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Silicon based solar cells using a multilayer oxide as emitter

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In this work, n-type silicon based solar cells with WO3/Ag/WO3 multilayer films as emitter (WAW/n-Si solar cells) were presented via simple physical vapor deposition (PVD). Microstructure and composition of WAW/n-Si solar cells were studied by TEM and XPS, respectively. Furthermore, the dependence of the solar cells performances on each WO3 layer thickness was investigated. The results indicated that the bottom WO3 layer mainly induced band bending and facilitated charge-carriers separation, while the top WO3 layer degraded open-circuit voltage but actually improved optical absorption of the solar cells. The WAW/n-Si solar cells, with optimized bottom and top WO3 layer thicknesses, exhibited 5.21% efficiency on polished wafer with area of 4 cm2 under AM 1.5 condition (25°C and 100 mW/cm2). Compared with WO3 single-layer film, WAW multilayer films demonstrated better surface passivation quality but more optical loss, while the optical loss could be effectively reduced by implementing light-trapping structures. These results pave a new way for dopant-free solar cells in terms of low-cost and facile process flow. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4960836]

I. INTRODUCTION

Silicon based heterojunction (SHJ) solar cells with 24.7% power conversion efficiency (PCE) has been substantiated by Panasonic,1 which implementing high quality intrinsic a-Si:H as passivation layer and B2H6 doped a-Si:H as emitter. However, several limitations of SHJ solar cells may restrict its practical application, such as explosive dopant-gas precursors and costly film deposition equipment. Since transition metal oxides (TMOs), compromising MoO3, WO3, V2O5 and TiO2, show the merits of highly transparent, selective charge extraction and facile deposition,2–9 they are explored extensively as candidates for substituting boron/phosphorous doped a-Si:H.10–13 In the last few years, MoO3, WO3, V2O5 with nm-thickness capped directly on n-type silicon (n-Si) show extraordinary hole-selectivity,14,15 which favour charge-carriers’ separation by transporting holes while blocking electrons, and reaching the efficiency of 14.3% for MoOx/a–Si:H/n-Si heterojunctions.14 Moreover, when inserting an intrinsic a-Si:H layer into MoOx/a–Si:H/n-Si heterojunctions for passivation, PCE as high as 22.5% has been recorded for this novel structure (MoOx/a–Si:H/n-Si) solar cells.12 Analogously, TiO2 exhibits superior electron-selective and surface passivation property,8,9 proving dopant-free TMOs are ideal candidates for replacing doped a-Si:H.

Since the nm-thickness TMOs exhibit ultra-high sheet resistance on the order of 108Ω/sq,13 a TCO (e.g. ITO, IO:H) layer covered on TMOs is essential for charge-carriers lateral transportation.

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and collection. However, the sputter deposition of ITO would degrade surface passivation severely and increase O-deficiency of MoO$_3$.\textsuperscript{12,15,16} A followed low-temperature annealing process is routinely carried out to cure sputter damage.\textsuperscript{17} Whereas TMOs are sensitive to temperature significantly, the post-deposition anneal may impair their (MoO$_3$ and V$_2$O$_5$) high work-function and carrier selectivity, resulting in the degradation of FF as well as PCE.\textsuperscript{11,13,16}

Here, we incorporate oxide/metal/oxide (OMO) multilayer into silicon based solar cells as emitter, charge-carriers lateral transportation and collection are achieved through inserting one thin metal film into TMOs. OMO multilayer, such as MoO$_3$/Ag/MoO$_3$ (MAM),\textsuperscript{18,19} WO$_3$/Ag/WO$_3$ (WAW),\textsuperscript{20,21} and V$_2$O$_5$/Ag/V$_2$O$_5$ (VAV),\textsuperscript{22} has been developed as transparent electrode in organic devices due to high- transmittance, low-resistivity and low-damage deposition. Compared with MAM and VAV, WAW multilayer is more transparent and environmentally friendly. What’s more, high work-function of 6.334 eV has been reported for WAW multilayer,\textsuperscript{23} which is the key factor for hole-selectivity contact. In this work, we develop a novel solar cell structure using WAW multilayer as emitter on n-type silicon (WAW/n-Si solar cells), neither any TCO film nor any post-deposition annealing is employed in device fabrication process. The WAW/n-Si solar cells are fabricated via physical vapor deposition (PVD). We investigate the microstructure, composition and optimum thickness of WAW multilayer in WAW/n-Si solar cells. Furthermore, we compare the electrical and optical performance of WAW multilayer and WO$_3$ layer in terms of application in silicon based solar cells.

