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Rectification and tunneling effects enabled by Al$_2$O$_3$ atomic layer deposited on back contact of CdTe solar cells

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Atomic layer deposition (ALD) of Aluminum oxide (Al$_2$O$_3$) is employed to optimize the back contact of thin film CdTe solar cells. Al$_2$O$_3$ layers with a thickness of 0.5 nm to 5 nm are tested, and an improved efficiency, up to 12.1%, is found with the 1 nm Al$_2$O$_3$ deposition, compared with the efficiency of 10.7% without Al$_2$O$_3$ modification. The performance improvement stems from the surface modification that optimizes the rectification and tunneling of back contact. The current-voltage analysis indicates that the back contact with 1 nm Al$_2$O$_3$ maintains large tunneling leakage current and improves the filled factor of CdTe cells through the rectification effect. XPS and capacitance-voltage electrical measurement analysis show that the ALD-Al$_2$O$_3$ modification layer features a desired low-density of interface state of $8 \times 10^{10}$ cm$^{-2}$ by estimation.

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The performance of a CdTe thin film solar cell strongly depends on the nature of the back contact because it is challenging to compromise the CdTe material to most electrode materials.\textsuperscript{1–3} To date, extensive efforts have been devoted to optimize the back contact based on nano-structures and physical concepts.\textsuperscript{3–5} For example, we have shown previously that copper-nanowire back contact could be a controllable intermediate layer to enhance CdTe cell performances.\textsuperscript{1} In the meantime, Al$_2$O$_3$ has been reported to be a promising candidate to passivate $p$-type silicon (Si) material due to its good chemical and field-effect passivation, which is induced by the negative charge in the Al$_2$O$_3$ layer from Al vacancies, O interstitials, and extrinsic H.\textsuperscript{6–11} Additionally, Al$_2$O$_3$ is a good candidate as an modification material for CdTe, because the lattice mismatch is only 3.7\% between the unit cell of (0001) surface of Al$_2$O$_3$ and the unit cell of (111) surface of CdTe.\textsuperscript{12} Therefore, a smooth interface of Al$_2$O$_3$/CdTe with strong chemical bonding and surface modification is expected to enhance the performance of CdTe solar cells.

Among the various methods for depositing Al$_2$O$_3$, atomic layer deposition (ALD) is attractive due to the ultra-thin film with excellent coverage. A 0.5–10 nm thickness is sufficient to tune the tunneling current by controlling the thickness.\textsuperscript{5} In this letter, we demonstrate a nano-structured back contact of CdTe solar cells with Cu dopant and ALD-Al$_2$O$_3$ with thickness from 0.5 nm to 5 nm. The CdTe solar cells based on such Al$_2$O$_3$ ALD layer displays superior performance of efficiency due to the optimized rectification and tunneling effects.

CdTe solar cells were fabricated as following: 200 nm thick CdS window layers were grown by radio frequency magnetron sputtering (RF sputter), and then CdTe absorber layer was deposited by close space sublimation (CSS). For the back contact treatments, the ultrathin and uniform Al$_2$O$_3$ films were deposited by ALD using alternating pulses of Al(CH$_3$)$_3$ (Trimethylaluminium, TMA) and water as the precursors. Au was then evaporated as electrode. The procedure details were described in supplementary material, and the material properties are shown in Figures S1, S2, and S3.\textsuperscript{20} The structure photo of CdTe solar cell is shown in Figure 1(a). The surface of ALD-Al$_2$O$_3$ CdTe layer shows smooth curvature, as shown in Figures 1(b) and S3, and the process is described in Figs. S1–S4.\textsuperscript{20} From the XPS analysis (Figure 1(c)), the Cu sign gradually reduces reversely with the thickness of Al$_2$O$_3$ until it vanishes at 5 nm. Considering the XPS probe depth of around 2–5 nm, this result indicates an excellent coverage of the Al$_2$O$_3$ thin film on CdTe layer. The FTO/CdS/CdTe/Cu dopant/Al$_2$O$_3$/Au solar cell structure and modification mechanism are shown in Figure 1(d). Without the Al$_2$O$_3$ film deposition, a potential field points from fixed positive charges at CdTe/Cu$_2$Te shallow surface to the interior of CdTe. With depositing Al$_2$O$_3$ with a high-density negative charge, the interface on the CdTe surface is chemically modified, and an electrical field at the surface is established to neutralize the built-in field from the positive charge on the surface.

