Application of ALD-Al₂O₃ in CdS/CdTe Thin-Film Solar Cells

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Abstract: The application of thinner cadmium sulfide (CdS) window layer is a feasible approach to improve the performance of cadmium telluride (CdTe) thin film solar cells. However, the reduction of compactness and continuity of thinner CdS always deteriorates the device performance. In this work, transparent Al₂O₃ films with different thicknesses, deposited by using atomic layer deposition (ALD), were utilized as buffer layers between the front electrode transparent conductive oxide (TCO) and CdS layers to solve this problem, and then, thin-film solar cells with a structure of TCO/Al₂O₃/CdS/CdTe/BC/Ni were fabricated. The characteristics of the ALD-Al₂O₃ films were studied by UV–visible transmittance spectrum, Raman spectroscopy, and atomic force microscopy (AFM). The light and dark J–V performances of solar cells were also measured by specific instrumentations. The transmittance measurement conducted on the TCO/Al₂O₃ films verified that the transmittance of TCO/Al₂O₃ were comparable to that of single TCO layer, meaning that no extra absorption loss occurred when Al₂O₃ buffer layers were introduced into cells. Furthermore, due to the advantages of the ALD method, the ALD-Al₂O₃ buffer layers formed an extremely continuous and uniform coverage on the substrates to effectively fill and block the tiny leakage channels in CdS/CdTe polycrystalline films and improve the characteristics of the interface between TCO and CdS. However, as the thickness of alumina increased, the negative effects of cells were gradually exposed, especially the increase of the series resistance (Rₛ) and the more serious “roll-over” phenomenon. Finally, the cell conversion efficiency (η) of more than 13.0% accompanied by optimized uniformity performances was successfully achieved corresponding to the 10 nm thick ALD-Al₂O₃ thin film.

Keywords: atomic layer deposition; Al₂O₃; CdS/CdTe thin-film solar cells

1. Introduction

In order to improve the short-wave response and increase the short circuit current density (J_sc) of the cadmium sulfide (CdS)/cadmium telluride (CdTe) cell, it is necessary to reduce the photon absorption of the CdS window layer. One useful method is to reduce the thickness of the CdS film [1]. When the thickness of CdS exceeds 100 nm, there is a strong absorption of photons with energy measuring greater than 2.4 eV, meaning that the number of photons reaching the junction region is substantially reduced, which leads to a reduction in photocurrent [2]. However, when the thickness of CdS is reduced to below 50 nm, some fine pinholes begin to emerge because of the reduction of compactness and continuity of the CdS film, resulting in the destruction of the CdS/CdTe heterojunction. In extreme cases, some local short circuit channels are formed by the direct contact of...
the absorption layer of CdTe with the front electrode transparent conductive oxides (TCO) through larger pinholes. Therefore, in the case of the thinner window layer, a buffer layer having a relatively high resistance between TCO and CdS is necessary to block the direct contact between the CdTe and the front electrode [3,4]. Furthermore, this buffer layer must also have a high transmittance in the full spectrum to avoid the loss of absorbed light. As one of the candidate materials for the buffer layer, alumina has the advantages of abundant resources, low cost, and good thermal and chemical stability. Furthermore, Al2O3 has been currently employed as passivation and anti-diffusion layers in solar cells [5–7], especially in the passivated emitter and rear cell, which is attributed to alumina that has a band gap of 8.8 eV greater than that of the TCO substrate but has a stable interface with a low density of states at Al2O3 and TCO and also has a high density of fixed negative charges (~10^{13} \text{cm}^{-2}). As a passivation layer, Al2O3 has been mainly used in p-type materials, because it can significantly reduce the surface electron concentration [8]. It is well known that the resistance of the aluminum oxide film is very large. So, it is especially important to precisely control the thickness of alumina to avoid the effect of the extra series resistance in cells brought by the Al2O3 buffer layer, as well as to ensure the formation of a dense continuous Al2O3 thin film to avoid extra leakage channels in the case of relatively small thickness (<20 nm) of the Al2O3 thin film. Thus, choosing an appropriate fabrication technology is critical for achieving the corresponding blocking function of the Al2O3 buffer layer.

