# INVESTIGATION OF LOW TEMPERATURE SINTERING Cu-DOPED GRAPHITE INK AS BACK ELECTRODE OF CdTe SOLAR CELLS

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This paper has investigated the change of CdS/CdTe thin film crystal microstructure after CdCl $_2$  vapor post-treatment and the effect of Cu- and Cu compound (Cu $_2$ - $_x$ Zn $_x$ Te)-doped graphite ink as back electrode on the performance of CdTe solar cells. It reveals that the post-treatment of CdCl $_2$  vapor significantly increased crystal size of both CdS and CdTe thin films and improved their crystal structure. The post-treatment of CdTe with CdCl $_2$  vapor and the addition of Cu $_2$ - $_x$ Zn $_x$ Te in graphite ink as back electrode of CdS/CdTe solar cells eliminated the etching process before back electrode was applied, enhanced the efficiency of CdTe solar cells from 6.9% using pure graphite to 13.5%, reduced the optimal sintering temperature of graphite ink from 240 °C to 200 °C, and greatly improved the thermal stability of CdTe solar cells.

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Keywords: CdTe solar cells, graphite ink, back electrode, Cu dopping

### 1. Introduction

Cadmium telluride (CdTe) thin film solar cell has been one of research focuses in solar cell industry. With the success of CdTe solar technology in commercializaton by First Solar, CdTe solar cell has been applied widely in solar farms. In the current solar industry, 90% is Si-based and 10% is thin film solar, of which CdTe has 80%. So the total share of CdTe thin film in the solar industry is 8%, exhibiting its importance in the solar industry. In order to increase the application of CdTe solar cells and reach grid-parity using CdTe solar cells in electricity generation, it is necessary and critical to improve solar cell efficiency and reduce manufacturing cost further by developing new manufacturing technique.

The work function of CdTe is as high as 5.5eV, much higher than that of most conventional metals. Depositing a metal, such as Ni, Al and Ag, et al., directly on the surface of CdTe thin film will lead to the formation of high contact resistance between metal and CdTe thin film, resulting in the decrease of solar cell performance significantly. Therefore, forming an ohmic-contact layer between CdTe thin film and back electrode is the key in obtaining high performance CdTe solar cells. One of typical methods in obtaining ohmic-contact layer is to dope CdTe thin film with dopants, forming a highly doped p+ region after heat treatment at a certain temperature. As a result, an ohmic-contact between CdTe thin film and back electrode is achieved. Cu can be used to dope the CdTe surface as a p+ dopant and form a back contact with a lower barrier height and has been widely used in high efficiency CdTe solar cells. Currently, there are several methods to form ohmic contact between CdTe thin film and back electrode using Cu as dopant. One of them is to deposit 2-5 nm Cu layer using vacuum sputtering technique or vacuum

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electron evaporation technique [1, 2], and then sputter a layer of metal back electrode. After heat treatment, a layer of highly-doped p+ region is formed. The second is to deposit a layer of Cu-doped ZnTe or ZnTe/Cu using vacuum evaporation technique [3, 4]. A phase of ZnTeCu which has a lower barrier height is formed after heat treatment. The third method is to screen-print or spray a layer of Cu-doped graphite ink, such as 40wt% HgTe:CuTe doped graphite ink [5, 6] on the surface of CdTe thin film. CdTe solar cell which efficiency is as high as 16.5% is thus obtained after heat treatment at 250 °C for 30 min in helium environment. Another example is to use Cu:Te doped graphite ink as back contact [7]. It has been reported [7] that an efficiency of 10.2% is obtained on the Cu:Te doped graphite ink pasted CdTe solar cell after sintered at 240 °C for 30 min.

When vacuum sputtering method is used to deposit a Cu layer as thin as 2-5 nm, a highly précised sputtering machine is required to control the thickness uniformity of the Cu layer on a large substrate surface. However, the machine is extremely expensive. In industry, vacuum evaporation deposition technique is widely used for depositing a thin metal layer on a small area substrate. However, it is hard to get uniform film on a substrate as large as 60x120 cm. Moreover, the cost of vacuum evaporation deposition system is extremely high, preventing its application in solar cell industry. Screen-printing or spraying technique is a simple method, and requires only a screen-printer, roll-coater, doctor blade or sprayer. Therefore, it is practical in large-scale application and beneficial to reducing the manufacturing cost of CdTe solar cells.