II. EXPERIMENTAL DETAILS

One side polished n-type (100) oriented CZ silicon wafers (1–3 $\Omega$·cm, 300 $\mu$m) were used for all the device fabrications in this study. Silicon wafers were cleaned with standard RCA processing prior to the WO$_3$ film deposition. After cleaning and dewatered, the substrates were immediately loaded into the evaporating chamber. 99.99% pure WO$_3$ powder and 99.999% silver wire were placed into alumina-coated tungsten boat separately as source materials, the deposition rate of WO$_3$ and Ag were controlled to be 0.5Å/s and 2Å/s. WO$_3$ films (0, 5, 10, 15 nm thickness), Ag (12 nm thickness), WO$_3$ (5, 30, 55, 80 nm thickness) were thermally evaporated sequentially at room temperature, and film thicknesses were monitored using a quartz crystal monitor (Model SQM 200, Filtech). For intermediate Ag layer, the deposition pressure was kept at 8 $\times$ 10$^{-4}$ Pa. For both WO$_3$ layers, O$_2$ gas was introduced to ensure that the vacuum pressure was 1.5–2.5 $\times$ 10$^{-2}$ Pa, detailed procedure could be found in Ref. 23. The front electrode was fabricated by depositing 500-nm-thick Ag through a shadow mask, and 500 nm Ag film was evaporated onto the rear side of the silicon as electrode. The effective area of the solar cells was controlled at 2 $\times$ 2 cm$^2$ through shadow mask. The image of a finished device is shown in Fig. S1.

The microstructure and composition of the device were evaluated by transmission electron microscope (TEM, JEM-2100, JEOL) and X-ray photoelectron spectrum (XPS, Thermo ESCALAB 250XI, Thermo Scientific), separately. Reflectance of devices were obtained using an UV-Vis-NIR spectrophotometer (U-4100, HITACHI). PV measurements were employed on a NewPort system under AM 1.5G sunlight and J–V curves were recorded by Keithley 2400. The External Quantum Efficiency (EQE) measurement was performed on Quantum Efficiency Measurement System (QEX10, PV Measurements). Contact resistivity ($\rho_{sc}$) of WO$_3$/n-Si contact was investigated using transfer-length-method (TLM) and more details can be found in Ref. 24. The illumination-implied $V_{oc}$ curves\textsuperscript{25,26} and the implied J–V curve\textsuperscript{27} are measured by lifetime test instrument (WCT-120, Sinton Instruments) using Quasi-Steady-State-Photo-Conductance (QSSPC) method. The optical loss of the devices are simulated by Wafer Ray Tracer.\textsuperscript{28}

III. RESULT AND DISCUSSION

The WAW/n-Si device was characterized by cross sectional TEM. The analyzed structure consists of two WO$_3$ layers (10 nm bottom layer, 55 nm top layer) and an intermediate Ag layer (12 nm) deposited on silicon wafer (covered with ~1 nm of native SiO$_2$), as shown in Fig. 1(a). The surface
oxidation of n-Si is invoked by the reaction between WO₃ and silicon substrate, in accordance with Ref. 29. It can be seen that the intermediate Ag layer is continuous but not uniform, the top WO₃/Ag interface is clearly resolved, whereas the interface of bottom WO₃/Ag is ambiguous, suggesting the implantation of Ag atoms into amorphous WO₃ layer during evaporation process.

The tungsten 4f XPS spectrum (squares) for top WO₃ layer is shown in Fig. 1(b). Obviously, the 4f profile can be fit by two Gaussian peaks centered at 37.9 and 35.8 eV, which are corresponding to the W 4f₅/₂ and W 4f₇/₂ orbital of tungsten in the W⁺⁶ valence state. Similar spectra is revealed in Fig. 1(d), indicating that both WO₃ layers are stoichiometric WO₃, in contrary to sub-stoichiometric WOₓ evaporated in vacuum. Since the deposition was carried out under O₂ atmosphere, the oxygen deficiency of WO₃, which would adversely affect its high-work-function, could be effectively eliminated. XPS signal of intermediate Ag layer and bottom WO₃ layer are obtained by depth profile. The Ag 3d spectrum (Fig. 1(c)) consists of double peaks of Ag 3d₃/₂ and Ag 3d₅/₂, which are located at 374 eV and 368 eV respectively, indicating the zero valence (Ag⁰) of Ag layer.

