# *Review Article* **Achievements and Challenges of CdS/CdTe Solar Cells**

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Thin film CdS/CdTe has long been regarded as one promising choice for the development of cost-effective and reliable solar cells. Efficiency as high as 16.5% has been achieved in CdS/CdTe heterojunction structure in laboratory in 2001, and current techniques for CdS/CdTe solar cells gradually step toward commercialization. This paper reviews some novel techniques mainly within two years to solve this problem from aspects of promotion of fabrication technology, structural modification, and choice of back contact materials.

## 1. Introduction

As the world is suffering from impending death of fossil fuels and serious pollution resulted from the fuels, solar energy is now regarded as one promising solution to the global energy crisis. Among various means for generating energy from the sun, solar cells are an effective approach to convert solar energy into practical electrical energy. In 2009, the global production of photovoltaic cells and modules in 2009 was 12.3 GW [1], and it increased to over 20 GW one year later [2]. Many kinds of solar cells based on Si [3], thin film [4, 5], or even organic materials [6, 7] are gradually developed these years. According to the US Department of Energy, solar energy should only be economically viable for large-scale production if the cost can be reduced to \$0.33/Wp (Wp = wart peak) [8].

Thin-film cadmium telluride (CdTe) is now regarded as one leading material for the development of cost-effective photovoltaics (PV), and it is also the first PV technology with the price for Wp below \$1 (\$0.85) [9]. CdTe has a band gap of ~1.5 eV, which is close to the ideal value for photovoltaic conversion efficiency. Meanwhile, high optical absorption coefficient and high chemical stability also appear in CdTe. All of them make CdTe a very attractive material for thinfilm solar cells. The theoretical efficiency of CdTe thin-film solar cells is expected to be 28%–30% [10, 11]. Currently, First Solar has announced a new world record this year for CdTe PV solar cell efficiency of 17.3% with a test cell constructed using commercial-scale manufacturing equipment and materials, and its average efficiency of modules produced in the first quarter of 2011 was 11.7% [12].

One of best choices for CdTe cells are heterojunction structures with n-type cadmium sulfide (CdS) as a transparent window layer, and they are generally fabricated in a superstrate configuration (Figure 1). Despite the lattice mismatch of 10% between CdTe and CdS, the formed heterojunction has an excellent electrical behavior, leading to a high fill factor of 0.77 in produced solar cells [13]. Therefore, this structure is favored by a variety of worldleading corporates. For example, First Solar has launched one project to double its manufacturing capacity of CdS/CdTe solar cells from 1.5 GW at the beginning of 2011 to nearly 3 GW by the end of 2012 [14]. Calyxo also expended their capacity up to 25 MWp in 2008 and expects to finish their second production line with capacity of 110 MWp in 2011 [15]. In CdS/CdTe heterojunction structure, efficiency up to 16.5% has been achieved in lab as early as 2001 [16], while the best commercial modules are approximately 10%-11% [17]. However, these are still much lower than the theoretical value. There are currently several challenges for further making CdS/CdTe thin-film solar cells more competitive: (1) short minority carrier lifetime due to the recombination of electron-hole pairs at the defect centers in CdTe layers and at the interface between CdS and CdTe, (2) insufficient transparency of transparent conductive oxide (TCO) and CdS window layers, (3) lack of good ohmic contact between CdTe layers and back contacts, and (4) possibility in doping p-type CdTe films in a stable way. Techniques coming up



FIGURE 1: An example of the structure of standard CdS/CdTe thinfilm solar cells.

in recent years are mainly concentrated on the first three challenges above.

Instead of summarizing the history, this paper aims to review the progress of CdS/CdTe photovoltaics by evaluating some current techniques to deal with first three challenges above from three aspects: fabrication technology, structural design, and choice of back contact, respectively.

