Approaches to Fabricating High-Efficiency Ultra-Thin CdTe Solar Cells

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Biographical Sketch

The author was born in Wuhan, Hubei Province, China on August 5, 1981. He attended the University of Science and Technology Beijing from 1999 to 2003 and graduated with a Bachelor of Engineering degree in 2003. Afterwards, he started his graduate studies at the Institute of Process Engineering, Chinese Academy of Sciences and was awarded a Master’s degree in Chemical Engineering in 2006. He came to the University of Rochester in the summer of 2007 to pursue his Ph.D. studies in Chemical Engineering. His thesis research was to fabricate high-efficiency ultra-thin CdTe solar cells under the supervision of Professor Ching W. Tang.

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Abstract

This thesis is an investigation of the fabrication, characterization and performance of high-efficiency and ultra-thin CdTe solar cells with an aim of reducing the material usage and cell manufacturing cost. Several approaches have been successfully carried out to directly or indirectly improve the device performance. Major achievements are listed below:

1) A close-spaced sublimation (CSS) process with an improved control of the deposition temperature-time profile was developed to fabricate high-quality ultra-thin CdTe films. Three key factors in the CSS process including oxygen pressure, substrate temperature and thermal etch duration were optimized.

2) A two-stage post-deposition treatment including a high temperature annealing (HTA) followed by a vaporous cadmium chloride treatment (VCC) was developed and optimized for the growth of high-quality CdTe films. The effects of HTA and VCC on ultra-thin CdTe solar cells were revealed by a combination of characterization techniques, including photoluminescence.

3) In a collaborative effort two new back contact buffers, MoOx and Te/Cu, were identified and applied in ultra-thin CdTe solar cells. Substitution of a conventional acid etching method with the new back contact buffers was found to enhance the cell efficiency from ~10% to ~13.5%. Moreover, the new buffers improved the reproducibility of cell fabrication.
A low-resistance electrical back contact based on the Te/Cu buffer and Ni as electrode was developed. A thermal activation process was found necessary to promote ohmic contact formation. Cu diffusion into the Te layer and CdTe bulk layer occurred during the thermal activation process and must be controlled to prevent excessive diffusion into the CdS/CdTe junction. The effects of Cu concentration and Te thickness on device performance and cell stability were systematically investigated and a cell efficiency as high as ~15% with good stability has been achieved using an optimized Te/Cu buffer.

4) A novel vaporous zinc chloride treatment was developed for the formation of Cd$_{1-x}$Zn$_x$S from CdS films. Compared with conventional fabrication methods, the VZC method features simple setup and operation and is capable of producing Cd$_{1-x}$Zn$_x$S films with a homogenous structure. The Zn to Cd doping ratio in Cd$_{1-x}$Zn$_x$S can be easily controlled by adjusting the process parameters. By replacing CdS with a more transparent Cd$_{1-x}$Zn$_x$S as the window layer, CdTe solar cells with a higher (12-14%) short-circuit current, $J_{sc}$, have been demonstrated.
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The development, optimization and characterizations of MoO$_x$ back contact buffer in Chapter 4 were mainly conducted by Hao Lin. The optimization of metal electrode deposition was conducted by Hsiang Ning Wu. The experimental work of a new vapor zinc chloride treatment for Cd$_{1-x}$Zn$_x$S fabrication was mainly conducted by Jonathan A. Welt. All other work conducted for the dissertation was completed by me independently.

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1. **Introduction**

1.1 **Background of thin film CdS/CdTe solar cells**

A solar cell is a device which can convert solar energy directly into electric energy. According to “Marketbuzz™ 2012: Annual world solar photovoltaic industry report”, the world solar photovoltaic (PV) market installations reached a consolidated figure of 27.4 GW in 2011, representing an annual growth of 40% over the previous year. However, more than 80% of the current PV production is based on single-crystal silicon. The high cost of single-crystal silicon based PV remains to be the main barrier which limits their applications. It is also the driving force for developing low-cost PV technologies such as thin film solar cells. In silicon-based PV, the wafer cost accounts for over 50% of the total module cost. Replacing wafers by thin-film of semiconductor can greatly reduce the manufacturing costs. Additional benefits include lower energy consumption for solar cell production and consequently a shorter energy payback time.

Cadmium telluride (CdTe) has been regarded as a very promising material for thin-film solar cells. The maximum power that a solar cell can theoretically deliver is proportional to the product of the short circuit current \( J_{sc} \) and open circuit voltage \( V_{oc} \) produced by the cell under illumination. The \( J_{sc} \) decreases with increasing bandgap whereas the \( V_{oc} \) increases. The maximum theoretical efficiency of a single-junction solar cells is around 27% which corresponds to a bandgap of 1.5 eV, which is a good match with the 1.45 eV bandgap of CdTe. Furthermore, CdTe is a direct bandgap semiconductor with a strong absorption coefficient of \( 10^4 \sim 10^5 \text{ cm}^{-1} \) in the range of 300~850 nm, which means that
more than 99% of the photons with energy greater than the bandgap will be absorbed within 2 μm. Thus the raw material usage and therefore cost per unit area for CdTe solar cell is expected to be low. Moreover, high-quality polycrystalline CdTe films can be deposited via a number of fabrication techniques including sputtering, close-space sublimation (CSS), high vacuum thermo-evaporation, and electro-deposition. The CSS method in particular is relatively simple and has been adopted for high-speed, large-area manufacturing of CdTe PV modules.

Thin film CdTe solar cells are based on a heterojunction formed between p-CdTe and n-type semiconductor, typically II-VI compound such as n-CdS, n-CdSe, n-ZnSe or n-Cd_{1-x}Zn_xS. Among these compounds, CdS is the most commonly used. Fahrenbruch et al. compared the physical properties of several II-VI heterojunctions and their applications in the solar cell. The p-CdTe/n-CdS heterojunction possesses one of the smallest lattice mismatch of 9.7% and thermal expansion mismatch of 9%. A power conversion efficiency of 18.5% can be expected from CdS/CdTe solar cells, which is among the highest in thin film photovoltaics.

A typical configuration of thin film CdS/CdTe solar cell is shown in Fig. 1-1. It is known as the superstrate configuration with light illumination through the substrate, which is typically a soda lime or borosilicate glass with a thickness of 2~4 mm. The glass substrate provides mechanical support for the entire cell and protection against the environment for the active layers. Transparent conducting oxide (TCO) on the glass substrate acts as the front contact to the device. Indium tin oxide (ITO) and fluorine
doped tin oxide (FTO) are widely used as the TCO. $n$-CdS, as the window layer, permits the absorption of photons and the generation of electro-hole pairs largely in the $p$-CdTe layer. In conventional CdS/CdTe solar cells, gold or nickel is commonly used as the back contact to the CdTe layer.

![Diagram of CdS/CdTe solar cell structure](image)

**Figure 1-1.** A thin film CdS/CdTe solar cell structure with a superstrate configuration

### 1.2 Fabrication of thin film CdS/CdTe solar cells

Since the CdS/CdTe heterojunction is the critical part of CdTe solar cells, the fabrication of the CdTe and CdS has a strong effect on the device performance.

For the deposition of CdS films, the common methods include sputtering,\textsuperscript{14} chemical pyrolysis deposition,\textsuperscript{15} co-evaporation,\textsuperscript{16} close spaced sublimation\textsuperscript{17} and chemical bath deposition (CBD)\textsuperscript{18}. Among these deposition methods, CBD has been widely used in the laboratory scale because it is a relatively simple to achieve a compact CdS film that adheres well on a TCO substrate\textsuperscript{19,20}. 

In a CBD process, CdS film is produced via the decomposition of thiourea in an alkaline solution of cadmium salts according to the reaction (Eqn. 1-1) \(^{20}\).

\[
Cd(NH_3)_4^{2+} + SC(NH_2)_2 + 2OH^- = CdS + CH_2N_2 + 4NH_3 + 2H_2
\] (1-1)

In this reaction, cadmium acetate (Cd(CH₃CO₂)₂) and thiourea provide the cadmium and sulfur ions, respectively in an alkaline solution with ammonium hydroxide (NH₄OH) and ammonium acetate (CH₃CO₂NH₄) as the pH buffers. The CdS film growth rate is determined by the initial concentration of metal ions and the bath temperature.

A CSS method has been widely used to deposit CdTe films in most high-efficiency CdS/CdTe cells. In laboratory scale the highest efficiency in CdS/CdTe cells is produced with CdTe films deposited by the CSS method.\(^{21-23}\) The CSS method was first suggested by Nicoll et al.\(^{24}\) for the hetero-epitaxial growth of GaAs on Ge substrates. Its key feature is the short distance between the source and the substrate as illustrated in Fig.1-2. The CSS technique offers higher deposition rate and more efficient material utilization than other techniques such as sputtering and electro-deposition. Moreover, it can be scaled up for manufacturing with wide process window in terms of vacuum range and process temperature below 700 °C.\(^{25}\) The key parameters for a CSS deposition include substrate temperature \(T_{sub}\), source temperature \(T_{src}\), spacing between the source and substrate \(d\), and ambient oxygen pressure \(P_{O2}\).\(^{26}\)
Figure 1-2. Schematic illustration of experimental setup for CSS deposition of CdTe films

\[
\text{CdTe}(s) + \text{CdCl}_2(s) \rightarrow 2\text{Cd}(g) + \frac{1}{2}\text{Te}_2(g) + \text{Cl}_2(g) \rightarrow \text{CdCl}_2(s) + \text{CdTe}(s)
\]

(1-2)

To improve the crystallinity quality of the CdTe films produced by the CSS or other methods, it is necessary to subject the as-deposited CdTe films to various post-deposition thermal treatments, including the CdCl\(_2\) treatment. A CdCl\(_2\) treatment usually leads to prominent grain growth in CdTe films as a result of vapor phase induced re-crystallization\(^{27}\) described in the reaction shown in Eqn. 1-2.\(^{12,20}\) For CdTe films deposited with a high substrate temperature, though the average grain size is large, a CdCl\(_2\) treatment can still promote grain boundary re-growth and eliminate small grains. It is believed that the presence of Cl\(_2\) promotes the crystalline growth of CdTe by means of local vapor phase transport.\(^{20}\)

In addition to enhancing the CdTe grain structures, a CdCl\(_2\) treatment can also cause inter-diffusion of sulfur and tellurium ions at the CdTe/CdS interface resulting in improved junction characteristics.\(^{28}\) Moreover, a CdCl\(_2\) treatment can also create V\(_{\text{Cd-Cl}}\)
complexes, known to be shallow acceptors in CdTe films.\textsuperscript{28} Generally, a typical CdCl\textsubscript{2} treatment includes three steps as follows:

1) Apply a layer of CdCl\textsubscript{2} on top of CdTe film either by dip-coating or by evaporation;
2) Anneal the CdS/CdTe/CdCl\textsubscript{2} stack layers in air at 380~420 °C for 20~40 min;
3) Remove CdCl\textsubscript{2} residues from the treated CdTe films.

A CdCl\textsubscript{2} treatment has also been applied to improve crystallinity and optical properties of the CdS window layer.\textsuperscript{29,30}

Back contact formation is the last step in the cell fabrication. In the band diagram shown in Fig.1-3a \textsuperscript{31}, a contact barrier, $\Phi_b$, for holes exists at the CdTe/metal interface, which can be calculated using Eqn. 1-3,

$$\Phi_b = \frac{E_g}{q} + \chi - \varphi_m$$

(1-3)

where $E_g$, $\chi$ and $\varphi_m$ represent the bandgap of CdTe, the electron affinity of CdTe and the work function of the contact metal, respectively. Because of the high work function of CdTe (5.6~5.7 eV), the contact between CdTe and most common metals (with a work function lower than that of CdTe) invariably results in a barrier, $\Phi_b$, which is too high to allow the hole carriers to transport across the $p$-CdTe/metal junction efficiently.
Figure 1-3. Band diagrams of (top) CdS/CdTe solar cell (the subscript b represents the diode CdTe/metal), and (bottom) CdTe/MX/metal.

In order to reduce this contact barrier and thus promote the formation of ohmic contact to $p$-CdTe, a back contact buffer layer (through an etching process) was introduced into the fabrication process$^{32}$. The as-fabricated glass/ITO/CdS/CdTe stack is dipped in an etching solution for certain duration and dried after the residual etching solution is removed by rinsing in deionized water. The etchant is a solution of nitric and phosphoric
acids, commonly known as NP solution, or a solution of bromine and methanol, named as BM solution. In addition to solution treatments, direct introduction of a buffer layer MX (MX = Cu₅Te, ZnTe, Sb₂Te₃, Ni₂P, Te, etc.) between p-CdTe and the back contact metal can also produce a low-resistance back contact. As Fig. 1-3b shows, the high space charge density in the MX layer at the MX/metal junction can allow tunneling of charge carriers. Cu and Sb from the MX layer are known to form shallow acceptors in CdTe. Besides the high work function of MX layer also reduce the energy barrier for the hole transfer at the CdTe/MX junction.

1.3 Deficiencies of thin film CdS/CdTe solar cells

The potential environmental hazard of CdS/CdTe solar cells resulting from the toxicity of cadmium compounds is one of its deficiencies. Acute inhalation exposure to high levels of cadmium in humans may cause effects on the lung such as pulmonary and bronchial irritation. Chronic inhalation and oral exposure to cadmium results in a build-up in the kidneys which can result in kidney diseases and reproductive effects. According to experimental investigations and life cycle analysis of cadmium in CdTe PV productions, if CdTe PV modules are used under normal conditions, no emission of any kind can be generated. The emission of cadmium from CdTe PV modules during accidents (e.g. fire, breakage) is negligible. But the possible emission of cadmium during the Cd mining and PV manufacturing and recycling cannot be completely avoided.
In order to reduce the environmental hazards resulting from cadmium compounds, several approaches have been adopted in the research and manufacturing of CdS/CdTe solar cells:

1) Reducing the cadmium content of CdS/CdTe solar cells;
2) Increasing the raw material utilization in the fabrication of CdS/CdTe solar cells;
3) Minimizing the emission of cadmium in the cadmium mining and PV manufacturing process;
4) Developing advanced technologies to recover cadmium from the recycled CdTe PV modules and from cadmium waste generated from PV manufacturing.

1.4 Developing ultra-thin CdTe solar cells and its challenges

Reducing the thickness of CdTe film, a.k.a. developing ultra-thin CdTe solar cells (~1 µm), is a primary solution to reduce cadmium usage. Additional advantages include extending the tellurium supply, which is a limited reserve, and reducing the material cost as well as the waste treatment cost.\(^{36}\) Furthermore, reduction of the CdTe layer thickness also makes it easier to incorporate the CdTe layer in tandem solar cells and potential PV glazing devices.\(^{37}\)

In most high-efficiency CdTe solar cells the CdTe thickness is typically in the range of 5 to 10 µm.\(^{21,38}\) A thick absorber layer can avoid pinholes, which can result in shorting the cell.\(^{37}\) However, the recombination loss of charge carriers in a thicker CdTe layer is more prominent.\(^{37}\) Moreover, a thicker CdTe layer also has a larger series resistance. These drawbacks can adversely affect cell performance.
Reducing the thickness of CdTe layer from 5~10 µm to ~1 µm can alleviate the aforementioned drawbacks. Due to the high absorption coefficient of CdTe, the minimum thickness required to directly absorb ~90% of the incident irradiation is approximately 1 µm. Theoretical calculation of carrier generation in CdS/CdTe solar cells by Amin et al shows most of the charged carriers are generated within the first 1 µm-CdTe layer from the CdS/CdTe junction, and beyond this region the carrier generation is reduced by two orders of magnitude. Therefore, in principle, only 1~2-µm CdTe layer is needed to produce highly efficient CdS/CdTe solar cells.

So far, the most popular methods for fabricating ultra-thin CdTe film are magnetron sputtering deposition and metal organic chemical vapor deposition (MOCVD). Gupta et al fabricated an 11.8%-CdTe solar cell in which the CdTe layer thickness was 0.9 µm. The CdTe film was deposited by magnetron sputtering. Jones et al achieved an efficiency of 11.4% in an ultra-thin CdTe solar cell in which the 1-µm-thick CdTe layer was deposited by MOCVD. Both the magnetron sputtering and MOCVD methods require complicated setup and costly maintenance; moreover, the deposition rates of CdTe using these methods are very low (<100 nm/min), which is not applicable in large-scale PV manufacturing. Because of the many advantages of the CSS technique as mentioned, it is important to explore the optimized deposition conditions for ultra-thin CdTe film using a CSS method.
As shown in Fig. 1-4, one of the intrinsic characteristics of CdTe films deposited by a CSS method is large grain size. As a result of high substrate temperature, CdTe crystals nucleated on CdS films are thermodynamically favorable to grow in both horizontal and vertical directions. It has been proved that the grain size of CdTe film scales with its thickness\textsuperscript{25,42}. Therefore, in order to fabricate pinhole-free CdTe film with a thickness around 1 µm, it is critical to control the growth of CdTe crystals and limit the grain size to within 1 µm.

A CdCl\textsubscript{2} treatment on CdTe films has been widely acknowledged as a critical step to achieve high device efficiency. However, if CdTe films were over treated by CdCl\textsubscript{2}, excessive inter-diffusion at the CdS/CdTe heterojunction will create pinholes on CdS films and thus deteriorate cell performance. Partial delamination of CdTe film from the substrate has been observed in the extreme case. Thus optimized cadmium treatment is the key to the high device efficiency.
The optimal cadmium chloride treatment conditions, which include annealing temperature, duration and ambient pressure, are influenced by the thickness of CdTe and CdS films, the morphology of the CdTe films and the post-treatment conditions of CdS films. The optimal treatment conditions for normal CdTe films may not be suitable for ultra-thin CdTe films and need to be systematically investigated.

Figure 1-5. Schematic illustration of recombination pathways generating low shunt resistance along grain boundaries of CdTe films, (a) before and (b) after NP etching, and (c) after NP etching and electrode deposition.

As discussed in section 1.2, there are mainly two types of method to form ohmic contact to p-CdTe: etching CdTe films with NP or BM solutions, and introducing a MX buffer layer between p-CdTe and metals. For CdTe films with a normal thickness (3~10 µm), the NP or BM etching method is equivalent or even better than inserting a MX
buffer layer in forming ohmic contact to $p$-CdTe. However, as illustrated in Fig.1-5 \textsuperscript{43}, one of the drawbacks of NP or BM treatment is that the tellurium rich layer on CdTe films resulting from the treatment produces low shunt resistance along grain boundaries, which leads to large leakage current and thereof low $V_{oc}$. The drawback will be amplified if the CdTe film is not compact enough (Fig. 1-5b) or the etching duration is too long or the CdTe film is too thin. Alternative methods are required to replace the conventional back contact formation schemes.

1.5 Summary

As a promising and commercialized PV technology, CdTe solar cells still face a lot of challenges including increasing material cost as a result of limited tellurium supplies, and environmental hazards associated with potential cadmium emission and waste management.

Developing ultra-thin CdTe solar cells with the CdTe thickness of $\sim$1 μm or less is a feasible approach to solving the challenges. Reducing the thickness of CdTe from 4~6 μm to $\sim$1 μm will reduce the materials cost, alleviate the environmental impact of cadmium compound, and improve manufacturing productivity.

Reducing the thickness of CdTe while maintaining the high-efficiency (15~17 %) is technically challenging and will require significant development efforts, including the following:

1) Improving the fabricating techniques for the production of ultra-thin CdTe films with high throughput.
2) Addressing the low-crystallinity and corresponding defects issues of ultra-thin CdTe films deposited at low substrate temperature.

3) Developing new back contact materials to replace the conventional solution etching method which is not applicable to ultra-thin CdTe cells.

This thesis work is aimed to producing high-efficiency ultra-thin CdTe solar cells by providing solutions to these issues.
2. Fabrication of ultra-thin CdTe films

To achieve high-efficiency in ultra-thin CdTe solar cells, the most important step is to deposit pinhole-free CdTe films with sufficient crystallinity. As discussed in Section 1.2, deposition methods such as sputtering are better suited for depositing ultra-thin CdTe films. However, due to their limitations especially low deposition rate, these methods are not as compatible to large-scale manufacturing as the CSS method. This chapter will discuss the fabrication of ultra-thin CdTe films using a CSS method with a modified temperature-time profile, and the effects of CSS deposition conditions on CdTe film morphology and device performance.

2.1 Close-spaced sublimation with modified temperature-time profile

2.1.1 Control factors of fabricating pinhole-free CdTe films

As discussed in Section 1.4, in order to fabricate pinhole-free CdTe films with a thickness around 1 µm, it is critical to control the crystal growth and to limit the grain size to within 1 µm. To deposit CdTe films with the grain size of ~1 µm, the conventional CSS deposition conditions will have to be modified.

According to Luschitz et al., the grain size of CdTe films deposited by a CSS method is highly dependent on the substrate temperature. CdTe films deposited with $T_{\text{sub}}$ between 350 °C and 460 °C exhibit pyramidally shaped grains which extend throughout the whole film. The surface grain size linearly increases from ~0.5 µm at $T_{\text{sub}} = 350$ °C to ~1.5 µm at $T_{\text{sub}} = 460$ °C. In order to limit the grain size of CdTe to within 1 µm, $T_{\text{sub}}$ between 350 °C and 460 °C should be used. However, the high density of deep pinholes
in the CdTe films deposited with $T_{\text{sub}}$ between 350 °C and 460 °C can impair the device performance and stability.