As a special chemical vapor deposition technology with lower temperature, quasi-continuous and self-limiting characteristics atomic layer deposition (ALD) is a preferred method to deposit an ultra-thin-film layer due to its ability to deposit high-quality and uniform materials with an atomic-level precise control of layer thickness. For this technology, gaseous chemical precursors are alternately introduced into the reaction chamber in a pulsed manner to generate a gas–solid chemical reaction on the substrate, thereby forming a dense, uniform, pinhole-free, and continuous film containing fewer impurities on the substrate. This deposition technique is very suitable for those substrates with undulating surfaces and facilitates the formation of a continuous ultra-thin film on the grooves or channels in substrate, thus effectively blocking the potential leakage paths, which cannot be achieved by other deposition techniques [9,10]. Al2O3 films were widely used as a passivation layer in p-silicon solar cells, while its application in cadmium telluride thin film solar cells was relatively rare [11,12]. Kephart et al. studied the application of sputter-deposited oxides for interface passivation in CdTe photovoltaics and found that Al2O3 shows the strongest passivation effect at the front interface and the highest lifetime and Photoluminescence (PL) intensity improvement at the rear interface. It is worth noting that the basic structure of their cells was MZO/CdTe, in which the window layer CdS was totally replaced with MgZnO [13].

Based on the above analysis, in this work, ALD technology was used to fabricate Al2O3 films with different thicknesses on TCO. The optical, electrical, and structural properties of TCO/Al2O3 films were analyzed. Then these films were applied in CdS/CdTe solar cells with a 40-nm-thick CdS, and the performances of the cells were studied at the same time. Finally, the potential application of alumina as a buffer layer in CdS/CdTe thin film solar cells was clarified.

2. Experimental

Atomic layer deposition equipment ALD100-R produced by GuoKai Electronic Co., Ltd. was employed to prepare Al2O3 films. The TCO films commonly used in our laboratory were selected as the substrate, namely TEC 10, which was a commercial glass coated with FTO (SnO2:F).

The experimental conditions of ALD-Al2O3 fabrication were as follows: Substrate temperature was 150 °C, purge time was 30 s, dose time was 0.3 s, and the action time was 15 s. High-purity water supplying element O of Al2O3 and trimethylaluminum (TMA) supplying Al of Al2O3 with a purity of 99.999% were used as precursors, and ultrahigh purity 99.9999% N2 was used as the carrier and purging gas with a constant flow rate of 20 sccm throughout all cycles during ALD deposition. ALD cycling began with H2O exposure to the substrate surface with a hydroxyl group for action with the first TMA pulse. After each precursor exposure, the ALD chamber and gas feeding lines were
purged with N₂ to prevent chemical vapor deposition from occurring, followed by the next cycle. The test method for the thickness of ALD-Al₂O₃ is shown in Figure 1, and the schematic of the reaction mechanism of ALD is shown in the inset of Figure 1. The thickness \( d \) of the aluminum oxide film was calculated according to the following formula: \( d = \varepsilon_0 \varepsilon_r / SC \), where \( C \) is the capacitance value of the capacitor device composed of p-Si as one electrode and an ALD-Al₂O₃ and Ti(3 nm)/Au(40 nm) electrode prepared by electron beam evaporation (EBE) with an area of 0.05 mm², \( \varepsilon_0 \) is \( 8.85 \times 10^{-12} \) F/m, and \( \varepsilon_r \) is 9 [14]. In this work, a complete cycle corresponded to a thickness of 0.33 nm for Al₂O₃ deposition, which was twice greater than other published results of ~0.15 nm/cycle [11,15]. Therefore, the corresponding Al₂O₃ thickness was obtained by controlling the number of cycles, i.e., 3 cycles corresponded to 1 nm, 15 cycles to 5 nm, 30 cycles to 10 nm, and 60 cycles to 20 nm, respectively. Next, after the CdS thin film with a thickness of 40 nm was deposited by using chemical bath deposition (CBD) technique on the surface of ALD-Al₂O₃ at about 85 °C, CdTe thin film with a thickness of 5 μm was prepared by using close-space sublimation (CSS) method. The deposition conditions of CdTe were as follows: The chamber was initially evacuated to a pressure of 5 × 10⁻² Pa, and a mixture of 99.999% pure argon and 99.999% oxygen (the oxygen partial pressure was 8%) was then charged into the chamber to maintain a pressure of 1 KPa; the space from the substrate to the source was 2 mm; and the source and substrate were simultaneously heated to about 650 °C and 550 °C, respectively, and the deposition time for CdTe was 5 min. Afterwards, the CdTe films were annealed for 30 min with the CdCl₂ source in a tube furnace preheated to 380 °C under 1 atmospheric pressure of mixed N₂ + O₂ gas (volume ratio 4:1). Before the back-contact deposition, the CdTe film was etched by bromine methanol solution to purify the surface. The concentration of the bromine methanol solution was 0.2%, and the duration was 4 s. Then, a back-contact layer of ZnTe:Cu which was used to reduce the contact resistance between CdTe and the back-electrode metal, was fabricated by using a vacuum thermal evaporation technique. Then, 99.999% pure ZnTe and 99.999% pure Cu powder were put into quartz crucibles and heated indirectly by tungsten heater and molybdenum heater, respectively. Two quartz crystal monitors were employed to monitor the deposition rates of ZnTe and Cu on-line, respectively. Finally, unit cells with areas of 0.24 cm² were achieved by depositing a 100-nm-thick nickel electrode using EBE with a shadow mask. The structure of the solar cells is shown in Figure 2.