## 2. Promotion in Fabrication Techniques

Fabrication methods for CdS/CdTe layers could have a significant effect on cell efficiency and cost. Samples have been obtained successfully by several common techniques: radio frequency sputtering (R. F. Sputtering) [18], close-spaced sublimation (CSS) [19], and chemical bath deposition (CBD) [20] for CdS preparation, while electrodeposition (ED) [21], screen printing (SP) [22], and CSS [23-25] for CdTe thin-film formation. However, these methods are still not sufficient good due to their inherent drawbacks. For example, R. F. Sputtering for preparing CdS window layer can be rather fast but with poor quality that reduces the cell efficiency, while CBD could provide a dense and smooth CdS layer but the solution waste recycling and management cause extra cost. Therefore, the techniques should be carefully chosen with the consideration of high quality thin-film structure (high efficiency), proper pollution control, and commercial production prospect. Currently, the emerging problems related to fabrication mainly focus on (1) the short circuit of TCO and the CdTe layer caused by the partial grain covering and pinholes in CdS with extremely small thickness and (2) short minority carrier life time due to the defects inside the CdTe layer. Fortunately, several modifications to conventional methods and new techniques have been explored to improve the problems above these years [26-36].

2.1. Sputtering in  $Ar + CHF_3$  Atmosphere. One excellent improvement to the fabrication of CdS layers is employing R. F. sputtering in the atmosphere of argon (Ar) containing ~3% of CHF<sub>3</sub> [11, 26–29]. This gas is decomposed and ionized during the sputtering discharge, delivering electronegative fluorine (F) to the substrate. Although it has been proved that F does not reduce the resistance of CdS layers [11, 27, 29], compared with undoped CdS, F-doped CdS still exhibits a larger forbidden gap [26], a stronger photoconductivity, and, most importantly, gives higher-efficiency solar cells [27]. This phenomenon probably results from the presence of F.



FIGURE 2: The structure of CdS/CdTe thin-film solar cell with bilayer CdS.

On one hand, it strongly reduces the growth rate of CdS and bombards the CdS films during the growth, which can eliminate the excess of Cd and S, hence producing a dense film with excellent thickness and quality control [28, 29]. On the other hand, it also promotes the formation of CdF<sub>2</sub>, which could passivate the grain boundaries and forming good CdS/CdTe junctions [11, 28, 29]. Efficiency as high as 15%–15.8% has been obtained by Bosio et al. [11] in this approach. Therefore, this technique can be treated as a good choice for the fabrication of CdS layers in industrial production of photovoltaic modules.

2.2. Bilayer CdS Thin-Film Preparation. The structure of the bilayer CdS thin-film solar cell is shown in Figure 2. In this technology, the first CdS layer is made by standard CBD process with reduced time (compared with standard structure shown in Figure 1), and then the second CdS layer is deposited by CBD at lower temperature (55°C). Approximately 14.6 nm's roughness was observed in atomic force microscopy (AFM) for standard CBD of CdS thin film, while it could be reduced to 7.2 nm in bilayer case (see in Figures 3(a) and 3(b), resp.). Then smaller grain size would be obtained since the bilayer structure could provide the compact and uniform CdS layers without pinholes and cracks among grain boundaries. The dense and smooth CdS thin films could generate isolation between TCO and CdTe layers, which could solve the shunt problem between these two layers. Moreover, thinner CdS film results in higher short-circuit current (Figure 4) and improved the efficiency by around 6.1% with less demand of material (only 80 nm thickness of CdS layer shown in Figure 2) compared with standard CBD process [30, 31].

2.3. Low-Temperature Deposition Method. An innovative low-cost trial through vacuum deposition (VD) is investigated to fabricate both CdS and CdTe on low-temperature  $(-55^{\circ}C)$  substrate [32]. The substrate holder was cooled by liquid nitrogen, while a secondary heater can adjust the temperature in a desired range. This process could provide higher optical transparency of CdS thin film and similar grain size (average 300 nm) for both layers (see in Figures 5(a) and 5(b)) compared with conventional techniques. As the performance of the solar cell is closely related to the quality of the interface between CdS and CdTe, the similar grain size does favor to good intermixture of these



FIGURE 3: AFM of (a) standard CBD CdS with roughness of 12.2 nm, (b) CBD CdS with CdCl<sub>2</sub> annealing treatment at  $300^{\circ}$ C with roughness of 14.6 nm, (c) bilayer CdS with total 80 nm thickness with roughness of 7.2 nm. Figures are taken from [30].



FIGURE 4: J-V characteristics of CdS/CdTe solar cells with different CdS films: Sample A: standard CBD CdS; Sample B: CBD CdS with CdCl<sub>2</sub> annealing treatment at 300°C; Sample C: bilayer CdS with total 80 nm thickness. Figures are taken from [30].

two materials and could dramatically decrease the defects inside interface. The resulted conversion efficiency >14% is rather high since it is the first successful operation of CdS/ CdTe-based solar cell prepared by low-temperature deposition, and more work should be done to optimize the process before actually applying for commercial purpose [33].

