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journal homepage: [www.elsevier.com/locate/matlet](http://www.elsevier.com/locate/matlet)Nb<sub>2</sub>O<sub>5</sub> hole blocking layer for hysteresis-free perovskite solar cells

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## ABSTRACT

Perovskite solar cells have attracted attention due its high conversion efficiency and low cost. In this work, Nb<sub>2</sub>O<sub>5</sub> is used as an alternative compact hole blocking layer in conjunction with mesoporous TiO<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> in perovskite solar cells. The influence of Nb<sub>2</sub>O<sub>5</sub> layer thickness was studied and it was found to strongly influence the *J*-*V* hysteresis of the cells. Devices constructed with 50 nm Nb<sub>2</sub>O<sub>5</sub> have small or undetectable hysteresis, which becomes detectable and increases with increasing Nb<sub>2</sub>O<sub>5</sub> layer thickness. For the best device, energy conversion efficiency of up to 12%, short-circuit currents of 17 mA/cm<sup>2</sup> and fill factors of 74% were found. These parameters are comparable to the best performance of similar devices where the compact layer is TiO<sub>2</sub>. In addition, the use of Nb<sub>2</sub>O<sub>5</sub> improved the stability of the solar cells under illumination. These improvements are attributed to a better extraction of photo-generated 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 PSC are a new class of photovoltaic materials, 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-super-structured solar cells [5], and in general they are composed by a hole-blocking layer (HBL), the perovskite CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub> (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 TiO<sub>2</sub>, [11,12] but also organic materials such as PCBM were studied [13]. Nb<sub>2</sub>O<sub>5</sub> is a promising material because of its similar electronic properties to TiO<sub>2</sub> (band gap and charge transfer kinetics) and due to its better chemical stability. Nb<sub>2</sub>O<sub>5</sub> 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 Nb<sup>5+</sup> 4*d*-orbitals and it is 0.2–0.4 eV below the CB in TiO<sub>2</sub> [16,17]. Very recently, Miyasaka et al. reported the use of Nb<sub>2</sub>O<sub>5</sub> as HBL in PSC, however, the results showed lower power conversion efficiency compared to analogous devices using TiO<sub>2</sub> [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 PSCs 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*-dimethoxyphenylamine)-9,9'-spirobifluorene (spiroOMeTAD). However, it is known that the electron transfer between the perovskite and the anode (TiO<sub>2</sub>) is more challenging. The use of mesoporous TiO<sub>2</sub> offers a partial solution. It lowers the contact resistance for forward electron transfer with respect to flat TiO<sub>2</sub> 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 TiO<sub>2</sub>, resulting in lower *J*-*V* hysteresis

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due the higher conductivity of PCBM [19]. However, PCBM has a higher cost which is not ideal for large scale production of PSC.

In this work we have reduced the *J-V* hysteresis in mesoscopic  $\text{CH}_3\text{NH}_3\text{PbI}_3$  PSCs using a  $\text{Nb}_2\text{O}_5$  compact layer in association with mesoporous  $\text{TiO}_2$ . In this system,  $\text{Nb}_2\text{O}_5$  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  $\text{Nb}_2\text{O}_5$ /mesoporous  $\text{TiO}_2$ / $\text{CH}_3\text{NH}_3\text{PbI}_3$ /Spiro-OMeTAD/Au.  $\text{Nb}_2\text{O}_5$  films were obtained by reactive magnetron sputtering using a metallic 3" 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  $5.0 \times 10^{-3}$  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  $\text{Nb}_2\text{O}_5$  films was estimated from the optical absorption coefficients using Tauc's Plot. The other layers were prepared following standard procedures [4]. In short, the  $\text{TiO}_2$  mesoporous layer was deposited on top of the compact  $\text{Nb}_2\text{O}_5$  by spin-coating using a commercial paste from Solaronix (Ti-Nanoxide T/SP) diluted in anhydrous ethanol (1:3.5). A two-step deposition technique was used to synthesize 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<sup>2</sup>. 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 solar irradiation of 100 mW cm<sup>-2</sup> from a calibrated solar simulator (Spectra-Nova). The voltage sweep rate used was 5mV/s for all measurements. For comparison, solar cells with a dense  $\text{TiO}_2$  layer was deposited by sputtering at 300 °C using 20 sccm of argon flow and 20% of oxygen flow and a chamber pressure of  $4.0 \times 10^{-3}$  Torr. The film thickness was controlled using different depositions time, analogous to the  $\text{Nb}_2\text{O}_5$  deposition.