![Figure 1](image1.png)

**Figure 1.** Schematic diagram of test method for the thickness of atomic layer deposition (ALD)-Al₂O₃ thin films, the schematic of reaction mechanism of ALD is also shown in the left inset.

![Figure 2](image2.png)

**Figure 2.** The structure of a cadmium sulfide (CdS)/cadmium telluride (CdTe) solar cell with ALD-Al₂O₃.
3. Results and Discussion

3.1. Optical Properties

Figure 3a shows the transmittance spectra of TCO/Al2O3 films utilized by UV/Vis spectrometer (Lambda 9500 PerkinElmer). One may find that the curves of all the samples exhibited a relatively insensitive variation in transmittance with the increase of the thickness of Al2O3, and a high transmittance (>85%) for visible light with a wavelength of >400 nm was easily observed. Additionally, all the curves showed an obvious sharp absorption edge at the wavelengths of around 300 nm, which was anticipated from the band gap $E_g$ of the substrate calculated by Tauc formula as follows:

$$ahv = A(hv - E_g)^n$$

where $a$ is the absorption coefficient, which is related to the thickness of the film, $hv$ is defined as photon energy, $A$ is a constant, and the value of $n$ depends on the energy-band structure of the material. For direct energy-band semiconductor materials, such as SnO2, $n$ is 0.5 [16]. The obtained $E_g$ was 4.33 eV for TEC 10, agreeing well with the former result [17]. Notably, no obvious extra absorption of photons was caused, as Al2O3 was introduced onto the substrate because of the fact that the $E_g$ of Al2O3~8.8 eV is far greater than that of the substrate. So, according to the change in Figure 3a, ALD-Al2O3 films with excellent light transmittance are suitable to be served as buffer layers between the front electrode TCO and the window layer CdS.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** (a) Transmittance vs. wavelength spectra, (b) sheet resistance, and (c) Raman spectra of the TEC 10/ALD-Al2O3 thin films with different Al2O3 thickness.

3.2. Electrical Properties

Figure 3b shows the sheet resistance of the TEC 10/Al2O3 thin film tested by a four-point probe resistivity measurement system (PROBES TECH). With the increase of the thickness of Al2O3, not only an upward tendency but also the appreciable variations of the sheet resistance of the samples were observed. As compared with the bare substrate, the sheet resistance of the TEC 10 substrate coated by 10 nm Al2O3 increased by 15.22%. Furthermore, the resistance non-uniformity of the TEC 10 substrate with 10 nm thick Al2O3 was 4.83% while that of TEC 10 with 20 nm thick Al2O3 increased to 11.11%, with the magnitude of the increase exceeding 130%. This is caused by the modification of the surface characteristics of the substrate. With the increase of the ALD deposition cycle, Al2O3 accumulated locally in the pores or cavities on the substrate surface leading to the local ALD-Al2O3 thickness exceeding the designed deposition thickness, which resulted in the increase of electrical non-uniformity [18]. Combined with the device performance, the non-uniform sheet resistance had a great influence on the device performance, especially in the fill factor.