CdTe films deposited with $T_{\text{sub}} > 460$ °C, which has been widely used in the state-of-the-art process of CSS deposition, are featured by irregularly shaped grains, a high surface roughness and non-uniformly distributed grain size. Bulk diffusion processes including recrystallization and grain growth result in the as-mentioned morphological characteristics. Although the grain size of CdTe films is much larger than 1 µm and not uniform, it is better to choose $T_{\text{sub}} > 460$ °C because the resulting films are more dense and compact. It will be necessary to reduce the grain size through other means.

The introduction of oxygen into the CSS deposition of CdTe films was due to Tyan et al. Apparently incorporating oxygen in the deposition ambient can increase the amount of nucleation sites on the CdS film and thus reduce the grain size of CdTe film grown on top of the CdS film. O$_2$ react with CdS to form CdO which serve as nucleation sites for CdTe growth. By tailoring the O$_2$ partial pressure in the ambient, it is possible to deposit ultra-thin CdTe film at a high substrate temperature to produce crystalline CdTe films with a grain size < 1 µm while retaining good film quality.

2.1.2 Modified temperature-time profile for depositing ultra-thin CdTe films

Fig.2-1a shows typical temperature profiles of depositing CdTe films with a thickness of 3~8 µm. $T_{\text{sub}}$ was maintained at 600 °C during the preheating step and the deposition process in order to achieve high Voc. The deposition rate was set at 1~1.5 µm/min by adjusting $T_{\text{src}}$, $d$ and $P_{O_2}$. 
Figure 2-1. (a) Conventional temperature-time profile for depositing normal CdTe films, and (b) modified temperature-time profile for depositing ultra-thin CdTe films.

In order to deposit ultra-thin CdTe films with a thickness of 1~1.5 µm, a new temperature-time profile was used, as shown in Fig.2-1b. $T_{\text{sub}}$ was reduced from 600 °C to 525 °C. Compared with the conventional temperature-time profile in which $T_{\text{src}}$ was
unchanged during the deposition process, in the new temperature profile, $T_{src}$ was varied from 550 °C to 625 °C. Before $T_{src}$ reached the maximum value, $T_{src}-T_{sub}$ ranged from 0 to 100 °C. Small $T_{src}-T_{sub}$ leaded to a low deposition rate and might result in dense film at the beginning of the deposition, a critical step to reduce pinhole formation. The average deposition rate was ~500 nm/min.

The ramping rate of the source was decreased from 300 °C/min to 100 °C/min. Since the heat transfer was more thorough with a longer ramping duration, the thermal equilibrium between the graphite holder and the CdTe granules was more easily to achieve.

2.1.3 Comparison between conventional and modified temperature-time profile

As shown in Fig. 2-2, in terms of roughness or roughness/thickness ratio, the CdTe films deposited by a CSS method with the new temperature-time profile have a much smoother surface than the film deposited with the conventional temperature-time profile. Small roughness of the film deposited by a CSS method with the new temperature-time profile indirectly suggests small grain size from low deposition rate.

Fig.2-3 shows the SEM images of CdTe films deposited using the conventional and new temperature profile. The terrace-type texture on the CdTe grains, which is similar to the CdTe grains shown in the SEM images in Fig.1-4, indicates good film crystallinity. The grain size of the CdTe film deposited using the modified temperature-time profile is much smaller than that using the conventional temperature-time profile. The difference
in morphology is due to the lower substrate temperature in the modified temperature-time profile.

Figure 2-2. Thickness profiles of CdTe films deposited by a CSS method using the conventional and modified temperature-time profile.
As the X-ray diffraction spectra (XRD) in Fig. 2-4 exhibit, the CdTe films deposited using both temperature-time profile are (111)-orientation favored\textsuperscript{25,26}. Moreover, the crystallinity of CdTe films deposited using the modified temperature-time profile is poorer than that using the conventional temperature-time profile.

Figure 2-4. XRD spectra of the CdTe films deposited by a CSS method using the conventional and modified temperature-time profile.
Although CdTe films deposited using the modified temperature-time profile have smaller grain size and lower crystallinity, they feature smooth surface and compact grains. The issues related to film crystallinity can be solved by post-deposition treatment, which will be addressed in Chapter 3.

2.2 Effects of deposition conditions on ultra-thin CdTe film

2.2.1 Oxygen pressure

Figure 2-5. AFM images of ultra-thin CdTe films deposited by a CSS method at different oxygen partial pressure in nitrogen. (a) 100%, (b) 75%, (c) 50%, (d) 25% and (e) 0%.
As discussed in Section 2.1.1, oxygen can increase the amount of nucleation sites on CdS films and thus reduce the grain size of CdTe. Fig.2-5 presents the atomic force microscopy (AFM) images of ultra-thin CdTe films deposited at different oxygen partial pressures. These AFM images clearly show the evolution of CdTe morphology with increasing oxygen partial pressure. The grain size and surface roughness of CdTe decreases as oxygen partial pressure was increased, which is consistent with previous studies.\textsuperscript{47,48}

Furthermore, oxygen has been proved to increase the acceptor concentration and enhance the \textit{p}-type characteristics of CdTe film.\textsuperscript{47,49-51} Hsu \textit{et al} \textsuperscript{49} found that the oxygen content in CdTe film deposited by a CSS method in the oxygen ambient was unusually high ($10^{19}$-$10^{20}$ cm\textsuperscript{-3}), which did not result in band-gap narrowing. Besides, the increase in oxygen concentration did not decrease the impurity ionization energy. Considering that the experimental results did not follow the conventional theory of simple impurity doping, he suggested that oxygen atoms did not behave as a simple shallow acceptor but promoted the formation of \textit{p}-type complexes. Hernández-Fenollosa \textit{et al} \textsuperscript{52} affirmed Hsu’s results by conducting photoluminescence (PL) studies on CdS/CdTe solar cells treated with oxygen. They found that oxygen enhanced the concentrations of \textit{p}-type complexes, Cl\textsubscript{Te} and V\textsubscript{Cd}, in CdTe. Hernández-Fenollosa’s findings have been validated by several independent research groups.\textsuperscript{48,53}

Although oxygen is beneficial in enhancing the \textit{p}-type characteristics of CdTe film, it can also produce problematic issues. Excess oxygen can result in severe oxidation of
CdTe source and laterally non-uniform deposition. Rose *et al.*\textsuperscript{54} revealed that source oxidation can decrease sublimation from the source and reduce the reproducibility and manufacturing-suitability of the process. Vora *et al.*\textsuperscript{55} found that higher oxygen partial pressure resulted in larger oxygen concentration gradient in the CSS system and thus different reaction rates between oxygen and Cd vapor at different positions.

![Graph](image1)

*Figure 2-6.* (a) Photo and (b) dark *J*-V characteristics of ultra-thin CdTe solar cells with CdTe films deposited by a CSS method under different oxygen pressures
Table 2-1. Device performance of ultra-thin CdTe solar cells with CdTe deposited by a CSS method under different oxygen pressures*1

<table>
<thead>
<tr>
<th>Cell</th>
<th>CSS deposition conditions</th>
<th>VCC*2 treatment conditions</th>
<th>J-V characteristics</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$T_{\text{sub}}$ (°C)</td>
<td>$T_{\text{src}}$ (°C)</td>
<td>$P_{\text{O}_2}$ (°C)</td>
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<tr>
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<td>525</td>
<td>615</td>
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<tr>
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<tr>
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</tr>
<tr>
<td>1360C</td>
<td>525</td>
<td>615</td>
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</table>

*1: The thickness of CdTe films is 1.5 ± 0.2 μm. The back contact for the CdTe solar cells is 40 nm MoO$_x$ and 200 nm Ni, deposited by thermal evaporation and DC sputtering respectively.

*2: VCC stands for vaporous cadmium chloride treatment
Figure 2-6 shows the photo and dark $J$-$V$ characteristics of CdTe solar cells with CdTe films deposited under different oxygen pressures. The cell fabrication details and device performance are listed in Table.2-1. In order to compensate the effects of chamber pressure on deposition rate, the deposition durations were adjusted accordingly so that the as-deposited CdTe films had similar thicknesses. Based on the $J$-$V$ characteristics and device performance, the optimum oxygen pressure is 1.5 Torr which produces the highest efficiency. If the oxygen pressure is much lower, e.g. 0.5 Torr, the CdTe solar cell has a lower $V_{oc}$ of 730 mV, which is consistent with the larger leakage current. The inferior device performance is presumably due to the lower density of nucleation sites and less effective doping effect. If the oxygen pressure is higher, e.g. 2.0 Torr, the device efficiency is almost not affected, although the $V_{oc}$ is slightly lower.

2.2.2 Substrate temperature

As discussed in Section 2.1.1, in order to deposit pinhole-free CdTe films, it is better to choose $T_{sub} > 460 ^\circ \text{C}$ and to reduce the grain size through other means. As discussed in Section 2.2.1, oxygen can reduce the CdTe grain size by increasing the density of nucleation sites on CdS films. With a low substrate temperature of 525 $^\circ \text{C}$, the optimum oxygen pressure is $\sim 1.5$ Torr. However, low $T_{sub}$ can result in poor crystallinity and thus more defects and impurities, which is detrimental to device performance. In order to compensate the effects of poor crystallinity, a post-deposition annealing treatment is required to improve film quality, which will be discussed in detail in Chapter 3. Alternatively, CdTe film crystallinity can be enhanced by increasing $T_{sub}$. Although
higher $T_{\text{sub}}$ tends to produce larger grain size, the suppression effects of oxygen on grain growth can be utilized to balance the grain size.

Figure 2-7. (a) Photo and (b) dark $J$-$V$ characteristics of ultra-thin CdTe solar cells with CdTe deposited by a CSS method under different substrate temperatures.
Table 2-2. Device performance of ultra-thin CdTe solar cells with CdTe deposited by a CSS method under different substrate temperatures. *3

<table>
<thead>
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<th>Cell</th>
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<th>VCC treatment conditions</th>
<th>J-V characteristics</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td>$T_{\text{src}}$ (°C)</td>
<td>$P_{\text{O}_2}$ (°C)</td>
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<td>635</td>
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</tr>
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</table>

*3: The thickness of CdTe films is 1.5 ± 0.2 μm. The back contact for the CdTe solar cells is 40 nm MoO$_x$ and 200 nm Ni, deposited by thermal evaporation and DC sputtering respectively.
Fig. 2-7 shows the photo and dark J-V characteristics of CdTe solar cells with CdTe films deposited under different substrate temperatures. The cell fabrication details and device performance are listed in Table.2-2. The SEM images of these CdTe films with a thickness of ~1.5 μm are displayed in Fig.2-8.

The average grain sizes of CdTe films were statistically measured using the SEM images. As shown in Fig.2-8, CdTe film deposited at $T_{\text{sub}} = 520$ °C has an average grain size of ~0.7 μm. As $T_{\text{sub}}$ was increased from 520 °C to 560 °C, the average grain size increased to ~1.1 μm which is still much smaller than the film thickness, suggesting the suppression effects of oxygen on grain growth. The increase of grain size resulted in the reduction of grain boundaries and the defects at the boundaries. As for the device
performance, the cells with CdTe film deposited at higher $T_{\text{sub}}$ (550~560 °C) show higher $V_{\text{oc}}$ and $FF$ than that at lower $T_{\text{sub}}$ (520~535 °C). However, in order to balance the grain growth for $T_{\text{sub}} = 560$ °C, the oxygen pressure has to be increased to 2.5 Torr. Higher oxygen pressure will readily result in more oxides (CdO, CdTeO$_3$) on the CdTe surface and increase the series resistance of the cell, which explains the fact that cell 1400D has lower $FF$ than cell 1400C, as shown in Table 2-2.

2.2.3 Thermal etch duration

In order to increase the density of nucleation sites on glass/FTO/CdS substrate (or CdS substrate for short), facilitate the growth of CdTe crystal and therefore reduce the amount of pinholes in CdTe films, oxygen was introduced in the CSS process. Apart from the introduction of oxygen, a surface pre-treatment on CdS substrate at elevated temperature, named thermal etch, is also important and necessary\textsuperscript{56}. In addition to promote the formation of nucleation sites, thermal etch also cleans the substrate surface prior to CdTe growth. Rose et al\textsuperscript{48} also found that the thermal etch could alter the stoichiometry of the surface.

Fig. 2-9 shows the SEM images of CdTe films with a thickness of ~1.5 μm deposited with a thermal etch on the CdS substrate at 550 °C for different durations. The photo and dark $J$-$V$ characteristics of CdTe solar cells using these CdTe films are displayed in Fig.2-10. The cell fabrication details and device performance are listed in Table 2-3.
As shown in Fig. 2-9, compared with the CdTe film deposited without thermal etch (0 min), the films with thermal etch have larger grain size. As the thermal etch duration was increased from 0 min to 6 min, the average grain size increased from ~0.9 μm to ~1.3 μm. Larger grain size results in fewer defects at the grain boundaries and better film crystallinity.

As shown in Fig. 2-10 and Table 2-3, the cells in which CdTe films were deposited with thermal etch have significantly higher $V_{oc}$, $FF$ and $\eta$ than that without thermal etch. However, if the thermal etch was carried out for a long duration (> 6.0 min), the $V_{oc}$ started to deteriorate. Rose et al.\textsuperscript{55} believed that CdS is sublimated from the substrate.
during the thermal etch process which may result in the increase of leakage current and the reduction of $V_{oc}$.

Figure 2-10. (a) Photo and (b) dark $J$-$V$ characteristics of ultra-thin CdTe solar cells with CdTe deposited by a CSS method with different thermal etch durations at 550°C.

It is noted that often the minimum of the absolute dark current density, as shown in dark J-V traces of in Fig.2-10b as well as many other figures, is not at zero voltage bias.
This anomaly may be due to measurement errors related to hysteresis of the J-V traces which is due to charge trapping in some of the cells. Another possible cause for the voltage offsets is leakage light from room light during the dark J-V measurements.

2.3 Summary

To fabricate pin-hole free CdTe films with a thickness of ~1 μm by a CSS method, it is important to control the growth of CdTe crystals and limit the grain size to <1 μm. Since the conventional temperature-time profile of a CSS method features high deposition rate (>1 μm/min) and high substrate temperature (~600 °C), it is inherently difficult to fabricate ultra-thin CdTe films with a good reproducibility. With the modified temperature-time profile, ultra-thin CdTe films with a small roughness/thickness ratio and very few pinholes can be reproducibly deposited.

Three key parameters, oxygen pressure, substrate temperature and thermal etch duration, have been systematically investigated. Although low substrate temperature (<525 °C) is favorable for the deposition of pinhole-free ultra-thin CdTe films, the poor crystallinity in these films and associated defects are problematic. By optimizing the substrate temperature, oxygen pressure, and thermal etch of CdS, ultra-thin CdTe films with very few pinholes and good film crystallinity have been fabricated.
Table 2-3 Device performance of ultra-thin CdTe solar cells with CdTe deposited by a CSS method with different thermal etch durations on the substrate*4,5

<table>
<thead>
<tr>
<th>Cell</th>
<th>$T_{sub}$ (°C)</th>
<th>$T_{src}$ (°C)</th>
<th>$P_{O2}$ (°C)</th>
<th>$t_{dep}$ (min)</th>
<th>$t_{etch}$ (min)</th>
<th>$T_{ann}$ (°C)</th>
<th>$P_{O2/N2}$ (Torr)</th>
<th>$t_{ann}$ (min)</th>
<th>$J_{sc}$ (mAcm$^{-2}$)</th>
<th>$V_{oc}$ (mV)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
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<td>625</td>
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<td>2.0</td>
<td>0</td>
<td>400</td>
<td>2/8</td>
<td>4.5</td>
<td>21.4</td>
<td>706</td>
<td>69.7</td>
<td>10.5</td>
</tr>
<tr>
<td>1917B</td>
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<td>625</td>
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<td>2.0</td>
<td>1.5</td>
<td>400</td>
<td>2/8</td>
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<td>21.4</td>
<td>750</td>
<td>70.7</td>
<td>11.3</td>
</tr>
<tr>
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<td>625</td>
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<td>2.0</td>
<td>3.0</td>
<td>400</td>
<td>2/8</td>
<td>4.5</td>
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<tr>
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<td>21.6</td>
<td>760</td>
<td>78.2</td>
<td>12.8</td>
</tr>
</tbody>
</table>

*4: The back contact for the CdTe solar cells is 100 nm Te/1.1 nm Cu and 200 nm Ni deposited by DC sputtering. The cell was subjected to a thermal activation at 275°C for 10s.

*4: The thickness of CdTe film is 1.6 ± 0.2 μm
3. **Post-deposition treatments on ultra-thin CdTe films**

According to the conclusions of Chapter 2, the substrate temperature should be kept at 500~525 °C for CSS deposition of ultra-thin CdTe films. Note for depositing CdTe films of normal thicknesses, the substrate can be maintained at a higher temperature of 550~600 °C. The relatively low substrate temperature tends to produce films of poor crystallinity with more defects. It also lessens inter-diffusion at the CdS/CdTe junction, which is beneficial to device performance. To further enhance the film crystallinity of the ultra-thin CdTe films, post-deposition treatments are necessary. This chapter will discuss two post-deposition treatments that were found to be highly beneficial: CdCl$_2$ treatments and a high-temperature annealing (HTA) treatment.

3.1 **Vaporous cadmium chloride treatment**
In the conventional CdCl₂ treatment, a layer of CdCl₂ was first applied on the CdTe film either by dip-coating\textsuperscript{57} or by vacuum deposition\textsuperscript{58} followed by thermal annealing at a suitable temperature typically below 400 °C. After this treatment, unreacted CdCl₂ residues are often left on the CdTe film. These residues need to be removed from the CdTe film (usually by water rinsing) before the back contact formation. Although the process steps are relatively straightforward, they nevertheless involved an additional step and management of Cd compound waste in cell fabrication\textsuperscript{59}. With vapor chloride treatment (VCC) treatment, as illustrated in Fig.3-1, the CdTe film is directly subjected to CdCl₂ vapor and annealed in an enclosed environment. Because the substrate temperature is equal to or higher than the source temperature, there is almost no
condensation of CdCl₂ on the substrate. Moreover, as a result of the small gap between the source and the substrate in the VCC treatment, CdCl₂ vapor can be effectively utilized in treating the CdTe film with little waste.

![SEM images of CdTe films](image)

Figure 3-2. SEM images of an ultra-thin (1.2 μm) CdTe film (a) before and (b) after a VCC treatment; a CdTe film (4.0 μm) before (c) and after (d) a VCC treatment.

As shown in Fig.3-2, VCC treatments significantly change the morphology of CdTe films. Before VCC treatments, both the ultra-thin and normal CdTe films featured a terrace-type texture. The small grain size of ultra-thin CdTe film was due to lower substrate temperature. After VCC treatments, CdTe grains became less faceted or
smoother and had narrower grain boundaries. The grain size of CdTe films was not significantly increased after VCC treatments.

![XRD spectra](image)

**Figure 3-3.** XRD spectra of a ultra-thin CdTe film before and after a VCC treatment.

CdCl₂ acts as “fluxing agent” in promoting grain growth. The recrystallization of CdTe, illustrated by the XRD spectra in Fig.3-3, occurs during VCC treatments and takes two forms: primary and secondary recrystallization. The primary or intra-grain recrystallization changes grain orientation, which accounts for the morphology changes in Fig. 3-2. The secondary or inter-grain recrystallization results in grain coalescence and thus increases grain size. However, as seen in Fig. 3-2b and 3-2d, depending on the thermo-chemical history of CdTe film and the initial grain size, the secondary recrystallization does not always occur. For the films deposited at high temperature or
containing native oxide, little observable grain growth occurs during VCC treatments. Under such a circumstance, the surface energy has been already minimized or pinned by the presence of the oxide.

In addition to recrystallizing CdTe films, VCC treatments also influence the inter-diffusion at the CdS/CdTe junction, which can be characterized by UV/Vis spectroscopy and PL spectroscopy.

### 3.2 VCC process optimization

#### 3.2.1 Annealing duration and temperature

Annealing duration and temperature are two important factors in a VCC treatment. They determine the amount of CdCl$_2$ vapor flux that will react with the CdS/CdTe stack layers. The amount of CdCl$_2$ vapor flux increases with the increasing annealing duration and/or temperature. Neither under-treatment nor over-treatment will produce the optimum device performance. The optimized annealing duration and temperature are determined by several factors including the thermo-chemical history of CdS and CdTe films, thickness and crystallinity of CdTe films. In terms of the effects of VCC treatments, prolonging annealing duration at a given temperature above the sublimation point of CdCl$_2$ is equivalent to elevating annealing temperature for a fixed duration.
Figure 3-4. (a) photo and (b) dark $J$-$V$ characteristics of ultra-thin CdTe solar cells treated by VCC for different durations.

Fig.3-4 shows the photo and dark $J$-$V$ characteristics of ultra-thin CdTe solar cells with CdTe films treated for different durations. As shown in Table.3-1, the cell with treatment
duration of 4 min has the highest $V_{oc}, FF$ and $\eta$. VCC treatments with a shorter duration are not sufficient to improve the CdTe film and CdS/CdTe junction quality. However, VCC treatments with a longer duration can cause serious sulfur diffusion from CdS to CdTe, partially depleting the CdS film $^{60}$ and causing a reduction in $V_{oc}$. The reverse saturation current of cell 1003112, which was over-treated with CdCl$_2$, is two or three orders of magnitude higher than the cells treated with a shorter duration. Along with the largest reverse saturation current, the $V_{oc}$ of this cell is the lowest.

