

Nb2O5 hole blocking layer for hysteresis-free perovskite solar cells

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A B S T R A C T

Perovskite solar cells have attracted attention due to their high conversion efficiency and low cost. In this work, Nb2O5 is used as an alternative compact hole blocking layer in conjunction with mesoporous TiO2 and CH3NH3PbI3 in perovskite solar cells. The influence of Nb2O5 layer thickness was studied and it was found to strongly influence the J-V hysteresis of the cells. Devices constructed with 50 nm Nb2O5 have small or undetectable hysteresis, which becomes detectable and increases with increasing Nb2O5 layer thickness. For the best device, energy conversion efficiency of up to 12%, short-circuit currents of 17 mA/cm² and fill factors of 74% were found. These parameters are comparable to the best performance of similar devices where the compact layer is TiO2. In addition, the use of Nb2O5 improved the stability of the solar cells under illumination. These improvements are attributed to a better extraction of photogenerated electrons in the perovskite layer.

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1. Introduction

Conversion efficiencies of perovskite solar cells (PSCs) have risen from 3% to more than 21% in just a few years [1], putting them in direct competition with Si solar cells, whose best commercial cells have an efficiency between 21% and 22% [2].

Since PSCs are a new class of photovoltaic material, several questions concerning their working principle, optimization and stability need to be addressed. Many different architectures have been proposed as planar, [3] mesoscopic, [4] and meso–superstructured solar cells [5], and in general they are composed by a hole-blocking layer (HBL), the perovskite CH3NH3PbI3 (X=I, Cl, Br) layer and a hole-transporting layer (HTL). HBL and HTL have the role to selectively and efficiently extract charge carriers from the perovskite semiconductor [6]. Most of the studies so far are focused either on the perovskite absorber or on the HTL, while the HBL are less studied. [7–10] Different materials have been used as HBL, the most common are compact oxides layers such as TiO2, [11,12] but also organic materials such as PCBM were studied [13]. Nb2O5 is a promising material because of its similar electronic properties to TiO2 (band gap and charge transfer kinetics) and due to its better chemical stability. Nb2O5 is a transparent, air-stable and water-insoluble material with extensive polymorphism. Tuning of the band gap of niobium oxides is possible by changing stoichiometry and crystallinity [14,15]. The conduction band (CB) is composed mainly by unoccupied Nb5+ 4o-orbitals and it is 0.2–0.4 eV below the CB in TiO2 [16,17]. Very recently, Miyasaka et al. reported the use of Nb2O5 as HBL in PSC, however, the results showed lower power conversion efficiency compared to analogous devices using TiO2 [18].

Although PSCs have high conversion efficiency, one of its characteristic that needs attention is the J-V hysteresis with respect to scan direction, which is commonly reported [19]. Currently, the hysteresis has been tentatively attributed to various factors like ion migration, dynamic charge trapping and detrapping and charge accumulation at the interface [20]. The connection of charge accumulation with hysteresis has been studied [19,21,22] in PSC. Charge accumulation are caused mainly by unbalanced photogenerated charge extraction. In the cathode, holes are well extracted by the HTL, due to the high hole conductivity of the materials used, typically 2,2'-7,7'-Tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiroOMeTAD). However, it is known that the electron transfer between the perovskite and the anode (TiO2) is more challenging. The use of mesoporous TiO2 offers a partial solution. It lowers the contact resistance for forward electron transfer with respect to flat TiO2 due its higher surface, reducing the hysteresis [20,21,23]. Another solution makes use of planar PCBM ([6,6]-phenyl-C61-butyric acid methyl ester) substituting TiO2, resulting in lower J-V hysteresis...
due the higher conductivity of PCBM [19]. However, PCBM has a higher cost which is not ideal for large scale production of PSCs.

In this work we have reduced the J-V hysteresis in mesoscopic CH$_3$NH$_3$PbI$_3$ PSCs using a Nb$_2$O$_5$ compact layer in association with mesoporous TiO$_2$. In this system, Nb$_2$O$_5$ is used to enhance electron extraction and to block holes from reaching the FTO anode.

2. Experimental

PSCs were constructed in the following configuration: FTO/compact Nb$_2$O$_5$/mesoporous TiO$_2$/CH$_3$NH$_3$PbI$_3$/Spiro-OMeTAD/Au. Nb$_2$O$_5$ films were obtained by reactive magnetron sputtering using a metallic 3\textdegree{} diameter Nb target (99.9% purity) in a Kurt J Lesker System I. The deposition temperature was 550 °C, while the chamber pressure, argon and oxygen flow were kept at 5.0 × 10$^{-3}$ Torr, 40 sccm and 8 sccm respectively. Films thicknesses were controlled using different deposition times, 8, 15, 30 and 40 min and determined by profilometry (Ambios XP1). UV-vis measurements were performed using a Varian Cary 50 UV-vis spectrophotometer and the optical band gap of the Nb$_2$O$_5$ films was estimated from the optical absorption coefficients using Tauc’s Plot. The other layers were prepared following standard procedures [4]. In short, the TiO$_2$ mesoporous layer was deposited on top of the compact Nb$_2$O$_5$ by spin-coating using a commercial paste from Solaronix (Ti-Nanoxide Ti/SP) diluted in anhydrous ethanol (1:3.5). A two-step deposition technique was used to synthetize the perovskite films [4]. Spiro-OMeTAD was deposited on top of the perovskite film. Finally, the gold cathode was thermally evaporated through a shadow mask defining the solar cell active area of about 0.34 cm$^2$. The FEG-VP Zeiss Supra 35 model was used for the FE-SEM (high resolution field emission scanning electron microscopy) cross section measurements. X-ray diffraction (XRD) was obtained using a Rigaku/RINT2000 from 10° to 50°. Current-voltage (I-V) characteristic were measured using a Keithley 2400 source/measure unit in the dark and under simulated AM 1.5G illumination. Current-voltage and J-V curves were estimated the resistance ($R_s$) of the devices was found to be ~340 Ω, while for the 220 nm devices it was found to be ~450 Ω. Thus the higher $R_s$ in the thick HBL based devices is responsible for the decrease in electron extraction, which results in charge accumulation and consequently J-V hysteresis [26]. The increase in $R_s$ decreased $J_{sc}$ and $V_{oc}$ as well the conversion efficiency [27,28], see Table 1. We have constructed devices using Nb$_2$O$_5$ layers with thickness lower than 50 nm, however these devices did not work due to shorts caused by pinholes. As already mentioned TiO$_2$ HBL based PSCs always presents hysteresis and the general trend with HBL layer thickness is the same. We attribute the hysteresis dependence to differences in electron extraction, as will be describe in the following.