## 3. Results and discussion

A transparent, homogeneous and flat  $\text{Nb}_2\text{O}_5$  film was obtained. The  $\text{Nb}_2\text{O}_5$  phase (JCPDS number 28-317) was confirmed by X-ray diffraction as shown in Fig. 1a. Cross section FE-SEM (Fig. 1b) and AFM images showed a homogeneous dense film; from AFM a root-mean-square (RMS) surface roughness of 2 nm was found. The thicknesses were measured by profilometry and found to be 50, 70, 110 and 220 nm for the different deposition times (8, 15, 30 and 40 min, respectively). UV–vis measurements confirmed the transparency of the films; for 50 and 70 nm thick  $\text{Nb}_2\text{O}_5$  films the transmittance is close to 100% and for 110 and 220 nm it is close to 90%. The optical band gap of the  $\text{Nb}_2\text{O}_5$  was found to be ~3.4 eV. Fig. 1a also shows the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  diffractions.

In Fig. 2 the *J-V* curves in the dark and under AM 1.5G illumination of the PSCs using two different  $\text{Nb}_2\text{O}_5$  thicknesses are shown. The relevant parameters are summarized in Table 1 for all devices studied. The  $\text{Nb}_2\text{O}_5$  based PSC gave conversion efficiencies ( $\eta$ ) > 12%, short circuit current ( $J_{sc}$ ) > 17 mA/cm<sup>2</sup>, open circuit voltage ( $V_{oc}$ ) > 0.9 V and a fill factor (*FF*) of 74%. As shown in a recent review [24] where the best performances found in different

technologies are presented, perovskites solar cells contrary to mature technologies like silicon based photovoltaics have still space to improve.

A solar cell with a 50 nm thin  $\text{Nb}_2\text{O}_5$  compact layer has no apparent hysteresis, contrary to the one with the 220 nm thick  $\text{Nb}_2\text{O}_5$  compact layer (Fig. 2). PSCs employing  $\text{TiO}_2$  as HBL with analogous thicknesses to the  $\text{Nb}_2\text{O}_5$  have lower performances compared to  $\text{Nb}_2\text{O}_5$  and the higher  $\eta$  obtained was 11%. More importantly as expected from the literature, the *J-V* hysteresis is observed in  $\text{TiO}_2$  HBL based devices at all thicknesses studied, as shown in Fig. 3.

Fig. 3 shows the difference in conversion efficiency ( $\eta$ ) between the two scanning directions of the solar cells as a function of the HBL thickness. We are using this difference as indicator of the hysteresis strength. As can be seen, the only hysteresis-free device is the one with HBL of 50 nm  $\text{Nb}_2\text{O}_5$ .

In a first approximation, the perovskite layer has balanced electron and hole transporting behavior. [25] Thus, when the photogenerated electrons and holes are equally collected, there is no charge accumulation and no hysteresis. From the maximum power point of the *J-V* curves we estimated the resistance ( $R_s$ ) of the 50 nm  $\text{Nb}_2\text{O}_5$  based devices 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  $\text{Nb}_2\text{O}_5$  layers with thickness lower than 50 nm, however these devices did not work due to shorts caused by pinholes. As already mentioned  $\text{TiO}_2$  HBL based PSC 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/ $\text{TiO}_2$  causes the hysteresis. In the case of the couple  $\text{TiO}_2$  mesoporous/ $\text{Nb}_2\text{O}_5$  compact, charge accumulation is reduced due the efficient electron transfer from  $\text{TiO}_2$  to  $\text{Nb}_2\text{O}_5$ ; since  $\text{Nb}_2\text{O}_5$  CB lays below  $\text{TiO}_2$  (see Fig. 1c). In addition, analyzing Fig. 1c it is clear that  $\text{Nb}_2\text{O}_5$  is a better hole-blocking material than  $\text{TiO}_2$  due to its lower valance band [18], which also favors electron extraction in this electrode.

The better electron extraction induced by the  $\text{Nb}_2\text{O}_5$  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,  $\text{Nb}_2\text{O}_5$  and  $\text{TiO}_2$ . As can be seen the  $\text{Nb}_2\text{O}_5$  based devices have higher stability compared to  $\text{TiO}_2$  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  $\text{O}_2^-$  species resulting in fast degradation of the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  [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  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and  $\text{ZnO}^-$  originating Zn–OH,  $\text{I}^-$ ,  $\text{PbI}_2$  and  $\text{CH}_3\text{NH}_2$ . This reaction is driven by deprotonation of  $\text{CH}_3\text{NH}_3^+$  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  $\text{Nb}_2\text{O}_5$  increases the photogenerated electron extraction from