The $J$-$V$ characteristics of ultra-thin CdTe solar cells with CdTe films treated under different annealing temperatures are shown in Fig.3-5. The detailed device performance is listed in Table. 3-2. The effects of annealing temperature are more prominent on the $V_{oc}$ and the roll-over of the photo $J$-$V$ curves. A higher annealing temperature tends to induce a larger reverse saturation current and roll-over. The former change affects $V_{oc}$, while the later indicates an energy barrier at the back contact side. The degradation of $V_{oc}$ at higher annealing temperature may be related to excess sulfur diffusion at the CdS/CdTe junction, analogous to that of over-treatment with VCC.
In order to study the effects of annealing duration and temperature on ultra-thin CdTe solar cells, PL measurements were carried out on CdTe solar cells that had been subjected to different annealing conditions. PL spectra, shown in Fig. 3-6, were obtained.
with excitation (He-Ne laser, 633 nm) directly at the CdS/CdTe interface through the glass substrate. The sample was cryogenically cooled to 10 K. Similar trend in the PL spectra was observed for CdS/CdTe stack layers with VCC treatments at various temperatures and with VCC treatments at same temperature for various durations. Only PL spectra with VCC treatments at various temperatures are discussed here.

Figure 3-6. PL spectra of CdS/CdTe stack layers with VCC treatments at various temperatures for 3 min. The spectra were obtained with interface excitation at 10 K.

As shown in Fig.3-6, the reference cell without any VCC treatments features a broad peak at ~1.43 eV which has been attributed to the defects at the CdS/CdTe interface. After VCC treatment, the 1.43 eV peak shifts to lower energy. This peak shift is caused by the evolution of the 1.43 eV defect band and a band located at ~1.38 eV. The 1.38 eV band has been attributed to the formation of CdTe$_{1-x}$S$_x$ at the CdS/CdTe junction.
It is known that CdCl$_2$ treatment can reduce the lattice mismatch between CdS and CdTe by promoting inter-diffusion at the CdS/CdTe junction and the formation of CdTe$_{1-x}$S$_x$. As a result, the lattice mismatch between CdS and CdTe is reduced along with the defects at the interface, including dislocations and dangling bonds. The decrease in intensity of the 1.43 eV defect band is due to a reduction of lattice mismatch and the evolution of the CdTe$_{1-x}$S$_x$ band. Though the PL spectra are normalized for a better comparison in Fig.3-6, the intensity decay of 1.43 eV defect band is still very obvious. The PL measurements show that the sulfur diffusion due to the VCC treatment at the highest temperature of 420 °C is the strongest. Since excessive sulfur diffusion can create pinholes in the CdS films and compromise $V_{oc}$, the PL spectra are consistent with the analyses on $J$-$V$ characteristics.

Lee et al $^{27}$ investigated the effects of annealing temperature and CdCl$_2$ treatment on CdS/CdTe solar cells. They found that the grain size in CdTe films increases with increasing annealing temperature. In addition, they were able to correlate the annealing temperature with device performance. Similarly, we have observed that the device performance is increased with increasing annealing temperature but only up a certain temperature threshold, beyond which the device will deteriorate. Nakamura et al $^{61}$ has reported similar findings.
Table 3-1. Device performance of ultra-thin CdTe solar cells treated by VCC for different durations*6

<table>
<thead>
<tr>
<th>Cell</th>
<th>CSS deposition conditions</th>
<th>VCC treatment conditions</th>
<th>J-V characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{\text{sub}}$ ($^\circ C$)</td>
<td>$T_{\text{src}}$ ($^\circ C$)</td>
<td>$P_{\text{O}_2}$ (Torr)</td>
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<td>625</td>
<td>1.5</td>
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</tbody>
</table>

*6: The thickness of CdTe films is 1.6 ± 0.2 μm. The back contact for the CdTe solar cells is 40 nm MoO$_x$ and 200 nm Ni, deposited by thermal evaporation and DC sputtering respectively.
Table 3-2. Device performance of ultra-thin CdTe solar cells treated by VCC under different temperatures*.

<table>
<thead>
<tr>
<th>Cell</th>
<th>CSS deposition conditions</th>
<th>VCC treatment conditions</th>
<th>J-V characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{\text{sub}}$ (°C)</td>
<td>$T_{\text{src}}$ (°C)</td>
<td>$P_{O_2}$ (°C)</td>
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<td>1.5</td>
</tr>
<tr>
<td>1148A</td>
<td>525</td>
<td>625</td>
<td>1.5</td>
</tr>
<tr>
<td>1148B</td>
<td>525</td>
<td>625</td>
<td>1.5</td>
</tr>
<tr>
<td>1148C</td>
<td>525</td>
<td>625</td>
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</tr>
<tr>
<td>1148D</td>
<td>525</td>
<td>625</td>
<td>1.5</td>
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</tbody>
</table>

*7: The thickness of CdTe films is 1.5 ± 0.2 μm. The back contact for the CdTe solar cells is 40 nm MoO$_x$ and 200 nm Ni, deposited by thermal evaporation and DC sputtering respectively.
3.2.2 Oxygen partial pressure

Most CdCl$_2$ treatments, including our VCC treatment, require a thermal annealing process in air to complete the activation$^{8,60,62,63}$. McCandless et al$^{30}$ found that oxygen concentration during VCC treatments does not appear to affect the solar cell efficiency, although it does influence the consumption of the CdS layer. The oxygen concentration they explored ranges from 0.01 Torr to 570 Torr out of 760 Torr. At very high oxygen concentration (570 Torr), S diffusion at CdS/CdTe junction is greatly enhanced forming CdTe$_{1-x}$S$_x$ where $x$ is increased from 0.7% to 2.9%. Zhou et al$^{64}$ found that CdTe solar cells treated by a VCC method in an ambient without oxygen perform poorly with a low $V_{oc}$ of 550 mV and a $FF$ of 46%. They showed that oxygen ambient is needed to yield substantial enhancement in $V_{oc}$ (up to 780 mV) and $FF$ (up to 66%). The optimized range of oxygen partial pressure was 5~15%. They did not observe significant S diffusion at the CdS/CdTe junction nor depletion of the CdS layer.

We studied the effects of oxygen partial pressure on ultra-thin CdTe solar cells in VCC treatments. The oxygen concentration in an oxygen/nitrogen mixture was varied from 0% to 80%. The total pressure was 50 Torr. The $J$-$V$ characteristics, PL spectra and device performance are shown in Fig.3-7, 3-8 and Table 3-3 respectively.
Figure 3-7. (a) photo and (b) dark $J$-$V$ characteristics of ultra-thin CdTe solar cells treated by VCC with different oxygen partial pressures at 400°C for 4.5 min.
Figure 3-8. PL spectra of CdS/CdTe stack layers with VCC treatment in different oxygen partial pressures at 400°C for 4.5 min. The total pressure of oxygen and nitrogen is 50 Torr. The spectra were obtained with interface excitation at 10 K.

As shown in Fig.3-7, the oxygen partial pressure has negligible effects on both the photo and dark J-V characteristics. Also, there is no obvious correlation between oxygen partial pressure and device performance listed in Table 3-3.

The PL spectra shown in Fig.3-8 indicates that the intensity of the CdTe$_{1-x}$S$_x$ band at 1.38 eV is unaffected by the oxygen ambient during VCC treatments, indicating that the S diffusion at the CdS/CdTe junction is insignificant.
Table 3-3. Device performance of ultra-thin CdTe solar cells treated by VCC under different oxygen partial pressures *8

<table>
<thead>
<tr>
<th>Cell</th>
<th>CSS deposition conditions</th>
<th>VCC treatment conditions</th>
<th>J-V characteristics</th>
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</thead>
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<td>$P_{O2}$ (°C)</td>
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<tr>
<td>1034D</td>
<td>525</td>
<td>625</td>
<td>1.5</td>
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</table>

*8: The thickness of CdTe films is 1.5 ± 0.2 μm. The back contact for the CdTe solar cells is 40 nm MoO$_x$ and 200 nm Ni, deposited by thermal evaporation and DC sputtering respectively.
3.2.3 Ambient pressure

As the limited studies on VCC treatments have shown, the role of ambient pressure is still ambiguous. Zhou et al.\textsuperscript{64} found that an ambient pressure higher than 10 Torr during VCC treatments tends to produce the best and also the most consistent device performance. McCandless et al.\textsuperscript{30}, however, showed that VCC at low pressure (0.04 Torr) does not induce inter-diffusion at the CdS/CdTe junction.

We studied the effects of ambient pressure on ultra-thin CdTe solar cells by carrying out the VCC treatments in an ambient pressure ranging from 2 to 760 Torr. The $J-V$ characteristics, PL spectra and device performance of these cells are shown in Fig.3-9, 3-10 and Table 3-4 respectively.

![Graph showing J-V characteristics](image-url)
Figure 3-9. (a) photo and (b) dark $J$-$V$ characteristics of ultra-thin CdTe solar cells treated by VCC with different ambient pressures.

Figure 3-10. PL spectra of CdS/CdTe stack layers with VCC treatments in different ambient pressures at 400°C for 4.0 min. The flow rate ratio between oxygen and nitrogen is 1:4. The spectra were obtained with interface excitation at 10 K
Table 3-4 Device performance of ultra-thin CdTe solar cells treated by VCC under different ambient pressures *

<table>
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<th>Cell</th>
<th>CSS deposition conditions</th>
<th>VCC treatment conditions</th>
<th>J-V characteristics</th>
</tr>
</thead>
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<td></td>
<td>$T_{\text{sub}}$ (°C)</td>
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<td>$P_{\text{O}_2}$ (°C)</td>
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<td>1387B</td>
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<td>625</td>
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</table>

*9: The thickness of CdTe films is 1.5 ± 0.2 μm. The back contact for the CdTe solar cells is 40 nm MoO$_x$ and 200 nm Ni, deposited by thermal evaporation and DC sputtering respectively.
Comparing cells with and without VCC treatment, it is clear that the performance of the treated cells is considerably higher than that of the untreated cell. The improvement in device performance is mainly because of reduced roll-over and improved contact resistance, as shown in Table 3-4. The PL spectra show a prominent shift to lower energy with VCC treatment, indicating the formation of CdTe$_{1-x}$S$_x$ at the junction. Sulfur diffusion (increasing $x$ values) is increased then saturated with increasing ambient pressure. The reverse saturation current, as shown in Fig.3-10b, decreases as the ambient pressure is increased, which is consistent with the improved $V_{oc}$. However, as the pressure is increased from 50 Torr to 760 Torr, both $V_{oc}$ and FF are reduced. Apparently the reduction in $V_{oc}$ is not related to the leakage current.

According to Rose et al $^{48}$, the growth mechanism of CdTe film in CSS deposition is pressure dependent. At high ambient pressure, the growth rate is diffusion limited while at low pressures it is limited by evaporation or condensation. Since VCC treatment is also carried out in the chamber with a CSS configuration, the growth mechanism can be utilized to explain the phenomena in the VCC treatment. At low pressure, the transport of CdCl$_2$ flux is determined by the evaporation or condensation. Because the source temperature and substrate temperature were the same, the condensation of CdCl$_2$ on the CdTe film was limited. At high pressure, the transport of CdCl$_2$ flux is facilitated by the carrier gases. Though the CdCl$_2$ vapor is also difficult to condense, it can accumulate and saturate in the gas surrounded the CdTe film, which might increase the residual time of CdCl$_2$ vapor on the CdTe surface.
3.3 High temperature annealing

One of the critical effects of VCC treatments is to reduce the lattice mismatch at CdS/CdTe junction by forming an inter-mixing layer of CdTe$_{1-x}$S$_x$. During VCC treatments, sulfur diffusion proceeds via Fickian bulk and grain-boundary diffusion.
processes which feature Arrhenius temperature dependence. The activation energy for sulfur diffusion via bulk and grain boundaries are ~3.0 eV and ~2.0 eV, respectively, indicating that sulfur diffusion via the grain boundaries is dynamically faster than that via the bulk. A similar conclusion is also valid for metal migration from the back contact to the CdTe bulk and/or CdS/CdTe junction. Excessive sulfur diffusion causes partial consumption of CdS and therefore tends to create pinholes in CdS films. Metal migration from the back contact is the main reason for device degradation.

As shown in Fig.3-11a and b, ultra-thin CdTe films have much more grain boundaries than the conventional CdTe films because of smaller grain size; therefore the problems associated with grain boundaries are more serious. Post-deposition processes, such as high-temperature annealing (HTA) treatment, which are intended to promote recrystallization, are beneficial in mitigating the fast grain boundary diffusion as they will increase grain size and thus reduce grain boundaries.

HTA treatments were carried out in a tube furnace under an inert ambient in a temperature range of 530 to 560 °C for a duration up to 45 min. The inert gas flow under atmospheric pressure was maintained during the entire HTA process to protect CdTe film from being oxidized.

3.3.1 Effects of HTA
Figure 3-12. (a) photo and (b) dark $J$-$V$ characteristics for ultra-thin CdS/CdTe solar cells with various HTA and VCC treatments
Table 3-5. Device performance of ultra-thin CdS/CdTe solar cells with various HTA and VCC treatments*10

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<tr>
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<td>Y</td>
<td>14971</td>
</tr>
</tbody>
</table>

*10: The thickness of CdTe films is 1.5 ± 0.1 μm. The back contact for the CdTe solar cells is 40 nm MoO$_x$ and 200 nm Ni, deposited by thermal evaporation and DC sputtering respectively.

*11: The CdTe films were subjected in N$_2$ at 550 °C for 40 min.

*12: The VCC treatment was carried out at 400 °C in 10 Torr O$_2$/40 Torr N$_2$ for 4 min.
Fig. 3-12a and b show the photo and dark $J$-$V$ characteristics of ultra-thin CdTe solar cells with various heat treatments. Compared to the reference cell (without any treatment), the cell with HTA alone exhibits significant improvement in $V_{oc}$, $J_{sc}$ and $FF$, although it is still substantially inferior to the cell with just VCC treatment. Combining HTA and VCC treatments further enhances the cell performance over the VCC treatment alone, yielding the best device performance, as shown in Table 3-5. The improvement in $V_{oc}$ is consistent with the reduction of reverse saturation current shown in Fig. 3-12b.

Table 3-5 includes the dynamic shunt resistance, $R_{sh}$, and dynamic series resistance, $R_s$, calculated from the slope of $dJ/dV$ at $J_{sc}$ and $V_{oc}$, respectively. The cell with both HTA and VCC treatments yields excellent $R_{sh}$ and $R_s$, as well as the highest efficiency of 11.6%. The improvement in $R_s$ is consistent with the finding that heat treatment on CdTe films at elevated temperature reduces film resistivity.$^{66,67}$

3.3.2 Optimization of HTA process

In order to confirm the beneficial effects of HTA treatments, the same annealing treatment as shown in Table 3-5 was applied on ultra-thin CdTe solar cells with different CdTe thickness. The $J$-$V$ characteristics and device performance are shown in Fig.3-13 and Table 3-6, respectively.
Comparing the J-V characteristics of the cells with and without a HTA treatment, several differences are noted as follows:
1) The curve bending at forward bias, also known as “roll-over”, is prominent in the cells without HTA treatments. There is hardly any roll-over in the cells with HTA treatments. Since the “roll-over” is an indication of a barrier at the back contact, it is conclusive that HTA treatments can reduce the energy barrier and help form a more ohmic back contact;

2) The current density at the forward bias of 1.0 V in the cells with HTA treatments is generally larger than that in the cells without HTA treatments, indicating that the cells are more photoconductive after the HTA treatments;

3) Regardless of the CdTe film thickness, the cells with HTA treatments have higher $V_{oc}$ than that without HTA treatments. The improvement of $V_{oc}$ is consistent with the observed decrease of leakage current, suggesting that CdTe films became denser after HTA treatments.

As listed in Table 3-6, HTA treatments increased $R_{sh}$ by 1.45~2 times and reduced $R_s$ by 16~38%, which contributed to the improvement in $FF$. In addition, the $J_{sc}$ was also enhanced by 0.7~1.3 mA/cm$^2$. In general, with HTA treatments, the cell efficiency can be repeatedly enhanced by 1.5~2.1%. 


Table 3-6. Device performance of various ultra-thin CdTe solar cells with different post-deposition treatments

<table>
<thead>
<tr>
<th>Cell</th>
<th>CdTe thickness (μm)</th>
<th>HTA</th>
<th>550°C /40min</th>
<th>$R_{sh}$ (Ω)</th>
<th>$R_s$ (Ω)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1080B</td>
<td>1.2</td>
<td>N</td>
<td>7133</td>
<td>107</td>
<td>19.3</td>
<td>695</td>
<td>60.2</td>
<td>8.1</td>
<td></td>
</tr>
<tr>
<td>1080D</td>
<td>1.2</td>
<td>Y</td>
<td>10356</td>
<td>66</td>
<td>20.6</td>
<td>750</td>
<td>65.8</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>1086A</td>
<td>1.5</td>
<td>N</td>
<td>12484</td>
<td>104</td>
<td>19.5</td>
<td>738</td>
<td>60.3</td>
<td>8.7</td>
<td></td>
</tr>
<tr>
<td>1086B</td>
<td>1.5</td>
<td>Y</td>
<td>24968</td>
<td>70</td>
<td>20.2</td>
<td>765</td>
<td>69.6</td>
<td>10.8</td>
<td></td>
</tr>
<tr>
<td>1098A</td>
<td>1.8</td>
<td>N</td>
<td>16644</td>
<td>96</td>
<td>19.5</td>
<td>752</td>
<td>61.5</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>1098c</td>
<td>1.8</td>
<td>Y</td>
<td>25050</td>
<td>81</td>
<td>20.4</td>
<td>775</td>
<td>66.6</td>
<td>10.5</td>
<td></td>
</tr>
</tbody>
</table>

*13: The CdS films were not treated by VCC. The VCC treatment was carried out at 400°C for 4.5 min. The back contact for the CdTe solar cells is 40 nm MoO$_x$ and 200 nm Ni, deposited by thermal evaporation and DC sputtering respectively.
Fig. 3-14 shows the correlation between device performance and the annealing duration and temperature. As expected, the cells with both HTA and VCC treatments show higher $V_{oc}$ (by 30~40 mV), larger $J_{sc}$ (by 0.6~0.8 mAcm$^{-2}$), and higher $FF$ (by 7~8%) than the cells with VCC treatment alone. The improvement is marginal for HTA
treatment temperature lower than 520 °C or for HTA treatment duration less than 20 min. However, if the HTA treatments were carried out at a too high temperature (≥ 560 °C) for a too long period (≥ 60 min), evaporation of CdTe occurred resulting in pinholes and compromising device performance. The optimized annealing temperature and duration were found to be 550 °C and 40 min, respectively.

3.4 Combinatorial effects of HTA and VCC

In this section, a series of characterization techniques were used to study the effects of HTA on device performance.

Figure 3-15. SEM images for: CSS-deposited ultra-thin CdTe film (a) without any treatment, (b) with VCC treatment, (c) with HTA treatment, and (d) with HTA+VCC treatments.
The evolution of CdTe grain growth as a result of HTA and VCC treatments is shown by the SEM images (a-d) in Fig. 3-16. The CSS-deposited CdTe film without any treatment (Image a) has a relatively small grain size of ~0.5 μm. The VCC treatment on the CdTe film (Image b) does not appear to change the grain size prominently but tends to smooth the grain facets. However, the HTA treatment induces large CdTe grain growth as shown in Image C. The average grain size of the HTA-treated film is significantly larger than that of the untreated film. A subsequent VCC treatment of the HTA-treated film results in further grain growth as well as more rounded grain facets, as shown in Image d.

Fig. 3-17 shows the PL spectra of CdTe films without any treatments, with only VCC treatment, with only HTA treatment, and with HTA plus VCC treatment. The laser excitation (He-Ne laser, 633 nm) was directed at the free CdTe surface. The prominent features are bands with peaks at ~1.430 eV and ~1.585 eV. Known as the “near-band-edge (NBE) band”, the ~1.585 eV band has been attributed to bound excitons and used as an indicator of CdTe crystallinity. As shown is Fig. 3-17a, the NBE peak increases significantly with HTA and VCC treatments, indicating improvements in CdTe crystallinity. The ~1.430 eV band, known as the “surface defect band (SDB)”, is presumably due to intrinsic defects. As shown in Fig. 3-17b, the NBE/SDB intensity ratio also increases with HTA and VCC treatments, further supporting that the CdTe quality is improved. Among various treatments, the HTA plus VCC treatment produces the strongest NBE peak intensity as well as the highest NBE/SDB intensity ratio, which corresponds to the largest CdTe grains as shown in Fig. 3-16.
Figure 3-16. PL spectra with surface excitation for: CSS-deposited ultra-thin CdTe film without any treatment, with VCC or HTA or HTA+VCC treatment.

The CdS/CdTe interface was also characterized by PL measurements. The PL spectra, taken with excitation through the substrate, feature a broad peak around 1.4 eV, which broadens and shifts to lower energy with HTA and VCC treatments. To further analyze the evolution of these spectra, they were deconvoluted into four Gaussian components using *MicroLab Origin 8.0* as shown in Fig.3-18.
Figure 3-17. PL spectra and the corresponding deconvoluted PL peaks for CSS-deposited ultra-thin CdTe film (a) without any treatment, (b) with HTA treatment, (c) with VCC treatment and (d) with HTA+VCC treatments. PL spectra were obtained with interface excitation at 40 K.
Figure 3-18. PL spectra with interface excitation showing the evolution of: (a) the interface defect band, and (b) the CdTe$_{1-x}$S$_x$ band with various HTA and VCC treatments.
The deconvoluted components with peaks at ~1.43, ~1.38, ~1.35, and ~1.30 eV have been attributed to various species in the literature. The ~1.43 eV band is the surface defect band also observed from the free surface in Fig.26. The ~1.38 eV band has been assigned to CdTe$_{1-x}$S$_x$ and the ~1.35 eV band to cadmium vacancy complexes. The small ~1.30 eV band, which is only observed in CdTe with treatments, has not been identified yet.

