell heated at 400°C for 30 min.

between carbon electrode and CdTe. The measurement of the electron voltaic (EV) effect on the CdS/CdTe cells shows there is no difference between the cells made from the carbon paste with 100 ppm Cu added and with no impurity, i.e., peaks of the EV curve for both cells were located at approximately 3 μm on the CdTe side from the CdS/CdTe interface.

I_{SC} increased slightly with increasing Cu addition up to 50 ppm and decreased monotonically upon any further addition. The spectral response of short circuit current for cells made from the carbon paste with 100 ppm Cu added and with no impurity is shown in Fig. 4. The cell with 100 ppm Cu-added carbon electrode showed poor response in the long wave length region. Large additions of Cu reduced the spectral response of the solar cell. Thus an appropriate amount of Cu in carbon paste and heat treatment at optimum condition might make CdTe layer p^+ type and lowered the contact resistivity of CdTe/carbon electrode through an optimum amount of Cu diffusion into CdTe. The highest efficiency solar cell with 0.78 cm^2 active area prepared by use of carbon paste with 50 ppm Cu added showed $V_{OC}=0.754$ V, $I_{SC}=0.022$ A, $FF=0.606$ and $\eta_i=12.8\%$. V/I characteristics of the cell is shown in Fig. 5. As for large area solar cells, $V_{OC}=1.478$ V, $I_{SC}=0.757$ A, $FF=0.531$ and $\eta_i=9.3\%$ were obtained for cells with 10×10 cm^2 substrate area having two small cells (5×10 cm^2) connected in series. Further investigation concerning fabrication of 30×30 cm^2 substrate solar cell was done and will be published at a later date.[13)]

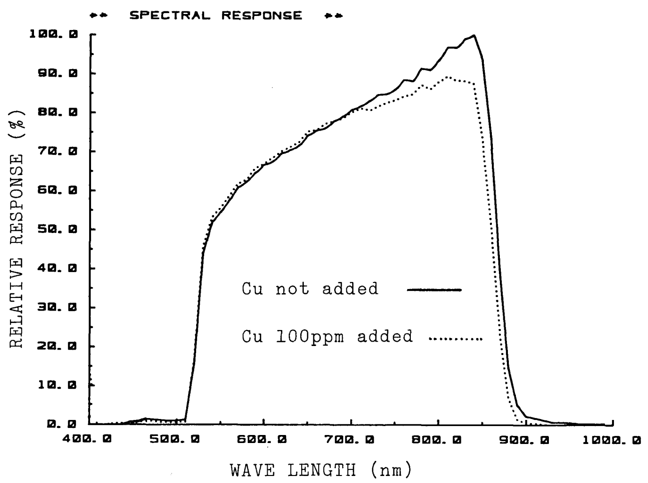

Fig. 4. Spectral response of the cells made from 100 ppm-Cu added carbon paste and no impurity added paste.

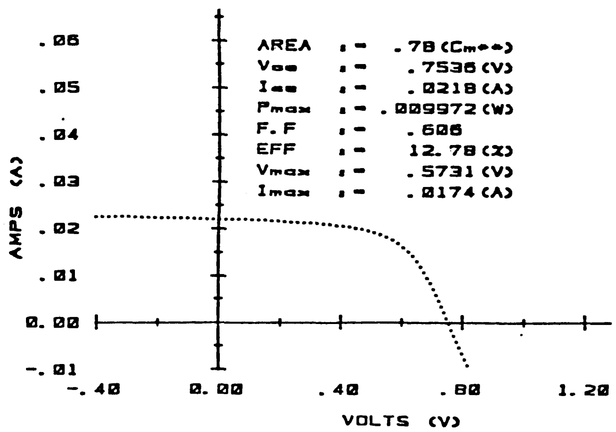

Fig. 5. V/I characteristic of the cell with 0.78 cm^2 active area made from 50 ppm Cu-added carbon paste.

Effects of additions of Ag and Au into the carbon paste on characteristics of solar cell are shown in Figs. 6 and 7. respectively. A slight improvement of η_i was observed the cell with Ag-added carbon electrode heated at 400°C for 30 min. No improvement was observed for the cell with Au-added carbon electrode heated at 400°C. Approximately 11 and 5% increase in η_i were observed for cells with 50 ppm Ag-added and 20 ppm Au-added carbon electrode heated at 500°C, respectively. As mentioned before, since the cell made by the heat treatment at 500°C for 30 min has approximately 10% lower η_i than that of the cell heated at 400°C for 30 min, the cell with 50 ppm Ag-added carbon electrode heated at 500°C has nearly the same η_i as the cell with no impurity-added carbon electrode heated at 400°C. Ionization energy of Ag and Au associated acceptors in CdTe is nearly the same as that of Cu.[12)] The ionic radius of Cu^+ (0.96A) is close to that of Cd^{2+} (0.95 A), making substitution for Cd easy. On the other hand, the ionic radii of Ag^+ (1.15 A) and Au^+ (1.37 A) are much larger than that of Cd^{2+}, making substitution for Cd difficult. Figure 8 shows the effects of Sb addition on characteristics of solar cell. About 6% increase in η_i was observed for the cell with 20 ppm Sb added carbon electrode heated at 400°C for 30 min. Approximately 2.5% increase in V_{OC} and 4.5% increase in I_{SC} were observed for the cell with 20 ppm Sb-added carbon electrode. *FF*, however, was not improved by adding Sb.

