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Enhancement of photoconversion efficiency in dye-sensitized solar cells exploiting pulsed laser deposited niobium pentoxide blocking layers

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ABSTRACT

Among all the photovoltaic technologies developed so far, dye-sensitized solar cells are considered as a promising alternative to the expensive and environmentally unfriendly crystalline silicon-based solar cells. One of the possible strategies employed to increase their photovoltaic efficiency is to reduce the charge recombination at the cell conductive substrate through the use of a compact blocking layer. In this paper, we report on the fabrication and characterization of dye-sensitized solar cells employing niobium pentoxide (Nb_2O_5) thin film blocking layer deposited through the pulsed laser deposition technique on conductive substrates. The careful selection of the optimal film thickness led to a 30% enhancement of the photoconversion efficiency with respect to reference cells fabricated without blocking layer. Open circuit voltage decay and electrochemical impedance spectroscopy techniques proved that the effective suppression of the charge recombination occurring at the substrate/electrolyte interface represents the main reason for the improvement of the photovoltaic efficiency.

1. Introduction

Dye-sensitized Solar Cells (DSCs), invented by O'Regan and Grätzel in 1991 [1], represent a low-cost alternative to the currently dominating technology in the photovoltaic market, i.e. the silicon-based devices, especially under low-irradiance and diffuse light conditions, like indoor ambient [2]. The core element of a DSC, which is referred to as photoanode, is constituted by a dye-sensitized mesoporous layer of titanium dioxide deposited on a glass slice covered with Fluorine-doped Tin Oxide (FTO). The counter electrode is constituted by another FTO-covered glass on which a thin film of Pt is deposited. All the volume between the two electrodes and inside the pores of TiO_2 layer is filled with an electrolytic solution, composed by the I^-/I_3^- redox shuttle dissolved into an organic liquid solvent [3]. The principle of operation is very simple: incident photons are absorbed by dye molecules, causing the promotions of electrons from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO). Photogenerated electrons are ultrafastly injected into the TiO_2 conduction band (CB). Through a tortuous path across the nanoparticle network, electrons arrive at the front electrode. Traveling along the external circuit, the negative charges reach the counter electrode, where, with the help of the Pt which catalyze the reduction reaction, they are transferred to the electrolytic solution. The final step is the dye regeneration via electron donation from I^-, which is in turn oxidized to I_3^- [4]. However there are two possible recombination pathways for CB electrons which work against the efficient functioning of the DSCs: the first one can occur with oxidized dye molecules, the second one with tri-iodide redox species in the electrolytic solution. Nevertheless, the first process is usually neglected, due to the very high (nearly equal to 100%) regeneration efficiency values of iodine-based electrolytes with a large class of sensitizers [5]. On the other hand, the recombination of CB electrons with the acceptor in the electrolyte (back electron reaction) remains the main loss mechanism in this kind of photovoltaic devices. This phenomenon can occur both at the interface between the TiO_2 and the electrolyte and at the part of the FTO that is uncovered with TiO_2, and it is therefore exposed to the electrolyte (as depicted in Fig. 1a). Different approaches have been exploited to reduce the back electron reaction occurring through the first route: deposition of a sub-nanometer layer of insulating oxide on the mesoporous semiconductor [6], $TiCl_4$ treatment in order to reduce the number of defect sites [7], or use of additives in the electrolytic solution able to saturate the TiO_2 pores that are not covered by dye molecules [8], just to cite some examples. On the other hand, for what concerns the recombination at the FTO/electrolyte interface, the back reaction can be efficiently suppressed by the deposition of a compact blocking layer (BL) of a metal oxide onto the conducting substrate [9]. Nevertheless, detailed studies about this second interface are not as numerous as

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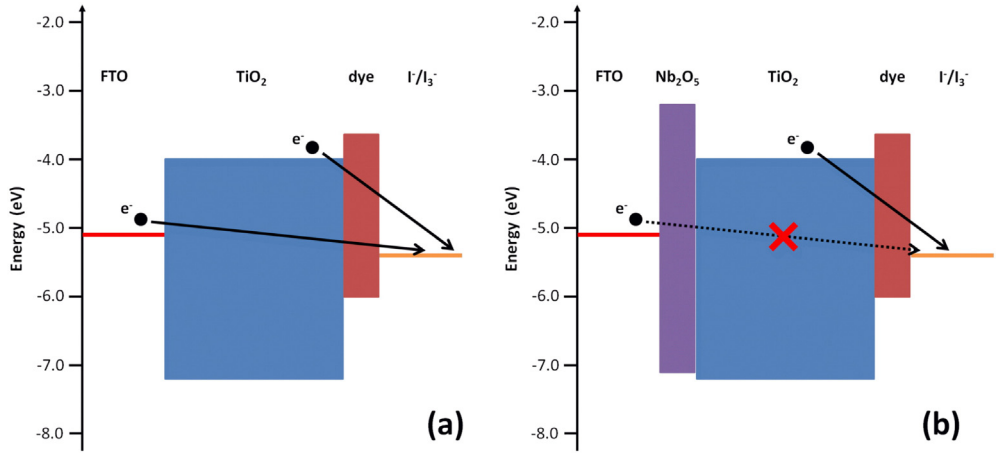

Fig. 1. Simplified energy level diagram for a DSC in absence (a) and in presence (b) of a Nb_2O_5 blocking layer.

the former [10]. Several different materials have been explored so far to this purpose, namely TiO_2 [11], ZnO [12], HfO_2 [13], and SnO_2 [14]. In addition to these, niobium pentoxide has been found to exhibit efficient back reaction suppression ability [15,16]. Nb_2O_5 is a dielectric material with high permittivity ($k \approx 53$) and high energy bandgap (3.3 eV) [17]. Since it presents a good insulating behavior, one would expect that a barrier potential which blocks the back electron reaction can be formed without lowering the conductivity of the injected carriers, thus making Nb_2O_5 very suitable as a blocking layer.

