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Citation: Appl. Phys. Lett. 103, 073903 (2013); doi: 10.1063/1.4818714
View online: http://dx.doi.org/10.1063/1.4818714
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Doping-free silicon thin film solar cells using a vanadium pentoxide window layer and a LiF/Al back electrode

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(Received 5 February 2013; accepted 27 July 2013; published online 16 August 2013)

This work describes the preparation of a doped layer-free hydrogenated amorphous silicon (a-Si:H) thin film solar cell consisting of a vanadium pentoxide (V2O5-x) window layer, an intrinsic a-Si:H absorber layer, and a lithium fluoride (LiF)/aluminum (Al) back electrode. The large difference between the work functions of the V2O5-x layer and the LiF/Al electrode permitted photogenerated carriers in the i-a-Si:H absorber layer to be effectively separated and collected. The effects of the V2O5-x layer thickness and the oxidation states on the photovoltaic performance were investigated in detail. X-ray photoelectron spectroscopy analysis confirmed that the major species of the sputtered V2O5-x thin films were V5+ and V4+. Optimization of the V2O5-x window layer yielded a power conversion efficiency of 7.04%, which was comparable to the power conversion efficiency of a typical a-Si:H solar cell (7.09%). © 2013 AIP Publishing LLC.

[http://dx.doi.org/10.1063/1.4818714]

Conventional a-Si:H solar cells typically have a p-type doped layer/intrinsic absorber layer/n-type doped layer configuration, in which photogenerated holes and electrons in the i-a-Si:H cell are effectively collected in the p-doped and n-doped layers, respectively.1–5 The p-doped and n-doped layers are formed by introducing hazardous doping gases, such as diborane (B2H6) and phosphine (PH3), which require cluster-type bulky deposition systems. The use of these toxic gases poses operational and environmental issues and can increase production costs. Additionally, doping has a detrimental effect on the quality of the i-a-Si:H layers because it leads to the creation of several additional Si dangling bonds that decrease the stabilized solar cell efficiency. These drawbacks of conventional a-Si:H thin film solar cells may be overcome by using a thermally evaporated molybdenum oxide window layer film in an a-Si:H solar cell.6–8 Such layers yield a power conversion efficiency (PCE) of 6.21%, a-Si:H rear Schottky junction solar cells with LiF/Al back electrodes (FTO/MoO3/i-a-Si:H/n-a-Si:H/Al).9 Such layers yield a power conversion efficiency (PCE) of 6.21%. a-Si:H rear Schottky junction solar cells with LiF/Al back electrodes (FTO/MoO3/i-a-Si:H/n-a-Si:H/Al).9 Such layers yield a power conversion efficiency (PCE) of 6.21%. a-Si:H rear Schottky junction solar cells with LiF/Al back electrodes (FTO/MoO3/i-a-Si:H/n-a-Si:H/Al).9 Such layers yield a power conversion efficiency (PCE) of 6.21%. a-Si:H rear Schottky junction solar cells with LiF/Al back electrodes (FTO/MoO3/i-a-Si:H/n-a-Si:H/Al).9 Such layers yield a power conversion efficiency (PCE) of 6.21%. a-Si:H rear Schottky junction solar cells with LiF/Al back electrodes (FTO/MoO3/i-a-Si:H/n-a-Si:H/Al).9

Vanadium pentoxide (V2O5) displays promising properties as a window layer, including a high optical band gap of 2.8 eV, a high work function of 6.85 eV, and good electrical properties.8,13 Accordingly, it has been widely used as a hole-selective layer in organic solar cells.9–13 In our a-Si:H solar cell design, a LiF/Al bilayer was used as a back electrode because it displayed a low work function (2.9 eV),14,15 thereby forming a Schottky junction between the i-a-Si:H and back electrode layers.1 LiF reduced the work function of Al when LiF was coupled to Al due to the large dipole moment of LiF.16 Therefore, a high internal electric field between the V2O5-x layer and the LiF/Al electrode formed, leading to effective charge separation in the i-a-Si:H. Optimizing the V2O5-x window layer produced a PCE of 7.04% with a short circuit current density (Jsc) of 14.17 mA/cm2, an open circuit voltage (Voc) of 0.80 V, and a fill factor (FF) of 0.62.