Since graphite ink contains a large amount of organic solvents and low-molecular resin, these organic solvents evaporate to discharge into the surrounding environment in sintering. When the sintering temperature is higher than the graphite ink sintering temperature specified by suppliers, a small amount of low molecular resin discharges into air as well, enhancing the effect of graphite ink sintering on the surrounding environment and limiting the application of graphite ink in CdTe solar cell industry. Based on the published literature [5-7], the lowest optimal sintering temperature is 240 °C, which is much higher than specified graphite ink sintering temperature, e.g., 170 °C. Therefore, it is necessary to develop a Cu-doped graphite ink with a lower sintering temperature.

In this study, the effect of CdCl<sub>2</sub> vapor treatment on the crystal structure of CdS/CdTe thin films was investigated to create a CdTe thin film which is suitable for lowering graphite ink sintering temperature. Furthermore, an attempt to reduce graphite ink sintering temperature and improve the efficiency of CdTe solar cells by doping Cu or Cu compound in the graphite ink used as back electrode was conducted. The primary goal of this study is to reduce the sintering temperature of graphite ink as back electrode effectively and improve the CdS/CdTe solar cell performance. The successful development of low temperature sintering Cu<sub>2-x</sub>Zn<sub>x</sub>Te doped graphite ink as back electrode is beneficial to manufacturing low cost CdTe solar cells.

### 2. Experimental

The CdS/CdTe thin films in this research were supplied by Zhejiang Jiayuan Green Energy Ltd.(ZJGE). The CdS and CdTe thin films were subsequently deposited on florin-doped tin oxide (FTO) purchased from Pilkington (product name is TEC15) in an automatic CdS/CdTe thin film vacuum vapour deposition system developed by ZJGE. CdS raw material was purchased from Hefei Keyang Electronic material, and CdTe was synthesized by ZJGE, respectively. The purity of both materials is 5N and 4N, respectively. The thickness of both CdS and CdTe thin films was controlled at 0.1-0.2 and 2-5 micrometer, respectively. After CdS/CdTe thin film deposition, the substrate which is deposited with CdS and CdTe thin films was sent to the CdCl<sub>2</sub> vapor treatment furnace for activation at 400 °C in N<sub>2</sub> for 30 min. After activation of CdS/CdTe thin film in the CdCl<sub>2</sub> vapor furnace, it was pasted with pure graphite ink and Cu- or Cu<sub>2-x</sub>Zn<sub>x</sub>Te-doped graphite ink and sintered in air, respectively. The concentration of Cu content in both graphite inks is 0.6 wt%. A CdS/CdTe thin film solar cell was thus obtained after sintering at a certain temperature in air. The Cu<sub>2-x</sub>Zn<sub>x</sub>Te was synthesized as follows: mix Cu, Zn, Te powder and a small amount of

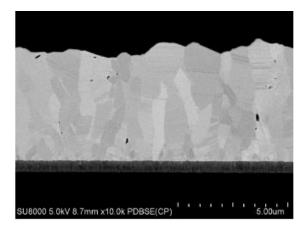
graphite ink, heat the mixture at 280°C for 60min in air, cool down to room temperature and grind to fine powder by hand.

The scanning electron microscope (SEM) analysis of CdS and CdTe thin films was carried out at CTF Solar GmbH in Germany. The performance of solar cells was characterized with a thin film solar cell J-V measurement device under AM1.5 irradiation. In order to do J-V performance measurement, the CdS/CdTe thin film around the CdTe solar cell was etched away to expose FTO substrate. No metallic conductive material was pasted on the surface of both graphite coating and FTO. The solar cell area is 0.25 cm². In the thermal stability test, a halogen lamp was used to heat a graphite plate on which CdTe solar cells were held. A thermal couple was inserted into the graphite plate and the temperature was controlled with a PID.