2.4. All-Electrodeposited Method. In the all-electrical-deposition (AE) processing for CdS thin film, a graphite anode and a glass/fluorine-doped tin oxide (FTO) cathode are applied to pass an electric current through the electrolyte with CdCl<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> dissolved in (pH = 1.40) as shown in Figure 6. Both Cd- and S-containing cations are deposited on the cathode surface with electrically discharging and chemically

reaction. The formation of CdS on the cathode can be represented by following mechanisms:

$$Cd^{2+} + 2e^- \longrightarrow Cd$$
 (1a)

$$Na_2S_2O_3 + H_2O + 2H^+ \longrightarrow 2Na^+ + H_2S_2O_3 + H_2O$$
 (1b)

$$H_2S_2O_3 \longrightarrow H_2SO_3 + S$$
 (1c)

$$Cd + S \longrightarrow CdS$$
 (1d)

Daily waste of toxic Cd-contained solution during the production could be avoided since the bath for ED-CdS can be used for at least 18 months without discarding the electrolyte compared with CBD process. Furthermore, the CdS/CdTe thin-film solar cells achieve a similar or superior performance by applying ED-CdS instead of CBD-CdS, because the crystal structure is hexagonal for former and cubic for latter. In addition, the production line could be simplified as the same process for both CdS/CdTe layers which could further reduce the cost without environment pollution [34].

2.5. Dry CdCl<sub>2</sub> Treatment for CdTe Recrystallization. Conventionally, CdS/CdTe samples are immersed into the solution containing CdCl<sub>2</sub> and heated at 400-500°C in order to enlarge the grains inside the CdTe layers and eliminate defects to increase the minority carrier lifetime. However, it seems to be unsuitable for large area manufacture considering industrial production and the residue of the solute may not be thoroughly cleared up. To solve this problem, Lee's work [35] shows that the dry CdCl<sub>2</sub> treatment by physical vapor deposition (PVD) on the sputtered CdTe layer. This method reveals effective process since no vacuum breaks are involved in production line, which agrees with commercial prospects. Furthermore, the average lower transmittance than wet treatment reflects its better light absorption property (Figure 7, the curve for dry CdCl<sub>2</sub> treatment is obviously below the wet one) [35].



FIGURE 5: SEM photomicrographs of (a) CdS thin films prepared at 218 K substrate temperature, (b) CdTe thin films prepared at 218 K substrate temperature. Figures are taken from [33].



FIGURE 6: Electrodeposition process of CdS with graphite anode and glass/FTO cathode.

2.6. Nontoxic Chlorine Ambient Treatment. As the heat treatment with  $CdCl_2$  would bring both pollutions to environment and toxic threats to operators, nontoxic process is expected to be explored while retaining the efficiency of solar cells. Romeo et al. [29] provide a solution: to anneal the CdS/CdTe structure in mixture of 100–500 mbar of Ar and 20–50 mbar of nontoxic gas containing  $Cl_2$  such as difluorochloromethane (HCF<sub>2</sub>Cl) for 5–10 minutes at 400°C. HCF<sub>2</sub>Cl is stable, inert, and nontoxic at room temperature, and it would be decomposed as  $Cl_2$  and other products during annealing. Hence, the reactions below are supposed to happen:

$$CdTe(s) + 2Cl_2(g) \longrightarrow CdCl_2(g) + TeCl_2(g)$$
 (2a)

$$CdCl_2(g) + TeCl_2(g) \rightarrow 2Cl_2(g) + CdTe(s)$$
 (2b)

The resultant CdTe solid in second chemical reaction (2b) would have larger grain size than the one in first reaction (2a) since annealing process in chlorine ambient assists the recrystallization of CdTe grains. The merits of this method are



FIGURE 7: Average transmittance in the range of 800-100 nm for CdTe films annealed at different temperatures with dry and wet CdCl<sub>2</sub> treatment. The films were deposited on ITO-coated glass substrate instead of CdS/ITO/glass substrate. Figure is taken from [35].

that it provides an effective way of producing high-quality CdTe layers with large grains and few defects (Figures 8(a) and 8(b)) to obtain less possibility of electron-hole recombination. The highest cell efficiency has reached 15.8%. In addition, any gas of Freon family can be applied for carrying Cl<sub>2</sub>. Although the Freon gas with Cl is harmful to the ozone belt, the recovering machines are already commercially available. This process has been patented by Romeo et al. [36].