V2O5-x thin films were deposited on fluorine-doped tin oxide (FTO, SnO2:F) glass substrates using RF magnetron sputtering with a V2O3 target (2 in. diameter, 99.95% purity). Sputtering was carried out in an Ar and O2 gas mixture with a base pressure of 2 × 10−5 Torr and a working pressure of 5 × 10−3 Torr. The O2 gas flow rate ranged from 0 to 0.5 sccm whereas the total flow rate was maintained at 50.0 sccm. The separation distance between the sputtering target and the substrate was 5 cm, and the RF power was maintained at 50 W during sputtering.17 A 500 nm thick i-a-Si:H absorber layer was deposited onto a 100 nm thick FTO glass using plasma-enhanced chemical vapor deposition (PECVD). A 1.5 nm thick LiF layer and a 100 nm thick Al layer were thermally evaporated using a shadow mask to define a cell active area of 0.25 cm2. The optimal LiF layer thickness is 1.5 nm, according to the literature;7 therefore, we did not investigate the effects of the LiF layer thickness on the photovoltaic performance in this work. The current density versus voltage (J-V) characteristics of the solar cell devices were measured under AM 1.5 simulated illumination with an intensity of 100 mW/cm2.

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0003-6951/2013(7)/073903/5/$30.00

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efficiency (EQE) was obtained by using a 200 W Xe lamp and a grating monochromator, and the light intensity was measured using a calibrated Si solar cell (PV measurement). The total transmittance spectra were obtained using a UV-vis spectrophotometer. The cross-sectional microstructures of the devices were observed using transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDX) was used to perform elemental analysis in the spherical aberration-corrected scanning transmission electron microscope (Cs-corrected STEM) mode. X-ray photoelectron spectroscopy (XPS) measurements were performed using a VG Microtech ESCA 2000 with an Al Kα photon source to analyze the chemical composition of the V_2O_5-x surface. Ultraviolet photoelectron spectroscopy (UPS) spectra were recorded using an AXIS-NOVA using a He I (21.22 eV) gas discharge lamp.

Figure 1 shows high-resolution TEM cross-sectional image and an EDX-based elemental mapping of a-Si:H solar cell with a V_2O_5-x window layer and a LiF/Al back electrode. A conformal V_2O_5-x layer with a thickness of 20 nm was deposited onto the textured FTO substrate. Uniform distributions of the component elements were clearly observed (Fig. 1(b)). No evidence of layer-by-layer mixing or physical damage, which could have occurred during the PECVD and thermal evaporation steps, was observed.

Figure 2 shows the J-V characteristics of our a-Si:H solar cells as a function of V_2O_5-x thickness sputtered under Ar ambient. In the device with no window layers (FTO/i-a-Si:H/LiF/Al), reasonable photovoltaic effects were observed with a J_sc of 11.93 mA/cm²; however, the V_oc and FF were poor, at 0.21 V and 0.35, resulting in a PCE of only 0.87%. The poor photovoltaic performance of the device arose from the absence of a built-in potential in the solar cell. The insertion of a sputtered V_2O_5-x window layer between the FTO and i-a-Si:H layers significantly improved the device performance (Fig. 2(b)). The J_sc clearly decreased with the thickness of the V_2O_5-x layer due to light absorption in the window layer. The device performance improvements, however, were mainly attributed to an increase in V_oc with increasing V_2O_5-x window layer thickness (Fig. 2(b)). The device with a 20 nm thick V_2O_5-x window layer exhibited the highest PCE of 6.32%, with a J_sc = 13.54 mA/cm², a V_oc = 0.75 V, and an FF = 0.62.

The ambient O_2 concentration during the sputtering step was critical for controlling the stoichiometry of the metal oxide. The metal-rich film can usually form under ambient Ar,
and a stoichiometric film can be obtained upon the addition of O₂. It should be noted that the films sputtered under 0.5 sccm O₂ and 49.5 sccm Ar appeared as transparent light yellow films, characteristic of vanadium pentoxide, whereas the films exhibited a light grey color when deposited under pure ambient Ar. The visual appearance agreed well with the total transmittance spectra (Fig. 3(a)). The 20 nm thick V₂O₅₋ₓ film sputtered under 0.5 sccm O₂ and 49.5 sccm Ar provided a much higher transparency, whereas the film sputtered under an Ar atmosphere provided a lower transmittance. The high transmittance of the V₂O₅₋ₓ window layer increased the Jsc for a given window layer thickness (Fig. 3(b) and Table I). In addition to increasing Jsc, Voc was also enhanced by adding small amounts of O₂ gas during the V₂O₅₋ₓ sputtering process. The solar cell with the best performance, that is, the device with a 20 nm V₂O₅₋ₓ layer sputtered under 0.5 sccm O₂ and 49.5 sccm Ar, exhibited a PCE of 7.04% with a Jsc = 14.17 mA/cm², a Voc = 0.80 V, and a FF = 0.62. The improvement in Voc was mainly attributed to an enhancement in the internal electric field between the V₂O₅₋ₓ layer and the LiF/Al electrode due to an increase in the work function of the V₂O₅₋ₓ sputtered in the presence of O₂, as confirmed by the UPS spectra. The performance of the optimized a-Si:H solar cell was comparable to that of a typical p-i-n a-Si:H solar cell (PCE = 7.09%, Jsc = 12.38 mA/cm², Voc = 0.79 V, and FF = 0.73), where the i-a-Si:H layer was prepared according to the same protocol as was used for preparing doping-free devices.