#### 3. Results and Discussion

## 3.1. Effect of CdCl<sub>2</sub> vapor treatment on the crystal structure of CdS/CdTe

The cross-sectional SEM images of CdS/CdTe thin films obtained directly from the CdS/CdTe thin film vacuum deposition production line using a modified close-spaced sublimation (CSS) technique, are shown in Figure 1. As shown in Figure 1 that there are a few holes along the CdTe crystal grains, the size of the CdTe crystals increases from the inner layer to the outer layer gradually. In the region close to CdS thin film, the CdTe crystal is only 200 nm, while its lateral crystal size increases to 1000 nm at the outer top surface. Compared with the CdTe crystal, the CdS crystal size is much smaller. Its lateral size is only 90 nm. This is likely related to low substrate temperature when CdS is deposited on the surface of florin-doped tin oxide (FTO). The cross-sectional SEM images of CdS and CdTe thin films after CdCl<sub>2</sub> vapor treatment at 400 °C for 30 min are shown in Figure 2 (Note: the CdS/CdTe thin films in Figures 1 and 2 were cut from different 60x120 cm panels). The CdTe thickness in Figure 1 is 5 micrometer, while it is only 2.4 micrometer in Figure 2. As shown in Figure 2, the CdTe crystal size is 2 micrometer, no holes is present in the CdTe thin film, and the CdTe surface is relatively smooth and uniform. The CdS thin film on the top of FTO in Figure 2 is about 140 nm thick, and its lateral crystal size is 250 nm. However, a small amount of holes is seen in the CdS thin film in its SEM image (Figure 2) after CdCl<sub>2</sub> vapor treatment. The above results show that CdCl<sub>2</sub> vapor treatment improves the CdTe crystal structure, increases its crystal size from 200-1000 nm to 2000 nm, and makes the holes along the CdTe crystal grains disappear. On the other hand, the lateral crystal size of CdS is also increases from 90 nm before treatment to 250 nm after treatment.



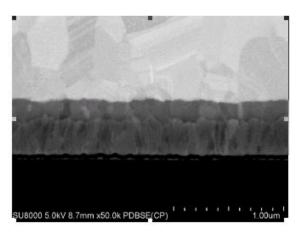
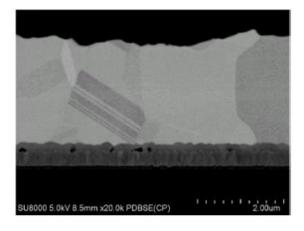
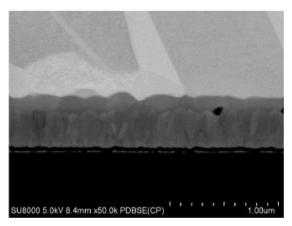


Fig. 1. SEM cross-sectional images of CdS/CdTe thin films before treatment in CdCl<sub>2</sub> vapor.

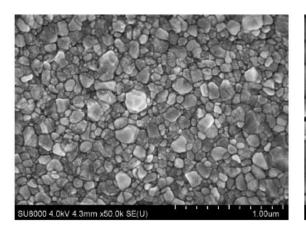
Left: CdTe thin film; Right: CdS thin film





 ${\it Fig.~2. SEM~cross-sectional~images~of~CdS/CdTe~thin~films~after~treatment~in~CdCl_2~vapor.}$ 

Left: CdTe thin film; Right: CdS thin film



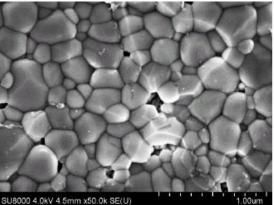


Fig. 3. SEM cross-sectional images of CdS surface morphology before (left) and after (right) CdCl<sub>2</sub> vapor treatment at 400 °C for 30 min

In order to further investigate the effect of CdCl<sub>2</sub> vapor treatment on the CdS crystal structure in CdS thin film, the CdTe thin film was etched away to expose CdS thin film before and after CdCl<sub>2</sub> treatment. After that, an analysis of CdS surface morphology using SEM technique was conducted. Figure 3 shows the SEM images of CdS thin film surface morphology before and after CdCl<sub>2</sub> vapor treatment. As revealed in Figure 3, the lateral crystal size of CdS is quite small before CdCl<sub>2</sub> vapor treatment, only 80±40 nm. This is likely related to the low substrate temperature during CdS thin film deposition. However, its lateral crystal size increased significantly after CdCl<sub>2</sub> vapor treatment, reaching at 200±90 nm. However, as shown in Figure 2, the morphology image of CdS thin film exhibits that a few holes in the CdS thin film were formed during CdCl<sub>2</sub> vapor treatment. It is likely that the lateral crystal size of CdS increases so fast that a few holes are left at some certain regions due to the movement of CdS crystals. It can also be seen in Figure 2 that the occurrence of holes in CdS thin film does not lead to the direct contact between CdTe thin film and FTO.