FIGURE 8: SEM photomicrographs of the surface of CdTe films: morphology of an untreated CdTe film deposited by the CSS method (a) before and (b) after thermal treatment in  $Ar + HCF_2Cl$  atmosphere at a temperature of 400°C for 5 min. Figure is taken from [29].

# **3. Structural Modification**

The second approach to improve efficiency is to modify the configuration of CdS/CdTe solar cells. The favorable formation enthalpy and good chemical stability of CdS/CdTe heterojunction have allowed many routes to be explored in novel device architectures. In this part, two of them, namely nanostructure and tandem cells, are discussed.

3.1. Nanostructured Geometries. Nanostructured geometries are believed to be the most promising method to achieve high efficiency and low cost from structural aspect [37, 38]. By employing nanopillar instead of planar CdS layer, on one hand, this provide excellent transparency of CdS layer, since the size of nanopillars is much smaller than the wavelength of visible light. On the other hand, light absorption is enhanced simultaneously due to quantum confinement effect. In addition, this approach also offers more flexibility, since the optical gap can be tuned by size variation of nanopillars. Currently, power conversion efficiency of 6.5% has been achieved by Liu et al. in this kind of structure [37], and it is expected to reach >20% after further optimization [38].

The nanopillars can be directly built on or even embedded into CdTe with several methods (details in reference [39]), and one popular way is to employ anodized aluminum membrane (AAM) as the molds [37-39]. An excellent work of one three-dimensional (3D) nanopillar-array CdS/CdTe solar cell done by Fan et al. [40] is shown in Figure 9(a). A  $\sim 2 \mu m$  AAM with near-perfect ordering after anodization is built on Al substrate (Figure 9(b)), followed by a barrier thinning process to branch out the pore channels and reduce the AAM film to a few nanometers. After electrodepositing a thin layer of Au at the bottom of the channel, the nanopillar structure of CdS is then carried out in a quartz tube furnace with two resistive heating. In the third step, the AAM layer is partially etched by NaOH (Figure 9(c)) and a p-type CdTe film with  $\sim 1 \,\mu m$  is deposited by chemical vapor deposition (CVD). Finally, Cu/Au bilayer is grown on CdTe film

by thermal evaporation to achieve low-barrier contact. This fabrication method can achieve high-density, single-crystal nanopillar array with good geometric control. This is an excellent breakthrough since it is difficult to keep highquality single-crystal structure when moving into nanometer level, and single crystal is usually required for high-efficiency solar cells to maintain high density of e-h pairs. Furthermore, it is also suggested that 3D nanopillar array can also improve the light absorption while enhancing the carrier collection efficiency [40]. The main limitation on its performance is the poor transparency of Cu/Au layer (currently 50% only). Conversion efficiency of ~6% has been reported in the initial design. To improve the efficiency, future research should focus on both the creation of high-quality singlecrystal nanopillar and understanding on pillar distribution and recombination rate of carriers in this structure.

3.2. Bifacial and Tandem Structure. Another popular structural solution of increasing efficiency is to build tandem cells. Bifacial configuration, the base of tandem connection, was developed in 1980s and then obtained renewed interests with intensive research after 2004 [41-44]. The basic idea is to replace conventional Cu/Au with transparent indium tin oxide (ITO) as back contact layers. In this way, the solar cells can be illuminated from both sides, and, more importantly, the long-term stability can be improved due to the absence of bulk Cu layer [20]. The equivalent circuit of bifacial cells is now modeled as two opposite illuminated diodes representing main separating barrier and the barrier near the back contact, respectively [45]. Current efficiency achieved in CdS/CdTe bifacial structure has exceeded 10% and 3% on the front side and back side illumination, respectively [43]. It has also been shown that a very thin Cu layer can be added between CdTe and ITO to decrease the series resistance but still keeping the transparency [43, 45]. If further reducing the thickness of CdTe layers in bifacial configuration, tandem cells can be built to increase the efficiency by absorbing a broader part of solar spectrum, though intensive researches are still required to make it into practice [45, 46].



FIGURE 9: (a) Cross-sectional schematic diagram of the solar nanopillar cell. (b) SEM images of an as-made AAM with perfectly ordered pores and (c) a CdS nanopillar array after partial etching of the AAM. Figures (b) and (c) are taken from [40].