As explained by Heo et al. [21] it is believed that the non-extracted electrons accumulated at the interface of perovskite/TiO$_2$ causes the hysteresis. In the case of the couple TiO$_2$/mesoporous/Nb$_2$O$_5$ compact, charge accumulation is reduced due the efficient electron transfer from TiO$_2$ to Nb$_2$O$_5$; since Nb$_2$O$_5$ CB layers below TiO$_2$ (see Fig. 1c). In addition, analyzing Fig. 1c it is clear that Nb$_2$O$_5$ is a better hole-blocking material than TiO$_2$ due to its lower valance band [18], which also favors electron extraction in this electrode.

The better electron extraction induced by the Nb$_2$O$_5$ compact layer does also influence the device stability. Fig. 4 shows a sequence of J-V measurements performed in air, under illumination, for both HBLs used, Nb$_2$O$_5$ and TiO$_2$. As can be seen the Nb$_2$O$_5$ based devices have higher stability compared to TiO$_2$ devices, even after twenty measurements, and independent of the scan direction.

This higher stability can be explained by the better electron extraction. Recently Bryant et al. [29] showed that the main cause of the perovskite degradation is oxygen rather than moisture. They found that molecular oxygen in presence of an excess of electrons produces O$_2^-$ species resulting in fast degradation of the CH$_3$NH$_3$PbI$_3$ [30]. Previously, Kelly et al. [31] showed that ZnO induces a fast degradation of the perovskite. ZnO is known to have a negatively charged surface which induces acid-base reaction between CH$_3$NH$_3$PbI$_3$ and ZnO$^-$ originating Zn-OH, PbI$_2$ and CH$_3$NH$_2$. This reaction is driven by deprotonation of CH$_3$NH$_3^+$ due the excess of electrons present at the ZnO surface.

Based on this, we propose that the same degradation mechanism occurs in our system depending on the density of accumulated electrons at the interface oxide/perovskite. In other words, in the specific case of Fig. 4, as discussed previously, the use of Nb$_2$O$_5$ increases the photogenerated electron extraction from
the oxide/perovskite interface thus hindering the device degradation. Despite Nb$_2$O$_5$ based devices showed an improvement in the stability, it is far from the lifetime of up to 25 years guaranteed by most manufacturers for Si based devices. Thus, a better understanding of the degradation mechanism is necessary to achieve a stability comparable to that one found in Si based devices [32]. Further investigations are ongoing in order to investigate the long term stability of these devices.

4. Conclusions

Nb$_2$O$_5$ have been successfully used as HBL in PSC, with comparable efficiency with TiO$_2$ HBL based devices. Our results show

Table 1

<table>
<thead>
<tr>
<th>HBL thickness</th>
<th>Scan</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
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<tr>
<td>50 nm</td>
<td>Reverse</td>
<td>924</td>
<td>17.9</td>
<td>74</td>
<td>12.3</td>
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<td></td>
<td>Forward</td>
<td>93</td>
<td>17.8</td>
<td>73</td>
<td>12.2</td>
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<tr>
<td>70 nm</td>
<td>Reverse</td>
<td>881</td>
<td>17.4</td>
<td>72</td>
<td>11.1</td>
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<tr>
<td></td>
<td>Forward</td>
<td>886</td>
<td>16.9</td>
<td>70</td>
<td>10.5</td>
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<tr>
<td>110 nm</td>
<td>Reverse</td>
<td>872</td>
<td>16.9</td>
<td>72</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>Forward</td>
<td>876</td>
<td>15.6</td>
<td>70</td>
<td>9.7</td>
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<tr>
<td>220 nm</td>
<td>Reverse</td>
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<td>15.3</td>
<td>75</td>
<td>9.6</td>
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<tr>
<td></td>
<td>Forward</td>
<td>850</td>
<td>13.8</td>
<td>68</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Fig. 1. (a) XRD of CH$_3$NH$_3$PbI$_3$ and Nb$_2$O$_5$ (b) FE-SEM cross-section image of the device (c) energy band diagram.

Fig. 2. $J$-$V$ curves in the dark and under AM 1.5G illumination of solar cells with different Nb$_2$O$_5$ layer thicknesses: 50 nm and 220 nm.

Fig. 3. Difference between the conversion efficiency in the reverse and forward scan as a function of HBL thickness. The size of the symbols represents the measurement uncertainties.
that the use of a thin Nb2O5 compact layers in combination with mesoporous TiO2 can result in PSC with small or undetectable hysteresis and improved solar cells short term stability due a better photogenerated electron extraction.

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References