### 3.2. The Effect of Cu-doped graphite ink on cell performance

The performance of a CdS/CdTe solar cell, prepared with pure graphite ink as back electrode, is shown in Figure 4. Before CdS/CdTe thin film was pasted with graphite ink, it was annealed with CdCl<sub>2</sub> vapor at  $400^{\circ}$ C for 30 min in N<sub>2</sub>. The cell was sintered at  $240^{\circ}$ C for 30 min

after the pure graphite ink was pasted on the surface of CdTe thin film. The shape of J-V curve in Figure 4 shows that no effective ohmic-contact layer was formed between CdTe thin film and pure graphite layer in sintering. As a result, the performance of the CdTe solar cell in Figure 4 is much lower than those having good ohmic-contact between CdTe thin film and back electrode [4-6]. As such, the effect of sintering temperature on the solar cell performance was investigated. Table 1 shows the performance results of solar cells which were sintered at various temperatures using pure graphite ink as back electrode. The sintering time is 30 min. It can be seen in Table 1 that the J-V measurement device is not sensitive enough to detect the performance of solar cell when the sintering temperature is less than 200 °C due to high series resistance and small short circuit current. At temperature above 200 °C, the efficiency increases with the increase of sintering temperature until the sintering temperature reaches at 240 °C. After that, the short circuit current (Jsc) and fill factor (FF) decrease, even the open circuit potential (Voc) remains constant, leading to the decrease of the cell efficiency ( $\eta$ ). The decrease of efficiency when sintering temperature is higher than 240 °C is likely related to the degradation of mechanical contact between CdTe thin film and graphite layer.

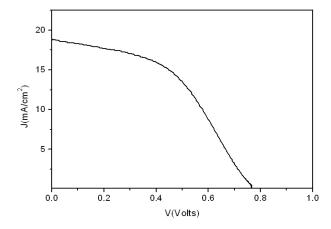


Fig. 4. J-V characteristic of CdS/CdTe thin film solar cell with pure graphite ink as back electrode.

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| Temperature/°C | Voc/V | Jsc/mAcm <sup>-2</sup> | FF/% | $\eta$ /% |
|----------------|-------|------------------------|------|-----------|
| 200            | 0.7   | 15.2                   | 38   | 4.04      |
| 210            | 0.72  | 16.5                   | 42   | 5         |
| 220            | 0.75  | 17.9                   | 43   | 5.77      |
| 230            | 0.76  | 18.4                   | 45   | 6.3       |
| 240            | 0.76  | 18.5                   | 48   | 6.75      |
| 250            | 0.76  | 17.6                   | 46   | 6.15      |

The above results indicate that using pure graphite ink as back electrode of CdTe solar cells cannot meet the requirement of fabricating high performance CdS/CdTe thin film solar cells. It has been reported [2, 8] that when the surface of CdTe is covered with Cu layer, the Cu can react with rich tellurium (Te) layer which is formed in the etching of CdTe thin film with

nitric-phosphoric acid (NP) or bromine-methanol (BM) to form a phase of Cu<sub>2</sub>Te, providing ohmic-contact layer for CdTe thin film and then improving the performance of CdTe solar cells greatly. Therefore, Cu powder was mixed with pure graphite ink at a certain ratio to make a Cu-doped graphite ink. Figure 5 shows the J-V characteristic of a CdTe solar cell using Cu-doped graphite ink as back electrode. The thickness of CdTe is 5 micrometer and CdS 140 nm. After the CdTe surface was pasted with Cu-doped graphite ink, it was sintered at 220 °C for 20 min. Unlike the J-V characteristic in Figure 4, the J-V characteristic with approximately linear relationship between J and V at a region close to Voc in Figure 5 demonstrates that the CdTe solar cell with Cu-doped graphite ink as back electrode is characterized with good ohmic-contact, indicating that Cu-doped graphite ink can be used to form ohmic-contact layer on the surface of CdTe thin film which was activated with CdCl<sub>2</sub> vapor.

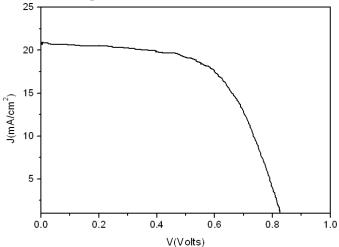


Fig. 5. J-V characteristic of CdS/CdTe thin film solar cell with Cu-doped graphite ink as back electrode.