Fig.3-19a shows that the intensity of the defect band is reduced with HTA and VCC treatments, indicating that the defect concentration at the CdS/CdTe interface is reduced. As discussed in Section 3.1, VCC treatments can promote sulfur diffusion from CdS to CdTe. As shown in Fig.3-19b, the intensity of the ~1.38 eV band increases significantly with VCC treatments, a clear evidence that CdTe$_{1-x}$S$_x$ is being formed near the interface. Note that the ~1.38 eV band for the films with HTA and HTA+VCC treatments is considerably weaker compared to the film with VCC treatments only. The phenomenon suggests that additional HTA treatment can mitigate excess sulfur diffusion in the VCC treatment.

In order to further analyze the effects of HTA treatments on sulfur diffusion, ultra-thin CdTe films with various heat treatments were characterized by UV/Vis absorption spectroscopy. Fig.3-20a shows the absorption of ultra-thin CdTe films near the absorption edge region. It is clearly that the absorption edge shifts to lower energy with post-deposition treatments, especially with VCC treatments. The red shift is consistent with the formation of CdTe$_{1-x}$S$_x$, a low bandgap component resulting from the
incorporation of sulfur in CdTe films with VCC treatments. As illustrated in Fig. 3-20a, the bandgap of CdTe\textsubscript{1-x}S\textsubscript{x} was extracted from the absorption spectra using a linear fit at the threshold region \textsuperscript{73}. Using the extracted bandgap of CdTe\textsubscript{1-x}S\textsubscript{x} and an established relation between the bandgap and stoichiometry of CdTe\textsubscript{1-x}S\textsubscript{x}\textsuperscript{62}:

\[ E_g = 1.74x^2 - 1.01x + 1.51 \]  

(4)

the values of \( x \) are calculated and presented in Fig.3-20b with relation to the bandgap of CdTe\textsubscript{1-x}S\textsubscript{x}.

As displayed in Fig.3-20b, a HTA treatment itself can promote the sulfur diffusion from CdS to CdTe because of high temperature, causing the \( x \) value in CdTe\textsubscript{1-x}S\textsubscript{x} to increase from 0.8\% in the cell without any treatments to 1.3\% in the cell with just HTA treatment. However, as for the efficiency in promoting sulfur diffusion, a HTA treatment is less effective than a VCC treatment with the latter producing an apparently higher \( x \) value of 2.3\% in the cell with just VCC treatment despite shorter treatment duration. Furthermore, it is noteworthy that a HTA treatment prior to a VCC treatment can suppress sulfur diffusion resulting from the VCC treatment. It can be seen in the cell with HTA plus VCC treatment where \( x \) value in CdTe\textsubscript{1-x}S\textsubscript{x} is only 1.8\%. The trend reflected in Fig.3-20b is very similar to that in Fig.3-19b.
Figure 3-19. Absorption at the band edge region for ultra-thin CdTe films with various HTA and VCC treatments, (b) the $x$ values of CdTe$_{1-x}$S$_x$ in relation to the bandgap of CdTe$_{1-x}$S$_x$. 
As discussed in the introduction of Section 3.3, sulfur diffusion via grain boundaries is thermodynamically favorable and dynamically faster than that via the bulk. The SEM observation in Fig.3-16 shows that HTA can reduce grain boundaries; therefore it helps mitigate sulfur diffusion, which has been confirmed by both PL and absorption analyses.

![Figure 3-20. Spectral response for ultra-thin CdS/CdTe solar cells with various HTA and VCC treatments](image)

Fig.3-21 shows the spectral response curves for the ultra-thin CdTe solar cells with various HTA and VCC treatments. The $J$-$V$ characteristics and device performance are illustrated in Fig.3-12 and Table 3-5 respectively. It is clear that the improvement in quantum efficiency is significantly higher in the long wavelength region and for cells that have been subjected to HTA and VCC treatments. The low quantum efficiency in ultra-thin CdTe solar cells, especially in the region near band edge, can be ascribed to incomplete light absorption and recombination loss at the back contact. According to the
analysis of the absorption edge in Fig. 3-20, the red shift in the band edge region is because of the formation of CdTe$_{1-x}$S$_x$ which is enhanced with HTA and VCC treatments. It is believed that the increase of quantum efficiency in high-wavelength region can be partly due to CdTe$_{1,x}$S$_x$. On the other hand, HTA and VCC treatments can reduce defects both on the surface and in the CdS/CdTe junctions. The reduction of surface defects on the back contact can also contribute to the increase of quantum efficiency.

3.5 Summary

Compared with conventional solution based cadmium chloride treatment, vaporous cadmium chloride treatment consumes much less cadmium compound, creates less cadmium waste, and is more compatible with vacuum based manufacturing processes. Three key parameters of VCC treatments on ultra-thin CdTe solar cells, annealing temperature/duration, oxygen partial pressure and ambient pressure, have been studied. Using $J-V$ and PL measurements, the correlation between device performance and treatment conditions has been established.

Apart from VCC treatments, another post-deposition treatment named high-temperature annealing was introduced in the device fabrication process. We have shown that the HTA process prior to a VCC treatment is useful for producing high-quality ultra-thin CdTe films. SEM, optical absorption and PL measurements show that substantial growth in CdTe grain size and reduction in defects related to grain boundary and excessive sulfur diffusion are realized with combined HTA and VCC treatments. An
efficiency of about 11.6% has been demonstrated for ultra-thin CdS/CdTe solar cells processed with these post-deposition treatments.
4. **Ohmic contact formation to ultra-thin CdTe**

As discussed in Section 1.4, the formation of a low-resistance electrical contact or ohmic contact to CdTe solar cells was a major obstacle. Self-compensation hampers efforts to achieve high $p$-doping in CdTe. The large work function of CdTe limits the choice of metals as the contact electrode. A conventional method for forming ohmic contact uses etching solutions such as nitric-phosphoric acid (NP) or bromine-methanol (BM) solutions to create a $p^+$ tellurium rich surface, which provides a buffer layer with a work function adequate for making ohmic contact to the underlying CdTe layer.

However the solution method for making ohmic contacts is not applicable for ultra-thin CdTe solar cells, because, through preferential etching on CdTe grain boundaries, it creates shunting paths in the CdTe film, which can seriously deteriorate the device performance. Furthermore, it is particularly difficult to control the final CdTe layer thickness and uniformity with solution etching. Among the alternatives to NP or BM method, Cu/Au and graphite paste mixed with Cu$_x$Te have been applied for the fabrication of ultra-thin CdTe solar cells with efficiencies of 11~12%. Cu$^+$ can readily substitute for Cd$^{2+}$ in CdTe to form Cu$_{Cd}$ complex which acts as a shallow acceptor and enhances the $p$-type characteristics of CdTe. In addition, Cu$_x$Te can reduce the energy barrier at the CdTe/metal junction to facilitate the hole transfer by producing tunneling states at the CdTe/Cu$_x$Te and Cu$_x$Te/metal interfaces.

Although the Cu containing back contact can form a low-resistance contact to $p$-CdTe and improve cell efficiency, it also can cause serious cell instability. Cu can be depleted
from the back contact by rapid diffusion into the CdTe bulk and by oxidation on the surface. Both processes reduce the beneficial effects of Cu as mentioned previously. Moreover, the diffusion of Cu through CdTe bulk to the CdS/CdTe junction is known to produce recombination centers at the junction and shunting paths along the stack layers. The device degradation associated with Cu diffusion in CdTe solar cells gets even more serious as the CdTe film thickness is decreased.

MoO$_x$ and Te/Cu bi-layer, have been identified as effective alternatives to replace NP treatment in forming ohmic contact to ultra-thin CdTe solar cells. In this chapter, we will discuss the fabrication, optimization and characterization of the new back contact buffer layers.

4.1 Effects of NP treatment on ultra-thin CdTe films

Fig.4-1 shows the photo and dark $J$-$V$ characteristics of CdS/CdTe solar cells with CdTe film thickness ranging from 5.0 μm to 1.5 μm and treated in NP solution for different durations. In a series of experiments the optimum NP treatment time was determined for each CdTe thickness and the solar cell data are presented in Table 4-1 and Fig.4-1. As the CdTe thickness is decreased, $V_{oc}$ and $FF$ deteriorate. The degradation of $V_{oc}$ corresponds to an increase in the reverse saturation current as shown in Fig.4-1b. The degradation of $FF$ is directly related to the decrease in the shunting resistance as a result of acid etching.
Figure 4-1. (a) Photo and (b) dark $J$-$V$ characteristics of CdS/CdTe solar cells with 1.5-5.0 μm CdTe thickness using NP treatment in back contact formation.

Table 4-1. Device performance of CdS/CdTe solar cells with various CdTe film thicknesses

<table>
<thead>
<tr>
<th>Cell</th>
<th>CdTe thickness (μm)</th>
<th>NP etching duration (s)</th>
<th>$J_{sc}$ (mAcm$^{-2}$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>$V_{oc}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5.0</td>
<td>40</td>
<td>21.4</td>
<td>810</td>
<td>68.0</td>
<td>11.8</td>
</tr>
<tr>
<td>B</td>
<td>2.5</td>
<td>30</td>
<td>21.3</td>
<td>780</td>
<td>66.2</td>
<td>11.0</td>
</tr>
</tbody>
</table>
The effects of NP etching on the ultra-thin CdTe film morphology are illustrated in Fig. 4-2. The SEM image (a: top view) of the as-deposited CdTe film looks diffuse and unfocused, which is attributable to charging effect. In contrast, the SEM image of the CdTe film (b: top view) after NP etching shows a sharper contrast, indicating the Te layer formed on the surface and possibly along the grain boundaries from NP etching is more conductive. Besides, this NP-treated CdTe film appears to have smoother grains with
fewer facets and broader grain boundaries. As shown in the cross-section view of the CdTe films in Figs 4-2c and d, the boundaries of the CdTe columns are more prominent after acid etching. These morphology changes suggest that the grain boundaries of CdTe are vulnerable to acid etching than the bulk of CdTe. The broad boundaries are indicative of altered surface composition and the presence of shunts and diffusion channels that are responsible for the deterioration of cell performance. These negative effects become more serious as the CdTe film thickness is decreased.

4.2 Comparison between NP treatment and MoOx buffer layer in ohmic contact formation

We have demonstrated the utility of MoOx as a buffer layer for forming a low-resistance contact to p-CdTe \(^{82,83}\). Depending on the deposition method, the work function of MoOx can be as high as 6.8 eV, which is significantly higher than that of CdTe\(^{65}\). The MoOx buffer layer does not contain Cu and thus avoids the conventional degradation issues caused by Cu diffusion. Moreover it also acts as a barrier to metal electrode diffusion and thus enhances cell stability\(^{84}\).
Figure 4-3. Comparison of the (a) photo and (b) dark J-V curves, and (c) diode factor extraction of a NP cell and a MoO_x cell. The CdTe film thickness is 1.5 μm.

Table 4-2. Device performance of ultra-thin CdTe solar cells with various back contacts. The CdTe film thickness is 1.5 μm.

<table>
<thead>
<tr>
<th>Cell</th>
<th>NP etching duration</th>
<th>MoO_x thickness (nm)</th>
<th>A</th>
<th>V_{oc} (mV)</th>
<th>J_{sc} (mA cm^{-2})</th>
<th>FF (%)</th>
<th>V_{oc} (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-1</td>
<td>25</td>
<td>-</td>
<td>3.2</td>
<td>750</td>
<td>21.5</td>
<td>63.0</td>
<td>10.2</td>
</tr>
<tr>
<td>E-2</td>
<td>-</td>
<td>40</td>
<td>2.1</td>
<td>770</td>
<td>22.0</td>
<td>68.2</td>
<td>11.6</td>
</tr>
</tbody>
</table>
As shown in Fig. 4-3a, CdTe solar cells with a MoO₅ back contact buffer exhibit a higher $V_{oc}$ and better $FF$. The improvement in $V_{oc}$ is consistent with the reduction of reverse saturation current as shown in Fig. 4-3b, which indicates that MoO₅ eliminated the shunting problem caused by NP etching. The enhancement of $FF$ demonstrates that the addition of MoO₅ layer to the cell does not necessarily lead to an increase in series resistance. The derivative $dV/dJ$ of the curves in Fig. 4-3a against $(J + J_{sc})^{-1}$ is plotted in Fig. 4-3c. According to Eqn. 4-1 and the procedure described by Hegedus et al.\textsuperscript{85}, the ideal diode factors $(A)$ of the CdTe solar cells with NP treatment and the MoO₅ buffer layer have been determined. As shown in Table 4-2, replacing NP treatment with a MoO₅ back contact buffer layer generally results in a smaller diode factor and consequently a higher power conversion efficiency.

$$\frac{dV}{dJ} = R + \frac{A k T}{q} \cdot (J + J_L)^{-1}$$ \hspace{1cm} (4-1)

Figure 4-4. Effect of thermal stress on efficiency for ultra-thin CdTe solar cells with different back contacts. The CdTe film thickness is 1.5 μm.
Ultra-thin CdTe solar cells with MoOₓ buffer layer or NP treatment were subjected to a thermal stress test at 200 °C for 1 to 9 hours in an inert ambient. Both cells exhibited degradation but in various degrees, as shown in Fig.4-4. After 6 hours, the efficiency of MoOₓ cell degraded by 8.3%, while NP cell degraded by 16.2%. The decreased efficiency is largely due to a decrease in FF. Compared to NP cell, the MoOₓ cell is more stable. Dobson et al.⁷⁶ found that the oxidation of Te and CdTe beneath the back
contact and the diffusion of metal from the back contact are two primary degradation mechanisms. The ease of oxidation of the Te-rich layer is probably the reason why the NP cells are inferior in stability relative to the MoO_x cell.

Fig.4-5 shows the photo and dark $J$-$V$ characteristics of ultra-thin CdTe solar cells with various back contacts compositions. Table 4-3 lists the photovoltaic parameters. In general, Ni forms a relatively ohmic contact with the NP-treated ultra-thin CdTe films. With Al, a low work function metal, the contact is blocking with serious roll-over in the $J$-$V$ characteristics and poor $V_{oc}$ and $FF$. Both NP cells show large leakage currents. However, as Fig.4-5a shows, both Ni and Al produce an ohmic contact with MoO_x as the buffer, resulting in fairly good $FF$ (66-68%). The leakage current of the MoO_x cell is about two orders of magnitude lower than that of the NP cell.

<table>
<thead>
<tr>
<th>Cell</th>
<th>NP etching duration</th>
<th>MoO_x thickness (nm)</th>
<th>Electrode/work function (eV)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-1</td>
<td>25</td>
<td>-</td>
<td>Ni/5.4</td>
<td>750</td>
<td>21.5</td>
<td>63.0</td>
<td>10.2</td>
</tr>
<tr>
<td>E-3</td>
<td>25</td>
<td>-</td>
<td>Al/4.3</td>
<td>660</td>
<td>18.0</td>
<td>20.9</td>
<td>2.5</td>
</tr>
<tr>
<td>E-2</td>
<td>-</td>
<td>40</td>
<td>Ni/5.4</td>
<td>770</td>
<td>22.0</td>
<td>68.2</td>
<td>11.6</td>
</tr>
<tr>
<td>E-4</td>
<td>-</td>
<td>40</td>
<td>Al/4.3</td>
<td>770</td>
<td>21.9</td>
<td>65.5</td>
<td>11.1</td>
</tr>
</tbody>
</table>

Table 4-3. Device performance of ultra-thin CdTe solar cells with various back contacts with Ni or Al electrode. The CdTe thickness is 1.5 μm.
4.3 Ohmic contact formation to ultra-thin CdTe using MoO$_x$ back contact buffer

(a) MoO$_x$ (10nm) - MoO$_x$ (20nm) - MoO$_x$ (40nm) - MoO$_x$ (80nm)

(b) MoO$_x$ (10nm) - MoO$_x$ (20nm) - MoO$_x$ (40nm) - MoO$_x$ (80nm)

Figure 4-6. (a) Photo and (b) dark $J$-$V$ characteristics of ultra-thin CdTe solar cells with different thicknesses of MoO$_x$ buffer layer.

The effects of MoO$_x$ thickness on the performance of ultra-thin CdTe solar cells are shown in Fig.4-6 and Table 4-4. The optimized thickness of MoO$_x$ is about 40 nm.
Table 4-4. Device performance of ultra-thin CdTe solar cells with various thicknesses of MoO\textsubscript{x} buffer layer. The thickness of CdTe films is 1.5\,μm

<table>
<thead>
<tr>
<th>Cell</th>
<th>MoO\textsubscript{x}</th>
<th>V\textsubscript{oc}</th>
<th>J\textsubscript{sc}</th>
<th>FF</th>
<th>η</th>
<th>R\textsubscript{sh}</th>
<th>R\textsubscript{s}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>thickness (nm)</td>
<td>(mV)</td>
<td>(mAcm\textsuperscript{-2})</td>
<td>(%)</td>
<td>(%)</td>
<td>(Ωcm\textsuperscript{2})</td>
<td>(Ωcm\textsuperscript{2})</td>
</tr>
<tr>
<td>F-1</td>
<td>10</td>
<td>740</td>
<td>22.2</td>
<td>65.0</td>
<td>10.7</td>
<td>1179</td>
<td>5.9</td>
</tr>
<tr>
<td>F-2</td>
<td>20</td>
<td>760</td>
<td>21.9</td>
<td>66.3</td>
<td>11.0</td>
<td>2367</td>
<td>6.1</td>
</tr>
<tr>
<td>F-3</td>
<td>40</td>
<td>780</td>
<td>22.1</td>
<td>69.0</td>
<td>11.9</td>
<td>1953</td>
<td>5.6</td>
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<tr>
<td>F-4</td>
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<td>780</td>
<td>22.0</td>
<td>66.0</td>
<td>11.3</td>
<td>1872</td>
<td>7.4</td>
</tr>
</tbody>
</table>

The average surface roughness of ultra-thin CdTe films measured by surface profilometer is 20~35 nm. To prevent direct contact of the metal electrode with the CdTe layer, the thickness of MoO\textsubscript{x} buffer layer should be conformal and continuous, and at least greater than the surface roughness of the CdTe film. On the other hand, thick MoO\textsubscript{x} film is undesirable as it can introduce additional series resistance.

Table 4-5. Device performance of ultra-thin CdTe solar cells with various CdTe film thicknesses and a 40-nm MoO\textsubscript{x} back contact buffer layer.

<table>
<thead>
<tr>
<th>Cell</th>
<th>CdTe thickness (μm)</th>
<th>MoO\textsubscript{x} thickness (nm)</th>
<th>V\textsubscript{oc} (mV)</th>
<th>J\textsubscript{sc} (mAcm\textsuperscript{-2})</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>1.1</td>
<td>40</td>
<td>720</td>
<td>21.7</td>
<td>60.9</td>
<td>9.5</td>
</tr>
<tr>
<td>H</td>
<td>1.3</td>
<td>40</td>
<td>750</td>
<td>22.1</td>
<td>68.1</td>
<td>11.3</td>
</tr>
<tr>
<td>I</td>
<td>1.5</td>
<td>40</td>
<td>770</td>
<td>22.2</td>
<td>69.8</td>
<td>11.9</td>
</tr>
<tr>
<td>J</td>
<td>1.6</td>
<td>40</td>
<td>780</td>
<td>22.3</td>
<td>70.2</td>
<td>12.2</td>
</tr>
</tbody>
</table>
Fig. 4-7 shows the photo and dark J-V characteristics of ultra-thin CdTe solar cells with different thicknesses of CdTe and a 40-nm MoOₓ back contact buffer. The device performance of these cells is listed in Table 4-5. Except for the cell with 1.1 μm CdTe, which has relatively low $V_{oc}$, $FF$ and $\eta$, the cells with 1.3~1.6 μm CdTe have efficiencies
of 11.3~12.2%, which are among the highest obtained in CdTe solar cells of similar CdTe thickness. The reason for the low device performance of the cell with 1.1 μm CdTe is not known. Clearly it is not due to a decrease in shunt resistance as the reverse saturation current of this cell is still 2~3 orders of magnitude lower than that of the reference NP cells.

4.4 Ohmic contact formation to ultra-thin CdTe using Te/Cu back contact buffer

We developed a new back contact buffer using Te/Cu bi-layer. Similar to MoOₓ, Te/Cu bi-layer is deposited by a vapor deposition method. Unlike MoOₓ, Te/Cu back contact buffer does not necessitate a surface cleaning step on the CdTe film but it requires a thermal activation step to promote contact formation.

Typically, after VCC treatment on ultra-thin CdTe films, a layer of 100 nm Te and a layer of 1.1 nm Cu are deposited on top of CdTe film in sequence by DC sputtering. A layer of 200 nm Ni is then applied as the back electrode. The cells are then subjected to a thermal activation at 200~285°C for 0 s to 20 min in N₂. The glass tube positioned in tube furnace for the thermal activation is purged with N₂ at a flow rate of 100 cm³/min for 30 min. The nitrogen flow is maintained during the heating-up, annealing and cooling processes.

The composition of Te/Cu bi-layer was first optimized for CdTe solar cells with normal CdTe thickness (~4.0 μm). The optimized Te/Cu bi-layer together with the optimum thermal activation is irrelevant to the CdTe film thickness. The details of the Te/Cu bi-layer study will be discussed in Chapter 5. The thermal activation duration in
this section and Chapter 5 refers to the duration for which the annealing step is maintained at constant temperature. It does not include a heating-up duration of 5 min and a cooling-down duration of 30 min.

