

One-dimensional TiO₂ by electrochemical anodization of DC sputtered Ti films

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In the present work, we have deposited titanium (Ti) thin films on FTO substrates by DC magnetron sputtering and subsequently formed nanoporous titanium dioxide (TiO₂) via electrochemical anodization of Ti films. The anodization was performed at different voltages ranging from 10 to 40 V in the electrolyte (NH₄F/H₂O/ethylene glycol). The nanopores with pore diameter of around 40–60 nm was achieved which is deduced from the SEM analysis. The investigated optoelectronic properties indicated the high mobility with reasonable carrier concentration, decreased resistivity and increased transmittance for nanoporous TiO₂. This paves the way for the fabrication of solid state heterojunction solar cells using nanoporous TiO₂ as efficient electron transporting layer.

Keywords: DC sputtering, anodization, nanoporous TiO₂, optoelectronics.

Introduction

One-dimensional semiconducting metal oxides have attracted much attention in recent years due to their size and tunable optoelectronic properties¹. Titanium dioxide (TiO₂) is one of the most important semiconducting metal oxides which find its potential applications in various fields that include energy storage and energy conversion devices².

Electron transporting layer (ETL) in solid state solar cells plays a vital role in extracting the excited electrons from the absorber layer and thus preventing the recombination of exciton pairs. In this direction, TiO₂ is being utilized as efficient ETL in heterojunction solar cells till date³. However, the morphological defects leads to the lowering of charge transport properties which lead to the poor performance of the solid state solar cells. Hence, it is imperative to develop methods to form nanostructured TiO₂ which could enhance the charge transport between the layers. Recently, Choi *et al.* fabricated perovskite solar cells using the well-defined nanostructured TiO₂ as ETL⁴.

In the present investigation, we have deposited titanium (Ti) thin films on FTO substrates by DC magnetron sputtering. We performed electrochemical anodization of Ti thin films

to give nanoporous TiO₂. Nanoporous structure was confirmed by SEM analysis. Effect of anodization voltage on optical and electrical properties of nanoporous TiO₂ thin films on FTO substrates were also analyzed.

Experimental

The ultrasonically cleaned glass and FTO substrates were placed in the deposition chamber of RF/DC magnetron sputtering (PLASSYS, France) and evacuated to the base vacuum of around 5×10^{-6} mbar using the mechanical pumps. The 2" diameter Ti target was utilized for the deposition of Ti layer. DC power of 100 W was applied to the target and sputtering was carried out using argon gas (20 SCCM) at 400°C.

The deposited Ti layer was subjected to electrochemical anodization using the APLAB DC power supply in a two electrode configuration. The cathode was platinum sheet while the anode was the DC sputtered Ti layer onto the FTO substrates. The anodization was done at various applied voltages such as 10, 20, 30 and 40 V. The combination of ammonium fluoride and deionized water (0.3 wt% NH₄F/2 vol% DI water) in ethylene glycol was used as electrolyte for this anodization in two electrode configuration as shown in Fig. 1.



Fig. 1. Optical pictures of (a) RF/DC magnetron sputtering system and (b) electrochemical anodization.

The sputtered Ti layer and anodized TiO₂ layer was subjected to microscopic analysis (FESEM, Carl Zeiss, Germany) in order to confirm the formation of nanoporous structure. The compositional analysis was done by EDX analysis. The optoelectronic properties of TiO₂ layer was investigated using UV-VIS-NIR spectrophotometer (JASCO, Japan) and hall measurements system (ECOPIA HMS-7000).

Results and discussion

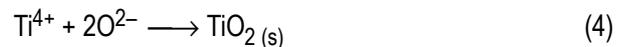
The thickness of DC magnetron sputtered Ti layer on FTO substrates was around 1 μm which was found out using the stylus profilometer. This layer was subjected to electrochemical anodization to form nanostructured TiO₂. As expected,

one-dimensional nanoporous TiO₂ was obtained. The applied voltages were also varied from 10 to 40 V in order to check the nanoporous formation. Beyond 40 V, the films were peeled off and hence we stopped at 40 V. The mechanism of formation of nanoporous TiO₂ from the DC sputtered Ti layer on FTO substrates is illustrated as follows^{2,5}:

At anode (Oxidation):



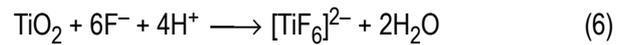
At metal/electrolyte interface:



At cathode (Reduction):



Oxide dissolution in F⁻ electrolyte:



The anodic oxidation of sputtered Ti layer gives Ti ions and releases the electrons (eq. (1)). Oxide anions are generated from the electrolyte at the electrolyte/metal interface and helps to form TiO₂ barrier layer which in turn creates the Ti/TiO₂ interface (eqs. (2–4)). Then, the formed barrier TiO₂ layer gets dissolved at this interface to form the soluble titanium hexafluoride (eq. (6)) and as a result, nanoporous structure was obtained.