Analysis of microelectronic and photonic structure device simulation program in one-dimension (wxAMPS-1D) was used for a numerical modeling of 12 nm thick p-a-Si:H/500 nm thick i-a-Si:H/25 nm thick n-a-Si:H configuration. The input parameters for a device modeling was obtained from the literature (Table II). To obtain the best matched simulation results with our experimental data for p-i-n configuration, the reflection ratio has been considered as 0.25 at front contact. Graded buffer layer has been simulated by two undoped a-Si:H layers with equal thickness (2 nm), with variable band gaps (Eg = 1.75 eV and 1.72 eV, respectively). The band gap profile and characteristic energy were also decreased gradually from the wide band gap p-a-Si:H layer (Eg = 1.78 eV) towards the lower band gap of i-a-Si:H layer (Eg = 1.72 eV) and n-a-Si:H layer (Eg = 1.72 eV). As seen in Fig. 3(b) and Table II, the best matched simulation results have the PCE of 7.03%, with a Jsc = 12.20 mA/cm², a Voc = 0.79 V, and an FF = 0.73, which correspond very well the experimental one.

Compared to the p-i-n configuration, doping-free a-Si:H solar cell exhibited lower FF (0.62, versus 0.73 for the p-i-n configuration). This is attributed to an increase in the series resistance of the device.

### Table I. Photovoltaic parameters and dark current fitting results for the a-Si:H solar cells with different window layers. For comparison, the device parameters of conventional p-i-n type a-Si:H solar cells are also presented.

<table>
<thead>
<tr>
<th></th>
<th>PCE (%)</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>Shunt resistance (kΩ·cm²)</th>
<th>Series resistance (Ω·cm²)</th>
</tr>
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<tr>
<td>FTO/ι-Si:H/LiF/Al</td>
<td>0.87</td>
<td>11.93</td>
<td>0.21</td>
<td>0.35</td>
<td>27.5</td>
<td>1185.0</td>
</tr>
<tr>
<td>FTO/V₂O₅₋ₓ (20 nm)/ι-a-Si:H/LiF/Al</td>
<td>6.32</td>
<td>13.54</td>
<td>0.75</td>
<td>0.62</td>
<td>9129.9</td>
<td>54.2</td>
</tr>
<tr>
<td>FTO/V₂O₅₋ₓ (20 nm)/ι-a-Si:H/LiF/Al</td>
<td>7.04</td>
<td>14.17</td>
<td>0.80</td>
<td>0.62</td>
<td>6215.9</td>
<td>41.6</td>
</tr>
<tr>
<td>FTO/p-a-Si:H (12 nm)/ι-a-Si:H/n-a-Si:H (25 nm)/Ag</td>
<td>7.09</td>
<td>12.38</td>
<td>0.79</td>
<td>0.73</td>
<td>3408.0</td>
<td>11.5</td>
</tr>
</tbody>
</table>

FIG. 3. (a) Total transmittance of the 20 nm thick sputtered V₂O₅₋ₓ thin films prepared in the presence of different O₂ flow rates. (b) Illuminated J–V characteristics, (c) EQE, and (d) dark J–V characteristics of the doped layer-free a-Si:H solar cell prepared with different O₂ flow rates.
resistance values. The FF (therefore, the PCE) may potentially be further enhanced by introducing a continuous vacuum system over the V$_2$O$_{5-x}$ window layer sputtering process and the i-a-Si:H layer PECVD process. However, the doping-free solar cell displayed higher values of $J_{sc}$ (14.17 mA/cm$^2$) than were observed for the p-i-n configuration (12.38 mA/cm$^2$). The improvements in $J_{sc}$ were mainly attributed to the enhanced QE in the short wavelength region due to the wide band gap properties of the V$_2$O$_{5-x}$ film, as shown in Fig. 3(c). Wide optical band gap properties are very useful in the window layers of a-Si:H solar cells. A wide band gap provides a high transparency, which is beneficial for tandem solar cells, because the thickness of the top a-Si:H solar cell can be reduced. This approach can improve the stable efficiency of a tandem solar cell. Figure 3(d) compares the dark currents of the doping-free a-Si:H solar cell to the corresponding currents of a conventional p-i-n-type a-Si:H solar cell. Table I also presents the shunt resistance and series resistance, determined from the data fitting. The series resistance of the doping-free a-Si:H solar cell exceeded that of the conventional p-i-n-type a-Si:H solar cell, indicating a lower FF in the doping-free a-Si:H solar cell. The FF and $V_{oc}$ in our a-Si:H solar cell may potentially be further improved by implementing a continuous vacuum system over the V$_2$O$_{5-x}$ sputtering and i-a-Si:H PECVD processes. The V$_2$O$_{5-x}$ film in our study displayed a lower work function than the value reported previously.