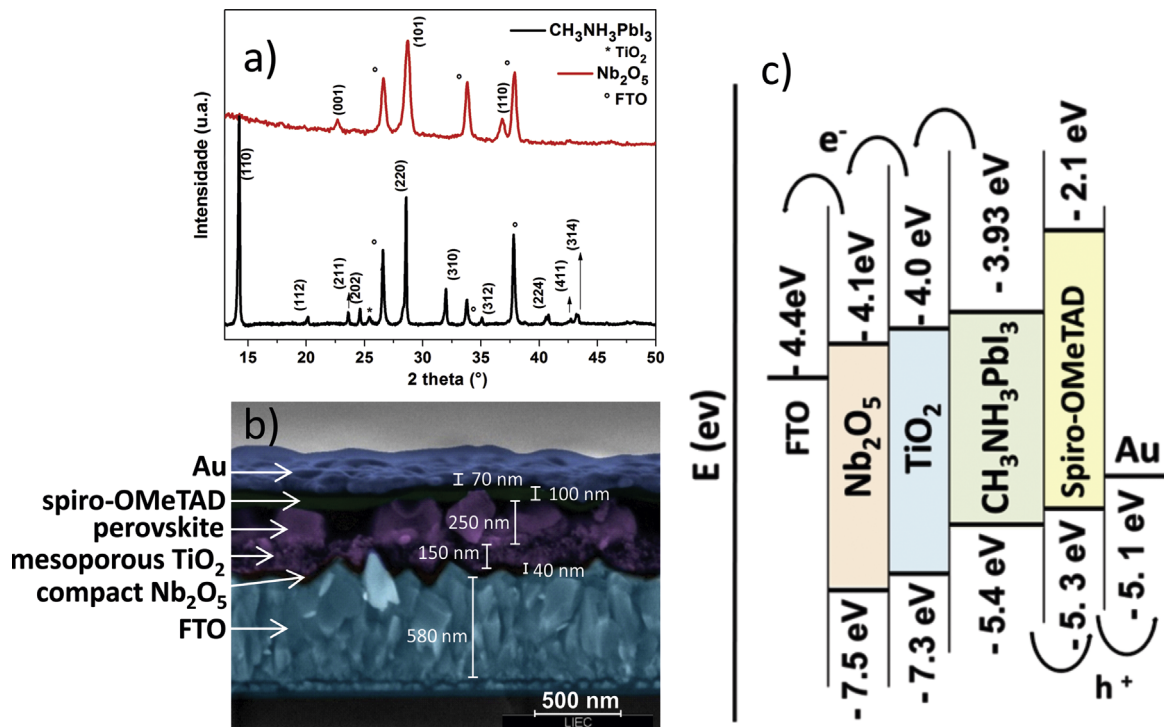


Fig. 1. (a) XRD of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and  $\text{Nb}_2\text{O}_5$  (b) FE-SEM cross-section image of the device (c) energy band diagram.

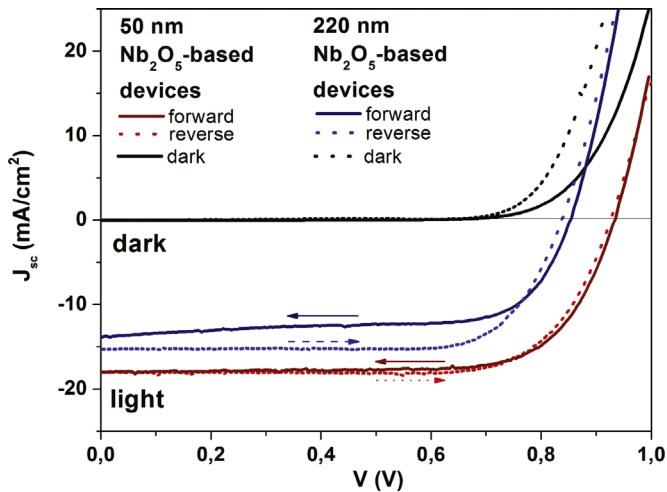


Fig. 2.  $J$ - $V$  curves in the dark and under AM 1.5G illumination of solar cells with different  $\text{Nb}_2\text{O}_5$  layer thicknesses: 50 nm and 220 nm.

Table 1

Photovoltaic parameters obtained from solar cells with different  $\text{Nb}_2\text{O}_5$  layer thickness under AM 1.5G illumination in forward (from short circuit to forward bias) and reverse (from forward bias to short circuit) scan. The numbers correspond to an average value obtained from 8 different cells.