Figure 4-8. (a) Photo and (b) dark $J$-$V$ characteristics of ultra-thin CdTe solar cells with MoO$_x$ or Te/Cu back contact buffer. The CdTe film thickness is 1.5 μm.

Fig.4-8 shows the photo and dark $J$-$V$ characteristics of ultra-thin CdTe solar cells using MoO$_x$ or Te/Cu as the back contact buffer layer with and without surface cleaning.
on CdTe film. It turns out that without surface cleaning, MoO$_x$ cannot form a low-resistance electrical contact to $p$-CdTe, featuring a serious roll-over. Only with the CdTe film being thoroughly cleaned by deionized water can MoO$_x$ form a good ohmic contact to $p$-CdTe. Lin et al $^{84}$ revealed that a chlorine-containing compound, Cd$_3$Cl$_2$O$_2$, was present on the CdTe films after VCC treatments. Cd$_3$Cl$_2$O$_2$ is non-volatile up to 600 °C $^{86}$ but is easily soluble in water. The existence of a thin layer (0.9~2.5 Å) Cd$_3$Cl$_2$O$_2$ is believed to reduce the work function of MoO$_x$ and consequently results in the occurrence of roll-over. Water rinse can remove this layer and recover the high work function of MoO$_x$. Lin’s explanation is plausible. Different from MoO$_x$, Te/Cu is not affected by the existence of Cd$_3$Cl$_2$O$_2$.

Table 4-6. Device performance of ultra-thin CdTe solar cells with MoO$_x$ or Te/Cu back contact buffer. The CdTe film thickness is 1.5 μm $^{14}$

<table>
<thead>
<tr>
<th>Cell cleaning</th>
<th>Back contact buffer</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mAcm$^{-2}$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without</td>
<td>MoO$_x$</td>
<td>740</td>
<td>21.4</td>
<td>33.9</td>
<td>5.4</td>
</tr>
<tr>
<td>With</td>
<td>MoO$_x$</td>
<td>780</td>
<td>21.8</td>
<td>70.2</td>
<td>11.9</td>
</tr>
<tr>
<td>Without</td>
<td>Te/Cu</td>
<td>809</td>
<td>21.8</td>
<td>76.2</td>
<td>13.4</td>
</tr>
<tr>
<td>With</td>
<td>Te/Cu</td>
<td>793</td>
<td>21.9</td>
<td>75.7</td>
<td>13.1</td>
</tr>
</tbody>
</table>

*14: The MoO$_x$ thickness is 40 nm. The Te and Cu thicknesses are 100 nm and 1.1 nm respectively. The cells with Te/Cu were thermally activated at 275 °C for 0 s.

As shown in Fig.4-8a and Table 4-6, the cells using Te/Cu back contact buffer show very similar $J$-$V$ characteristics and device performance with and without surface cleaning on CdTe films. Actually, the existence of Cd$_3$Cl$_2$O$_2$ results in slightly
improvement in both $V_{oc}$ and $FF$. Dobson et al.\textsuperscript{77} found that Cu$_{Cd}$ and Cl can form a Cl-Cu$_{Cd}$ type of complex which is a shallow acceptor. It is believed that Cd$_3$Cl$_2$O$_2$ may facilitate the Cu doping in CdTe and thus produces the beneficial effects.

Figure 4-9. (a) Photo and (b) dark $J$-$V$ characteristics of ultra-thin CdTe solar cells with Te/Cu back contact buffer with different thermal activation conditions. The CdTe film thickness is 1.5 μm
Table 4-7. Device performance of ultra-thin CdTe solar cells with Te/Cu back contact buffer with various annealing durations at 270°C. The CdTe film thickness is 1.5 μm

<table>
<thead>
<tr>
<th>Cell</th>
<th>Te/Cu thickness (nm)</th>
<th>Annealing duration (s)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mAcm$^{-2}$)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1838D</td>
<td>100/1.1</td>
<td>0</td>
<td>828</td>
<td>21.2</td>
<td>76.2</td>
<td>13.4</td>
</tr>
<tr>
<td>1838A</td>
<td>100/1.1</td>
<td>15</td>
<td>825</td>
<td>21.3</td>
<td>76.5</td>
<td>13.4</td>
</tr>
<tr>
<td>1838B</td>
<td>100/1.1</td>
<td>30</td>
<td>810</td>
<td>21.0</td>
<td>74.0</td>
<td>12.6</td>
</tr>
<tr>
<td>1838C</td>
<td>100/1.1</td>
<td>60</td>
<td>800</td>
<td>20.8</td>
<td>70.9</td>
<td>11.8</td>
</tr>
</tbody>
</table>

As shown in Fig.4-9, the thermal activation was carried out on CdTe solar cells with a Te/Cu back contact buffer at 270 °C for 0~60 s. An annealing duration of 0 s means that the heating-up step was followed by a cooling step once the temperature reached 270 °C. Thermal activation with a short duration of 0~15s produces higher $V_{oc}$ and FF than that with a long duration (30~60s). The deterioration in $V_{oc}$ is related with increased reverse saturation current and reduced shunting resistance. Similar to sulfur diffusion from CdS to CdTe, the diffusion of Cu from the back contact to the CdTe bulk also feature Arrhenius temperature dependence. A thermal activation at high temperature for a long duration may lead to excessive Cu diffusion to CdTe bulk even vicinity of CdS/CdTe junction, and therefore produces device deterioration. With an appropriate thermal activation, Te/Cu yields higher cell efficiency and FF than MoO$_x$ and NP treatment. The detailed discussion regarding to thermal activation will be discussed in Chapter 5.
Figure 4-10. (a) Photo and (b) dark $J$-$V$ characteristics of ultra-thin CdTe solar cells using Te/Cu back contact buffer with different Te thicknesses. The Cu thickness is 1.1 nm.

The effects of Te thickness on the ultra-thin CdTe solar cells using Te/Cu back contact buffer are illustrated in Fig.4-10 and Table 4-8. The cell without a Te layer shows much inferior device performance to the cells with a layer of 50~300 nm Te and a 1.1 nm-Cu
layer, meaning it is the tellurium not the copper that plays a critical role in the ohmic contact formation. Although the cells with and without a Te layer have a similar reverse saturation current, the cell without a Te layer has a lower $J_{sc}$. Besides, its photo current in the forward bias of 1.0 V is prominently higher, suggesting the CdS/CdTe stack is photoconductive. As the Te thickness is increased, both $V_{oc}$ and $FF$ are slightly improved. In general, the optimum Te thickness is 100 nm.

Table 4-8. Device performance of ultra-thin CdTe solar cells using Te/Cu back contact buffer with various Te thicknesses

<table>
<thead>
<tr>
<th>Cell</th>
<th>Te/Cu thickness (nm)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
<th>$R_{sh}$ (Ωcm$^2$)</th>
<th>$R_s$ (Ωcm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1805D</td>
<td>0/1.1</td>
<td>500</td>
<td>20.1</td>
<td>63.8</td>
<td>6.4</td>
<td>500</td>
<td>4.5</td>
</tr>
<tr>
<td>1845A</td>
<td>50/1.1</td>
<td>810</td>
<td>21.6</td>
<td>74.0</td>
<td>12.9</td>
<td>2966</td>
<td>4.0</td>
</tr>
<tr>
<td>1845B</td>
<td>100/1.1</td>
<td>820</td>
<td>21.4</td>
<td>77.1</td>
<td>13.5</td>
<td>4709</td>
<td>3.5</td>
</tr>
<tr>
<td>1845C</td>
<td>200/1.1</td>
<td>825</td>
<td>21.3</td>
<td>74.0</td>
<td>13.0</td>
<td>4149</td>
<td>4.3</td>
</tr>
<tr>
<td>1845D</td>
<td>300/1.1</td>
<td>820</td>
<td>21.3</td>
<td>74.8</td>
<td>13.1</td>
<td>4199</td>
<td>4.0</td>
</tr>
</tbody>
</table>

*15: The thermally activation was carried out on the cells at 275°C for 0s.

The effects of Cu thickness on ultra-thin CdTe solar cells using a Te/Cu back contact buffer are illustrated in Fig.4-11 and Table 4-9. The cell without a Cu layer shows inferior device performance, suggesting Cu is necessary to achieve high efficiency. The Te-only cell has $R_{sh}$ and $R_s$ similar to the Cu/Te cells. It is difficult to determine the optimum Cu thickness from the $J$-$V$ characteristics. But it will be shown in Chapter 5 that the concentration of Cu is critical to device degradation.
Figure 4-11. (a) Photo and (b) dark $J-V$ characteristics of ultra-thin CdTe solar cells using Te/Cu back contact buffer with different Cu thicknesses. The Te thickness is 100 nm.
Table 4-9. Device performance of ultra-thin CdTe solar cells using Te/Cu back contact buffer with various Cu thicknesses *16

<table>
<thead>
<tr>
<th>Cell</th>
<th>Te/Cu thickness (nm)</th>
<th>Voc (mV)</th>
<th>Jsc (mAcm(^2))</th>
<th>FF (%)</th>
<th>η (%)</th>
<th>Rsh (Ωcm(^2))</th>
<th>Rs (Ωcm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1805D</td>
<td>100/0.0</td>
<td>790</td>
<td>21.0</td>
<td>71.0</td>
<td>11.8</td>
<td>1361</td>
<td>4.7</td>
</tr>
<tr>
<td>1845A</td>
<td>100/0.3</td>
<td>815</td>
<td>21.2</td>
<td>75.0</td>
<td>13.0</td>
<td>3397</td>
<td>3.9</td>
</tr>
<tr>
<td>1845B</td>
<td>100/0.6</td>
<td>810</td>
<td>21.1</td>
<td>73.7</td>
<td>12.6</td>
<td>1717</td>
<td>3.5</td>
</tr>
<tr>
<td>1845C</td>
<td>100/1.1</td>
<td>800</td>
<td>21.3</td>
<td>74.4</td>
<td>12.7</td>
<td>4315</td>
<td>3.9</td>
</tr>
<tr>
<td>1845D</td>
<td>100/2.2</td>
<td>810</td>
<td>21.1</td>
<td>74.7</td>
<td>12.8</td>
<td>3277</td>
<td>4.9</td>
</tr>
</tbody>
</table>

*16: The thermally activation was carried out on the cells at 275°C for 0s.

Table 4-10. Device performance of ultra-thin CdTe solar cells with various CdTe film thicknesses and a Te/Cu back contact buffer layer

<table>
<thead>
<tr>
<th>Cell</th>
<th>CdTe thickness (μm)</th>
<th>Te/Cu thickness (nm)</th>
<th>Voc (mV)</th>
<th>Jsc (mAcm(^2))</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>0.9</td>
<td>100/1.1</td>
<td>790</td>
<td>20.4</td>
<td>69.0</td>
<td>11.1</td>
</tr>
<tr>
<td>G</td>
<td>1.2</td>
<td>100/1.1</td>
<td>790</td>
<td>20.7</td>
<td>70.8</td>
<td>11.6</td>
</tr>
<tr>
<td>H</td>
<td>1.4</td>
<td>100/1.1</td>
<td>790</td>
<td>21.6</td>
<td>76.5</td>
<td>13.1</td>
</tr>
<tr>
<td>I</td>
<td>1.5</td>
<td>100/1.1</td>
<td>820</td>
<td>21.5</td>
<td>76.4</td>
<td>13.5</td>
</tr>
<tr>
<td>J</td>
<td>1.7</td>
<td>100/1.1</td>
<td>830</td>
<td>21.5</td>
<td>76.8</td>
<td>13.7</td>
</tr>
</tbody>
</table>

Fig.4-12 shows the photo and dark J-V characteristics of ultra-thin CdTe solar cells with different thickness of CdTe. The Te/Cu thickness ratio for these cells is held at 100:1.1. The device performance is listed in Table 4-10. The efficiency of these cells is among the highest ever achieved using ultra-thin CdTe films as the absorber. As far as we know, this is the first time a fill factor as high as 76~77% in ultra-thin CdTe solar cell.
Figure 4-12. (a) Photo and (b) dark J-V characteristics of ultra-thin CdTe solar cells with different thicknesses of CdTe and a Te/Cu back contact buffer layer. The thickness of Te and Cu are 100 nm and 1.1 nm respectively.

4.5 Summary

NP treatment has been demonstrated to be inapplicable to ultra-thin CdTe solar cells because the problem of preferential etching on CdTe grain boundaries seriously affects the physical integrity of ultra-thin CdTe films. We have identified two back contact
buffers, MoO$_x$ and Te/Cu, which are suitable for the fabrication of ultra-thin CdTe solar cells. Compared with the NP method, our dry methods by physical vapor deposition avoid etching damage on CdTe films and are better suited for large scale in-line manufacturing of CdTe PV modules.

As a back contact buffer, MoO$_x$ can be produced to match the high work function of $p$-CdTe, thus it enables the formation of an ohmic back contact and enhances the efficiency of the CdTe solar cells, featuring high $FF$ and $V_{oc}$. MoO$_x$ is compatible with various metal electrodes including metals with a low work function or high reactivity with CdTe. We have also demonstrated that CdTe solar cells with MoO$_x$ as the back contact buffer is relatively stable.

In another approach, Te/Cu was developed as a contact buffer for application in ultra-thin CdTe solar cells. Te, prepared by vapor deposition directly on CdTe, has been found to be highly effective as a high work function buffer, and in addition it limits Cu diffusion into the underlying CdTe layer. Efficiencies up to 13.1% have been demonstrated in CdTe solar cells with the CdTe thickness as low as 1.4 μm.
5. Low-resistance electrical back contact buffer to p-CdTe

Among the approaches to achieving high-efficiency and long-lifetime thin film CdS/CdTe solar cells, the formation of a low-resistance and stable ohmic contact to p-CdTe is critical, and perhaps the most difficult. In general, a metal forming an ohmic contact to p-CdTe should have a work function aligned at least with the top of the CdTe valence band. However, since p-CdTe has a work function as high as 5.7 eV, most common metals are incapable of matching the work function and thus are not useful for making ohmic contact to p-CdTe.

One strategy to overcome this difficulty is to chemically modify the CdTe surface and create a degenerate $p^+$ Te-rich layer by chemical etching with bromine-methanol (BM) solution or nitric-phosphoric (NP) acid solution. The etching process produces a highly conductive Te layer with a thickness determined by the etching conditions and the CdTe surface morphology. There are several key issues associated with the etching process including the tendency of over etching along grain boundaries resulting in the creation of electrical shunts in the CdTe layer.

Alternatively, semiconductor materials MX, such as Cu$_x$Te$^{88}$, NiTe$_2^{89}$, ZnTe:N$^{90}$, ZnTe:Cu$^{91}$, Sb$_2$Te$_3^{92}$ and As$_2$Te$_3^{93}$, have been variously used as the contact buffer placed between the p-CdTe layer and the metal electrode. The MX layer is presumed to enhance charge tunneling across the MX/metal junction, and to reduce the energy barrier at the CdTe/MX junction through the creation a heavily p-doped CdTe surface. Cu and Sb from the MX layer are known to form shallow acceptors in CdTe. Among the MXs,
Cu$_x$Te results in the best CdS/CdTe solar cells $^{21}$. The control of Cu amount as well as the stoichiometry in the MX layer is critical and delicate to achieve the desired ohmic behavior. Cu deficiency will lead to non-ohmic behavior, while excessive Cu will cause fast device degradation. Besides, most of these schemes require the chemical etching of the CdTe surface.

In Chapter 4, we have described a new back contact buffer based on Te/Cu bi-layer. This buffer forms a low-resistance contact to p-CdTe and has been shown to produce superior device performance, especially $FF$, in ultra-thin CdTe solar cells. This Chapter describes the optimization and characterization of Te/Cu bi-layer.

### 5.1 Effects of Te/Cu bi-layer and thermal activation on device performance

**Table 5-1. Device performance of CdTe solar cells with and without back contact buffer layer.**

<table>
<thead>
<tr>
<th>Cell</th>
<th>Back contact buffer thickness (nm)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mAcm$^{-2}$)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
<th>$R_{sh}$ (Ω cm$^2$)</th>
<th>$R_s$ (Ω cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1805A</td>
<td>NA</td>
<td>478</td>
<td>20.9</td>
<td>60.5</td>
<td>6.0</td>
<td>515</td>
<td>3.7</td>
</tr>
<tr>
<td>1805D</td>
<td>NP</td>
<td>780</td>
<td>21.5</td>
<td>71.5</td>
<td>12.0</td>
<td>2399</td>
<td>3.1</td>
</tr>
<tr>
<td>1805C</td>
<td>100 Te</td>
<td>800</td>
<td>21.4</td>
<td>73.9</td>
<td>12.7</td>
<td>3817</td>
<td>2.7</td>
</tr>
<tr>
<td>1805B</td>
<td>100 Te/1.1 Cu</td>
<td>820</td>
<td>22.2</td>
<td>77.6</td>
<td>14.1</td>
<td>3784</td>
<td>2.4</td>
</tr>
</tbody>
</table>
Cu is used as a shallow acceptor in CdTe, but excessive Cu can result in device degradation as Cu diffuses rapidly in CdTe. Te is designed to buffer Cu diffusion and therefore prolongs the lifetime of the device.
Fig. 5-1 shows the photo and dark $J$-$V$ characteristics of CdTe solar cells with and without a back contact buffer. The device performance of these cells is listed in Table 5-1. The back contact buffer is either Te or Te/Cu. The Te layer was created either by NP etching or by sputtering deposition. A thermal activation at 270 °C for 10 s was carried out on all the four cells after completing the electrode deposition.

The cell without a back contact buffer shows significantly lower $V_{oc}$ and $FF$ than the cells with a back contact buffer. Our recent study \textsuperscript{84} shows that Ni reacts with CdTe at elevated temperature to form Ni$_x$Te, resulting in abstraction of Te from the CdTe and the formation of a Te-deficient CdTe layer adjacent to the Ni electrode surface. This leads to a non-ohmic contact, a roll-over behavior in the $J$-$V$ characteristics, and a low $V_{oc}$ and $FF$. The cells with a back contact buffer show normal $V_{oc}$ of 780–820 mV.

Among NP treatment, Te and Te/Cu back contact buffers, Te/Cu yields the highest $FF$ and $\eta$. The slightly inferior device performance, especially $V_{oc}$ and $FF$, of the NP cell is presumably due to the large leakage current as shown in Fig. 5-1b. As discussed in Chapter 4, the increased leakage current is correlated with the preferential etching on CdTe grain boundaries. Compared with NP etching, sputtering deposition does not affect the physical integrity of CdTe film and therefore avoids the increase of leakage current. As for the difference in device performance resulted from the evaporated Te and Te/Cu, it is believed that Cu in Te/Cu enhances the $p$-doping in bulk CdTe, increases the built-in voltage, and thus improves $V_{oc}$ and $FF$. 
Figure 5-2. (a) Photo and (b) dark $J$-$V$ characteristics of CdTe solar cells with Te/Cu back contact before and after accumulative thermal activation.
Table 5-2. Device performance of CdTe solar cells with Te/Cu back contact before and after accumulative thermal activation. The Te and Cu thickness is 100 nm and 4.5 nm, respectively.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Thermal activation</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>Duration (min)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0$^{th}$</td>
<td>-</td>
<td>-</td>
<td>21.2</td>
<td>744</td>
<td>62.7</td>
</tr>
<tr>
<td>1$^{st}$</td>
<td>150</td>
<td>20</td>
<td>21.3</td>
<td>740</td>
<td>64.6</td>
</tr>
<tr>
<td>2$^{nd}$</td>
<td>150</td>
<td>20</td>
<td>21.0</td>
<td>740</td>
<td>64.5</td>
</tr>
<tr>
<td>3$^{rd}$</td>
<td>150</td>
<td>20</td>
<td>20.8</td>
<td>735</td>
<td>65.3</td>
</tr>
<tr>
<td>4$^{th}$</td>
<td>225</td>
<td>4</td>
<td>22.7</td>
<td>810</td>
<td>71.7</td>
</tr>
</tbody>
</table>

Figure 5-2 shows the $J$-$V$ characteristics of CdTe solar cells with Te/Cu back contact buffer before and after thermal activations. The corresponding device performance is shown in Table 5-2. Without a thermal activation, the as-made CdTe solar cell had a low $V_{oc}$ of 744 mV and $FF$ of 62.7%. The roll-over at forward bias indicated a non-ohmic back contact. After the cell was subjected to a thermal activation at 150 °C for 20 min, the roll-over was prominently reduced. Correspondingly the $FF$ was increased from 62.7% to 64.6%. However the efficiency was only slightly improved because the $V_{oc}$ and $J_{sc}$ almost remained constant. With additional (2$^{nd}$ and 3$^{rd}$) thermal activations under the same conditions, the roll-over and $FF$ were further improved, but the overall efficiency was reduced because of the decrease in $V_{oc}$ and $J_{sc}$. Further thermal activation in which the annealing temperature was increased from 150 °C to 225 °C was found to produce significantly higher device performance with efficiency as high as 13.2%.
Figure 5-3. (a) $J$-$V$ characteristics of CdTe solar cells with Te/Cu back contact buffer before and after thermal activation at different temperatures. (b) Expanded view of the power-quadrant.

