

The formation of ZnTe:Cu and Cu_xTe double layer back contacts for CdTe solar cells

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ARTICLE INFO

Article history:

Received 5 November 2009

Received in revised form 8 February 2010

Accepted 12 February 2010

Available online 19 February 2010

Keywords:

CdTe solar cell

Back contacts

Cu_xTe

ZnTe

ABSTRACT

Processes to form a Cu_xTe layer on a ZnTe:Cu layer were investigated by various deposition methods and heat treatment. These were to make ZnTe:Cu/Cu_xTe double layer contacts for CdTe solar cells and to have benefit from both the well-matched interfacial property of ZnTe:Cu and low-resistivity Cu_xTe. The method to form Cu_xTe compounds was annealing the bi-layer of copper and tellurium which were deposited by sputtering. At an adequate annealing condition, Cu_xTe alloy was formed while maintaining underlying ZnTe without intermixing. Cu_xTe was also formed using co-deposition method. However, in terms of crystallinity, the bi-layer deposition method was considered to be better. According to this experiments, ZnTe:Cu/Cu_xTe double layer contact was successfully formed. This double layer contact is expected to be a good candidate for high efficiency CdTe solar cell.

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1. Introduction

CdTe has been regarded as an attractive material for solar cell because of its optimum band gap (1.45 eV) and high optical adsorption coefficient (over 10^5 cm^{-1} in optical range). Recently CdTe solar cells have been growing rapidly at photovoltaic markets because of its reasonably high module efficiency of 10% and cost competitiveness of under $1\$/\text{W}$ [1].

However, CdTe solar cells still need higher efficiency to lower the module cost and to increase the market share. There are several challenging points to improve the efficiency such as high-transparency window, low resistance contacts, low-defect density junction and so on. Among these points, back contact is an important issue that affects both efficiency and stability [2]. High work function of CdTe (5.9 eV) makes it difficult to form low resistance ohmic contacts. General method to make an ohmic contact is heavily doping the CdTe surface. The shallow highly doped region facilitates the carrier tunneling. Copper doped ZnTe (ZnTe:Cu) [3–5] and Cu–Te alloy (Cu_xTe) have been popular contact materials [6–10].

ZnTe:Cu is an advantageous contact material which has well-matched interfacial properties. The lattice parameter of ZnTe and CdTe is very similar. Additionally, the valence band of ZnTe:Cu is well aligned with that of CdTe [3]. This well-matched interface makes the movement of carriers across the interface easier. However, the carrier density of ZnTe:Cu is not high enough. It has been reported that the contact resistivity between ZnTe:Cu and elec-

trode metal is high and the contact resistivity largely depends on the kind of the metal electrode [4]. Cu_xTe has been another popular contact material. The interfacial property of Cu_xTe does not match with CdTe as nicely as ZnTe:Cu. However, Cu_xTe is a degenerated p-type semiconductor. Thus, ohmic contact can be easily formed using common conductors such as Aluminum [9,10]. Considering the material properties mentioned above, it is expected that the combination of Cu_xTe and ZnTe:Cu can make a back contact layer which has both low resistivity ohmic contact and good interfacial property with CdTe.

Conventionally, ZnTe:Cu has been deposited by sputtering method using an alloy target. Cu_xTe has been formed by making CdTe surface tellurium-rich and then depositing copper. After that, annealing follows to make the Cu_xTe alloy [8]. However, this method cannot be used to make ZnTe:Cu and Cu_xTe bi-layer back contact because Cu_xTe has to be formed on ZnTe:Cu, not on CdTe. So we need to form Cu_xTe layer using deposition of both copper and tellurium. Although Yun et al. reported the deposition of Cu_xTe contact on CdTe using thermal evaporation of Cu₂Te powder [6], formation of Cu_xTe contacts using deposition of both copper and tellurium has been relatively less studied than reacting copper with tellurium-rich CdTe surface. Additionally, it is necessary to form Cu_xTe while maintaining the underlying ZnTe:Cu layer. If the ZnTe:Cu layer is intermixed with the Cu_xTe layer, back contact layer will lose its beneficial property.

In this paper, various processes to form a Cu_xTe layer on a ZnTe:Cu layer were investigated. Especially, process parameters were controlled so that the Cu_xTe formation process did not damage the existing ZnTe:Cu layer.