3.3. Structural Properties

Raman spectra of ALD-Al2O3 with different thicknesses on the TEC 10 substrate were taken using laser Raman spectrometer (Lab RAM HR HORIBA) with a grating of 600 g/mm, and the exciting lasers of a wavelength of 785 nm were employed with comparable beam spots ~2 μm in diameter.
Only two peaks at 370 cm\(^{-1}\) and 560 cm\(^{-1}\) could be observed in Figure 3c. The peak shape was not sharp enough, accompanied by a distinct shoulder peak, and the full width of the half maximum of the peaks was also big, which verified that the ALD-Al\(_2\)O\(_3\) film deposited at 150 °C had an amorphous structure [19]. The first peak at about 370 cm\(^{-1}\) might be attributable to alumina, but it could also be a result of the combination of SnO\(_2\):F (this mode B\(_{1g}\) often corresponded to 360 cm\(^{-1}\)) and amorphous Al\(_2\)O\(_3\), which may be attributable to the fact that the phonon scattering range was closely related to the grain size and the surface stress of the film. The peak at 560 cm\(^{-1}\) was assigned to the characteristic Raman shift peak of the substrate SnO\(_2\):F [20–22].

3.4. Surface Morphology

Surface morphology characterization for ALD-Al\(_2\)O\(_3\) deposited on TEC 10 was accomplished by employing atomic force microscopy (AFM, Bruker Multi Mode 8), as shown in Figure 4. Meanwhile, the corresponding roughness was also listed in Table 1. Arithmetic mean roughness (R\(_q\)) and root-mean-square roughness (Ra) of the substrate without alumina were 17.2 nm and 13.9 nm, respectively, while the R\(_q\) and Ra of the substrate with 1 nm alumina increased to 19.0 nm and 15.1 nm, respectively. This change might be due to the substrate temperature 150 °C. However, it could be seen that as the number of Al\(_2\)O\(_3\) deposition cycles increased, the surface roughness of the film gradually decreased. The R\(_q\) of 1 nm thick Al\(_2\)O\(_3\) film was 19.0 nm while that of 20 nm thick Al\(_2\)O\(_3\) film was 15.5 nm, with a 18.4% reduction, and the corresponding Ra also decreased by 17.2%, which revealed that the surface smoothness of TCO/ALD-Al\(_2\)O\(_3\) thin films was improved and this variation was attributed to the filler Al\(_2\)O\(_3\) in the pores or cavities on the substrate surface. Furthermore, it could also be seen that the particle size was uniform, and there was no large-particle alumina clusters or obvious wrinkles on the film surface, which indicated that the Al\(_2\)O\(_3\) was uniformly distributed on the surface of the TEC 10 substrate. These change trends were quite conducive to promoting the quality of the subsequent deposition process of CdS films and reducing the interface defect states. However, as shown in Figure 4, because the thickness of the ALD-Al\(_2\)O\(_3\) was not more than 20 nm while the peak-to-valley distances of the substrate exceeded 100 nm, a very smooth surface had not yet been obtained in this work, although the roughness of the surface of the sample had improved to some extent.

**Figure 4.** Atomic force microscopy (AFM) pictures of the TEC 10/ALD-Al\(_2\)O\(_3\) thin films with different Al\(_2\)O\(_3\) thickness, (a–e) corresponding to the thickness of 0 nm, 1 nm, 5 nm, 10 nm, and 20 nm, respectively.
Table 1. The properties of the TEC 10/ALD-Al$_2$O$_3$ films, arithmetic mean roughness (Rq), root-mean-square roughness (Ra) and the average performances of solar cells, conversion efficiency (η), shunt resistance (R$_{sh}$), series resistance (R$_s$), fill factor (FF), short circuit current density (J$_{sc}$), open circuit voltage (V$_{oc}$), dark reverse saturation current density (J$_0$).