The XPS core level spectra of V$_2$O$_{5-x}$ deposited under different sputtering conditions are displayed in Figs. 4(a) and 4(b). The spin-orbit split 2p$_{3/2}$ and 2p$_{1/2}$ peaks were observed together with the O1s line in the experimental spectrum. Charge accumulation effects in all XPS spectra were calibrated with reference to the O1s (VO$_x$) peak at 530.0 eV. The binding energy (BE) of the V2p level increased with the oxidation state of the V cation. The oxidation states of the V and O species were determined using a peak deconvolution process, and the background was subtracted using a Shirley model. The major species of the sputtered vanadium oxide thin films were found to be V$^{5+}$ and V$^{4+}$. The V 2p$_{3/2}$ XPS spectra were deconvoluted into V$^{5+}$ (517.1–517.2 eV) and V$^{4+}$ (515.8–516.0 eV). The assigned binding energies of the V 2p$_{3/2}$ peaks, which were characterized by different chemical environments, agreed well with the values reported previously. The oxidation states of the V$_2$O$_4.53$ deposited under an Ar atmosphere were: 47% V$^{5+}$ and 53% V$^{4+}$. The V$^{5+}$ content increased to 73% upon the addition of 0.5 sccm O$_2$. The net stoichiometries of the sputter-deposited vanadium oxide films were determined to be V$_2$O$_{4.53}$ and V$_2$O$_{4.73}$, respectively. The higher oxidation states were related to the higher work functions of the vanadium oxide films. The work functions of the V$_2$O$_4.53$ and V$_2$O$_4.73$ films were measured to be 5.74 and 5.78 eV, respectively. The higher work function of the V$_2$O$_4.73$ thin film deposited under 0.5 sccm O$_2$ and 49.5 sccm Ar led to a high $V_{oc}$ of 0.80 V.

In summary, we developed a doped layer-free a-Si:H solar cell architecture including a V$_2$O$_{5-x}$ window layer/i-a-Si:H absorber layer/LiF/Al back electrode. The large difference between the work functions of the V$_2$O$_{5-x}$ layer and the LiF/Al electrode resulted in effective separation between the photogenerated carriers in the i-a-Si:H due to the establishment of a strong internal electric field. The effective separation resulted in a high $V_{oc}$ of 0.80 V. Furthermore, the wide band gap properties of V$_2$O$_{5-x}$ increased the quantum efficiency of the solar cell.

<table>
<thead>
<tr>
<th>Parameters used in the simulation</th>
<th>Device performance</th>
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<tr>
<td>p-a-Si:H midgap DOS (cm$^{-3}$)</td>
<td>Buffer layer midgap DOS (cm$^{-3}$)</td>
</tr>
<tr>
<td>3.2 × 10$^{18}$</td>
<td>2.0 × 10$^{19}$</td>
</tr>
<tr>
<td>8.0 × 10$^{18}$</td>
<td>7.03</td>
</tr>
<tr>
<td>3.0 × 10$^{19}$</td>
<td>5.58</td>
</tr>
</tbody>
</table>

FIG. 4. XPS spectra of the V2p region for a V$_2$O$_{5-x}$ layer deposited under (a) 50 sccm Ar, (b) 49.5 sccm Ar, and 0.5 sccm O$_2$. The black dotted lines and green solid lines indicate the experimental data and Shirley backgrounds, respectively. Red lines indicate the fitting envelope, with blue and pink lines representing the V$^{5+}$ and V$^{4+}$ contributions.
efficiency in the short wavelength region relative to the efficiency of a conventional p-i-n-type a-Si:H solar cell. Optimization of the V_{2}O_{5-x} window layer yielded a PCE of 7.04%, which was comparable to the value typical of a-Si:H solar cells (PCE = 7.09%).