Table 2. Effect of Cu-doped graphite ink sintering temperature on the performance of CdS/CdTe solar cells

| Temperature/°C | Voc/V | Jsc/mAcm <sup>-2</sup> | FF/% | η/%  |
|----------------|-------|------------------------|------|------|
| 190            | 0.768 | 18.3                   | 52   | 7.3  |
| 200            | 0.802 | 19                     | 56   | 8.5  |
| 210            | 0.82  | 19.2                   | 58   | 9.1  |
| 220            | 0.825 | 20.8                   | 59   | 10.1 |
| 230            | 0.792 | 19.6                   | 57   | 8.8  |
| 240            | 0.762 | 17.5                   | 55   | 7.3  |

Table 2 shows the performance of CdTe solar cells which used Cu-doped graphite ink as back electrode and were sintered at various temperatures. Compared with pure graphite ink as back electrode shown in Table 1, Voc, Jsc and FF are much higher when Cu-doped graphite ink is used as back electrode. The efficiency of the best CdTe solar cell is 10.1% for Cu-doped graphite vs. 6.9% for pure graphite as back electrode in Table 1. Since the CdTe thin films were not etched with NP or BM solution before the application of Cu-doped graphite ink, the improvement of solar cell performance is likely due to the formation of Cd<sub>1-x</sub>Cu<sub>x</sub>Te (0<x<1) phase at the surface of CdTe thin film during sintering. It can be seen in Table 2 that the CdTe solar cell sintered at 220 °C shows the best performance, indicating that 220 °C of sintering temperature is enough to form a

good ohmic-contact between CdTe thin film and back electrode. This optimal sintering temperature using Cu-doped graphite ink as back electrode is not only much lower than the optimal sintering temperature using pure graphite ink, 240 °C, but also lower than those reported in literature [5-7].

# 3.3. Effect of Cu compound ( $Cu_{2-x}Zn_xTe$ ) doped graphite ink on solar cell performance

Though the application of Cu-doped graphite ink as back electrode of CdTe solar cell improves the solar cell performance greatly, it is still much less than that of CdTe solar cells using 40wt% HgTe:CuTe-doped graphite ink as back electrode [5, 6]. Obviously, Cu-doped graphite ink needs to be modified in order to meet the requirement of fabricating high performance CdTe solar cells. An attempt to use Cu compound (Cu<sub>2-x</sub>Zn<sub>x</sub>Te) as dopant in graphite ink instead of Cu powder was made. Figure 6 shows the J-V characteristic of CdTe solar cell using Cu<sub>2-x</sub>Zn<sub>x</sub>Te -doped graphite ink as back electrode. As above, the CdS/CdTe thin film was treated with CdCl<sub>2</sub> vapor at 400°C for 30min in N<sub>2</sub>. The solar cell was sintered at 200 °C for 20 min after the graphite ink was pasted on the surface of CdTe thin film. As shown in Figure 6, the application of Cu<sub>2-x</sub>Zn<sub>x</sub>Te -doped graphite ink as back electrode improves the solar cell performance further vs. Cu-doped graphite ink. Voc and FF are increased to 0.84V and 65%, respectively, and the efficiency reaches at 12.8%, higher than that using graphite ink mixed with Cu and Te as back electrode and sintered at 240°C [7]. These results indicate the formation of an effective ohmic-contact layer between back electrode and CdTe thin film. In addition, the sintering temperature of 200 °C is much less than those reported in literature [5-7] for obtaining high performance CdTe solar cells using Cu2-xZnxTe doped graphite ink as back electrode, creating an opportunity for the application of graphite ink in CdTe solar cell large scale manufacturing.

Compared with the J-V characteristic in Figure 5, the J-V characteristic in Figure 6 shows that the application of  $Cu_{2-x}Zn_xTe$ -doped graphite ink as back electrode reduces the series resistance of solar cell and improves the technical criteria of solar cell, including Voc, Jsc and FF, indicating that the application of  $Cu_{2-x}Zn_xTe$  as dopant in graphite ink is beneficial to the formation of ohmic-contact layer at a low sintering temperature. During sintering in air, it is most likely that the Cu element in  $Cu_{2-x}Zn_xTe$  is more effective than pure Cu in the graphite ink to form a highly concentrated p+ region and a good ohmic-contact layer, leading to the reduction of the contact resistance between back electrode and CdTe thin film, and the improvement of the solar cell performance.