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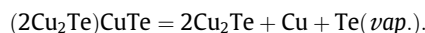
2. Experiment

ZnTe:Cu layer was deposited at 200 °C on corning glass by R.F. sputtering. ZnTe compound doped with 6 at.% copper was used as the target. It was deposited at an elevated temperature for good uniformity and electrical properties. The layer thickness was fixed to 150 nm. Cu_xTe was deposited on the ZnTe:Cu layer. It was deposited by either thermal evaporation or sputtering. In thermal evaporation, Cu_2Te powder was used as the evaporation source. In sputtering, copper and tellurium were used as the targets. In sputtering, two methods were investigated – one was to deposit copper and tellurium bi-layer and then anneal the layers to make alloy phase of Cu_xTe , the other was to co-sputter copper and tellurium at the same time. In the former process, Cu was deposited with various thicknesses for phase control while Te layer was fixed to 140 nm. After bi-layer deposition, the samples were annealed in a vacuum furnace ($\sim 1 \times 10^{-3}$ torr) at 150 °C and 250 °C for 30 min, respectively. After the Cu_xTe formation, the films were characterized. Phase variation was characterized using XRD, composition change across the film thickness was investigated using AES, and the resistivity was measured using 4-point probe method.

3. Results

ZnTe:Cu was easily sputtered from the alloy target. When it was deposited at room temperature, the film resistivity was high and the copper concentration was not uniform. However, when the film was deposited at 200 °C, copper concentration became uniform throughout the film area and the resistivity decreased from 570 to 16 mΩ cm. The results reported by other researchers were the same [5]. When the film is deposited at an elevated temperature, the diffusion of elements enhances, and as the result, the composition of the film gets uniform and closer to stoichiometric value.

Deposition of Cu_xTe alloy is a more challenging work than ZnTe:Cu. Firstly, Cu_xTe layer was deposited by thermal evaporation of Cu_2Te powder. But it was very difficult to form the reproducible Cu_xTe layer using this method. The film resistivity of the deposited Cu_xTe film varied one experiment to another in this experiment due to the difference of composition. This can be explained according to Eq. (1). Cu_2Te alloy dissociates into copper and tellurium in the evaporation source. The dissociated copper remains with Cu_2Te while Te vaporizes [7]. As the result, the evaporation source becomes more copper-rich as the deposition goes on



In Yun's experiment, a fixed amount of Cu_2Te powder was loaded in a tungsten boat and all of the powder was consumed during each deposition [6]. In this way, the total amount of evaporated copper and tellurium could be fixed in every deposition. This method may be a solution of the reproducibility problem, but it is not suitable for mass production.

Sputtering method was investigated to form Cu_xTe layer. In this paper, copper and tellurium targets were used separately. Two approaches were investigated in this experiment – copper and tellurium bi-layer deposition followed by thermal annealing and co-deposition of copper and tellurium at the same time. Fig. 1 shows the phase variation results of the bi-layer approach after annealing at 150 °C and 250 °C. The thickness of copper and tellurium layers were 100 nm and 140 nm, respectively. This thickness gives the atomic ratio of copper and tellurium to make Cu_2Te . The sample before annealing showed separate phases of copper, tellurium

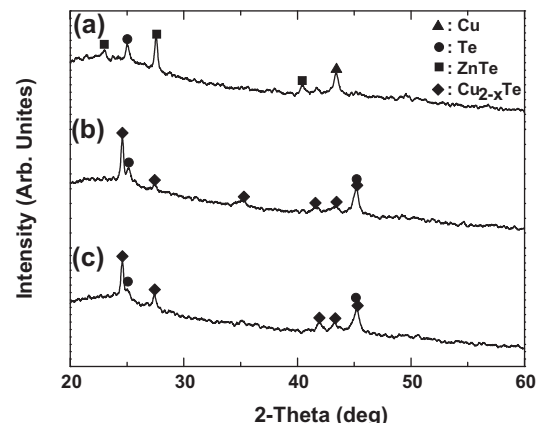


Fig. 1. XRD patterns of the samples annealed at different temperature: (a) as-deposition, (b) 150 °C, and (c) 250 °C.

and ZnTe, as expected. When the bi-layer was annealed at 150 °C, the formation of Cu–Te alloy was observed. When copper and tellurium reacted at higher temperature, for example at 250 °C, the phase rarely changed from that formed at 150 °C.

