

# The Study of Dye Sensitized Solar Cells with Thin HfO<sub>2</sub> Barrier Layers

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## 1. Introduction

In the past decades, titanium dioxide (TiO<sub>2</sub>)-based dye sensitized solar cells (DSSCs), as reported by O'Regan and Grätzel, were considered one of the most promising photovoltaic solar cells [1, 2]. In general, the nanoporous TiO<sub>2</sub> electrode introduces charge recombination, which mainly occurs at the electrode/electrolyte interface because of the absence of the energy barrier layer [3]. Therefore, some coating materials that function as the barrier layer onto the TiO<sub>2</sub> layer were investigated to reduce recombination at the interface and improve the efficiency [4-6]. Among these methods, hafnium oxide (HfO<sub>2</sub>) can effectively passivate the recombination centers on the TiO<sub>2</sub> surface and reduce the recombination rate in DSSCs. The conduction band edge of HfO<sub>2</sub> was more negative than that of the TiO<sub>2</sub>, and thus, the formation of an inherent energy barrier at the electrode/electrolyte interface is expected and provided. This paper presents the fabrication and characterization of DSSCs with hafnium oxide (HfO<sub>2</sub>) barrier layer deposited by the sputtering method. The influence of inserting the HfO<sub>2</sub> barrier layer onto the top of the TiO<sub>2</sub> porous layer on the performance of DSSCs is also discussed.

## 2. Experimental procedure

We first cleaned the ITO glass substrates. The solgel solution of TiO<sub>2</sub> paste includes an 25 nm TiO<sub>2</sub> (P25, Degussa) nanometer powders, an acetic acid, an acetylacetone (pentanedione-2,4), and a surfactant (Triton X-100). Then, the working electrode layer of TiO<sub>2</sub> paste was coated on the ITO glass plates by spincoating methods, subsequently allowed to dry in air, and followed by heat-treatment at 450 °C for 45 min. The thickness of the TiO<sub>2</sub> film was measured at approximately 10 μm. The HfO<sub>2</sub> barrier layers were subsequently deposited on TiO<sub>2</sub> film by using an RF sputtering system to fabricate the TiO<sub>2</sub>/HfO<sub>2</sub> electrodes. The flow rate ratio of O<sub>2</sub> and Ar was regulated at 1:10. The RF power and chamber pressure were controlled at 80 Watt and 5×10<sup>-6</sup> torr, respectively, during the sputtering. The sputtering time of the HfO<sub>2</sub> barrier layers was controlled at 15 min. The fabricated TiO<sub>2</sub>/HfO<sub>2</sub> films were subsequently immersed into a cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium (N719) dye solution and maintained at room temperature for 24 hours to ensure a complete sensitizer uptake. The light-reflected counter electrode was used, which consisted of ITO glass onto which a 5 nm Pt counter electrode was

deposited by an e-gun beam-evaporating system. The counter electrode was placed directly on the top of the N719 dye-coated TiO<sub>2</sub>/HfO<sub>2</sub> film. Both electrodes were clamped tightly together. A thin layer of electrolyte, which consists of a propylene carbonate, a 0.5 M tetrabutylammonium iodide (TBAI), an ethylene carbonate, and a 0.05 M iodine (I<sub>2</sub>) in solvents of acetonitrile, was injected into the gap between the working electrode and counter electrode. For comparison, the standard DSSC with only an N719 dye-coated TiO<sub>2</sub> film (that is, without the HfO<sub>2</sub> layer) was also fabricated. Figure 1 shows the schematic structure of the fabricated N719 DSSC based on TiO<sub>2</sub> with the HfO<sub>2</sub> barrier layer.

## 3. Results and discussion

Figure 2 shows the dark J-V characteristics measured in the 0-1 V forward bias condition. It was observed that the ultra thin HfO<sub>2</sub> barrier layer interface treatment changed the dark J-V behavior of the DSSCs. It was also found that the dark current density of TiO<sub>2</sub>-based DSSCs with HfO<sub>2</sub> barrier layer was smaller than that of TiO<sub>2</sub>-based DSSCs without HfO<sub>2</sub> barrier layer. When a 0 V applied bias was administered, the measured saturation current density of the fabricated DSSCs with HfO<sub>2</sub> barrier layer was 1.25×10<sup>-6</sup> A/cm<sup>2</sup>, while the saturation current density was 7.84×10<sup>-6</sup> A/cm<sup>2</sup> for the DSSCs without HfO<sub>2</sub> barrier layer. This higher saturation current density in low forward bias region denotes large density and activity of the surface states. The insertion of HfO<sub>2</sub> thin layer in DSSCs can generate the smaller particle size and high specific surface area, which results in the large density and activity of the surface states. In other words, because of the large density of surface states, the mesoporous TiO<sub>2</sub> spheres electrode with an HfO<sub>2</sub> barrier layer (Device B) results in enhanced light harvesting and a larger amount of dye loading.