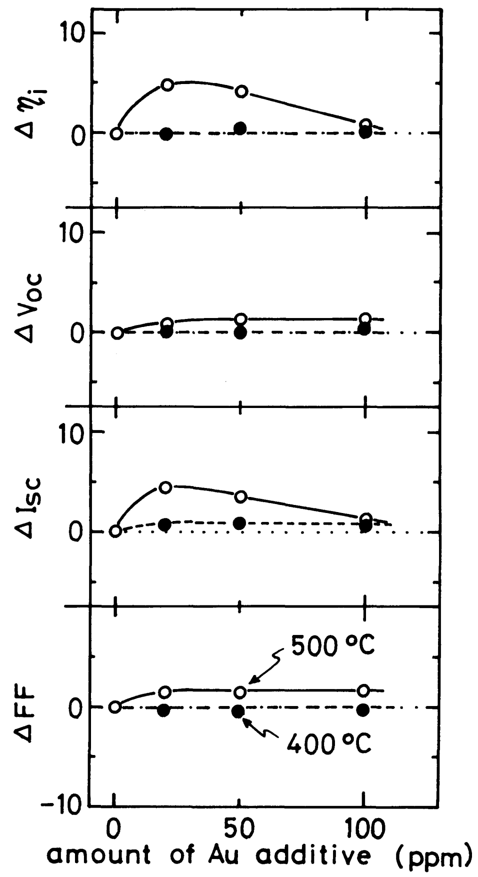

Fig. 6. Effects of Ag addition on the characteristics of solar cell heated at 400 (●) and 500°C (○) for 30 min.

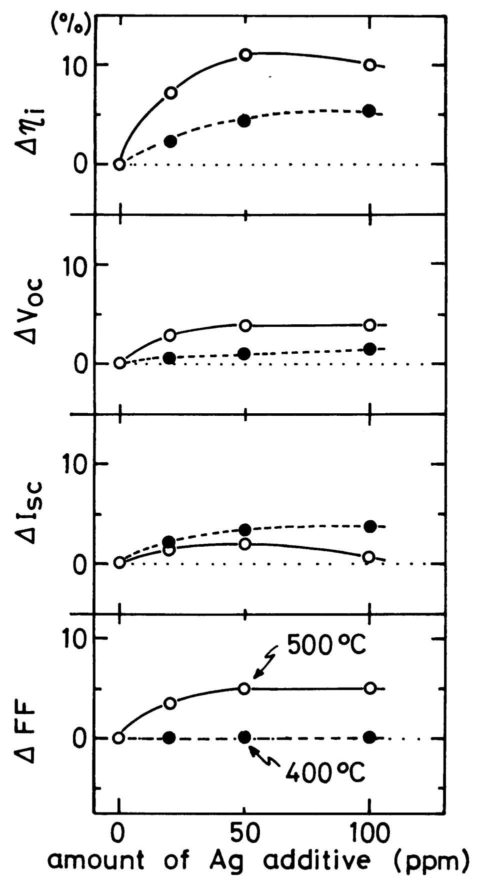

Fig. 7. Effects of Au addition on the characteristics of solar cell heated at 400 (●) and 500°C (○) for 30 min.

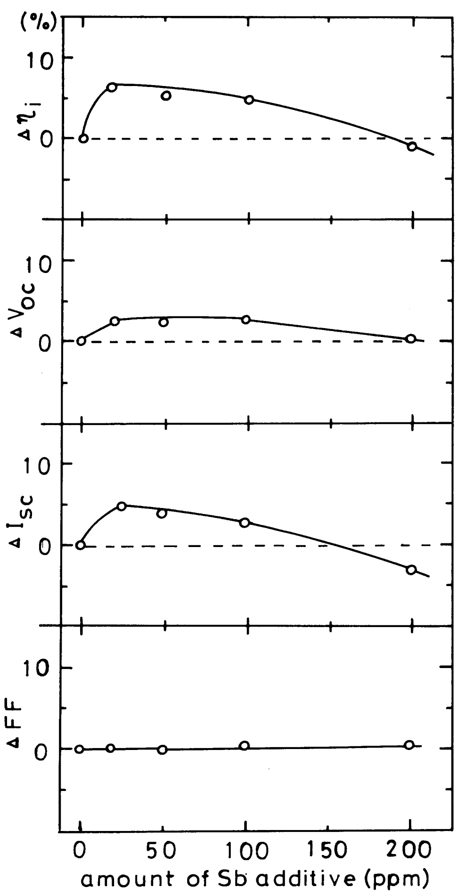

Fig. 8. Effects of Sb addition on the characteristics of solar cell heated at 400°C for 30 min.

No improvement of η_i was observed for the cells made from carbon paste with P and Bi added. Since P has high vapor pressure at the heating temperature of the carbon electrode, it vaporizes instead of substituting for Te. Even if P substitutes for Te, the defect is compensated by a donor such as Cd interstiticals.[12]

§4. Conclusion

1) An optimum heating condition of the carbon electrode for CdTe was investigated. The low resistance contact between the carbon electrode and CdTe, and consequently the higher efficiency solar cell were obtained by heating the electrode at 400°C for 30 min in an atomosphere including 1.0–1.5 mol% O_2.

2) An appropriate amount of Cu in carbon paste and heat treatment at optimum conditions might make CdTe layer p^+ type and lower the contact resistivity of CdTe/carbon electrode.

3) Remarkable improvement of η_i was observed for cells with 50 ppm Cu and 100 ppm Cu carbon electrodes heated at 400°C for 30 min in 1.0–1.5 mol% O_2 atmosphere. The highest efficiency solar cell with 0.78 cm^2 active area made from carbon paste with 50 ppm Cu added showed $V_{oc}=0.754$ V, $I_{sc}=0.022$ A, $FF=0.606$ and $\eta_i=12.8\%$. The cell with a 10×10 cm^2 substrate area consisting of two small cells connected in series showed $V_{oc}=1.478$ V, $I_{sc}=0.757$ A, $FF=0.531$ and $\eta_i=9.3\%$.

4) Adding Ag, Au, and Sb also increased η_i.

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