To further investigate the thermal activation process, CdTe solar cells with a Te/Cu buffer were subjected to thermal activations for a range of temperatures of 150~225 °C
and a fixed duration of 20 min. Figure 5-3 shows the photo $J$-$V$ characteristics and the expanded power-quadrant of these cells. It is very clear that significant improvement occurred at a temperature of $> 180$ °C. The thermal activation at 225 °C for 20 min results in slightly degradation, indicating the activation duration also matters when the activation temperature is higher than the threshold.

Table 5-3. Device performance of CdTe solar cells with Te/Cu back contact buffer and different thermal activations

<table>
<thead>
<tr>
<th>Cell</th>
<th>Thermal activation</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>Duration (min)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1790A</td>
<td>200</td>
<td>20.0</td>
<td>810</td>
<td>22.2</td>
<td>76.2</td>
</tr>
<tr>
<td>1790D</td>
<td>225</td>
<td>4.0</td>
<td>810</td>
<td>22.1</td>
<td>76.3</td>
</tr>
<tr>
<td>1790B</td>
<td>235</td>
<td>2.0</td>
<td>810</td>
<td>22.3</td>
<td>75.1</td>
</tr>
<tr>
<td>1790E</td>
<td>245</td>
<td>1.5</td>
<td>810</td>
<td>22.5</td>
<td>74.8</td>
</tr>
<tr>
<td>1810E</td>
<td>260</td>
<td>0.5</td>
<td>812</td>
<td>22.7</td>
<td>77.0</td>
</tr>
</tbody>
</table>

The device performance CdTe solar cells with a Te/Cu back contact buffer and a thermal activation at various temperatures and durations are shown in Table 5-3. The corresponding $J$-$V$ characteristics are shown in Figure 5-4. It can be seen that as the thermal activation temperature is increased, the device performance remains high as long as the activation duration is reduced correspondingly.
Figure 5-4. (a) $J$-$V$ characteristics of CdTe solar cells with Te/Cu back contact buffer and thermal activation at different temperatures; (b) expanded view of the power-quadrant.

In general, the optimum thermal activation should be carried out at the temperature above a temperature threshold (~180 °C) for a duration commensurate with the temperature. The optimum duration decreases as the temperature increases.
5.2 Device stability of Te/Cu back contact buffer

The instability of CdS/CdTe solar cells can be attributed to several causes including degradation in CdS/CdTe junction and the back contact, and the development of shunting defects in CdTe. In general, the beginning of cell degradation occurs with the development of “roll-over” in the $J$-$V$ characteristics causing a decrease in $V_{oc}$ and $FF$. The $J_{sc}$ is generally less affected.

Among the possible degradation mechanisms of the back contact, the most suspicious one is metal diffusion from the back contact into the CdS region. For the Cu-containing back contacts, it is well-known that Cu diffuses fast in CdTe especially along grain boundaries. At the CdS/CdTe junction, Cu was proposed to form recombination centers and shunt pathways, limiting the device lifetime. For Te/Cu back contact buffers developed in this work, the Cu/Te molar ratio ranges from 0.008 to 0.25, which is much smaller than that in Cu$_x$Te ($1 \leq x \leq 2$). The Cu concentration is deliberately reduced to avoid excess Cu diffusion to the CdTe bulk layer and the CdS/CdTe junction. Te is designed to buffer Cu diffusion and to further control Cu diffusion.

In order to evaluate the device stability of CdTe solar cells with a Te/Cu back contact buffer, the cells were subjected to two testing environments. The thermal stress test was conducted at 200 °C in a tube furnace filled with pure nitrogen. The light soaking test was carried out in a custom-made light box with compact fluorescence lamps with a light intensity of $\sim 1$ kW/m$^2$. 
Figure 5-5. Device degradation (a) $J_{sc}$, (b) $V_{oc}$, (c) $FF$ and (d) $\eta$ of CdTe solar cells with Te/Cu back contact buffer in thermal stress tests. The Te thickness is 100 nm. The Cu thickness is 0–9.0 nm.
As discussed in Section 4.4, the Te/Cu back contact without Cu results in device performance slightly inferior to the one with Cu. A back contact without Te cannot achieve ohmic contact to $p$-CdTe and produces poor device performances. Therefore, in order to form ohmic contact to $p$-CdTe, Cu is important but not indispensable whereas Te is an essential ingredient. For stability tests, the Cu thickness was varied from 0 to 9.0 nm; and the Te thickness was varied from 50 nm to 300 nm.

Fig.5-5 exhibits the degradation of $J_{sc}$, $V_{oc}$, $FF$ and device efficiency for a series of CdTe solar cells with various Te/Cu compositions. The thermal stress tests were carried out at 200 °C for up to 9 h. The Cu/Te molar ratio was varied from 0 (no Cu) to 0.25 (9 nm Cu). As discussed in Section 4.4 (Figure 4-11), the cell with a Te-only back contact buffer has inferior device performance to the cell with a Te/Cu back contact buffer. The Cu amount in the Te/Cu bi-layer only slightly affects the initial device performance. The $y$-axe of the Fig.5.5 represents the relative degradation rate in comparison with the initial device performance.

As shown in Fig.5-5a, b and c, the cell with a Te/Cu back contact buffer is much more stable than the cell with only Te. The cells with a Te/Cu buffer show a degradation of 3~9% after 9 h thermal stress test compared to 20% for the cell with Te only.
Figure 5-6. $J-V$ characteristics (a) photo and (b) dark of CdTe solar cells using Te/Cu back contact buffer with different Cu thicknesses before and after a thermal stress test at 200 °C for 9h. The Te thickness is 100 nm.
Fig. 5-6 displays the $J$-$V$ characteristics of CdTe solar cells using a Te/Cu buffer with various Cu thicknesses. Among the Cu thicknesses discussed in Fig. 5.5, three thicknesses, 0 nm Cu, 0.3 nm Cu and 9 nm Cu, were chosen in this comparison because they are very typical in terms of device degradation. The photo $J$-$V$ curves show that the roll-over behavior at the forward bias emerged in all three cells after a thermal stress test at 200°C for 9h; and the cell without Cu in the back contact has the largest deterioration in shunting. The dark $J$-$V$ characteristics show that the reverse saturation current only slightly increases as the Cu thickness is increased. In terms of leakage current, the cell with the highest amount of Cu exhibits the largest increase with thermal stress.

Although with thermal stress, the reverse saturation current is increased by ~300% for the cell with 9 nm Cu, the $V_{oc}$ remains relatively unaffected. On the other hand, the cell with 0 nm Cu had a deterioration of 40 mV in $V_{oc}$. It is believed that the enhancement in $V_{oc}$ from Cu doping in CdTe is negated by $V_{oc}$ degradation with thermals stress caused by Cu diffusion. The enhanced stability of the CdTe cells with a Te/Cu buffer suggests that Te plays a role of controlling Cu diffusion into the CdTe layer.

In order to find the optimum Cu amount in Te/Cu back contact with respect to stability under thermal stress, the correlation between the efficiency degradation and the Cu/Te molar ratio were established, which is shown in Fig. 5-7. In this plot, the thickness of the Cu layer is converted into Cu/Te molar ratio assuming uniform distribution of Cu in Te. In terms of producing the highest initial device efficiency (>13%), the optimum molar ratio of Cu/Te is in the range from 8.4e-3 to 1.3e-1. In terms of device stability
(degradation rate < 1%/h), the ratio is between 2.8e-3 to 2.5e-1. The optimal Cu/Te molar ratio is 8.4e-3 in terms of efficiency and stability.

Figure 5-7. Efficiency degradation of CdTe solar cells using Te/Cu back contact buffer with different Cu/Te molar ratios in the thermal stress test (200 °C, 0~9h)

Zhang et al\textsuperscript{95} found that Cl can accumulate at the CdTe grain boundaries and improve p-doping by creating a shallow acceptor complex $V_{\text{Cd-Cl}}$. There was also evidence that the diffusion and accumulation of Cu and Cl may be correlated, in the form of a Cu$_{\text{Cd}}$-Cl$_{\text{Te}}$ complex. Energetic studies have shown that Cu favors Cd (Cu$_{\text{Cd}}$) substitution and Cl favors Te (Cl$_{\text{Te}}$) substitution. The defect states created by the Te core have an energy level below the conduction band minimum and can be removed by co-passivation of Cl and Cu. Neither Cl nor Cu itself can completely passivate the Te core. The co-
passivation of Cl and Cu on the defects states of Te core may be beneficial for device stability. According to Zhang’s theory, Cu may be important for stabilized back contact, therefore Te/Cu is more stable than Te.

Fig.5-8 exhibits the degradation of $J_{sc}$, $V_{oc}$, $FF$ and efficiency of CdTe solar cells under thermal stress tests at 200 °C for up to 9 h. The Te thickness of the Cu/Te buffer was varied from 50 nm to 300 nm. Clearly the cell with only 50 nm-Te is very unstable with respect to thermal stress. After 9 h thermal stress test, all the device parameters, especially $FF$, have deteriorated significantly.

The degradation rate decreased with increased Te thickness, implying that the degradation mechanism might be related to Cu diffusion. Considering 50 nm is on the order of CdTe film roughness, some local areas of CdTe film with a high roughness may not be completely covered with Te, which allows Cu to diffuse in readily. In addition, Cu concentration in Te/Cu also determines the Cu diffusion. Fig. 5-5 demonstrates that the Te/Cu with a thicker Cu layer (4.5~9.0 nm) is less stable than that with a thinner Cu layer (0.2~1.1 nm), which affirms the speculation.
Figure 5-8. Device degradation (a) $J_{sc}$, (b) $V_{oc}$, (c) $FF$ and (d) $\eta$ of CdTe solar cells with Te/Cu back contact buffer in thermal stress test. The Cu thickness is 1.1 nm. The Te thickness is 50–300 nm.
Figure 5-9. Device degradation (a) $J_{sc}$, (b) $V_{oc}$, (c) $FF$ and (d) $\eta$ of CdTe solar cells with Te/Cu back contact buffer in thermal stress test at different temperatures. The Cu and Te layers are 1.1 nm and 100 nm thick respectively.

Fig.5-9 exhibits the degradation of $J_{sc}$, $V_{oc}$, $FF$ and efficiency of CdTe solar cells with a Te/Cu back contact buffer in the thermal stress test at 50~200 °C for up to 9 h. $V_{oc}$
remained relatively unchanged after thermal stress test for 9 h over a wide temperature range, which is consistent with the observation in Fig.5-5 and Fig.5-8. Actually, for the cells tested at 150~175 °C, $V_{oc}$ slightly increased by ~10 mV after 9h. As for the $J_{sc}$ and $FF$, the cells tested at 50~150 °C have marginal degradation (≤1%). The degradation increased with the increasing test temperature indicated by a clear trend in Fig.5-9a, c and d.

Similar to sulfur diffusion in the CdTe grain boundaries, the diffusion of Cu in Te and/or CdTe layers also features Arrhenius temperature dependence. High temperature facilitates Cu diffusion and thus accelerates device degradation. The observation in Fig.5-9 further consolidates the speculation that Cu diffusion accounts for the device degradation in the previous discussions. Moreover, Fig.5-9 also demonstrates that the Te/Cu contact is very stable under the temperature up to 150 °C.
Figure 5-10. Device degradation (a) $FF$ and (b) $\eta$ of CdTe solar cells with Te/Cu back contact buffer in light soaking test. The Cu layer was varied from 0 to 9.0 nm. The Te layer was 100 nm thick.

In addition to thermal stress test, light soaking test was also conducted on CdTe solar cells to evaluate the stability of Te/Cu back contact. Fig.5-10 displays the degradation of $FF$ and $\eta$ of CdTe solar cells with Te/Cu back contact buffer in the light soaking test for up to 35 days. The Cu/Te molar ratio was varied from 0 (no Cu) to 0.25 (9 nm Cu). The degradation of $V_{oc}$ and $J_{sc}$ is very minor and thus is not displayed.

Compared with Fig.5-5 c and d, Fig.5-10 shows the same correlation between Cu amount and device degradation rate. Neither low Cu concentration ($\leq 0.1$ nm Cu per 100 nm Te) nor high Cu concentration ($\geq 9.0$ nm Cu per 100 nm Te) produces a good stability (a degradation no higher than 5% after 30 days of light soaking). Contrary to the thermal stress test, the light soaking test did not produce deterioration in $V_{oc}$ for all the cells. Dobson et al.\textsuperscript{77} believed that a decrease in $V_{oc}$ in the stability test is ascribed to the degradation of PV junction, while a decrease in $FF$ is considered a result of the contact
degradation. The stress conditions in the light soaking test for 30 days may not be sufficient to cause junction degradation. The deterioration in $FF$ suggests that Te contact is not as stable as Te/Cu contact. The fact that certain amount of Cu produces a more stable back contact was affirmed by both the light soaking test and thermal stress test.

It is well known that illumination during stress at open circuit accelerates cell degradation\textsuperscript{97}. Under illumination, the built-in voltage at the CdS/CdTe heterojunction is reduced and slows the concentration gradient-driven diffusion of Cu$^+$ towards the junction. The subsequent Cu accumulation in the CdS results in device deterioration. Fig.5-10 c and d clearly display that higher Cu concentration (9.0 nm Cu per 100 nm Te) causes more significant deterioration in $FF$ and $\eta$ comparing with lower Cu concentration (0.3 nm Cu per 100 nm Te).
Figure 5-11. Device degradation (a) $FF$ and (b) $\eta$ of CdTe solar cells with Te/Cu back contact buffer in light soaking test. The Te layer was varied from 50 to 100 nm. The Cu layer was 1.1 nm thick.

Fig.5-11 displays the degradation of $FF$ and $\eta$ of CdTe solar cells with a Te/Cu back contact buffer in the light soaking test for up to 35 days. The Cu layer is 1.1 nm thick. The Te layer thickness was varied from 50 nm to 300 nm. The degradation of $V_{oc}$ and $J_{sc}$ is insignificant and therefore the results are not displayed.

Comparing Fig.5-8 and Fig.5-11, it is noted that the device degradation of the cell with 50 nm Te is close to that with a thicker Te (100~300 nm). The correlation between Te thickness and device degradation rate is not as obvious as that displayed in Fig.5-8. It is speculated that with the Te buffer layer, the Cu diffusion in Te and CdTe layers is not very strong under light soaking test. The amount of Cu in CdTe bulk layer might be very low and thus results in limited impact on device degradation.
In short, our stress tests suggested that the primary degradation mechanism associated with Te/Cu contact is Cu diffusion. Cu diffusion can be alleviated by reducing Cu concentration to a certain level or increasing Te thickness. A Thicker Te layer produces better stability, suggesting that Te acts as a buffer layer for Cu diffusion.

5.3 Characterization of Te/Cu back contact buffer

Figure 5-12. (a) and (b) CdTe film, (c) and (d) 100 nm Te on top of CdTe film, (e) and (f) 100 nm Te/CdTe after a thermal activation at 225 °C for 4 min.

According to the previous discussions, thermal activation is necessary to promote ohmic contact formation in CdTe solar cells with a Te/Cu as the contact buffer. To further understand the effects of thermal activation, several techniques including SEM, XPS and PL were used to characterize this process.
Fig. 5-12 shows the SEM images of CdTe film, 100 nm Te on CdTe film before and after a thermal activation at 225 °C for 4 min. Unlike NP treatment, the deposition of 100 nm Te on CdTe did not change its morphology. After the thermal activation at 225 °C for 4 min, there is an obvious change in the morphology. The smooth facet of Te/CdTe grains became rough after the thermal activation, featuring tiny grains on the large CdTe grains. Considering the thermal activation was carried out at low temperature under inert ambient, the tiny grains are likely due to the formation of tellurium crystallites.

XPS was conducted on the CdTe solar cells without back electrode. The device structure of the XPS sample is glass substrate/FTO/200 nm-CdS/4.0 μm-CdTe/50 nm-Te/4 nm-Cu. The sample was in-situ annealed in the XPS system at 260 °C for up to 1 hour. XPS signals were collected between two consecutive in-situ annealing after the sample was cooled down to room temperature. The XPS spectra of Te$_{3d}$ and Cu$_{2p}$ peaks before and after different annealing duration were overlapped for comparison as shown in Fig. 5-13.

After annealing for 5 min, there was ~2 eV shift towards the lower binding energy (BE) in both two figures, which was most probably due to removal of some surface impurities. The position of Te$_{3d}$ and Cu$_{2p}$ peaks remained unchanged at 572.5 eV and 932.6 eV respectively after in-situ annealing for up to 20 min, suggesting both Te and Cu were still in the elemental form. After annealing for 60 min, the Te$_{3d}$ peak shifted towards the
lower BE for ~0.3 eV. At the meantime, the Cu$_{2p}$ peak shifted towards to the higher BE for ~0.1 eV. The XPS peak shifts indicate that a reaction between Te and Cu occurred.

![XPS peak shift of Te 3d and Cu 2p](image)

Figure 5-13. XPS peak shift of Te$_{3d}$ and Cu$_{2p}$ during the in-situ annealing at 260 °C for certain duration between two consecutive XPS measurements. The sample structure is: glass substrate/ FTO/CdS/CdTe/50 nm Te/4 nm Cu.

Wu et al $^{88}$ and Zhou et al $^{98}$ investigated the formation of different phases of Cu$_x$Te and their effects on CdTe/CdS solar cells. In their studies, a 150-nm Te layer was fabricated through NP etching on the CdTe film. A layer of 0~130 nm Cu were deposited on top of the Te layer by thermal evaporation. The Te/Cu stack layers were annealed in helium at 250 °C for 30 min. If the Cu layer is thinner than 30 nm or the Cu/Te molar ratio is less than 0.556 (30 nm Cu per 150 nm Te), no Cu$_x$Te signal was detected by XRD after the annealing.
The Cu/Te molar ratios (0.0028–0.25), which have been previously investigated and discussed in the CdTe solar cells, are much lower than 0.556. Besides the typical thermal activation conditions (225 °C, 4 min) are milder than the annealing conditions in Wu’s study. Therefore, under typical thermal activation conditions, it is unlikely to form Cu₅Te compound. The XPS results validated this conclusion. It is believed that Cu diffuses into the Te layer and just forms a Cu-Te mixture after thermal activation. A small amount of Cu might diffuse into the CdTe bulk layer and acted as p-type dopants.

Figure 5-14. Normalized PL spectra of CdS/4.0 μm-CdTe/100 nm-Te/1.1 nm-Cu/200 nm-Ni without and with thermal activation; with thermal activation and 9h thermal stress test. PL spectra were obtained with interface excitation at 40 K

In order to trace the Cu diffusion in CdTe bulk layer, PL measurements were conducted on CdTe solar cell with interface excitation (He-Ne laser, 633 nm) at 40 K. The structure of the cell is glass substrate/200 nm-CdS/4.0 μm-CdTe/100 nm-Te/1.1 nm-Cu/200 nm Ni. PL signals were collected before and after a thermal activation on Te/Cu,
and after a thermal activation plus 9 h thermal stress test at 200 °C on Te/Cu. The PL spectra are normalized and displayed in Fig.5-14.

The prominent features are bands with peaks at ~1.380 eV and ~1.542 eV. According to Halliday et al.\textsuperscript{70} and Caraman et al.\textsuperscript{99}, the 1.542 eV band is ascribed to donor-accepter pair recombination associated with Cu dopants in CdTe. It can be regarded as a fingerprint of Cu dopants in CdTe. As shown in Fig.5-14, before the thermal activation, the 1.542 eV band is not observable in the PL spectra. After the thermal activation, the 1.542 eV band evolved, suggesting Cu actually diffused into CdTe bulk layer even into the vicinity of CdS/CdTe junction.
(b) After TA

- Sum of deconvoluted peaks
- Deconvoluted peak
- Deconvoluted peak
- Deconvoluted peak
- Deconvoluted peak
- Deconvoluted peak

Normalized PL intensity (arb. units)

$h\nu$ (eV)

1.366 eV

1.378 eV

1.448 eV

1.425 eV

(c) After TA and 9h TST

- Sum of deconvoluted peaks
- Deconvoluted peak
- Deconvoluted peak
- Deconvoluted peak
- Deconvoluted peak

Normalized PL intensity (arb. units)

$h\nu$ (eV)

1.365 eV

1.379 eV

1.452 eV

1.428 eV
Figure 5-15. PL spectra and the corresponding deconvoluted PL peaks of CdS/4.0 μm-CdTe/100 nm-Te/1.1 nm-Cu/200 nm-Ni (a) without and (b) with a thermal activation; (c) with a thermal activation and 9h of thermal stress test; (d) the evolution of the Cu$^+$/V$_{Cd}$ band. PL spectra were obtained with interface excitation at 40 K.

Table 5-4. Position and relative intensity ratio of the deconvoluted peaks in Fig.5-15

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Cd$_{1-x}$S$_x$Te Peak (eV)</th>
<th>I/I0</th>
<th>Surface defects Peak (eV)</th>
<th>I/I0</th>
<th>V$<em>{Cd}$-Cl$</em>{Te}$ Peak (eV)</th>
<th>I/I0</th>
<th>Cu$^+$/V$_{Cd}$ Peak (eV)</th>
<th>I/I0</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-made</td>
<td>1.381</td>
<td>0.675</td>
<td>1.438</td>
<td>0.263</td>
<td>-</td>
<td>-</td>
<td>1.421</td>
<td>0.038</td>
</tr>
<tr>
<td>After TA</td>
<td>1.378</td>
<td>0.532</td>
<td>-</td>
<td>-</td>
<td>1.448</td>
<td>0.118</td>
<td>1.425</td>
<td>0.108</td>
</tr>
<tr>
<td>TA + TST</td>
<td>1.379</td>
<td>0.563</td>
<td>-</td>
<td>-</td>
<td>1.452</td>
<td>0.102</td>
<td>1.428</td>
<td>0.157</td>
</tr>
</tbody>
</table>

*I$_0$ is the intensity of the primary peak located at 1.380 eV

As discussed in Section 3-4, the 1.380 eV has been assigned to CdTe$_{1-x}$S$_x$ phase. Considering the 1.380 eV band in Fig.5-14 is not a symmetric Gaussian curve, it is not solely ascribed to CdTe$_{1-x}$S$_x$ phase. It is composed of several PL peaks. The 1.380 eV
bands in Fig.5-14 were deconvoluted into several Gaussian components using *MicroLab Origin 8.0*. The 1.380 eV bands and its deconvoluted peaks are illustrated in Fig. 5-15. The sum of the deconvoluted peaks fits the original PL spectra very well.

