Fabrication of dye sensitized solar cells using BaTiO₃ blocking layer

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Dye-sensitized solar cells (DSSCs) have great potential for solar generation due to their low cost and simplicity of fabrication compared with silicon-based photovoltaic devices. One of the major problems with TiO_2-based DSSCs is the recombination loss at the substrate–electrolyte interface due to the mesoporous nature of the TiO_2 film. It was proposed earlier that introduction of a blocking layer at the substrate–TiO_2 interface could reduce this recombination loss by preventing direct contact of the substrate and electrolyte. In this present work, Barium titanate ($BaTiO_3$) nanoparticles prepared by using wet chemical method. The prepared nanoparticles were thermally evaporated on to well cleaned fluorine-doped tin oxide (FTO) glass under the vacuum of 2×10^{-5} torr at different thickness and used as electron-blocking layer of dye-sensitized solar cell (DSSC). The $BaTiO_3$ blocking layer functions as an energy barrier at the FTO–electrolyte interface to prevent back transfer of electrons to the electrolyte from the FTO. The blocking effect of the $BaTiO_3$ blocking layer was verified by an enhancement of the fill factor (FF) and open-circuit photovoltage (Voc) of the DSSC, leading to an improvement in the power conversion efficiency (PCE) from 3.86% to 4.34% for the $BaTiO_3$ blocking layer with optimum thickness of 80 nm. The TiO_2 layers were printed on top $BaTiO_3$ to assemble for a dye sensitized solar cells. DSSCs with the structure of FTO/$BaTiO_3$/TiO_2/Dye/EL/Pt/FTO have been prepared, and their solar-cell performance was evaluated.

1. Introduction

Since dye sensitized solar cells (DSSCs) was first demonstration by Ragen and Gratzel [1] in 1991.There have been several efforts to increase the energy conversion efficiency of the solar cells. In DSSC, the dyes adsorbed on the surface of titanium dioxide (TiO_2) absorb light and inject electrons into the conduction band of TiO_2. The overall energy conversion efficiency of DSSCs is greatly dependent on the electron transport from TiO_2 to transparent electrode. But the electron transport is delayed by charge recombination at the interface between TiO_2 and dye due to electron leakage at the interface between TiO_2 and electrode [2]. Over the last decade, several types of metal oxides have been deposited to form the BL in DSSCs, including TiO_2 [3], Nb_2O_5 [4], ZnO [5], SnO2 [6], etc. Among them, $BaTiO_3$ has been extensively investigated and is the most effective blocking layer in DSSCs. $BaTiO_3$ thin film was prepared by Vacuum evaporation method on FTO substrate to improve the DSSCs performance. Nevertheless, most methods reported for BL deposition have high manufacturing cost, for example, sputtering [7], atomic-layer deposition [8], nanocluster deposition [6], pulsed laser deposition [9], etc. Among the various methods, vacuum evaporation is an excellent method to produce thin films on various substrates with good stoichiometry. In this study we have prepared $BaTiO_3$ thin film by vacuum evaporation method. The advantages of Vacuum evaporation method include high purity, good chemical, and mechanical stability, and homogenous film formation on a large substrate. In our previous work, we have reported preparation and characterization of $BaTiO_3$ nanoparticles, and their thin films of various thickness prepared by Vacuum evaporation method [10-12]. To the best of our knowledge, there is no work reported in $BaTiO_3$ blocking layer of DSSCs. An attempt has been made to fabricate DSSCs by using $BaTiO_3$ as a blocking layer and their solar-cell performance carried out in the present work.

2. Experimental details

2.1. Preparation of BaTiO₃ thin films

The prepared nanoparticles of $BaTiO_3$ placed in the molybdenum boat (200 amps) and get heated with high current by energizing transformer. The transformer capable of supplying 150 amperes at 20 volts is used to provide the necessary current for heating the molybdenum source. Prior to evaporation, the evaporate material was carefully degassed at a lower temperature for about thirty minutes with the shutter closed. Deposition of the material on to pre-cleaned glass substrates under the pressure of about 10^{-5} Torr was achieved by slowly varying the current. A constant rate of evaporation 1Å/sec was maintained throughout the film preparation. The adhesion of the films to the substrate seems to be extremely good. The substrate to source distance was optimized to be at 0.175 m and

source to crystal distance was optimized to be at 0.21 cm inside the vacuum chamber.