| Thickness | Roughness (nm) | η (%) | R$_{sh}$ (Ω) | R$_s$ (Ω) | FF (%) | J$_{sc}$ (mA/cm$^2$) | V$_{oc}$ (mV) | J$_0$ (10$^{-8}$ mA/cm$^2$) |
|-----------|----------------|-------|--------------|-----------|--------|---------------------|--------------|--------------------------|
| 0         | Rq17.2/Ra13.9  | 11.03 | 1869         | 22.90     | 60.35  | 26.47               | 701.2        | 9.2                      |
| 1 nm      | Rq19.0/Ra15.1  | 11.10 | 1894         | 23.09     | 60.10  | 26.57               | 712.1        | 10.2                     |
| 5 nm      | Rq18.9/Ra15.2  | 11.66 | 2115         | 25.09     | 61.36  | 26.69               | 734.6        | 7.6                      |
| 10 nm     | Rq16.9/Ra13.6  | 12.82 | 2590         | 25.17     | 64.79  | 26.65               | 762.8        | 7.9                      |
| 20 nm     | Rq15.5/Ra12.5  | 10.26 | 1460         | 27.71     | 58.76  | 26.09               | 686.8        | 13.0                     |

3.5. Devices Performances

Finally, according to the International Electrotechnical Commission (IEC) 61646, the transient photocurrent-voltage was tested by using a specialized solar cell tester under an irradiance of 1000 W/m$^2$ at 25 °C, and the dark current versus voltage curves were also measured at a bias range of −0.8 V to 1.2 V by using an Agilent 4155C semiconductor parameter analyzer. The characterization was carried out on 10 champion cells with different Al$_2$O$_3$ thickness and the results were summarized in Figure 5 while the average parameters were listed in Table 1. As the thickness of the alumina increased from 0 nm to 20 nm, some parameters showed a more fluctuating change. For example, the shunt resistance (R$_{sh}$) increased first and then decreased while the series resistance (R$_s$) maintained a tendency to increase. The J$_{sc}$ of the cells was relatively insensitive to variations in the change of ALD-Al$_2$O$_3$ thickness due to the fact that the thickness of the window layer CdS was fixed at 40 nm in all cells. Interestingly, the conversion efficiency (η) showed exactly the same open circuit voltage (V$_{oc}$) and fill factor (FF) behavior with an optimized value corresponding to the 10 nm thick ALD-Al$_2$O$_3$ buffer layers. Furthermore, as can be seen in Figure 5, after the alumina was introduced between TCO and CdS, the uniformity of the cell performance was significantly improved. Taking the conversion efficiency as an example, for the cells without alumina, the efficiency variation (Δη/η$_{max}$) was 21.34%, and those of the cells with an alumina thickness of 1 nm, 5 nm, and 10 nm were 18.23%, 9.85%, and 7.37%, respectively. However, as the thickness of the alumina continually increased, the fluctuation in efficiency began to increase. Finally, a cell with a conversion efficiency of 13.40% was obtained, which was attributed to the fact that the leakage paths (including grain boundaries and pinholes) generated by the very thin CdS can be effectively blocked by introducing the ALD-Al$_2$O$_3$ between TEC 10 and CdS. At the same time, the increase in sheet resistance of TEC 10/10 nm ALD-Al$_2$O$_3$, as shown in Figure 3b, also helped block the leakage channels caused by the pinholes formed in the thinner CdS layer and optimized the CdS/CdTe heterojunction characteristics, which provided evidence of the existence of the alumina blocking effect. Furthermore, the thickness of the ALD-Al$_2$O$_3$ thin film as a buffer layer had multiple effects on the performances of the cells: the average performance degradation of cells with the 20 nm thick ALD-Al$_2$O$_3$ was visible with a 10.0% and 9.3% decrease in V$_{oc}$ and FF, respectively, compared to those of cells with the 10 nm thick ALD-Al$_2$O$_3$. As a result, the η of the cell declined by 20.0%. This degradation was caused not only by the increase in R$_s$ (9.2%), but also by the decrease in R$_{sh}$ as a function of the transportation properties of thermally excited electrons through the barriers at the interface [23].
the “roll-over” phenomenon will then be induced by the Schottky barrier formed at the CdTe/back electrode interface in the J–V which verifies the attenuation of the junction characteristics. It was worth noted that when the bias when the thickness of the alumina increased to 20 nm, the J

Energies

Figure 5. The performance parameters of Cds/CdTe solar cells with different Al2O3 thicknesses, (a–f) corresponding to conversion efficiency (η), Rsh, Rs, FF, Jsc, and Voc, respectively.