Fig. 2(a) shows the J-V curves of WAW/n-Si solar cells with different thicknesses of bottom WO₃ layer, while the thickness of intermediate Ag layer and top WO₃ are fixed at 12 and 30 nm, respectively. The detailed performances are provided in Table I. In absence of bottom WO₃ layer, the WA/n-Si solar cell exhibits rather low efficiency of 0.16%. When 5 nm thick WO₃ layer is introduced into the solar cell, the open-circuit voltage (V_oc), current density (J_sc) and fill factor (FF) improve significantly, reaching 4.00% efficiency, indicating that the added bottom WO₃ mainly induces strongly-inverted surfaces (p-type) in n-type silicon substrate and definitely favors carriers separation. Further increasing the bottom WO₃ thickness leads to an increase of FF but a negative effect on J_sc (indicated by the blue arrow), whereas the differences in V_oc values are slightly. 10 nm-thick WO₃ bottom layer leads to the highest 4.23% PCE of WAW/n-Si solar cells, and is therefore used in the subsequent investigation.
FIG. 2. Illuminated J-V characteristic (a), EQE (b) of WAW/n-Si solar cells with various bottom WO$_3$ thicknesses, the Ag and top WO$_3$ thickness are fixed at 12 and 30 nm respectively.

The corresponding EQE of the same samples is shown in Fig. 2(b). The $J_{sc}$ calculated by integrating the EQE vs wavelength and the AM 1.5G spectrum are 9.1, 17.4, 16.8 and 14.9 mA/cm$^2$, separately, which matches well with the $J_{sc}$ calculated from light J-V curves considering 7% electrode fraction (supplementary material, Table S1). It is observable that the EQE values decrease gradually with increasing the thickness of WO$_3$ layer (5∼15 nm), which is in conformity with the $J_{sc}$ in Fig. 2(a). The decreased EQE values as well as $J_{sc}$ are attributed to the fact that a thicker bottom WO$_3$ layer results in higher reflection loss (supplementary material, Fig. S2). As depicted in Table I, The series resistance ($R_s$) of WAW/n-Si solar cells decreases initially from 7.18 $\Omega$·cm$^2$ to 3.53 $\Omega$·cm$^2$ with increasing WO$_3$ film thickness, and climbs to 4.21 $\Omega$·cm$^2$ subsequently. The contact resistivity ($\rho_c$) of WO$_3$/n-Si hetero-contact, one of main components of $R_s$, drops rapidly from 6.43 $\Omega$·cm$^2$ to 0.31 $\Omega$·cm$^2$ when the thickness of WO$_3$ film is increased from 5 nm to 10 nm, and demonstrates the lowest value of 0.15 $\Omega$·cm$^2$ in 15 nm thickness (supplementary material, Fig. S3). Therefore, the initial decrease of $R_s$ is potentially because of the reduced $\rho_c$. Since fully stoichiometric WO$_3$ exhibit extremely high resistivity on the order of $10^{-6}$ S/cm, the followed rising of $R_s$ is probably a result of the bulk resistance of WO$_3$ film.

The thickness of top WO$_3$ layer in WAW/n-Si solar cells is further optimized and the result is shown in Fig. 3. The bottom WO$_3$ and Ag thickness are fixed at 10 and 12 nm respectively. Fig. 3(a) shows the J-V characteristic of WAW/n-Si solar cells with various thicknesses of top WO$_3$ layer, detailed parameters are summarized in Table II. Obviously, it can be noted that the $J_{sc}$ improves dramatically with increasing the top WO$_3$ layer thickness up to 80 nm (gray arrow), while the $V_{oc}$ is negatively affected at the meantime (violet arrow), the FF shows similar variation as $J_{sc}$ in the beginning, but saturates at 55 nm. These collective effects make WAW/n-Si solar cells with 55 nm-thickness top WO$_3$ layer process the highest PCE of 5.21%.