2.2. Fabrication of dye-sensitized solar cell

The DSSCs were made using a procedure similar to the one reported previously [13, 14]. The TiO_2 electrode of 8.5 µm of transparent layer (Ti-nanoxideT/SP, Dyesol) was screen printed on to FTO substrate coated with vacuum evaporated $BaTiO_3$ thin film of thickness 80 nm and 165 nm. Prior to the deposition of TiO_2, FTO substrates were treated with 40mM $TiCl_4$ for 60 min by chemical bath deposition. The deposited films were annealed in air, and allowed to cool, before having another $TiCl_4$ treatment (40mM for 30 min). The electrodes were annealed at 450 ˚C for 30 min at air. The electrodes were then sensitized with a 0.5mM solution dye molecules in THF solvent for 20h. Platinised counter electrodes were made by placing a solution of hexachloro platinicacidin propanol on FTO substrates, and heated at 450 ˚C for15 min. The counter and working electrodes were then sealed together using a hot melt polymer gasket, before a solution of 0.6M1- buty l - 3 - methylimidazoliumiodide, 0.03M I_2, 0.5M tert butyl pyridine and 0.1M guanidine thiocyanate in a 85:15 volume ratio of acetonitrile and valeronitrile was introduced into the cell through a pre-drilled hole in the counter electrode. The device was then sealed with the hot melt polymer and glass cover. In the present work, ruthenium dye was used to fabricate the solar cell.
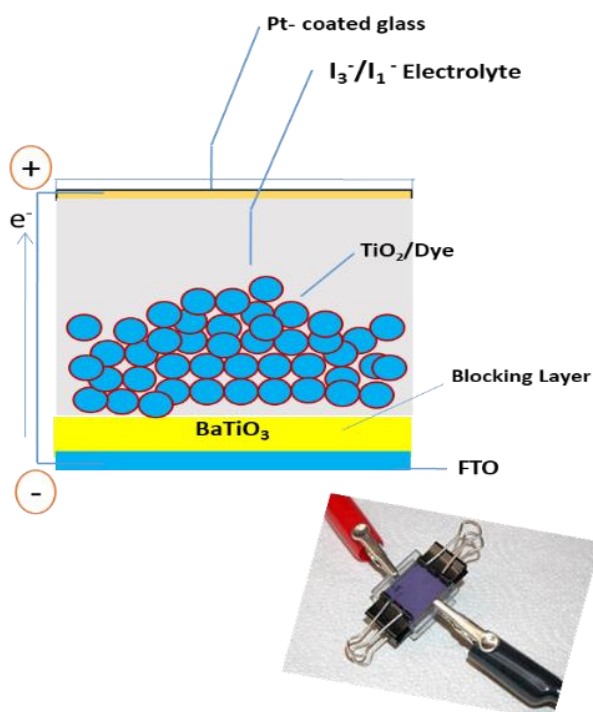

Fig. 1. Graphical diagram for the fabrication of cell (color online)

3. Results and discussions

The $BaTiO_3$ blocking layers were made through vacuum evaporation method. The TiO_2 layers were printed on top $BaTiO_3$ to assemble for a dye sensitized solar cells. The J – V of the DSSCs have shown in Fig. 2 and the results were given in Table 1.

3.1. Open –circuit Voltage *(Voc)*

The open circuit voltage (V_{OC}) is the potential measured when there is no current in the circuit. The mathematical expression for the (V_{OC}) is derived as

$$I_{ph} = I_s \left[\exp\left(\frac{V}{n.V_{th}} - 1 \right) \right] \qquad (1)$$

$$V_{OC} = n.V_{th} \log\left[\frac{I_{ph}}{I_s} + 1 \right] \qquad (2)$$

So, open circuit voltage (V_{OC}) varies logarithmically with incident illumination.

3.2. Short-circuit current (Isc)

The short circuit current is the photo current measured at zero potential, where the series resistance is minimal. At V=0, equation (2) becomes,

$$I_{sc} = I_{ph} - I_s \exp\left[\frac{V + I.R_s}{n.V_{th}} - 1 \right] \qquad (3)$$

Equation (3) depicts the linear relation between short-circuit photocurrent and incident illumination. Since I_{ph} is the function of illumination area, short-circuit current density (I_{sc}) is often used in solar cell characterization.

3.3. Fill Factor (FF)

The fill factor is a measure of cell quality as a power source, defined by the ratio of maximum power of the product of external open circuit voltage and short circuit current

$$FF = \frac{V_m \times I_m}{V_{oc} \times I_{sc}} \qquad (4)$$

3.4. Efficiency (η)

The efficiency describes the performance of the solar cell and is defined as the ratio of the maximum electric power extracted to the incident radiation power on the solar cell surface

$$\eta = \frac{P_{out}}{P_{in}} = \frac{V_m \times I_m}{P_{in}} \tag{5}$$

By substituting equation (4) in (5)

$$\eta = \frac{V_{oc} \times I_s \times FF}{P_{in}} \% \tag{6}$$

The efficiency is a function of the V_{OC}, the I_{SC} and the FF of the cell. Accordingly, improvement of the photovoltaic yield is the result of the optimization of these three parameters, these three parameters depend on the measurement condition and strongly on light intensity.

To have good comparison, photo current is often normalized to active area of the device and represented as photocurrent density with unit of mA. Cm^{-2}. The incident solar illumination was calibrated to 1 sun condition [$100mW.cm^{-2}$, Air mass 1.5] by using either photometer or reference si photodiode equipped with KG -5 filters.