Among the deconvoluted peaks shown in Fig.5-15, the peaks in the range of 1.354–1.366 eV are probably due to cadmium vacancy complexes. The emission mechanisms for the other deconvoluted peaks are listed in Table 5.

The peaks located at ~1.450 eV are assigned to deep accepter V$_{Cd}$-Cl$_{Te}$~70~. The level of V$_{Cd}$-Cl$_{Te}$ complex slightly decreased after 9h thermal stress test. The reason is still unclear.

The features centered at ~1.420 eV is related to the Cu dopants, which are known to form a relatively deep level Cu$^+$-V$_{Cd}$~100~ in CdTe. Cu forms accepter by substituting at the Cd sites. At a high concentration, Cu forms interstitial donors ~100~. The peak intensity increased from 0.038 I$_0$ to 0.108 I$_0$ after the thermal activation, suggesting the level of Cu$^+$-V$_{Cd}$ complex was enhanced by Cu diffusion. Additional thermal stress test further facilitated Cu diffusion and thus increased the peak intensity to 0.157 I$_0$.

Though not all the observations related to the PL spectra in Fig.5-15 are well-understood, it is still plausible to make a conclusion based on the information acquired in the PL spectra and their deconvoluted peaks. The thermal activation and thermal stress test exerted an influence on the Cu diffusion in the CdTe bulk layer. The 1.542 eV and ~1.420 eV bands, which are directly related to Cu dopants, validate the speculation.
In conclusion, the thermal activation mainly has two impacts on the Te/Cu back contact buffer. It promotes the crystallization of Te layer and results in Cu diffusion in the Te and CdTe layer. No reaction occurs between Cu and Te during a typical thermal activation process.

5.4 Summary

Te/Cu bi-layer was developed as an effective back contact buffer to p-CdTe in the fabrication of ultra-thin CdTe solar cells. The first intent is to avoid NP treatment, which is prone to produce shorts in ultra-thin CdTe solar cells. Another intent is to address the instability issue related to Cu as a dopant in CdTe.

Unlike NP treatment, Te/Cu does not necessitate acid etching. As a contact buffer, Te/Cu performs better than the Te buffer produced by NP treatment in terms of efficiency enhancement, particularly for ultra-thin cells.

The effects of Te and Cu thickness on Te/Cu back contact buffer have been systematically studied. The optimized Te and Cu thicknesses are 100 nm and 0.3~2.2 nm respectively. The optimum temperature and duration to activate the Te/Cu buffers are 225~260 °C and 4~0.5 min respectively. Higher thermal activation temperature corresponds to a shortened duration. The temperature threshold for thermal activation is ~180 °C. With the optimum conditions as mentioned, CdTe solar cells using a Te/Cu back contact with $V_{oc}$ up to 856 mV, $FF$ up to 78.6% and $\eta$ of 14.8% have been demonstrated.
The stability of CdTe solar cells with a Te/Cu back contact buffer have been evaluated under thermal stress and light soaking tests. Neither low Cu concentration (<0.1 nm Cu per 100 nm Te) nor high Cu concentration (>9.0 nm Cu per 100 nm Te) results in good device stability. The device instability is due to Cu diffusion which was proved by XPS and PL. With an appropriate Cu amount (0.2~1.1 nm) and Te thickness (100~300 nm), the Te/Cu back contact is stable.
6. Fabrication of Cd\(_{1-x}\)Zn\(_x\)S films by vapor zinc chloride treatment

As \(n\)-type semiconductors with a large and viable bandgap between 2.42 and 3.54 eV, the ternary Cd\(_{1-x}\)Zn\(_x\)S compounds have been used as a window layer to form heterojunction solar cells with CdTe\(^{101}\), Cu(In, Ga)Se\(_2\) (CIGS)\(^{102}\), CuGaSe\(_2\)\(^{103}\), CuInSe\(_2\)\(^{104}\) and Si\(^{105}\). For commercial CdS/CdTe and CdS/CIGS solar cells, CdS is the standard window layer despite its relatively low bandgap (2.42 eV) and considerable absorption in the short wavelength region (below 500 nm). To maximize the blue response in these solar cells, the CdS layer thickness is usually kept at a minimum, typically on the order of \(~100\) nm. Although thinner CdS films are favorable, they are impractical because of excessive pinhole formation and possible electrical shunting across the heterojunction. These issues can affect adversely the \(V_{oc}\) and \(FF\). Replacing CdS with Cd\(_{1-x}\)Zn\(_x\)S is a viable alternative because Cd\(_{1-x}\)Zn\(_x\)S can provide a more transmissive window without compromising the thickness. Oladeji et al.\(^{101}\) and others\(^{106,107}\) have already demonstrated that the spectral response in the 400-600 nm wavelength region can be prominently improved by substituting Cd\(_{1-x}\)Zn\(_x\)S for CdS in CdTe solar cells.

Various methods have been used to fabricate Cd\(_{1-x}\)Zn\(_x\)S films, which can be categorized into physical vapor deposition (PVD) and solution deposition method (SD). The PVD methods including metal organic chemical vapor deposition \(^{108}\) and molecular beam epitaxial \(^{109}\) require complicated apparatus and costly maintenance. While the SD methods, including chemical spray deposition \(^{110,111}\), co-evaporation \(^{112}\), photochemical
deposition \(^{107}\), and chemical bath deposition \(^{113,114}\), require additional annealing process to improve film quality. In this work, Cd\(_{1-x}\)Zn\(_x\)S films were fabricated using a vaporous zinc chloride treatment (VZC), by which the incorporation of Zn in a CdS film can be conveniently adjusted by annealing CdS film in the zinc chloride vapor ambient. This chapter will discuss the fabrication and characterization of Cd\(_{1-x}\)Zn\(_x\)S films made by VZC method, and the application of Cd\(_{1-x}\)Zn\(_x\)S in CdTe solar cells.

### 6.1 Experimental setup and process

![Figure 6-1](image)

**Figure 6-1.** (a) Schematic illustration of a two zone tube furnace setup and (b) a typical temperature profile for VZC treatment

The experimental setup for a typical VZC treatment based on a two-zone tube furnace is illustrated in Fig.6-1a. \(^{73}\) A glass tube (1” diameter and 24” long), containing both the ZnCl\(_2\) source (50-500 mg) and the FTO/CdS substrates in separate zones, was purged with nitrogen at a flow rate of 100 cm\(^3\)/min for 10 min. The zone containing FTO/CdS
substrates was firstly heated to 300-380 °C, then the temperature of the zone containing the ZnCl$_2$ sources was raised to 300-320 °C and kept at this temperature for 0~4 min. Nitrogen flow was maintained during the entire VZC process. The temperature profile for a typical VZC treatment is shown in Fig.6-1b.

6.2 Characterizations of Cd$_{1-x}$Zn$_x$S films fabricated by a VZC method

![Figure 6-2. XRD spectra of FTO substrate, CdS film on FTO substrate before and after a VZC treatment](image)

The XRD spectra of the FTO substrate, the as-deposited CdS film and the CdS after VZC treatment are shown in Fig.6-2. The (111), (200), (102), (112) and (004) peaks of the cubic CdS overlap closely with the (110), (101), (200), (211) and (220) peaks of the FTO, respectively, and are not easily distinguishable from each other. The pronounced (110) peak indicates that the as-deposited CdS has a zincblende structure. The standard
XRD spectra of cubic CdS and Cd$_{1-x}$Zn$_x$S show that as the $x$ value increases from 0 to 1, the (110) peak shifts from 43.9° to 48.2°. After the VZC treatment, the (110) CdS peak shifts from 43.7° to 46.2°, which clearly indicates the incorporation of Zn into the CdS. Similar peak shifts have been observed by Dzhafarov et al.\textsuperscript{115} and Gunasekaran and Ichimura et al.\textsuperscript{116}. The increase of XRD peak intensity, particularly the (200), (102) and (112) peaks, suggests that the CdS film crystallinity was improved as a result of VZC treatment.

![SEM images of (a) as-deposited CdS film and (b) CdS film treated by VZC treatment.](image)

**Figure 6-3.** SEM images of (a) as-deposited CdS film and (b) CdS film treated by a VZC treatment.

Fig.6-3a and b shows the SEM images of an as-deposited CdS film and a CdS film treated by VZC. The as-deposited CdS film is composed of closely-packed clusters with an average size of ~120 nm. High-resolution SEM images show that each cluster contains many small CdS grains. The morphological features of as-deposited CdS film are presumably due to low-deposition temperature. After the VZC treatment, the actual
The grain size of CdS increased to 30~80 nm. The grain growth is consistent with the improvement of crystallinity reflected in Fig. 6-2. In addition to grain growth, CdS grains appear to be more spherical before the VZC treatment and become more faceted and crystalline after the treatment. Also noted is the appearance of pinholes in the VZC-treated films, which are of concern and will be addressed in device fabrication.

Fig. 6-4 shows that optical transmission and the corresponding absorption edge of CdS and Cd$_{0.36}$Zn$_{0.64}$S. The bandgap of the CdS film before (2.3 eV) and after VZC treatment (2.92 eV) was extracted from the absorption spectra using a linear fit at the threshold region. According to Oladeji $^{107}$, the sharp absorption is a characteristic of homogeneous structure, in other words Cd$_{1-x}$Zn$_x$S with a fixed $x$ value. Using a well-established relation between the bandgap and stoichiometry of Cd$_{1-x}$Zn$_x$S $^{115,117}$:

$$E_g(x) = E_g(CdS) + \left[E_g(ZnS) - E_g(CdS) - b\right]x + bx^2$$  \hspace{1cm} (6-1)$$

a value of 0.635 was obtained from $x$ corresponding to a bandgap of 2.92 eV for the VZC-treated film. Bandgap values of cubic CdS (2.42 eV) and ZnS (3.54 eV) and the value of $b$ (0.91 eV) were used in this estimation. $^{118}$
Figure 6-4. Transmission spectra of a CdS film and the CdS film treated by VZC and (inset) the extraction of bandgaps of the CdS film from absorption measurement before and after a VZC treatment.

Table 6-1. Zn doping ratios ($x$) of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ calculated via absorption spectra and measured by EDX measurements.

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Optical measurement</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bandgap (eV)</td>
<td>2.36</td>
<td>2.45</td>
<td>2.60</td>
</tr>
<tr>
<td>Zn doping ratio (%)</td>
<td>0</td>
<td>8.9</td>
<td>33.8</td>
</tr>
<tr>
<td><strong>EDX measurement</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S K (atom%)</td>
<td>46.61</td>
<td>46.49</td>
<td>45.49</td>
</tr>
<tr>
<td>Cd L (atom%)</td>
<td>53.39</td>
<td>48.80</td>
<td>37.66</td>
</tr>
<tr>
<td>Zn K (atom%)</td>
<td>0</td>
<td>4.71</td>
<td>16.85</td>
</tr>
<tr>
<td>Zn doping ratio (%)</td>
<td>0</td>
<td>8.8</td>
<td>30.9</td>
</tr>
</tbody>
</table>
Figure 6-5. EDX spectra of a CdS film before and after a VZC treatment

The energy dispersive X-ray (EDX) spectra of in Fig. 6-5 clearly indicated the appearance of zinc in the CdS film after VZC treatment. As shown in Table 6-1, the Zn to Cd ratios in the Cd\(_{1-x}\)Zn\(_x\)S films as measured by EDX are consistent with the values calculated from the absorption spectra.
6.3 Process exploration of VZC treatment

There are several process parameters involved in a VZC treatment, including annealing temperature, annealing duration, nitrogen flow rate, ZnCl$_2$ source amount, and substrate temperature. Among these parameters, three critical parameters have significant effects on Zn doping ratio in CdS, and thus are important in controlling the composition of Cd$_{1-x}$Zn$_x$S films.

![Graph showing the relation between the bandgap of Cd$_{1-x}$Zn$_x$S films and different annealing temperatures](image)

**Figure 6-6. Relation between the bandgap of Cd$_{1-x}$Zn$_x$S films and different annealing temperatures (the annealing duration was 2 min)**

As shown in Fig.6-6, blue shift appears on the absorption edge of CdS film after VZC treatment. The bandgap of Cd$_{1-x}$Zn$_x$S increases with the increasing annealing temperature, suggesting ZnCl$_2$ vapor with higher thermal energy tends to react with the CdS film. It is quite straightforward that under the same annealing temperature, the Zn doping ratio or
the $x$ value in Cd$_{1-x}$Zn$_x$S increases with the increase of annealing duration, as shown in Fig. 6-7.

Figure 6-7. Relation between the bandgap of Cd$_{1-x}$Zn$_x$S films and different annealing durations (the annealing temperature was 360 °C)

Figure 6-8. Relation between the bandgap of Cd$_{1-x}$Zn$_x$S films and various nitrogen flow rates (the annealing temperature and duration were 360 °C and 2 min respectively)
In the VZC treatment, nitrogen plays the role as the carrier gas to transfer ZnCl$_2$ vapor from the source to the substrate. It also protects ZnCl$_2$ vapor from being oxidized at elevated temperature. As shown in Fig.6-8, the flow rate of nitrogen can prominently affect the Zn doping ratio in Cd$_{1-x}$Zn$_x$S films. In general, given the same duration, larger flow rate can bring more ZnCl$_2$ vapor to the substrate, and therefore result in higher Zn doping ratio or larger bandgap.

6.4 Fabrication of Cd$_{1-x}$Zn$_x$S /CdTe solar cells

![Graph of J-V characteristics](image)

Figure 6-9. Photo J-V characteristics of CdTe solar cells with CdS and Cd$_{1-x}$Zn$_x$S window layers.

In order to evaluate the effects of Cd$_{1-x}$Zn$_x$S as the window layer, a series of Cd$_{1-x}$Zn$_x$S/CdTe solar cells were fabricated with $x$ varied from 0 to 0.5. As shown in Fig.6-9, the $V_{oc}$ and $FF$ of the Cd$_{1-x}$Zn$_x$S/CdTe solar cells are significantly lower than that of the reference cell, resulting in an overall reduction in cell efficiency. At very high zinc
doping ratio \( x = 0.5 \), the \( J_{sc} \) is also much reduced in addition to severe degradation in \( V_{oc} \) and \( FF \). These adverse effects can be primarily attributed to an increase in the lattice mismatch between \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) and \( \text{CdTe} \) \(^{119}\) and in the electrical resistivity of the \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) film with increase in Zn doping ratio \(^{120}\).

As shown in Fig. 6-10, the spectra responses for the \( \text{Cd}_{0.95}\text{Zn}_{0.05}\text{S}/\text{CdTe} \) and \( \text{Cd}_{0.60}\text{Zn}_{0.40}\text{S}/\text{CdTe} \) solar cells are considerably enhanced in the blue region compared with that in the reference cell. The values of \( J_{sc} \) were both measured by \( J-V \) measurement and calculated from integrating the photo response of the cells with AM 1.5 solar spectrum. The values of \( J_{sc} \) obtained from different approaches are very consistent,
which are listed in Fig. 6-10. In general, substituting CdS with Cd$_{1-x}$Zn$_x$S (0.05 < x < 0.40) yields a promising enhancement of 12~14% in $J_{sc}$.

Figure 6-11. (a) Photo and (b) dark $J$-$V$ characteristics of CdTe solar cells with i-SnO$_2$/CdS, i-SnO$_2$/Cd$_{0.91}$Zn$_{0.09}$S and Cd$_{0.95}$Zn$_{0.05}$S window layers.

As discussed in Section 6.2, VZC treatment produces pinholes in the Cd$_{1-x}$Zn$_x$S films, which can lead to electrical shunts across the Cd$_{1-x}$Zn$_x$S/CdTe junction, and consequently a larger leakage current and a lower $V_{oc}$. To alleviate the pinhole issue, a bi-layer front
contact including an intrinsic i-SnO$_2$ layer on top of the more conductive FTO layer was used in the Cd$_{1-x}$Zn$_x$S/CdTe solar cells. The i-SnO$_2$ layer is intended to eliminate localized contacts present between FTO and CdTe, which can cause electrical shunts. What’s more, it has been suggested that the i-SnO$_2$ layer may also act as an “etching stop layer” for the NP solution treatment in forming the back contact.

Figure 6-12. Photo $J$-$V$ characteristics of CdTe solar cells with 150 nm i-SnO$_2$/Cd$_{0.90}$Zn$_{0.10}$S, 100 nm i-SnO$_2$/Cd$_{0.91}$Zn$_{0.09}$S, 50 nm i-SnO$_2$/Cd$_{0.92}$Zn$_{0.08}$S and Cd$_{0.95}$Zn$_{0.05}$S window layers.

Fig.6-11a shows the $J$-$V$ characteristics of several CdTe solar cells with and without the i-SnO$_2$ buffer layer. It can be seen that $V_{oc}$ is largely recovered in the cell with a buffer layer, even for a Cd$_{0.91}$Zn$_{0.09}$S film, which has a high content of Zn. The reverse saturation current of the cells with an i-SnO$_2$ buffer layer is reduced as much as four orders of magnitude compared with the cell without the i-SnO$_2$ layer, as can be seen in the dark $J$-$V$ curves in Fig.6-11b.
The effect of i-SnO$_2$ layer thickness is shown in Fig.6-12. The optimal thickness of the i-SnO$_2$ layer was about 50 nm. A thicker i-SnO$_2$ layer was found to decrease $J_{sc}$ due to an increase in series resistance and possible light interference from the intrinsic SnO$_2$ layer.

Figure 6-13. Photo and dark $J-V$ characteristics of CdTe solar cells with 100 nm i-SnO$_2$/CdS, 100 nm i-SnO$_2$/Cd$_{0.90}$Zn$_{0.10}$S, 100 nm i-SnO$_2$/Cd$_{0.81}$Zn$_{0.19}$S and 100 nm i-SnO$_2$/Cd$_{0.68}$Zn$_{0.32}$S window layers.
Fig. 6-13 shows the photo and dark $J$-$V$ characteristics of CdTe solar cells with 100 nm-i-SnO$_2$/CdS or 100 nm-i-SnO$_2$/Cd$_{1-x}$Zn$_x$S ($0.1 < x < 0.32$) as the window layer. Compared with the i-SnO$_2$/CdS/CdTe solar cell, the i-SnO$_2$/Cd$_{1-x}$Zn$_x$S/CdTe solar cells ($0.1 < x < 0.19$) have significantly higher $J_{sc}$, which is consistent with the results in Fig. 6-11. However, the $V_{oc}$ of the cell decreases from 800 mV to 400 mV as $x$ increases from 0.1 to 0.32. It is noted that as the content of Zn in Cd$_{1-x}$Zn$_x$S increases, both the resistivity of Cd$_{1-x}$Zn$_x$S and the lattice mismatch between CdTe and Cd$_{1-x}$Zn$_x$S increase, causing a drop in $V_{oc}$ and $FF$. Compared with the Cd$_{0.96}$Zn$_{0.04}$/CdTe solar cell, the cell with 100 nm i-SnO$_2$/Cd$_{0.81}$Zn$_{0.19}$/CdTe has higher $V_{oc}$ and $FF$ even though its Zn doping ratio is higher.
Figure 6-14. (a) Photo and (b) dark J-V characteristics of CdTe solar cells with CdS film and Cd$_{1-x}$Zn$_x$S film as window layers. The Cd$_{1-x}$Zn$_x$S films were made by VZC treatment using hydrated or ultra-dry ZnCl$_2$ source.
Table 6-2. Device performance of CdS/CdTe and Cd$_{1-x}$Zn$_x$S/CdTe solar cells with Cd$_{1-x}$Zn$_x$S films treated by VZC using different ZnCl$_2$ sources *17

<table>
<thead>
<tr>
<th>Cell</th>
<th>VZC</th>
<th>Cd$_{1-x}$Zn$_x$S</th>
<th>Device performance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°C)</td>
<td>t (min)</td>
<td>ZnCl$_2$</td>
</tr>
<tr>
<td>100426a</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100426b</td>
<td>360</td>
<td>0.5</td>
<td>Hydrated</td>
</tr>
<tr>
<td>100426c</td>
<td>360</td>
<td>0.5</td>
<td>Ultra-dry</td>
</tr>
<tr>
<td>100426d</td>
<td>360</td>
<td>1.0</td>
<td>Ultra-dry</td>
</tr>
<tr>
<td>100426e</td>
<td>360</td>
<td>1.2</td>
<td>Ultra-dry</td>
</tr>
</tbody>
</table>

*17 The CdTe film thickness is 4.5 μm. The back contact was formed by treating CdTe films with NP solution for 20s and depositing a layer of 200 nm Ni as electrode.
As a very hydroscopic compound, ZnCl\textsubscript{2} tends to absorb moisture easily. At elevated temperature, ZnCl\textsubscript{2} can react with H\textsubscript{2}O (Eqn. 6-2 and 6-3) and generate HCl vapor which can etch CdS films and create pinholes.

\[
ZnCl_2 + 2H_2O \rightarrow Zn(OH)_2 + 2HCl \\
Zn(OH)_2 \rightarrow ZnO + H_2O
\] (6-2) (6-3)

Reducing the exposure time of ZnCl\textsubscript{2} source to the air and decreasing the hydration content in the ZnCl\textsubscript{2} source can alleviate the above reactions, and therefore help to reduce the detrimental effects of HCl vapor.