HBL thickness	Scan	$V_{oc}$ (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	$\eta$ (%)
50 nm	Reverse	924	17.9	74	12.3
	Forward	93	17.8	73	12.2
70 nm	Reverse	881	17.4	72	11.1
	Forward	886	16.9	70	10.5
110 nm	Reverse	872	16.9	72	10.7
	Forward	876	15.8	70	9.7
220 nm	Reverse	835	15.3	75	9.6
	Forward	850	13.8	68	8.0

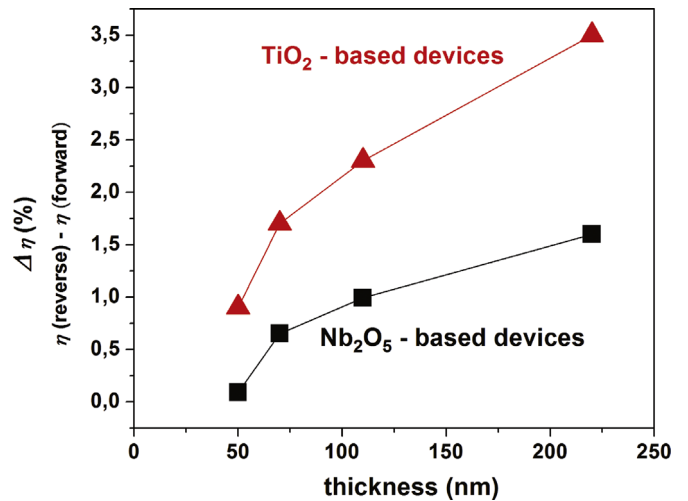


Fig. 3. Difference between the conversion efficiency in the reverse and forward scan as a function of HBL thickness. The size of the symbols represents the measurement uncertainties.

the oxide/perovskite interface thus hindering the device degradation.

Despite  $\text{Nb}_2\text{O}_5$  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

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

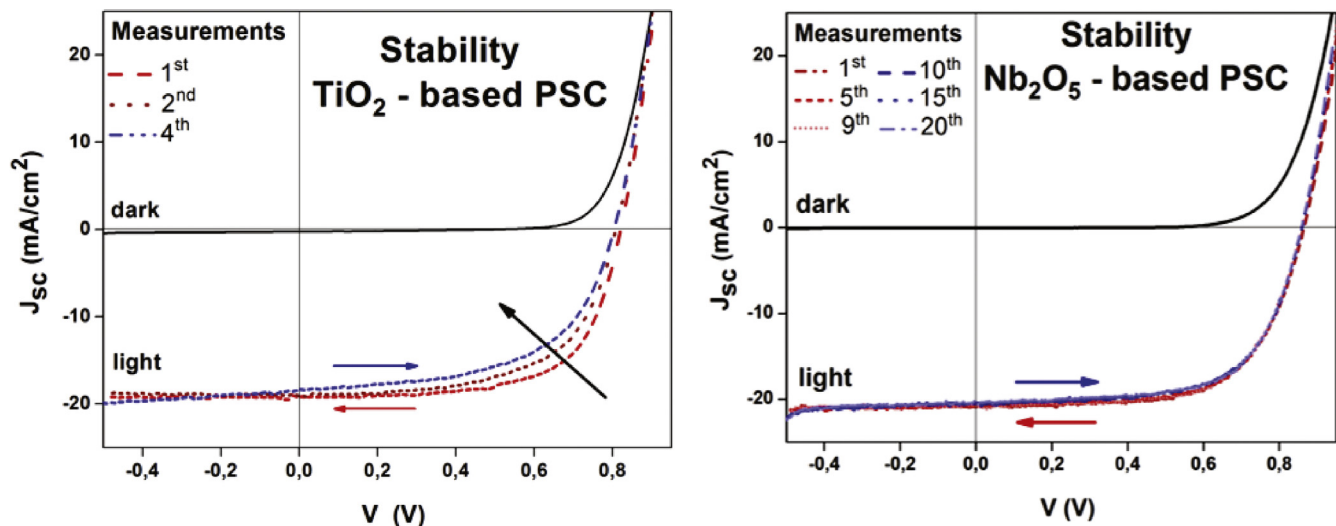


Fig. 4.  $J$ - $V$  curves measured after and increased number of scans for different HBLs (a)  $\text{Nb}_2\text{O}_5$  and (b)  $\text{TiO}_2$ .

that the use of a thin  $\text{Nb}_2\text{O}_5$  compact layers in combination with mesoporous  $\text{TiO}_2$  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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