Current Applied Physics 16 (2016) 131–134

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Optimization of ZnO thin film through spray pyrolysis technique and its application as a blocking layer to improving dye sensitized solar cell efficiency

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ARTICLE INFO

Article history:
Received 15 July 2015
Received in revised form
26 September 2015
Accepted 28 October 2015
Available online 2 November 2015

Keywords:
Spray pyrolysis
Thin film
ZnO
Blocking layer
Dye sensitized solar cell

ABSTRACT

ZnO thin films have been deposition with three techniques, spray pyrolysis, spin coating and dip coating. Based on results of UV, XRD, four-probe resistance and ellipsometry analysis, the spray pyrolysis technique was the best one. In order to optimize the thin film deposition, the temperature and the height parameters were investigated. For the first time the thin film prepared by this technique was used as a blocking layer between FTO/TiO_2 in dye sensitized solar cell. By employing the blocking layer J_{sc} increases from 12.63 mA/cm^2 to 15.60 mA/cm^2 and efficiency was 20% higher than that of the cell without the blocking layer.

1. Introduction

Nowadays the use of thin films technology is widespread. Deposition techniques affect the quality of the film which among these spray-pyrolysis, spin-coating and dip-coating techniques are simplest and create films with good quality. Compared to other thin film deposition techniques, spray-pyrolysis is the best choice because of the facility and the low cost and it doesn't need vacuum equipment. Thin films which make with this technique are smother and homogenous. Being able to simultaneously deposition and heating make the good adhesion of the film to the substrate [1]. The ZnO thin film has many applications in electronic, transistor, photodiode and nanostructure solar cells [2–4].

Dye sensitized solar cell (DSSC) has been recently attracted considerable attention because of low cost, availability, non–toxicity, flexibility, simple processing and etc. [5,6]. When the DSSC is irradiated with light, the dye molecules absorb photon and excite from the ground state to the excited state and inject into the TiO_2 conduction band. In the following, electrons diffuse to the transparent conducting film and during this process recombination may occur in the interface of TiO_2/FTO and TiO_2/dye [7–9]. In fact, recombination can be the most crucial issue which limit the performance of DSSC [10,11]. The surface of FTO is rough so it cannot be truly covered by TiO_2 and because of the contact between electrolyte and FTO surface, charge recombination occurs at the FTO/TiO_2 interface [12,13]. A great choice to prevent recombination is using blocking layer. The blocking layer causes the energy barrier and creates the compacted layer which can fill bare FTO sites and reduce the contact surface of electrolyte and FTO. Moreover this compact layer improved the contact between FTO and TiO_2. So by employing the blocking layer with the suitable thickness, the recombination will be reduced and the open-circuit-photovoltage (v_{oc}) increased which this leads to the DSSC efficiency improvement [14–16]. Several studies have done to investigate the effects of blocking layer in DSSC and employed different materials, for example TiO_2 [17], Nb_2O_5 [18], Al_2O_3 [9,19], In_2O_3 [20].

The compact ZnO can be the best choice as the blocking layer because of high electron mobility, high optical transparency, stability against photocorrosion and good connection with TiO_2. In addition, it has a higher conduction band than TiO_2 [13,21].

In this study, ZnO thin film was deposited with three simple techniques. The quality, optical and other properties of the films were compared. According to results and expectations the spray pyrolysis technique was the best one. Then a comprehensive report on effects of spray pyrolysis parameters on film quality was

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http://dx.doi.org/10.1016/j.cap.2015.10.015

demonstrated to optimize layers. For this purpose, deposition temperature and height was investigated by the homemade spray pyrolysis device. Then ZnO thin film deposited by spray pyrolysis was used as a blocking layer in DSSC for the first time and the efficiency enhancement was investigated by J–V characterization. Moreover, for comparison, the $TiCl_4$ treatment and ZnO blocking layer were investigated in DSSC.

2. Experimental

2.1. Material

Zinc acetatedihydrate (90% Sigma–Aldrich), absolute ethanol (Merck), triethanolamine (90% Sigma–Aldrich), dynamic light scattering (DLS, Malvern), spray pyrolysis which made by our group (national patent number: 85466), spin coat (Backer), dip coat (AirmatakDv 2842), UV–visible spectra transmission (Perkin–Elmer), X-ray diffraction (XRD-PANalytical), ellipsometry (Dektak 8000), Materials for cell fabrication: Fluorine doped tin oxide (FTO) (Solarmix), anatase 20 nm TiO_2 particles (Sharifsolar), N719 dye solution (Sharifsolar), spacer (Surlyn, 30 μm) redox electrolyte (Sharifsolar) and J–V characterization under AM1.5G illumination (Luzchem Solar Simulator).