From the literature, the metal oxide films exploited as compact blocking layers have been deposited through different techniques, such as spray pyrolysis [18], spin coating [10], sol–gel [11], sputtering [12], atomic layer deposition (ALD) [13], and electron beam evaporation [19]. Some of these methods (sol–gel, spin coating) do not allow obtaining a uniform coverage of the FTO substrate, while others (ALD) need expensive equipments. On the contrary, pulsed laser deposition (PLD) is a low cost and versatile thin film growth technique, which has already been proven to be an effective route to obtain high quality oxide semiconductors and dielectrics [20–22]. In particular, PLD has already been employed to deposit TiO_2 blocking layers [23], or Nb-doped TiO_2 films, acting as BL and transparent conductive layer at the same time [24].

In this work, we report on the fabrication of Nb_2O_5 thin films by PLD technique and on their effective use as blocking layers in microfluidic-based DSCs [25–27]. The exploitation of pulsed laser-deposited Nb_2O_5 films is expected to reduce the charge recombination occurring at the FTO/electrolyte interface, as illustrated in Fig. 1b. In this way an increment of the electron lifetime values and a subsequent enhancement in the photoconversion efficiencies should be obtained. The morphological and structural characterizations of the deposited films were carried out through field emission scanning electron microscopy and X-ray diffraction techniques, respectively. The photovoltaic performances of the DSCs fabricated with the Nb_2O_5 blocking layer films were evaluated through current–voltage measurements under AM1.5G illumination, and compared with those of cells fabricated without BLs. The recombination properties of the two classes of devices were studied by means of open circuit voltage decay and impedance spectroscopy measurements.

2. Experimental details

2.1. Materials

FTO-covered glasses (7 Ω/□, Solaronix) with area equal to 2×2 cm^2 were used as substrates for the deposition of the Nb_2O_5 thin films and for the fabrication of platinized counter-electrodes. For the morphological and structural characterizations, a Si substrate was inserted in the deposition chamber beside the glass/FTO substrate. Dyesol 18NR-AO paste was employed for the deposition of TiO_2 porous layers. N719 dye (Ruthenizer 535 bis-TBA) and I^-/I_3^--based electrolyte (Iodolyte AN50) were purchased from Solaronix.

2.2. Nb_2O_5 film deposition and characterization

The PLD system employed in this work is described elsewhere [21]. The target (99.9% purity) was a 10 mm diameter, 6 mm-thick, and sintered Nb_2O_5 ceramic disc supplied by Balzers. Before insertion in the deposition chamber, all samples were cleaned with acetone in ultrasonic bath, subsequently rinsed with isopropanol, and then dried up with compressed air. For all samples, PLD was carried out at 400 °C and at 1 Pa oxygen pressure. Table 1 summarizes all the Nb_2O_5 films deposited on both glass/FTO and Si substrates. All the samples differ one from another by the number of laser pulses employed in the deposition, which actually means different thickness of the films.

In order to determine the films' thickness and morphology, Nb_2O_5 films grown on Si substrate were inspected, by means of a ZEISS Auriga dual beam system, with Field Emission Scanning Electron Microscope (FESEM), either in cross section or at a 45° tilt. In order to have a fresh cross section to observe, all the samples were cleaved just before the measurements.

X-ray diffraction (XRD) patterns were acquired on as-deposited films and after an annealing treatment at 525 °C, by using a Panalytical PW3020 equipment in a parallel beam geometry with a fixed X-ray incident angle of $\omega = 1.5°$. The instrument was equipped with a Cu Kα radiation source ($\lambda = 1.54056$ Å).

2.3. Cell fabrication and characterization

A single layer of porous TiO_2 was deposited on top of conductive substrates, with a screen printer equipment (AT-25PA, Atma Champ

Table 1
Number of laser pulses used for growing the Nb_2O_5 films, corresponding thickness of the deposited films evaluated through FESEM analysis, and photovoltaic parameters of the DSCs fabricated exploiting the Nb_2O_5 films as blocking layers (J_{sc} short circuit current density, V_{oc} open circuit voltage, *FF* fill factor, *PCE* photoconversion efficiency). In the first row, sample A is a reference specimen without barrier layer (i.e. bare glass/FTO).

Sample name	Laser pulses	Thickness (nm)	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF*	*PCE* (%)
A	–	–	8.67	0.689	0.70	4.16
B	416	2	10.99	0.698	0.71	5.43
C	744	4	12.42	0.704	0.70	6.15
D	1612	8	11.53	0.697	0.70	5.65
E	2996	21	10.83	0.705	0.73	5.54