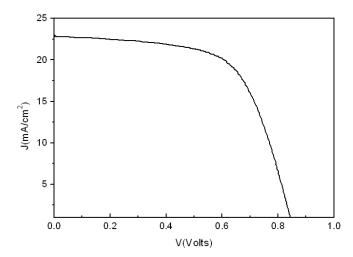


Table 3. Effect of sintering time of  $Cu_{2-x}Zn_xTe$ —doped graphite ink at 200 °C on the performance of CdS/CdTe solar cells

| Sintering time | Voc/V | Jsc/mAcm <sup>-2</sup> | FF/% | $\eta/\%$ |
|----------------|-------|------------------------|------|-----------|
| 5 min          | 0.83  | 20.2                   | 62   | 10.4      |
| 10 min         | 0.855 | 23.3                   | 68   | 13.5      |
| 15 min         | 0.85  | 23.1                   | 67   | 13.2      |
| 20 min         | 0.84  | 23                     | 66   | 12.8      |
| 25 min         | 0.83  | 22.5                   | 63   | 11.7      |
| 30 min         | 0.81  | 20.6                   | 61   | 10.2      |

The CdTe solar cell, shown in Figure 6, was sintered for 20 min, less than that reported in literature, 30 min, [5-7]. Therefore, further studies were performed to optimize sintering time at a sintering temperature of 200 °C. The results are shown in Table 3. The results in Table 3 show that the efficiency of CdTe solar cell increases with increasing sintering time, reaching the maximum at 10 min. However, the efficiency decreases with the increase of sintering time after the sintering time is longer than 15 min. These results indicate that 10-15 min of sintering time is enough to form a highly concentrated p+ region and a good ohmic-contact layer between back electrode and CdTe thin film. When the sintering time is longer than 15 min, the amount of Cu diffusing from the ohmic-contact layer to the heterojunction may be increased, resulting in the increase of recombination and decrease of Voc, similar to the results under illumination [9].

Table 4. Effect of sintering temperature of  $Cu_{2-x}Zn_xTe$ -doped graphite ink on the performance of CdS/CdTe solar cells

| Temperature/°C | Voc/V | Jsc/mAcm <sup>-2</sup> | FF/% | $\eta$ /% |
|----------------|-------|------------------------|------|-----------|
| 190            | 0.825 | 19                     | 58   | 9.1       |
| 195            | 0.836 | 22.4                   | 65   | 12        |
| 200            | 0.855 | 23.3                   | 68   | 14        |
| 210            | 0.843 | 23.2                   | 67   | 13        |
| 220            | 0.829 | 22.2                   | 65   | 12        |
| 230            | 0.806 | 21.6                   | 62   | 11        |
| 240            | 0.785 | 20.9                   | 59   | 9.7       |

The effect of sintering temperature on the performance of CdTe solar cells using  $Cu_{2-x}Zn_xTe$ -doped graphite ink as back electrode is shown in Table 4. The sintering time in Table 4 is 10 min. As shown in Table 4, the optimal sintering temperature is 200 °C, at which the CdTe solar cell has the highest efficiency. When the sintering temperature is lower than 190 °C, even the Voc is as high as 0.80V, the solar cell efficiency is less than that at 200 °C. Most likely, an effective p+ ohmic-contact region cannot be formed when the sintering temperature is lower than 200 °C. On the other hand, Voc, Jsc and FF decrease with the increase of sintering temperature when the sintering temperature is higher than 210 °C. As a result, the cell efficiency decreases with increasing sintering temperature. As expected, with the increase of sintering temperature, the diffusion rate of Cu from the ohmic-contact region to the heterojunction region is accelerated,

leading to the increase of recombination and deterioration of solar cell performance. Compared with the CdTe solar cells using Cu-doped graphite ink as back electrode in Table 2, the application of  $\text{Cu}_{2\text{-x}}\text{Zn}_x\text{Te}$  as dopant in graphite ink further decreases the sintering temperature and enhances the CdTe solar cell performance. The highest efficiency of CdTe solar cell increases from 10.1% in Table 2 to 13.5% in Table 4.