#### 4. Choice of Back Contact

Due to the high electron affinity of p-type CdTe, the Fermi level pinning would be formed between the absorption layer and the metal layer. A reverse-biased potential would be formed at the CdTe-metal interface to limit the holes' transport and would seriously reduce the cells' efficiency. Hence, an ohmic contact or tunneling contact is seriously required. Conventionally, an etching with nitric-phosphoric (NP) acid is applied to obtain Te-rich layers on the top of CdTe before copper deposition [11], so that a diffusion layer of Cu<sub>x</sub>Te alloy can be formed during the annealing after Cu deposition. Since  $Cu_x$  Te exhibits p-type characteristics, a large amount of holes appear in Cu<sub>x</sub>Te, and this offers a good ohmic contact with CdTe layers. Although it does help to provide tunneling contact and improve the cell performance, the roll over phenomenon can still not be avoided. Instead, a new etching technique employing nitric-acetic (NA) acid can be applied to avoid roll over phenomenon in J-V curve (Figure 10) and generate better ohmic contact with lower series resistance  $(4.3 \,\Omega \text{cm}^2)$  than that of NP acid etching method ( $6.5 \Omega \text{cm}^2$ ) as well as higher fill factor [47].

Several novel techniques have been explored to suppress the large Schottky barrier and reduce the contact resistance at the CdTe-metal interface. One popular solution is to use ZnTe as a buffer layer between the CdTe layer and the Cu back contact. ZnTe has a similar lattice parameter with CdTe, and the insertion of ZnTe layer produces an electrical field to reduce recombination loss of minority carriers at back contact surface [48, 49]. Kim et al. [50] also shows that



FIGURE 10: J-V characteristics of CdTe solar cells with different etching solutions applied. Figure is taken from [47].

double-layer structure with Cu doped ZnTe (ZnTe:Cu) buffer and  $Cu_x$ Te back contact can be very attractive for back contact fabrication, since ZnTe:Cu offers a good alignment of the valence band with CdTe, while  $Cu_x$ Te, produced by bilayer deposition method, has an excellent crystallinity and contact with CdTe:Cu. Park et al. [51] have also reported that doping ZnTe:Cu with Na<sub>2</sub>Te can further improve the performance by decreasing the film resistance of ZnTe layer to  $<1 \Omega$ cm. In addition, the stability can also be improved to a large extent if replacing the back contact metal of Cu into Al [52].

The use of Cu may reduce the long-term stability of solar cells, since Cu would gradually diffuse through grain boundaries reaching the interface of the junction and cause the shunt problem. Alternatively, some metals, such as Ni, Al, Mo, and W, can be employed to extend cell lifetime. Similarly, ohmic contact and metal diffusion barrier can be realized by a buffer layer inserted between CdTe and metal. Sb<sub>2</sub>Te<sub>3</sub> is considered as a low-resistivity p-type material  $(10^{-4}\Omega \text{ cm})$ [29] that suitable for buffer layer with Mo or W metal contact to provide stable high-efficiency solar cell [11]. However, the performance highly depends on process condition and material purity, and the doping effect of Te into Sb<sub>2</sub>Te<sub>3</sub> can be complicated [11].  $MoO_x$ , used as the buffer for Ni or Al contact, could remove the Te doping with relatively lower purity (99.95%) and ultrathin CdTe cells, and efficiency of >10% has been obtained [53]. An innovative way of As<sub>2</sub>Te<sub>3</sub>/Cu/Mo bilayer buffer structure provides efficiency as high as 16%, since the Cu<sub>x</sub>Te compound raises the conductivity in p-type material. As As<sub>2</sub>Te<sub>3</sub> is directly deposited onto CdTe layer, no etching process is required. Moreover, an extremely thin Cu layer (2–20 nm) is inserted to get a low contact resistance without varying the stability. The controlled affinity of  $x \leq x$ 1.4 ensures cell stability without rectification [29].

## **5.** Conclusion

This paper has summarized the latest research and techniques to solve the efficiency problem in CdS/CdTe solar cells from aspects of fabrication, structure, and back contact materials. Although there is no impressive progress for efficiency improvement these years, those techniques above offer some novel ideas for further development. Based on the previous analysis, we still believe that CdS/CdTe solar cell will be a crucial candidate for global low-cost solar cells market in future.

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