Fig.6-14 shows the \textit{J-V} characteristics of Cd\textsubscript{1-x}Zn\textsubscript{x}S/CdTe solar cells in which the Cd\textsubscript{1-x}Zn\textsubscript{x}S films were made by VZC treatment using hydrated ZnCl\textsubscript{2} (purity 98\%) and ultra-dry ZnCl\textsubscript{2} (purity 99.99\%). For the same Zn doping ratio (5-6\%), the cell with Cd\textsubscript{1-x}Zn\textsubscript{x}S treated using ultra-dry ZnCl\textsubscript{2} source has significantly higher \textit{V}_{oc} and better \textit{FF} than that using hydrate ZnCl\textsubscript{2} source, affirming the negative effects of moisture in ZnCl\textsubscript{2} source. However, as Table 6-3 shows, the device performance of CdTe solar cells in which Cd\textsubscript{1-x}Zn\textsubscript{x}S films were made by VZC treatment using ultra-dry ZnCl\textsubscript{2}, especially \textit{V}_{oc} and \textit{FF}, is still inferior to the reference CdS/CdTe solar cell. Thus reducing the hydration content in ZnCl\textsubscript{2} source alone cannot solve all the issues associated with Cd\textsubscript{1-x}Zn\textsubscript{x}S/CdTe solar cells.
Figure 6-15. (a) photo and (b) dark $J$-$V$ characteristics of $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{CdTe}$ solar cells with and without a HTA treatment ($550 \, ^\circ \text{C}, 40 \, \text{min}$)

Fig.6-15 shows the photo and dark $J$-$V$ characteristics of $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{CdTe}$ solar cells with and without HTA treatment. The device performance of these cells is listed in Table
6.3. The Cd$_{1-x}$Zn$_x$S films were made by VZC treatments using ultra-dry ZnCl$_2$ source. Interestingly, HTA resulted in enhancements of 50 mV and 3.6% in the $V_{oc}$ and $FF$ of the cell respectively. HTA can not only improve the crystallinity of CdTe film but also reduce film resistivity, which may result in the enhancement of device performance.

Table 6-3. Device performance of CdS/CdTe and Cd$_{1-x}$Zn$_x$S/CdTe solar cells with and without a HTA treatment $^{*18}$

<table>
<thead>
<tr>
<th>Cell</th>
<th>VZC</th>
<th>Cd$_{1-x}$Zn$_x$S</th>
<th>Device performance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T ($^\circ$C)</td>
<td>t (min)</td>
<td>ZnCl$_2$</td>
</tr>
<tr>
<td>1204a</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>1204b</td>
<td>360</td>
<td>0.5</td>
<td>Ultra-dry</td>
</tr>
<tr>
<td>1204c*19</td>
<td>360</td>
<td>0.5</td>
<td>Ultra-dry</td>
</tr>
</tbody>
</table>

$^{*18}$: The CdTe film thickness is 4.5 μm. The back contact was formed by treating CdTe films with NP solution for 20s and depositing a layer of 200 nm Ni as electrode.

$^{*19}$: After CdTe film was deposited, the cell was subjected to HTA at 550°C for 40min..

6.5 Summary

A useful technique using vapor zinc chloride treatment to fabricate Cd$_{1-x}$Zn$_x$S films has been demonstrated. The incorporation of Zn in CdS has been proved by a series of characterization techniques including XRD, absorption spectroscopy and EDX. The Zn doping ratio can be readily controlled by adjusting VZC treatment temperature, duration, nitrogen flow rate or the combination of both.
Substituting CdS with Cd\(_{1-x}\)Zn\(_x\)S in CdTe solar cells produces an increase of in \(J_{sc}\), up to 12~14\%. Inserting an intrinsic SnO\(_2\) as the front contact buffer was found to improve \(V_{oc}\), presumably due to a reduction of the shunting defects. Also, the use of ultra-dry ZnCl\(_2\) granules as the ZnCl\(_2\) source was found to be beneficial in reducing the pinhole formation during VZC treatments. The HTA process after CdTe deposition also improved \(V_{oc}\).
7. Summary and conclusions

This work is an investigation of (1) approaches to fabricating high-efficiency ultra-thin CdTe solar cells, (2) low-resistance electrical back contact buffer based on Te/Cu bi-layer, and (3) a novel vapor zinc chloride treatment method for making Cd$_{1-x}$Zn$_x$S films.

7.1 Approaches to fabricating high-efficiency ultra-thin CdTe solar cells

Three approaches were investigated to realize this objective, including the fabrication of high-quality ultra-thin CdTe films using an improved close-spaced sublimation method, an effective post-deposition treatment comprised of high-temperature annealing and vapor chloride treatment, and novel back contact formation based on MoO$_x$ and Te/Cu back contact buffers.

1) The conventional CSS method, featuring high deposition rate (>1 μm/min), and high substrate temperature, is not suitable for reproducibly making ultra-thin CdTe films without pinholes. The modified CSS method using an improved temperature-time profile control is able to deposit compact ultra-thin CdTe films with very few pinholes and a low roughness/thickness ratio. Three critical parameters including oxygen pressure, substrate temperature and thermal etch duration have been systematically studied. The best parameter combination to produce pinhole-free CdTe films with good crystallinity is high substrate temperature and oxygen pressure plus appropriate thermal etch prior to CdTe deposition.
2) A two-stage post-deposition treatment was found to be beneficial for producing high-efficiency ultra-thin CdTe cells. The high temperature annealing (HTA) step further enhances CdTe grain growth and reduces defects related to grain boundaries and excess sulfur diffusion during VCC treatment. The VCC step passivates the recombination centers along the grain boundaries and reduces lattice mismatch at the heterojunction. The combination of HTA and VCC steps yields higher efficiency than either HTA or VCC step alone.

3) In the conventional back contact formation using nitric-phosphoric acid (NP) solution, CdTe films, especially ultra-thin films suffer preferential etching on grain boundaries which results in pinholes and electrical shunting. In a collaborative effort, two back contacts based on MoO_3 and Te/Cu have been developed to replace the NP etching treatment. Deposited by thermal evaporation or sputtering, MoO_3 and Te/Cu avoid damages on ultra-thin CdTe films caused by acid etching. The high work function of MoO_3 and Te alters the effective electron affinity at the CdTe/metal interface and thus reduces the energy barrier for the hole transfer. Appropriate amount of Cu is deliberately introduced into the back contact to enhance p-type doping in CdTe.

Combining three approaches, CdS/CdTe solar cells with efficiency of 11.2~13.4 % have been demonstrated with CdTe films of only 0.9~1.5 µm

7.2 Low-resistance electrical contact based on Te/Cu bi-layer.
Te/Cu bi-layer was developed to replace NP treatment as a more reliable and effective back contact for CdTe solar cells. Similar to the Te-rich layer generated by NP treatment on CdTe surface, evaporated Te plays the same role to change the effective electron affinity of CdTe. Cu is deliberately introduced into the back contact because appropriate Cu diffusion can enhance the $p$-type doping in the CdTe layer. Different from NP treatment, Te/Cu bi-layer avoids damages on CdTe films caused by acid etching, which is of particular importance to ultra-thin CdTe solar cells.

It has been found that thermal activation is necessary to promote ohmic contact formation. Thermal activation on Te/Cu below the threshold temperature of 180 °C cannot form an ohmic contact and only produces insignificant improvement in device performance. The optimum thermal activation duration decreases from 20 min to 10 s as the activation temperature is increased from 200 °C to 270 °C. As a result of the ohmic contact formation, the device performance especially $V_{oc}$ and $FF$ is greatly enhanced.

SEM images show that the crystallinity of Te layer is improved with thermal activation. XPS analyses reveal that Cu diffuses into the Te layer with thermal activation above the threshold temperature. No reaction occurs until the activation duration is extended to one hour. PL spectra clearly show that Cu diffusion can reach vicinity of CdS/CdTe junction under certain activation condition.

Apart from thermal activation, the concentration of Cu in Te/Cu bi-layer and Te thickness also play an important role. The amount of Cu in Te/Cu does not affect the initial device performance but has a profound impact on device stability. Neither low Cu
concentration (<0.1 nm Cu per 100 nm Te) or high Cu concentration (>9.0 nm Cu per 100 nm Te) produces good device stability. Based on the thermal stress test and light soaking test, the optimum Cu concentration is (0.2~2.2 nm Cu per 100 nm Te). The thickness of the Te layer is also a critical factor. Good device stability can be only achieved with Te thickness greater than 50 nm. The overall device stability increases as the Te thickness is increased. It is concluded that the primary degradation mechanism associated with Te/Cu contact is the Cu diffusion. The Cu diffusion can be alleviated by reducing Cu concentration to certain level, increasing Te thickness or reducing stress temperature.

In general, Te/Cu has been proved to be an excellent back contact buffer for CdTe solar cells. CdTe solar cells with efficiencies up to 14.8% and low efficiency degradation rate (<0.4% /h at 200°C) have been demonstrated.

However, the understanding of the formation of Te/Cu back contact is still lacking. More characterizations will be needed to quantitatively determine the Cu diffusion profile in bulk CdTe and to understand how Te retards Cu diffusion.

7.3 A novel vaporous zinc chloride treatment for making Cd$_{1-x}$Zn$_x$S films.

As an effective window layer, Cd$_{1-x}$Zn$_x$S has been used in thin film CIGS and CdTe solar cells. However, the conventional methods to fabricate this ternary semiconductor including co-sputtering, co-evaporation, and MOCVD require complicated apparatus and costly maintenance. A novel method named vaporous zinc chloride treatment was
developed to fabricate $\text{Cd}_{1-x}\text{Zn}_x\text{S}$. The VZC method features simple setup and easy operation.

$\text{Cd}_{1-x}\text{Zn}_x\text{S}$ film with a homogeneous structure has been proved by a series of characterization techniques including XRD, absorption spectroscopy and EDX. The Zn to Cd doping ratio can be controlled by adjusting VZC treatment temperature, duration, nitrogen flow rate or the combination of these process parameters.

Although pinholes were founded in the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ film made by VZC, their negative effects on the CdTe solar cells can be largely eliminated by several approaches as follows:

1) Inserting an intrinsic SnO$_2$ layer between FTO and $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ to reduce localized contact between CdTe and front electrode.

2) Reducing the amount of hydration or moisture in ZnCl$_2$ source by replacing hydrated ZnCl$_2$ with ultra-dry ZnCl$_2$.

3) Applying a high temperature annealing process on the as-made $\text{Cd}_{1-x}\text{Zn}_x\text{S}$/CdTe stack layers before VCC treatment.

With $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ substituting CdS as the window layer, CdTe solar cells with a 12-14% higher $J_{sc}$ and without compromising in $V_{oc}$ and $FF$ have been demonstrated.

More characterizations including SEM, EDX and XRD will need to be carried out to further reveal the effects of moisture on VZC treatment and the impacts of HTA on $\text{Cd}_{1-x}\text{Zn}_x\text{S}$/CdTe solar cells. In addition, high quality $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films with appropriate
Zn doping ratio will be applied to ultra-thin CdTe solar cells to further improve the cell efficiency.
References


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Appendices

A.1 Fabrication of ultra-thin CdTe solar cells

A.1.1 Deposition of CdS films

CdS films were deposited on fluorine-doped tin oxide (FTO) glass substrate (Pilkington, TEC-15) using a chemical bath deposition method described by Chu et al.\textsuperscript{18} The procedure for our batch-wise preparation was as follows: the concentration of ammonium hydroxide, ammonium acetate, cadmium acetate, thiourea were typically 0.4 M, 20 mM, 1 mM and 5 mM, respectively. NH\textsubscript{4}Ac (405 mg), CdAc\textsubscript{2} (200 mg) and NH\textsubscript{4}H\textsubscript{2}O (40.5 ml, 28.0–30.0% as NH\textsubscript{3}) were firstly added to de-ionized water (DIW, 684 ml), stirred in a beaker (1000 ml) and heated to 92 °C on a hotplate. The FTO glass substrates with a dimension of 1.5” × 1.5” mounted on strips of stain steel plates were immersed in the solution. The preheated thiourea solution (286 mg in 25 ml DIW, 90°C) was then added into the solution. The solution was left stirring for 40 min before the substrates with the CdS deposits were removed from the bath. The substrates were cleaned ultrasonically in DIW for 5 min to remove loose CdS particulates on the substrates. They were then further rinsed with DIW and dried with nitrogen. The typical thickness of CdS deposited under the above conditions was 150 nm.

A.1.2 Deposition of ultra-thin CdTe films

Polycrystalline CdTe films were deposited on the CdS coated substrates by the close spaced sublimation \textsuperscript{39}. The CdTe source was CdTe granules (Alfa Aesar, 99.99%). The heating sources were halogen lamps (ELH, 300 W) mounted on the graphite plates,
which also serve as the source and substrate holders. A temperature-time profile for a typical deposition run is shown in Fig. 2-1b. The substrate and source temperatures were controlled independently by temperature controllers (Omega, CN 7800). The substrate temperature was maintained at 525°C. The source temperature was varied from 550°C to 625°C. The deposition duration is 2 min. The deposition chamber ambient was typically 1.5 Torr oxygen. Under these conditions, the deposition rate of the CdTe films was approximately 0.5 μm/min.

A.1.3 Post deposition treatments on CdS and CdTe films

Vapor CdCl$_2$ (VCC) treatments were conducted on CdS and CdTe films in a CSS system (Fig. 3-1a) similar to that used for the deposition of CdTe films. The CdCl$_2$ source was ultra-dry CdCl$_2$ granules (Alfa Aesar, 99.998% metals basis). The heating sources were halogen lamps (ELH, 300 W) mounted on the graphite plates, which also serve as the source and substrate holders. A temperature-time profile for a typical deposition run is shown in Fig. 3-1b. Both the source and substrate temperatures were maintained at 400 °C. The ambient during VCC treatments was an O$_2$:N$_2$ (1:4) ambient of 10 Torr. The typical treatment durations for CdS and CdTe films were 6 min and 4.5 min respectively.

Prior to the VCC treatment, a high-temperature annealing (HTA) treatment was conducted on CdTe films in a tube furnace under nitrogen at a temperature of 550°C for 40 min. Nitrogen flow (flow rate: 100 cm$^3$/min) under atmospheric pressure was maintained during the entire process. The ramping rate of the tube furnace was 80°C/min.
After the annealing process, the furnace was cooled down to room temperature with an average cooling rate of 17 °C/min.

A.1.4 Back contact formation

For NP treatment: after a VCC treatment, the CdTe films were etched in a solution (NP solution) of nitric and phosphoric acids with a volumetric ratio of 2.2 (HNO$_3$): 175 (H$_3$PO$_4$): 70 (H$_2$O) for 25 s, following by rinsing in DIW and drying with nitrogen.

For MoO$_x$ back contact buffer: the CdTe films were rinsed in DIW and dried with nitrogen. The back contact layer was formed by depositing a 40 nm-MoO$_x$ film on CdTe films by thermal evaporation of MoO$_x$ powder (Alfa Aesar, 99.95%) with a deposition rate of 5~7 Å/s in a vacuum level of 10$^{-5}$ Torr.

For Te/Cu back contact buffer, a layer of Te (100 nm) and a layer of Cu (1.1 nm) were deposited on CdTe films in sequence by DC sputtering using a Te target (0.125” x 2”, 99.9%) and a Cu target (0.063” x 2”, 99.9%) respectively. The vacuum level before the sputtering deposition was 10$^{-5}$ Torr. The deposition rates for Te and Cu were 7Å/s and 1 Å/s respectively.

For electrode deposition: after the formation of the back contact buffer, a layer of 200 nm Ni was deposited onto the buffer layer by DC sputtering with a deposition rate of 8 Å/s to form the back contact electrode.

For thermal activation on the Te/Cu back contact buffer: the cell completed with Ni electrode deposition was subjected to an annealing process. The typical annealing
temperature and duration are 225 °C and 4 min respectively. The average ramping rate and cooling rate were 45 °C/min and 10 °C/min, respectively. The annealing durations mentioned in the thesis were the durations for which the annealing temperature was stabilized at the temperature set-point.

A.1.5 Fabrication of Cd$_{1-x}$Zn$_x$S films

Cd$_{1-x}$Zn$_x$S films were fabricated by a vaporous zinc chloride (VZC) treatment in a two-zone tube furnace. A glass tube (1” diameter and 24” long) containing both the ZnCl$_2$ source (Alfa Aesar, ultra-dry: 99.999%, or hydrate: 99.99%) (50-500 mg) and the FTO/CdS substrates in separate zones was first purged with nitrogen to get rid of oxygen in the system. The VZC treatment was carried out at atmosphere pressure under a continuous nitrogen flow of about 100 cm$^3$/min. A temperature-time profile for a typical treatment run is shown in Fig. 6-1b.

A.2 Details about the characterizations and stability tests

The SEM images in Fig.1-4, 2-3, 3-2, 3-16, 4-2, and 6-3 were obtained using a scanning electron microscope (Zeiss, Supra 40 VP, operating voltage: 20 kV). The SEM images in Fig.2-8, 2-9, and 5-12 were obtained using a scanning electron microscope (Hitachi, TM 3000, operating voltage: 15 kV).

AFM images (Fig. 2-5) were obtained using an atomic force microscope (NT-MDT, Solver Next).
XRD spectra (Fig.2-4, 3-3, 6-2) were obtained using X-ray diffraction (XRD Philip, X’Pert MRD).

EDX spectra (Fig. 6-5) were obtained using EDX spectroscopy (Zeiss, Supra 40 VP)

XPS spectra (Fig. 5-13) were obtained using a Surface Science Laboratories’ SSX-100, equipped with a monochromatic Al anode X-ray gun (Kα 1486.6 eV). The base pressure of the system was $9 \times 10^{-11}$ Torr.

Transmission and absorption curves (Fig.6-4, 6-6, 6-8) were obtained using a spectrometer (Perkin-Elmer, Lambda 900)

Photoluminescence spectra (Fig.3-6, 3-8, 3-10, 3-17, 3-18, 3-19, 5-14, 5-15) were obtained using a He-Ne laser (Research Electro-Optical, 30992, 12 mW, 633 nm) as the excitation source and fiber optics spectrometer (Ocean Optics, USB 4000) as the detector. The samples were cooled down to 40 K during PL measurement using a cryostat.

The J-V data were obtained using a sourcemeter (Keithley, Model: 2400) and a tungsten-lamp-based solar simulator (Solux 3SS4736 50 W solar simulator). The solar simulator was calibrated with a silicon photodiode (Hamamatsu S1787-12). The spectrum of the solar simulator and AM1.5 solar spectrum are shown in Fig.A-1. The active area of the cell, typically about 0.1 cm$^2$, was isolated by scribing the CdS/CdTe/back contact buffer/Ni layer stack with a razor blade. The minimum absolute values of dark J-V curves are not at zero bias in some cells (Fig. 2-10, 3-4, 3-5, 3-7, 3-9, 3-12, 3-13, 3-15, 4-5, 4-6, 4-8, 4-9, 4-10, 4-11, 4-12, 5-6, 6-11, 6-13 and 6-15).
voltage offsets were probably due to measurement errors related to hysteresis of the J-V traces which is due to charge trapping in some of the cells. Another possible cause for the voltage offsets is light leakage (from room light) during the dark J-V measurement.

![Graph of normalized response vs. wavelength]

**Figure A-1 Spectrum of Solux solar simulator and AM 1.5 solar spectrum.**

Spectral response measurements (Fig. 3-21 and 6-10) were obtained using a calibrated ¼ m monochromator (ARC SpectroPro 275).

In thermal stress tests, CdTe solar cells were annealed at 200 °C in atmospheric nitrogen ambient for up to 9 h. In light soaking tests, CdTe solar cells were stressed under the illumination of about 100 mW/cm² provided by compact fluorescent lamps. The light soaking test temperature was maintained at ~45 °C due to illumination.

**A.3 Lists of symbols and abbreviations**

A: didoe factor
AFM: atomic force microscopy

BE: binding energy

BM: bromine-methanol

CBD: chemical bath deposition

CIGS: Cu(In, Ga)Se2

CSS: close spaced sublimation

\( d \): distance between source and substrate in a CSS deposition

EDX: energy dispersive X-ray spectroscopy

EQE: external quantum efficiency

FF: fill factor

FTO: flurine doped tin oxide

HTA: high-temperature annealing

ITO: indium tin oxide

\( J_{sc} \): short-circuit current

\( J-V \): current-voltage curve

MOCVD: metal organic chemical vapor deposition
NBE: near band edge

NP: nitric-phosphoric acid

PL: photoluminescence

$P_{O_2}$: oxygen pressure in a CSS deposition

$R_s$: dynamic series resistance

$R_{sh}$: dynamic shunting resistance

PVD: physical vapor deposition

SD: solution deposition

SDB: surface defect band

SEM: scanning electron microscopy

TCO: transparent conducting oxide

$T_{src}$: source temperature in a CSS deposition

$T_{sub}$: substrate temperature in a CSS deposition

VCC: vaporous cadmium chloride treatment

$V_{oc}$: open-circuit voltage

VZC: vaporous zinc chloride treatment
XPS: X-ray photoelectron spectroscopy

XRD: X-ray diffraction

η: energy conversion efficiency