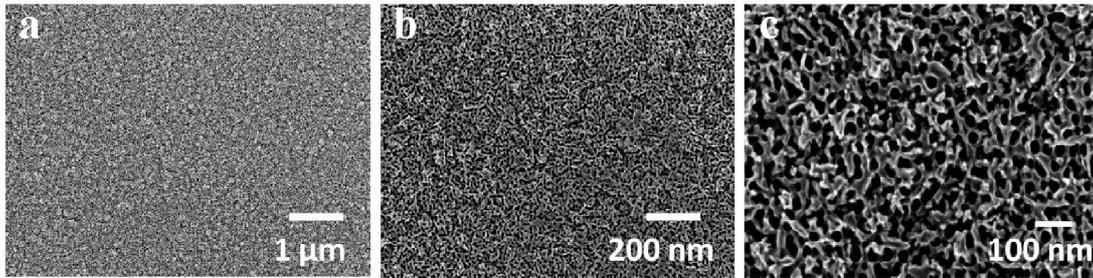


Fig. 2. SEM images of sputtered and anodized TiO₂ on FTO substrates at 40 V.

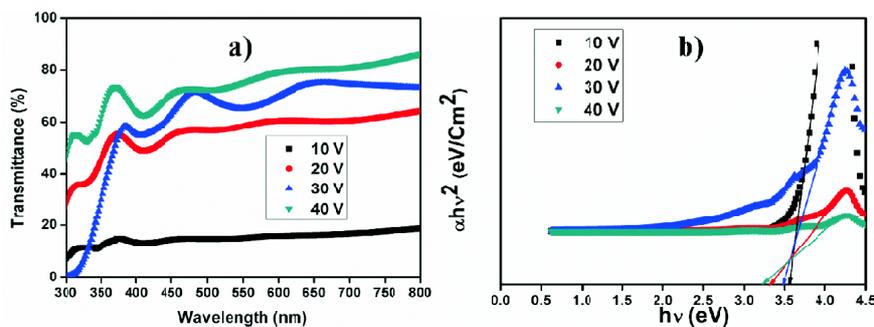


Fig. 3. Optical transmittance (a) and optical band gap (b) of anodized TiO₂ at various voltages ranging from 10–40 V.

Table 1. Optical and electrical parameters of 1-D nanoporous TiO₂ anodized at different voltages

Sample	Anodization voltage (V)	Carrier concentration (cm ⁻³)	Conductivity (ohm ⁻¹ cm)	Mobility (cm ² /V s)	% T at 600 nm	E _g (eV)
FTO	0	-4.37×10 ²⁰	1.59×10 ³	22.7	–	–
Ti-An 1	10	-3.3×10 ²⁰	9.60×10 ²	17.8	15	3.56
Ti-An 2	20	-2.09×10 ²⁰	7.44×10 ²	22.3	60	3.32
Ti-An 3	30	-1.30×10 ²⁰	4.85×10 ²	23.4	69	3.45
Ti-An 4	40	-1.62×10 ²⁰	7.08×10 ²	27.2	80	3.26

Fig. 2 clearly revealed the nanoporous structure of TiO₂. The pore diameter was found to be around 40–60 nm⁶. The nanopores are distributed throughout the surface which is evidenced by SEM image. The surface composition was confirmed by EDX analysis where it shows 29 at% for Ti and 71 at% for O. This nanopores will lead to the enhanced filling of the absorber layer which in turn may lead to the enhanced efficiency of solid state solar cells⁴.

Fig. 3 shows the optical properties of anodized TiO₂ at 10–40 V. It is noted that the transmittance increases when the applied voltage is increased due to the complete conversion of Ti layer to TiO₂ layer (Table 1). 80% transmittance was observed at 600 nm for 1-D TiO₂ anodized at 40 V. Direct optical band gap (E_g) was calculated from the photon energy ($h\nu$) and absorption co-efficient (α) which in turn calculated from the absorbance using Tauc's relation ($\alpha h\nu = A(h\nu - E_g)^n$). The plot of $\alpha h\nu^2$ versus $h\nu$ gives the direct optical band gap which is found to be 3.56 to 3.26 eV (Table 1) for TiO₂ anodized at 10–40 V.

Electrical properties were studied using Hall effect measurement system in Vander pauw configuration and the obtained electrical parameters such as carrier concentration, mobility and conductivity are outlined in Table 1. N-type conductivity was observed for all the samples with decrease in carrier concentration of around -1.62×10²⁰ cm⁻³ and increase in mobility (27.2 cm² V⁻¹ s⁻¹) as compared to bare FTO (Table 1). It is also noteworthy that the mobility increases from 17.8 to 27 cm² V⁻¹ s⁻¹ when the applied voltage is increased. This is attributed to the complete conversion of Ti layer to 1-D nanoporous TiO₂ layer with enhanced transmittance and hence it can serve as efficient ETL in heterojunction solar cells.

Conclusions

Ti thin films (thickness – 1 μm) were deposited on FTO substrates by DC magnetron sputtering and successfully converted to one-dimensional nanoporous TiO₂ by electrochemical anodization with pore diameter around 40–60 nm. Effect of anodization voltage (10–40 V) on optical and electrical properties of nanoporous TiO₂ was studied. High transmittance of around 80% with optical band gap of 3.26 eV was obtained for TiO₂ anodized at 40 V. N-type conductivity with high mobility and reasonable high carrier concentration was also achieved. The collective results suggested that it could be effectively used as ETL in heterojunction solar cells due to the enhanced optical and electrical properties.

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