Fig. 3(b) presents the EQE of WAW/n-Si solar cells, the corresponding integrated $J_{sc}$ values are consistent with the $J_{sc}$ from J-V measurements (supplementary material, Table S1). A red-shift of EQE peaks are clearly seen for top WO$_3$ layer with increased thickness (30∼80 nm), as well as the reflectance peaks (supplementary material, Fig. S4). Increase the thickness of top WO$_3$ layer from 30 nm to 80 nm, the transmittance peaks of WAW multilayer would demonstrate red-shift due to light coupling. Since the transmitted photons are absorbed by n-type silicon underneath.

<table>
<thead>
<tr>
<th>NO: bottom</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>Eff. (%)</th>
<th>$R_s$ ($\Omega$·cm$^2$)</th>
<th>$R_{sh}$ (k$\Omega$·cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30-12-0</td>
<td>0.09</td>
<td>7.98</td>
<td>22.17</td>
<td>0.16</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>30-12-5</td>
<td>0.44</td>
<td>16.00</td>
<td>56.86</td>
<td>4.00</td>
<td>7.18</td>
<td>0.51</td>
</tr>
<tr>
<td>30-12-10</td>
<td>0.43</td>
<td>15.44</td>
<td>63.68</td>
<td>4.23</td>
<td>3.53</td>
<td>2.01</td>
</tr>
<tr>
<td>30-12-15</td>
<td>0.43</td>
<td>13.67</td>
<td>66.93</td>
<td>3.93</td>
<td>4.21</td>
<td>1.26</td>
</tr>
</tbody>
</table>
WAW multilayer to generate current, the EQE curves are red-shifted. The red-shift of reflectance peaks are expected to better match the AM 1.5G spectrum, which has the maximum photon flux in 600 nm \(^{33}\) (as depicted in Fig. S4), resulting in a gradual increase of \(J_{sc}\) in WAW/n-Si solar cells. As films deposited via thermal evaporation always display island growth (Volmer-Weber nucleation), \(^{34}\) WO\(_3\) layer in 5 nm-thickness is potentially discontinuous and with rough surface, which may hinder charge carriers transportation and contribute to enhanced resistive loss. When WO\(_3\) top layer becomes continuous and the thickness within 60 nm limit, \(R_s\) is independent of the thickness of the top WO\(_3\) layer. \(^{35-37}\) After that, further increase of the top WO\(_3\) layer would lead to the gradual increase of \(R_s\) due to bulk resistance. Considering the light-coupling ability, carriers transport and \(V_{oc}\), top WO\(_3\) layer in 55 nm-thickness is the optimum thickness for WAW/n-Si solar cells in this work.

Surface passivation with excellent property is critical for high \(V_{oc}\) in SHJ. \(^{38}\) The quasi-steady-state open-circuit voltage (Qss\(V_{oc}\)) method has been proven an effective technique to evaluate the surface property and minority carrier lifetime. \(^{39}\) As shown in Fig. 4(a), implied \(V_{oc}\) (i-\(V_{oc}\)) as high as 621 mV is obtained by n-Si sample capped with WAW multilayer (55/12/10 nm), while n-Si sample capped with single WO\(_3\) layer (65 nm) displays inferior i-\(V_{oc}\) of 576 mV, which matches well with the reported i-\(V_{oc}\) value of \(\sim\)570 mV for n-Si/WO\(_3\) contact. \(^{15}\) Furthermore, compared with single WO\(_3\) layer, WAW multilayer demonstrates a bit higher implied FF of 80.4%, as seen in the inset of Fig. 4(a). So WAW multilayer exhibits better surface passivation performance and higher \(V_{oc}\) potential over WO\(_3\) layer. The real \(V_{oc}\) measured from light J-V curves in this work seems 150 mV lower than the typical WO\(_3\)/n-Si solar cells with a \(V_{oc}\) of \(\sim\)570 mV, \(^{13,15}\) which is largely due to the absence of back surface field (BSF) and surface passivation.