2.2. Preparation and optimization of thin film

ZnO nanoparticles were prepared by the sol–gel method according to the procedure. 0.25gr TEA was gradually added to 5 mL of absolute ethanol under vigorous stirring then 0.5gr ZnAc was added to this solution. The solution was stirred for one hour at ambient temperature to achieve transparent and sustainable sol. After the preparation of ZnO sol, we coated it directly on the substrate by spray pyrolysis, spin coating and dip coating and the resistance of thin film measured with four-probe resistance. Subsequently the quality and the resistance of films were compared and the best method was selected. In spray pyrolysis, the parameters such as substrate temperature and height (the distance between the nozzle and hot plate) play an important role in the specification and qualification of the films. So, we focused on this variability to optimize thin films. The thickness of the transparent film was measured by ellipsometry.

2.3. DSSC fabrication

The thin film with optimized condition was deposited on the cleaned FTO as the blocking layer. Since the $TiCl_4$ treatment is the common method for blocking layer creation in DSSC, we compared $TiCl_4$ treatment as a blocking layer with ZnO blocking layer, separately. For this purpose, in one cell only the $TiCl_4$ used as blocking layer and in another one the ZnO thin film just was used as a blocking layer. For $TiCl_4$ treatment FTO was immersed in 40 mM of $TiCl_4$ aqueous solution at 70 °C for 30 min. The commercial past containing 20 nm TiO_2 was deposited on FTO with and without blocking layer and FTO with $TiCl_4$ treatment by print screen technique and was dried at 120 °C for 6 min. After that films were calcined at 450 °C for 30 min. In order to dye absorption films had been immersed in the N719 dye solution for 24 h. Dye-anchored films were rinsed with acetonitrile to remove the accumulated dye on the surface. The counter electrode was prepared by coating H_2PtCl_6 on FTO glass substrate and the surlyn was used as a spacer between the electrodes. Then the counter electrode and TiO_2 working electrode were putted together. Finally the assembled cell gets filled with the electrolyte and sealed.

3. Results and discussion

To ensure the formation of ZnO sol we measured the absorption spectrum (Fig. 1). It can be seen that the absorption peak of ZnO is at 290 nm.

DLS spectrum has been measured for determining the particle size of the sample (Fig. 2). The resulting graph showed a uniform distribution of particles which have the size about 4 nm.

After preparing the solution, deposition was done by three techniques; spray pyrolysis, spin coating and dip coating under same condition. Substrates need to have high conductivity in DSSC, so the resistance of films was measured by four-probe resistance technique (Table 1). By the spray pyrolysis the sample was more uniform and has lower resistance.

The conductivity of FTO substrates that blocking layer was coated on them is so important to charge collection in DSSCs. If the resistance of thin films increases the electron transfer is reduced, so as a result the recombination will be increased. According to Table 1, since the resistance of dip-coating technique was much more, this technique was not suitable for the deposition of blocking layer. The resistance of thin films by spray-pyrolysis technique and spin-coating technique are almost the same. Therefore we measured the UV–vis analysis and compared the transmission of them. It is necessary for dye that can absorb maximum light in visible rang, so the ZnO blocking layer should be high transparent. Light passed through the ZnO blocking layer and absorb by the dye. According to Fig. 3 the spray pyrolysis technique has higher transmission than spin coating technique. Since the spray pyrolysis technique has lowest resistance and higher transmission, this technique was chosen to continue the work. To optimize thin films, deposition temperatures 250 °C, 350 °C and 450 °C and heights 15 cm, 20 cm and 25 cm were investigated.

In order to select the appropriate height, 1 mL of ZnO sol was deposited on quartz glass at 350 °C during 30 min (spray time). Due to the importance of the blocking layer transmission in DSSC, the UV–visible analysis was measured (Fig. 4). Results showed that the transmission of films in 15 cm and 20 cm height were better but the film in 20 cm was more uniform than the other. In 15 cm height, the solvent of sol will be evaporated before deposition of sol on substrate and a powder will be formed on the substrate. So the substrate does not cover by sol completely. As a result thin film quality is not good and thin film is not uniform. With these reasons, we chose 20 cm height to thin films deposition.

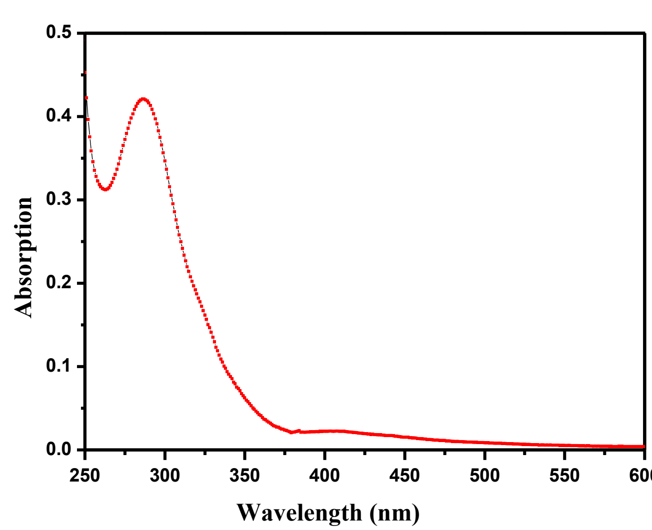

Fig. 1. UV–visible absorption spectra of ZnO solution.