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Sol–gel deposition of fluorine-doped tin oxide glasses for dye sensitized solar cells

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Abstract

Thin films of fluorine-doped tin-oxide (FTO) were prepared by a sol–gel process using the combination of $SnCl_2 \cdot H_2O$, NH_4F and isopropanol. The effects of annealing temperature on structural, electrical and optical properties of FTO were studied. It was found that films annealed at temperatures above 500 °C exhibit resistivity of around 30 Ω/sq with an optical transparency up to 90%, which is comparable with commercially available FTO coated glasses. A dye-sensitized solar cell was fabricated with the optimized thin film and yielded power conversion efficiency ~ 1.58%.

Keywords: A. Sol—gel processes; B. Nanocomposites; C. Electrical properties; E. Electrodes

1. Introduction

Recently, dye-sensitized solar cells (DSSCs) have attracted considerable attention due to their potential to lower the overall cost of solar cells [1–4]. Although power conversion efficiency greater than 12% has been achieved by DSSCs [5], however, the overall cost still remains high [6]. Past strategies for cost reduction have focused on three main areas. (1) Enhancing photo-anodes through adapting nanostructured materials (TiO_2 [3,7], ZnO [8,9] and SnO [10,11]); (2) replacing Pt counter electrodes with cheaper alternative nanomaterials (carbon nanotubes [12], carbon black [13] and cobalt sulfide [14]) or (3) developing higher performance dyes to replace the expensive Ru-based N719 dye [15,16]. Amid all the attentions on these related issues, the cost of FTO glasses has rarely been addressed. Break down cost analysis on DSSC productions have revealed that FTO coated glass substrate constitutes around 40% of the material costs [17]. Although a wide range of transparent conductive oxides (TCO), such as ITO [18] and AZO [19], have been investigated for DSSCs, FTO is preferred due to its superior chemical stability and greater tolerance during photo-anode annealing processes [20–22]. Currently, the commercially available FTOs are deposited by using the spray pyrolysis technique [23,24]. The primary costs associated with spray pyrolysis are the equipment expenditure, which is difficult to eliminate. Therefore, in order to reduce the overall production costs, alternative deposition techniques must be adopted [25]. The sol–gel process deposition is particularly attractive because it offers precise control of film composition, requires only simple equipment set-up and offers large-area deposition. Generally, sol–gel derived thin films are strongly affected by the deposition conditions such as sintering temperature, impurity incorporation, precursor ageing, pH and molar concentration. Previous studies on sol–gel derived FTO thin films have utilized combinations of $SnCl_2$, HF and alcohol [26]. To our best knowledge, there are very few studies on the sol–gel synthesis of FTO using NH_4F [25]. Furthermore, there is lack of studies on DSSCs fabrication using sol–gel derived FTO [27]. The main difference between the present study and Ray's study [25] is the deposition technique. Ray employed a dip-coating deposition method that coated both sides of the substrate, whereas, the films investigated in the present study were deposited by using a spin coating technique, which offers better thickness control and uniformity. In this study, the effects of temperature on the structure and optoelectronic properties of sol–gel derived FTO thin films were investigated. The derived FTO thin films were characterized through scanning

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electron microscope (SEM), X-ray diffraction (XRD) and the Hall effect measurements. For each sample, the Hall effect measurements were performed five times. By using the optimized FTO films, DSSCs were constructed and tested.

2. Experimental

All chemicals used in this study were of reagent grade and used without further purification. First, Corning Eagle 2000 glasses were cleaned using ultrasonic agitation in acetone, isopropanol, deionized water and were blown dry using an N_2 gun purge. Then 0.7 M of $SnCl_2 \cdot H_2O$ in IPA was mixed for 2 h at room temperature. Fluorine doping was achieved by adding NH_4F (F:Sn 50:1) into the pre-mixed solution. Previous studies [26] have revealed that fluorine-rich precursor are required to obtain sufficient doping through the sol–gel method due to non-vacuum deposition condition. The mixed FTO solution precursor was left to age for 48 h, which gave it a gel-like consistency. To deposit a uniform coating on the substrate, the precursor sol was spin coated onto the glass substrates at 3000 rpm for 30 s. Subsequently, the coated substrate was pre-heated at 250 °C and post sintered between 400 and 550 °C, respectively.