Fig. 4(b) shows the optical loss of various devices simulated by Wafer Ray Tracer, \(^{28}\) the optical constant of WO\(_3\) film is sourced from Ref. 40, additional optical constants required for simulation are acquired from refractive index library developed by PV Lighthouse. It is noticeable that WAW/n-Si solar cells with planar structure show ultra-high external reflection, which contributes to 13.5 mA/cm\(^2\) optical loss. Combining with remaining optical loss, the maximum possible photo-generation current density (\(J_g\)) of planar WAW/n-Si solar cells is 28.8 mA/cm\(^2\), approximately 6.7 mA/cm\(^2\) smaller than the typical WO\(_3\)/n-Si solar cells with planar structure. The reduced \(J_g\) is potentially attribute to the high-reflection and parasitic absorption of intermediate

### Table II. List of WAW/n-Si solar cells parameters with various thicknesses of bottom WO\(_3\) layer.

<table>
<thead>
<tr>
<th>NO: top</th>
<th>(V_{oc}) (V)</th>
<th>(J_{sc}) (mA/cm(^2))</th>
<th>FF (%)</th>
<th>Eff. (%)</th>
<th>(R_s) ((\Omega)-cm(^2))</th>
<th>(R_{sh}) (k(\Omega)-cm(^2))</th>
</tr>
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<tr>
<td>5-12-10</td>
<td>0.47</td>
<td>12.75</td>
<td>60.62</td>
<td>3.63</td>
<td>10.20</td>
<td>2.00</td>
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<tr>
<td>30-12-10</td>
<td>0.43</td>
<td>15.44</td>
<td>63.68</td>
<td>4.23</td>
<td>3.53</td>
<td>2.01</td>
</tr>
<tr>
<td>55-12-10</td>
<td>0.42</td>
<td>18.96</td>
<td>65.39</td>
<td>5.21</td>
<td>3.54</td>
<td>7.70</td>
</tr>
<tr>
<td>80-12-10</td>
<td>0.40</td>
<td>20.59</td>
<td>56.03</td>
<td>4.61</td>
<td>5.74</td>
<td>14.20</td>
</tr>
</tbody>
</table>
FIG. 4. (a) Implied $V_{oc}$ vs light intensity curves for n-Si samples in symmetrical structure capped with WO$_3$ or WAW. Inset: implied FF of the same samples. (b) Simulated optical loss of planar WAW/n-Si solar cells, typical planar WO$_3$/n-Si solar cells and textured WAW/n-Si solar cells (R-Reflected, A-Absorbed). Inset graphs show the corresponding structures of $J_g$.

Ag layer. However, when incorporate textured structure (random upright pyramids) into WAW/n-Si solar cells, the external reflection is greatly suppressed, which leads to an improvement of $J_g$ from 28.8 mA/cm$^2$ to 36.5 mA/cm$^2$. As a way forward, further investigation will be centered on implementing light-trapping structure on the front side, and electron-selective layer possessing excellent surface passivation quality on the rear side, e.g., TiO$_2$.

IV. CONCLUSIONS

In summary, the silicon based solar cells with WO$_3$/Ag/WO$_3$ as emitter (WAW/n-Si solar cells) were developed via simple PVD. The TEM and XPS characterizations showed that the intermediate Ag layer was continuous and in zero valence, while the top and bottom WO$_3$ layer were fully stoichiometric. Moreover, the effect of the thicknesses of the bottom and top WO$_3$ layer on photovoltaic behavior was investigated. The bottom WO$_3$ layer mainly induced band bending and separated electron-hole pairs, while the top WO$_3$ layer enhanced optical absorption by light coupling but impaired the $V_{oc}$ at the same time. After optimizing the thicknesses, highest PCE of 5.21% was obtained for the WAW/n-Si solar cells with 10 nm bottom WO$_3$ layer and 55 nm top WO$_3$ layer. Then we compared the electrical and optical performance of WAW multilayer and WO$_3$ layer for the application in silicon based solar cells. The results showed that WAW multilayer demonstrated better surface passivation quality but more optical loss (external reflected and front films parasitic absorption) than WO$_3$ layer. In addition, further improvement can be made by incorporating light-trapping structures, rear passivation and BSF into WAW/n-Si solar cells.

SUPPLEMENTARY MATERIAL

See supplementary material for the real image of a finished device, the reflectance of WAW/n-Si solar cells, the relationship between $\rho_c$ of WO$_3$/n-Si contact and WO$_3$ layer thickness and a comparison of the current density ($J_{sc}$) calculated from EQE and light J-V curves.

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