The efficiency characteristics of cells were estimated by photocurrent density–voltage ($J–V$) measurement (Figure 2(a)). All cells show good contact following the Ohmic conductivity, as shown in the inset of Figure 2(a). The best power conversion efficiency (PCE) is at 1 nm Al$_2$O$_3$, and the detailed photovoltaic parameters are listed in Table I. The performance improvement is clearly shown, resulted from the increased filled factor ($FF$) of the cell. This improvement originates from the optimization of the $p$–$n$ junction, including the metal-semiconductor contact. However, if the thickness of the Al$_2$O$_3$ layer is more than 3 nm, the efficiency shows obvious degradation. This can be explained by the tunneling current, which dominates the charge transportation with the ultra-thin (≤1 nm) dielectrics of Al$_2$O$_3$, but a thick Al$_2$O$_3$ film (≥3 nm) would block the charge transportation.\textsuperscript{13,14} Figure 2(b) shows...
the external quantum efficiency (EQE) of a series of CdTe solar cells with ALD-Al₂O₃ of different thicknesses. The cell with 1 nm Al₂O₃ presents more sensitive response at near infrared wavelength range (750 nm to 830 nm), as shown in the inset of Figure 2(b), which agrees well with the photocurrent $J-V$ characteristics. The high EQE at the visible wavelength range is mainly attributed to the reduced surface recombination by the ALD Al₂O₃. The high FF of cells with Al₂O₃ is related to the enhanced holes collection of the back contact due to the negative charges from Al₂O₃, which neutralizes the positive charge in the surface of CdTe and eliminates the defect state in the interface. The estimated density of interface state ($D_{it}$) is below $8 \times 10^{10}$ cm$^{-2}$ by fitting the $C-V$ curve of 1 nm Al₂O₃ sample, as shown in Figure S4. In order to quantitatively evaluate the surface modification of CdTe, small-amplitude intensity-modulated photovoltage spectroscopy (IMVS) was measured under a 560 nm light source with the structure of FTO/CdS/CdTe/Al₂O₃/Au. The back contact hole injection could be extracted from the formula, $\tau = (2\pi f_{\text{max}})^{-1},$ where $\tau$ is the carrier life time and

<table>
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<th>Al₂O₃ thickness (nm)</th>
<th>$V_{OC}$ (mA)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>$f_{\text{max}}$(Hz)</th>
<th>$\tau_c$ (ms)</th>
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<tr>
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<td>22.3</td>
<td>0.54</td>
<td>9.4</td>
<td>600</td>
<td>0.26</td>
</tr>
</tbody>
</table>
f_{\text{max}} \text{ is the max response frequency. Obviously, the best } \tau \text{ is achieved in the sample with 1 nm Al}_2\text{O}_3, \text{ as shown in Table I and Figure S5.}

In order to evaluate the tunneling function of ALD-Al_2O_3 directly, its conduction mechanism was analyzed by the I-V curves of the MIS devices, as shown in Figure 3(a). The leakage current reduces with the increasing thickness of Al_2O_3. Interestingly, there is an excellent rectification effect for the electrical field and shown that the density of current is linearly dependent on the mass of carrier and which reflects the direction of the built-in field at the interface of CdTe/Cu_xTe and Al_2O_3. The density of current (J) versus the electrical field (E) is shown in Figure 3(c). It is shown that the density of current is linearly dependent on the electrical field and $J \sim E$ follows the relation:

$$J \sim ET_C.$$

It is concluded that, if the Al_2O_3 thickness is less than 1 nm, a direct electron transport is prevented by the band gap of the insulator, so the electron transport is governed by an ballistic transport under a bias. By increasing the Al_2O_3 thickness to $\geq 3 \text{ nm}$, the leakage current curve fits the Frankel-Poole (F-P) mechanism very well. PF conduction is due to field-enhanced thermal excitation of trapped electrons into the conduction band. $J \sim E$ data should follow the relationship:

$$J \sim \exp \left( -\frac{q(B - \sqrt{\frac{4E}{\pi\varepsilon}})}{k_BT} \right),$$

where $B$ is the barrier, $\varepsilon$ is the dielectric constant, $k_0$ is Boltzmann’s constant, and $q$ is the electron charge. That different behavior of leakage current through Al_2O_3 layers with different thickness indicates the two competing mechanisms. In the ultra-thin film, the tunneling of electrons takes place in the ballistic transport mode. With a relative thick ALD-Al_2O_3 film, the charges in localized state dominate the tunneling current.

In summary, we have developed a CdTe back contact with ultra-thin Al_2O_3 films via ALD, which improves the performance of the solar cells. The modification of the back contact through ALD-Al_2O_3 leads to a high FF 67% due to the rectification and tunneling function. The efficiency of cell is improved, up to 12.1%. Our results show that the ALD-Al_2O_3 modification of the back contact is a promising approach for high efficiency solar cells.

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19. See supplementary material at http://dx.doi.org/10.1063/1.4926601 for the detailed fabrication process and property characterizations of the CdTe solar cells.