In order to make ZnTe:Cu/ Cu_xTe contact, ZnTe:Cu layer should not be damaged after Cu_xTe formation. At high process temperature, ZnTe and Cu_xTe layers may intermix with each other. In Fig. 2, the distribution of copper, tellurium and zinc after annealing was observed using AES. After the annealing at 150 °C, the zinc concentration profile did not change from that without annealing. However, after annealing at 250 °C, ZnTe:Cu and Cu_xTe layers intermixed with each other, and it was possible to observe diffusion of copper and tellurium atoms toward the ZnTe:Cu layer and diffusion of the zinc atom toward the Cu_xTe layer. Thus, it was possible to conclude that the heat treatment at 150 °C for 30 min was an adequate condition at which Cu_xTe alloy can be formed without damaging the underlying ZnTe:Cu layer.

The phase of the final Cu_xTe alloy is determined by the ratio of the reacting copper and tellurium. In order to control the phase of

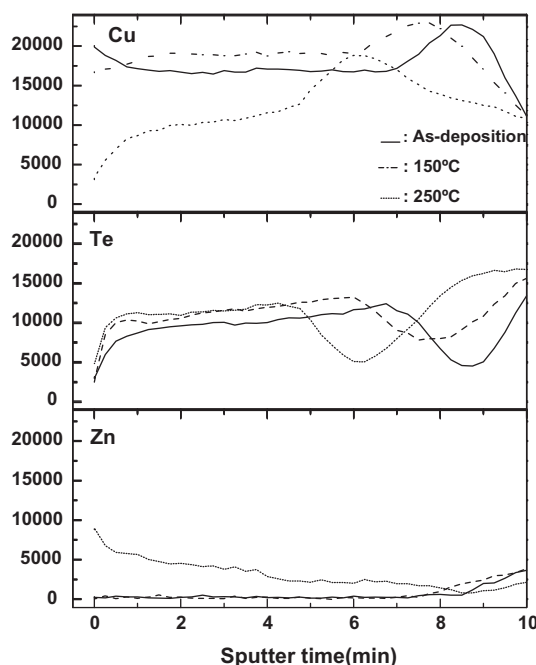


Fig. 2. AES analysis of the samples annealed at different temperature.

the film, the thickness ratio of the copper and tellurium was varied. Copper thickness was changed from 10 nm to 100 nm while tellurium thickness was fixed to 140 nm. All of samples were annealed at 150 °C for 30 min according to the result in Fig. 2. Fig. 3 shows the XRD patterns of Cu–Te alloys annealed from copper and tellurium bi-layers with different copper thickness. The phase became more copper-rich as the copper thickness increased. When a thin copper layer less than 30 nm was deposited, CuTe phase was observed. Cu₇Te₅ phase was the main phase for the sample with 50 nm copper. Sample of 100 nm copper thickness resulted in Cu₂Te phase.

Fig. 4 shows the resistivity of Cu_xTe layers as a function of copper thickness. The resistivity showed a large variation as copper thickness changed. The resistivity using 10 nm copper layer was about $1 \times 10^{-2} \Omega \text{ cm}$. Meanwhile, the resistivity of samples using 50 nm and 100 nm copper were 1×10^{-4} and $3 \times 10^{-5} \Omega \text{ cm}$, respectively. The phase control of Cu_xTe is very important because it is required to reduce the resistance while suppressing the excess copper diffusion into CdTe. It is expected that Cu_xTe contact could be optimized by controlling the copper and tellurium ratio and annealing condition.

Another method of Cu_xTe formation is using co-deposition. Copper and tellurium were deposited at the same time to form a mixture layer. With co-deposition, it is possible to be changed the two step process of bi-layer deposition and annealing to a single step process because of deposition and annealing can be conducted at the same time. Furthermore, copper and tellurium can react fast with adjacent atoms without long distance diffusion. Fig. 5 is the XRD pattern of Cu_xTe layers using co-deposition. Fig. 5a shows the result of the film co-deposited at room temperature without annealing. Fig. 5b shows the result of the film co-deposited at room temperature and then annealed at 150 °C, and Fig. 5c shows that of the film co-deposited at substrate temperature of 150 °C. Fig. 5a shows the Cu₂Te peaks even though the film was deposited at room temperature. However, the width of peaks was broad. This means that Cu_xTe does not form crystals with good crystallinity, even though copper and tellurium reaction may be enhanced by co-deposition. Fig. 5b shows nearly same peak position and shape, even though the co-deposited film was annealed at an elevated temperature. Thus, it seems that the co-deposited sample rarely changes crystallinity and phase by the annealing at 150 °C for 30 min. The sample co-deposited at the substrate temperature of 150 °C was similar to the sample annealed after co-deposition. It