The representative photocurrent and dark current curves of cells with performances close to the average performance of all the cells are shown in Figure 6. The typical cell performance shown in Figure 6a demonstrated the same tendency of change as analyzed above. As shown in Figure 6b, under the reverse bias or a small forward bias, the current was very small and relatively insensitive to variation in bias. However, an exponential increase trend of dark current could be clearly observed when the forward bias exceeded 0.6 V, close to the value of Voc of solar cells. The CdTe heterojunction current is described as follows [24]:

\[
I = I_0 \left( e^{\frac{(V-IR_s)}{AKT}} - 1 \right) + \frac{V - IR_s}{R_{sh}}
\]

where \(I_0\) is the dark reverse saturation current, \(K\) is Boltzmann’s constant, \(A\) is defined as the diode ideality factor representing the diffusion and recombination current components, and in this work, \(T\) is 298 K. The corresponding values of \(I_0\) (dark reverse saturation current density) are listed in Table 1, and the values of \(A\) in this work were close to 2. With the increase of alumina thickness, the \(I_0\) of cells decreased, revealing that the characteristics of the Cds/CdTe heterojunction were improved, and the negative effects of pinholes produced by Cds thin film were effectively suppressed. However, when the thickness of the alumina increased to 20 nm, the \(J_0\) increased to \(13.0 \times 10^{-8}\) mA/cm², which verifies the attenuation of the junction characteristics. It was worth noted that when the bias voltage exceeded 0.9 V greater than the Voc of the devices, an “inflection point” of the current could be obviously observed; this was the “roll over” phenomenon. Because the work function of CdTe is ~5.7 eV higher than that of the common metals used as the back electrode, the “roll-over” phenomenon will then be induced by the Schottky barrier formed at the CdTe/back electrode interface in the J–V curves was easily observed in the Cds/CdTe solar cells. An effective way to reduce this phenomenon is to introduce a back-contact layer between the CdTe and back electrode to form an ohmic back contact [25,26]. As shown in Figure 6b, in which the “roll over” phenomenon was greatly weakened, the difference was attributed to the fact that the buffer layer ZnTe:Cu was introduced as a back contact in all the solar cells fabricated in this work, and the effect of the metal/CdTe Schottky junction with a direction opposite to that of the main junction Cds/CdTe was effectively reduced. However, the “roll over” phenomenon became more serious when the alumina was introduced in the cells. According to reference [27], this “roll-over” phenomenon can also be introduced by other reasons, such as a relatively large positive conduction band offset at the interface of the Cds and CdTe films. In this work,
the cause of this phenomenon might have been that the alumina formed an energy barrier that could not be ignored at the interface of Al₂O₃/CdS [28].

![Figure 6.](image)

**Figure 6.** (a) Typical photocurrent and (b) dark current curves of the CdS/CdTe heterojunction solar cells for each ALD-Al₂O₃ thin film thickness.

4. Conclusions

In summary, we have successfully prepared alumina thin films by ALD and ALD-Al₂O₃ buffers have been incorporated into CdS/CdTe based solar cells. The amorphous ALD-Al₂O₃ is transparent to visible light and smoothens the surface of TCO. The device performance is significantly improved by the utilization of ALD-Al₂O₃ buffers and an optimized power conversion efficiency of over 13% has been achieved. Therefore, combined with the representative results of cells, the introduction of alumina is a comprehensive consideration process, especially in the control of its thickness. Fortunately, ALD technology meets the requirements for the precise control of alumina thickness. In this work, we confirm the possibility of the ALD-Al₂O₃ buffer in CdTe solar cells and pave a way to further optimize the device performance of CdTe and other photovoltaic devices which are suffered from surface/interface passivation problems.

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