Figure 3 shows the J-V characteristic curves of the fabricated DSSCs with and without the HfO<sub>2</sub> barrier layer. The short circuit current density (J<sub>sc</sub>), open circuit voltage (V<sub>oc</sub>), fill factor (FF), and the light-to-electric energy conversion efficiency (η) of DSSC may be extracted and calculated from Fig. 3, and the corresponding solar cell parameters are summarized in Table I. The TiO<sub>2</sub>-based DSSCs with HfO<sub>2</sub> barrier layer had higher J<sub>sc</sub> and V<sub>oc</sub> than that of TiO<sub>2</sub>-based DSSCs without HfO<sub>2</sub> barrier layer. The increased short-circuit current density may attest to the reduction of the interfacial resistance, which resulted from the large

density and activity of the surface states. In addition, the little increased open-circuit voltage can be attributed to the decrease of series and shunt resistance by the thin HfO<sub>2</sub> layer. Furthermore, the light-to-electric energy conversion efficiency ( $\eta$ ) of TiO<sub>2</sub>-based DSSCs with HfO<sub>2</sub> barrier layer was improved from 2.2% to 3.4%. This 54.5% efficiency enhancement in the DSSC was attributed to the HfO<sub>2</sub> barrier layer, which was used as a hole collector to improve the contact between the dye and the TiO<sub>2</sub> layer, and therefore, optimal charge separation. This indicates that the efficiency of a DSSC with the HfO<sub>2</sub> barrier layer can be improved.

#### 4. Conclusions

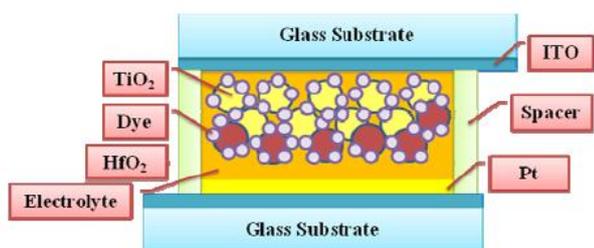
Dye-sensitized solar cells (DSSCs) with a sputtered HfO<sub>2</sub> barrier layer were successfully fabricated and investigated. With the HfO<sub>2</sub> barrier layer, the efficiency of the TiO<sub>2</sub>-based DSSC was improved from 2.2% to 3.4%. The efficiency of 3.4% with a  $J_{sc}$  of 8.94 mA/cm<sup>2</sup>, a  $V_{oc}$  of 0.72 V, and an FF of 53.3% was achieved by using the HfO<sub>2</sub> barrier and hole collector, which resulted in enhanced light harvesting and a larger.

#### 5. Acknowledgments

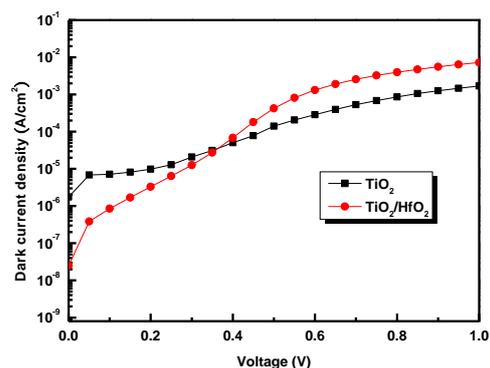
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#### 6. References

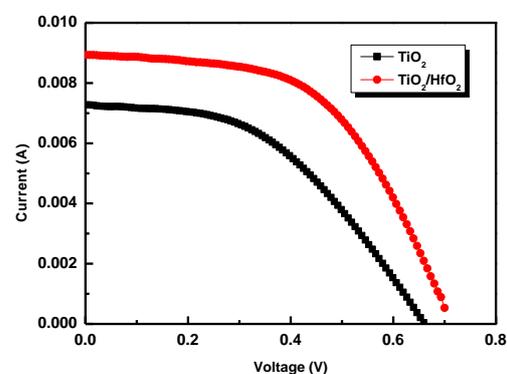
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**Fig.1** Schematic representation of the structure of fabricated DSSCs with HfO<sub>2</sub> barrier layer on mesoporous TiO<sub>2</sub> photoelectrode.



**Fig. 2** The dark current-voltage characteristics of the two kinds of DSSCs with and without HfO<sub>2</sub> barrier layer.



**Fig. 3** The photocurrent density-voltage characteristics of the two kinds of DSSCs with and without HfO<sub>2</sub> barrier layer.

**Table 1** List of the measured parameters for the DSSCs fabricated with and without HfO<sub>2</sub> barrier layer on mesoporous TiO<sub>2</sub> photoelectrode.

Device	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF (%)	$\eta$ (%)
Device A (TiO <sub>2</sub> )	7.27	0.66	46.3%	2.2%
Device B (TiO <sub>2</sub> /HfO <sub>2</sub> )	8.94	0.72	53.3%	3.4%