The morphology of the deposited FTO thin films was examined by using an FEI quanta 400F environmental scanning electron microscopy (SEM). Chemical composition was determined by energy dispersive spectroscopy equipped within the SEM. A Siemens D5000 X-ray diffractometer with Cu Kα radiation was used to obtain the crystalline orientation and grain size of the thin films. Hall effect measurements in a Van der Pauw configuration were used to determine the electrical conductivity type, resistivity and mobility. Optical transmittance and the Tauc gap were determined using a UV–vis NIR (Hitachi U-4100). DSSCs were fabricated by sandwiching a dye-sensitized TiO_2 photo-anode and a Pt counter electrode between two pieces of FTO coated glass substrates. Specifically, the TiO_2 photo-anode was prepared by using the doctor-blade method through a 3 M tape mask and heated to 450 °C in order to sinter and remove organic compounds. This coating process was repeated 3 times to yield a thickness of around 15 μm. Then the TiO_2 nanoparticle layer was immersed into a 0.3 M solution of N719 dye (Eversolar) mixed in dry ethanol at 60 °C for 24 h. Catalytic counter electrode was formed by sputtering 15 nm of Pt. The sandwich structure was partially sealed by hot compressing a Suryn sheet between the photo-anode and counter electrode at 125 °C. A mixture of 0.12 M I_2, 0.1 M LiI and 0.5 M tertbutylpyridine in 3-methoxypropionitrile was used as the electrolyte. This solution was injected through pre-drilled holes and fully sealed with Suryn thin film. Solar cell Illuminated current–voltage characteristics were measured by a solar simulator (Science tech).

3. Results and discussions

Fig. 1(a), (b), (c) and (d) shows the SEM image of the synthesized FTO thin films at different temperatures. The inserts show the same set of SEM images at lower magnifications. Clearly, at lower magnifications, it can be observed that

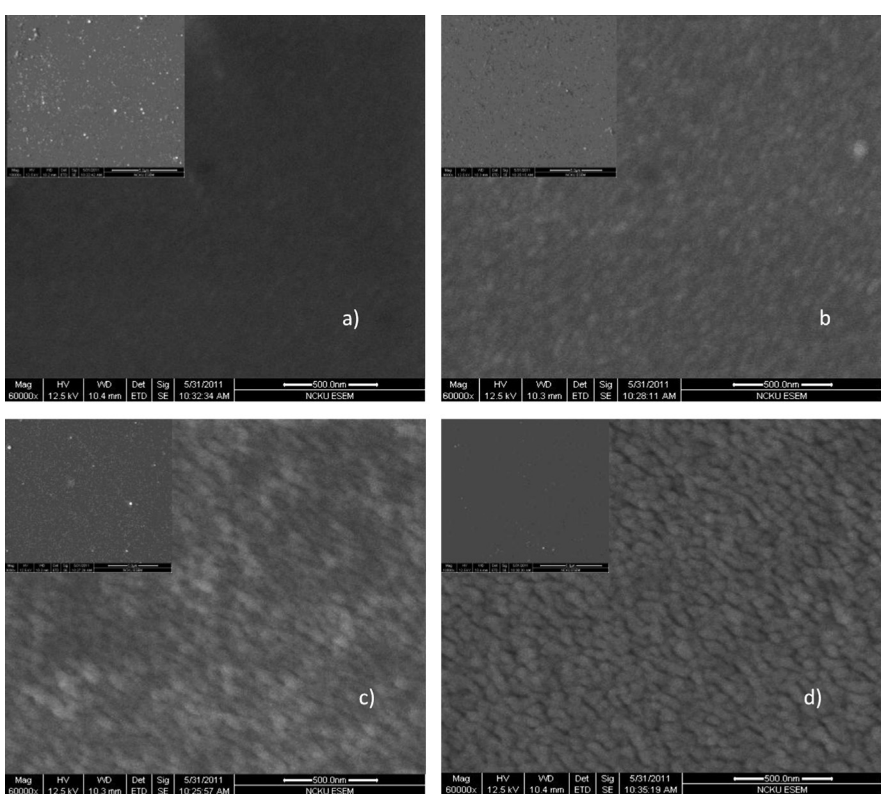

Fig. 1. SEM image of the sol–gel derived SnO_2:F films deposited at (a) 400, (b) 450, (c) 500 and (d) 550 °C. Insert shows the same SEM images at lower magnification (5 μm).