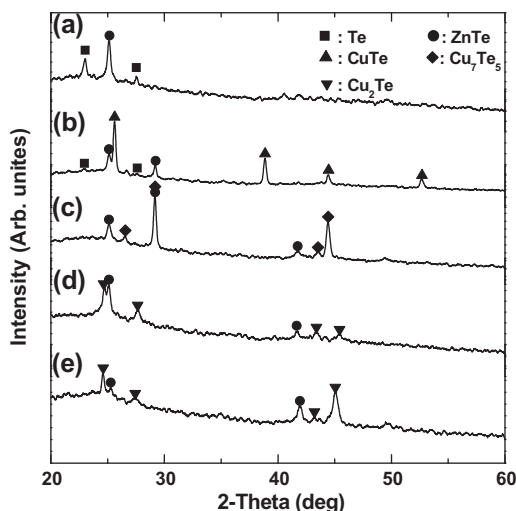


Fig. 3. XRD patterns of the samples with different Cu thickness: (a) 10 nm, (b) 30 nm, (c) 50 nm, (d) 70 nm, and (e) 100 nm.

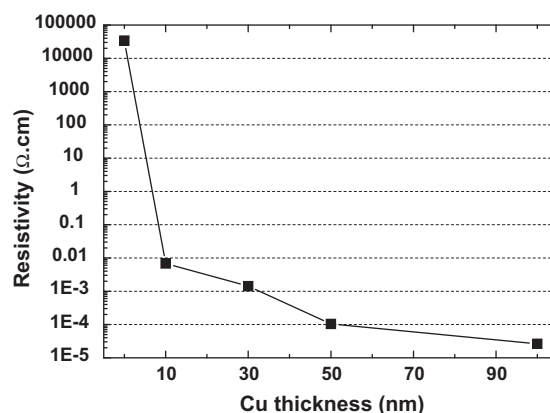


Fig. 4. Resistivity measurement results according to Cu thickness.

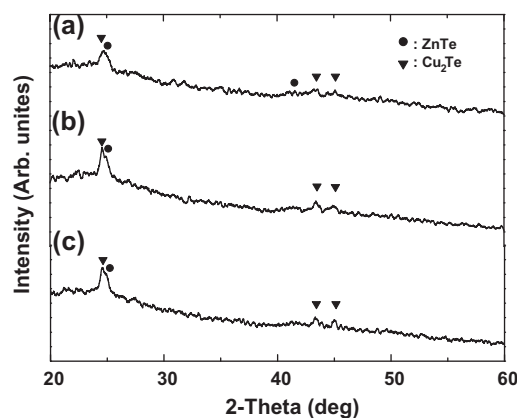


Fig. 5. XRD patterns of the samples formed at co-deposition condition: (a) co-deposition at R.T., (b) post annealing at 150 °C, and (c) co-deposition at 150 °C.

seems that the thermal energy at 150 °C is not sufficient enough to improve the crystallinity of Cu₂Te crystalline, the process at higher temperature might be able to improve the crystallinity. However, the process at high temperature may damage the underlying ZnTe:Cu layer.

4. Conclusion

Cu_xTe formation using vacuum deposition was investigated. It was difficult to make reproducible Cu_xTe films using thermal evaporation. This was probably because of the phase separation of tellurium-rich Cu_xTe phase and copper during the evaporation process. Reproducible Cu_xTe compounds were formed by annealing the bi-layer of copper and tellurium which were deposited by sputtering. In this experiment, annealing at 150 °C for 30 min was an adequate annealing condition which can make the Cu_xTe alloy while maintaining the underlying ZnTe:Cu layer without intermixing. A dominate phase of Cu_xTe changed from CuTe to Cu₂Te as copper thickness was increased and the resistivity of Cu_xTe layer was decreased as well. Cu_xTe layer also could be formed using co-deposition method. However, the crystallinity of the Cu_xTe film was not as good as the film formed by the bi-layer approach.

However, in this experiment, dual layer back contact of ZnTe:Cu and Cu_xTe was successfully formed. Detailed optimization of the Cu_xTe formation process and the application of the ZnTe:Cu/Cu_xTe dual contact to CdTe solar cells need further study.

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