# 3.4. Thermal stability of CdTe solar cells using Cu-doped and Cu<sub>2-x</sub>Zn<sub>x</sub>Te -doped graphite ink as back electrodes

As shown in Table 3, the solar cell performance degrades when the sintering time is longer than 15 min during sintering at 200 °C, indicating that the CdTe solar cell easily degrade at a certain high temperatrue. Since the surface temperature of solar cell panel under the Sun could reach at 70-90 °C in a hot temperature climate. Therefore, a modest temperature of 120 °C was chosen in this study to accelerate the degradation of solar cells. The efficiency change of several CdTe solar cells at a constant temperature of 120 °C is shown in Figure 7. As shown in Figure 7, the cell efficiency decreased after one day at 120 °C for both pure and Cu-doped graphite ink as back electrode, while the efficiency of the CdTe solar cell using Cu<sub>2-x</sub>Zn<sub>x</sub>Te-doped graphite ink started to degrade after 4 days at 120 °C. After 30 days at 120 °C, the efficiency of CdTe solar cells using pure, Cu-doped and Cu<sub>2-x</sub>Zn<sub>x</sub>Te-doped graphite inks as back electrode decreased by 10.2, 10.2 and 4.8%, respectively. The degradation rate of the CdTe solar cell using pure graphite as back electrode is the same as that using Cu-doped graphite as back electrode, while the CdTe solar cell using Cu<sub>2-x</sub>Zn<sub>x</sub>Te-doped graphite has the lowest degradation rate. When pure graphite ink is used as back electrode, the decrease of the CdTe solar cell efficiency is likely due to the degradation of mechanical contact between graphite back electrode and CdTe thin film, leading to the increase of contact resistance. It is also likely due to the poor ohmic-contact between graphite back electrode and CdTe thin film.

When graphite ink is doped with Cu powder, the initial CdTe solar cell performance is improved. However, the degradation of CdTe solar cell is also seen due to the existence of Cu, in agreement with that reported in literature [8]. As shown in Figure 7, using Cu<sub>2-x</sub>Zn<sub>x</sub>Te-doped graphite as back electrode of CdTe solar cells not only improves the performance of the solar cell, but also enhances the thermal stability of the solar cell. The strongly thermal stability of CdTe solar cell using Cu<sub>2-x</sub>Zn<sub>x</sub>Te-doped graphite as back electrode indicates that Cu in the Cu<sub>2-x</sub>Zn<sub>x</sub>Te at the interface between back electrode and CdTe thin film is quite stable. The diffusion of Cu from the ohmic-contact region to heterojunction is limited. This may be related to the compound structure of Cu in the ohmic-contact layer, the crystal structure of CdTe thin film treated with CdCl<sub>2</sub> vapor and CdTe thin film surface structure which is not etched with NP or BM.

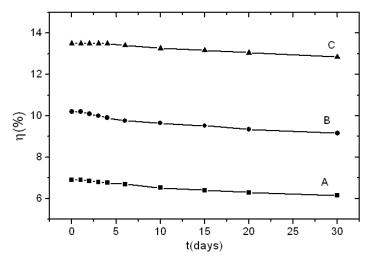


Fig.7.The change of efficiency of CdTe solar cells with pure graphite (A), Cu-doped graphite (B) and  $Cu_{2-x}Zn_xTe$ -doped graphite (C) as back electrode with exposure time at 120 °C in air.

### 4. Conclusions

After  $CdCl_2$  vapor treatment, the lateral crystal size of CdS thin film was increased from 90 nm to 200 nm, and that of CdTe thin film from 200-1000 nm to 2000 nm, the holes along CdTe crystal grains in the original CdTe thin film disappeared and the CdTe crystals became more regular in shape, while a few small holes in CdS thin film were formed during heat treatment with  $CdCl_2$  vapor.

The application of  $Cu_{2-x}Zn_xTe$ -doped graphite ink as back electrode of CdTe solar cells enhanced the performance of the solar cells significantly. A maximum efficiency of 13.5% was achieved.

The optimal sintering temperature using Cu<sub>2-x</sub>Zn<sub>x</sub>Te-doped graphite ink as back electrode of CdTe solar cells was 200 °C, much lower than that using pure or Cu-doped graphite ink.

The optimal time required to sinter  $Cu_{2-x}Zn_x$ Te-doped graphite ink pasted CdTe solar cells was shortened significantly. 10 min of sintering at 200  $^{\circ}$ C is enough to obtain a high efficiency CdTe solar cell.

The application of  $Cu_{2-x}Zn_xTe$ -doped graphite ink as back electrode of CdTe solar cells improved the thermal stability of CdTe solar cells.

The post-treatment of CdTe with  $CdCl_2$  vapor and the application of  $Cu_{2-x}Zn_x$ Te-doped graphite ink as back electrode eliminated the etching process before back electrode was applied.

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