According to basic theoretical considerations built-in potential evolves close to the interface between the nanoporous TiO_2 and the contacting FTO electrode. The origin of built-in voltage lies in the difference between the work function of the substrate material (ITO) and the redox potential of the electrolyte. The built-in voltage is caused by the negatively charged ions in the electrolyte surrounding the nanoporous TiO_2 close to its contact. Dependent on the size of the TiO_2 nanoparticles, the field region extends only 10 - 20 nm into the TiO_2 network [15]. The estimated built-in potential is approximately 0.7eV [16].   The origin of built-in potential can be explained based on Schottky diode model, barrier height representing the FTO/TiO_2 interface, and the main diode, which corresponds to the electron injection from the TiO_2 into the electrolyte.

When compact $BaTiO_3$ and FTO (fluorine doped tin oxide) are in contact (i.e. semiconductor–metal contact), a depletion region or Schottky barrier is formed by the difference of work function of FTO and $BaTiO_3$. Electrons have to overcome this barrier in order to be transferred from TiO_2 to ITO. Hence, the electron injection efficiency decreased while the back electron transfer increased. Moreover, the built-in potential will be very high in the open circuit conditions due to the blocking layer in between TiO_2 and FTO, which causes the electron life time decrease during electron injection from TiO_2 to FTO. The decrease in life time increases the recombination which leads to potential decrease in Voc. On the other hand, the contact between FTO and the $BaTiO_3$ coated TiO_2 layer forms a very narrow depletion region. Electrons injected rapidly from TiO_2 to FTO by tunnelling leads to Ohmic contact characteristics. Therefore, the $BaTiO_3$ coated TiO_2 layer remarkably reduces the interfacial charge transfer resistance and results in the enhancement of the performance of the DSSC especially increase in V_{OC}.

Fig. 2 presents the Current density–voltage characteristics, (A) The DSSCs assembled with TiO_2 electrode thicknesses of 8.5 μm without barrier layer. (B1) The DSSCs assembled with TiO_2 electrode thicknesses of

8.5 μm with $BaTiO_3$ barrier layer of 165 nm. (B3) The DSSCs assembled with TiO_2 electrode thicknesses of 8.5μm with $BaTiO_3$ barrier layer of 80 nm and photovoltaic parameters measured under simulated standard solar irradiation (AM1.5, 100 mWcm^{-2}). The Table 1 shows the J - V characteristics parameters of DSSCs with and without blocking layers. The efficiency of the devices decreased drastically with the increase of blocking layer thickness to 165 nm. This is due to the inefficient electron tunnelling through thicker layer. The V_{OC} is increased from 856 mV to 882 mV with 165 nm thick $BaTiO_3$ blocking layer may be due to the increase of electron population in the TiO_2 conduction band. The decrease in current shows the inefficient electron transport. However, the device quality improves by having 80 nm blocking layer which is due to the efficient recombination reduction via exposed FTO surface.

Table 1. J - V characteristics parameters of DSSCs with and without blocking layers

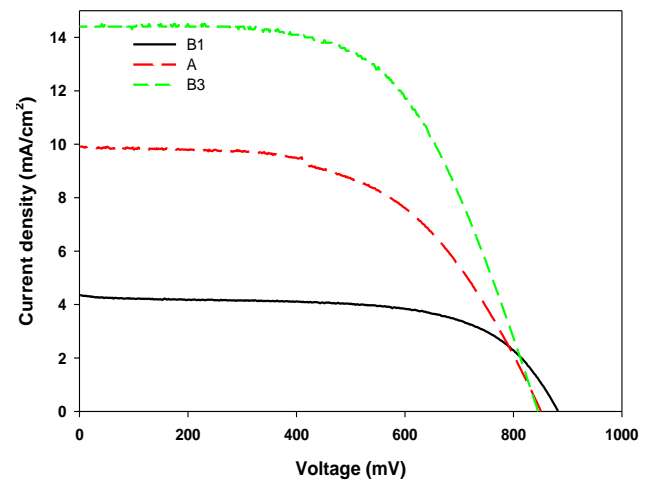| Sample Name	Voc (mV)	Jsc (mA/cm2)	ff (%)	η (%)
A	856	10.13	51.9	4.48
B1	882	4.36	64.9	2.49
B3	843	14.61	55.3	6.82

Fig. 2. J-V Characteristics of DSSC's with and without blocking layer (color online)

4. Conclusion

Dye sensitized solar cells (DSSCs) have been fabricated by using $BaTiO_3$ as blocking layer. Open circuit voltage (V_{OC}), short – circuit current density (J_{SC}), fill factor (FF) and efficiency (η) of the DSSCs have been estimated from the J – V characteristics current. $BaTiO_3$ barrier layer of 50 nm shows a maximum efficiency of 6.82 %.

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