Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Sheet resistance dependence of fluorine-doped tin oxide films for high-performance electrochromic devices

Kue-Ho Kim[a,1], Bon-Ryul Koo[b,1], Hyo-Jin Ahn[a,b,*]

[a] Department of Materials Science and Engineering, Seoul National University of Science and Technology, Seoul 01811, South Korea
[b] Program of Materials Science & Engineering, Convergence Institute of Biomedical Engineering and Biomaterials, Seoul National University of Science and Technology, Seoul 01811, South Korea

ARTICLE INFO

Keywords:
Films
Electrical properties
Optical properties
Transition metal oxides
Electrochromic performances

ABSTRACT

In the present study, we fabricated fluorine-doped tin oxide (FTO) films with different sheet resistances (~10 Ω/□, ~6 Ω/□, and ~3 Ω/□) prepared through the adjustment of deposition time during the horizontal ultrasonic spray pyrolysis deposition (HUSPD) and investigated the effect of electrochromic (EC) performances with different sheet resistances of the FTO films used as transparent conducting electrodes. The results demonstrated that, owing to the increased electrochemical activity, the decrease of sheet resistance accelerated switching speeds of the EC devices. However, for the coloration efficiency (CE), the FTO films with the optimum sheet resistance of ~6 Ω/□ exhibited the highest value as compared to the other samples. The improvement of the CE value can be mainly attributed to high transmittance modulation by the uniform surface morphology of the FTO films to reduce interfacial light-scattering between the WO_3 films and FTO films. Therefore, our results provide a valuable insight into the improvement of the performance of the EC devices using the optimum sheet resistance (~6 Ω/□) of the FTO films.

1. Introduction

With the development of energy-efficient and convenient applications such as smart windows, electronic displays, and adjustable mirrors, electrochromic devices (ECDs), with their unique characteristics of visibility in sunlight, colour variations, and a low operating voltage, have become increasingly important for researchers [1–3]. These devices can accurately control various optical properties (*e.g.,* transparency, absorption, reflection, and colour) under a small electric field, which is typically composed of three functional layers: the cathodic electrochromic (EC) layer, the electrolyte layer, and the anodic EC layer between transparent conducting layers [4,5]. For practical application of ECDs, it is necessary to improve the EC performances including coloration efficiency (CE) and switching speed, which is mainly determined by the components of the ECDs [6]. At this point, improving the performances of transparent conducting layers is an important research direction, as these layers perform a fundamental role in assigning transparency to the ECDs and connecting the devices with the external power supply [7]. Currently, indium tin oxide (ITO) is a representative material used as the transparent conducting layer in optoelectronic applications (touch screens, organic light emitting diodes, and sensors). ITO is characterized by low resistivity ($< 10^{-3}$ Ω cm), high transparency (> 80%), and relatively high work function (4.8 eV) [8,9]. However, ITO also has several critical drawbacks, such as high element cost and vulnerable mechanical and chemical stabilities [8]. In this context, it is imperative to develop alternative materials. Recently, due to its good transparent conducting performance, low cost, and good chemical durability, fluorine-doped SnO_2 (FTO) has received a noticeable interest as a transparent conducting layer for the ECDs or dye-sensitized solar cell [10]. Much effort has been invested into fabricating the FTO films with low sheet resistance or high optical transmittance so that to increase their performances for practical applications. To this end, several methods have been used, including ultrasonic spray pyrolysis deposition (USPD), magnetron sputtering, and chemical vapor deposition [10–12]. Among these methods, USPD has been widely used to form doped or undoped films with superb quantity, especially FTO, which makes it possible to fabricate the film structure on the substrate by pyrolysis of precursor droplets with 1–100 μm in size formed through the ultrasonic atomization [10]. In addition, this method can simply perform the adjustment of transparent conducting performances on the FTO films by controlling the deposition conditions such as deposition temperature, carrier gas, precursor, and additive [13,14]. For

* Corresponding author at: Department of Materials Science and Engineering, Seoul National University of Science and Technology, Seoul 01811, South Korea.
E-mail address: hjahn@seoultech.ac.kr (H.-J. Ahn).
[1] K.-H. Kim and B.-R. Koo contributed equally to this work.

https://doi.org/10.1016/j.ceramint.2018.02.157
Received 10 February 2018; Received in revised form 17 February 2018; Accepted 19 February 2018

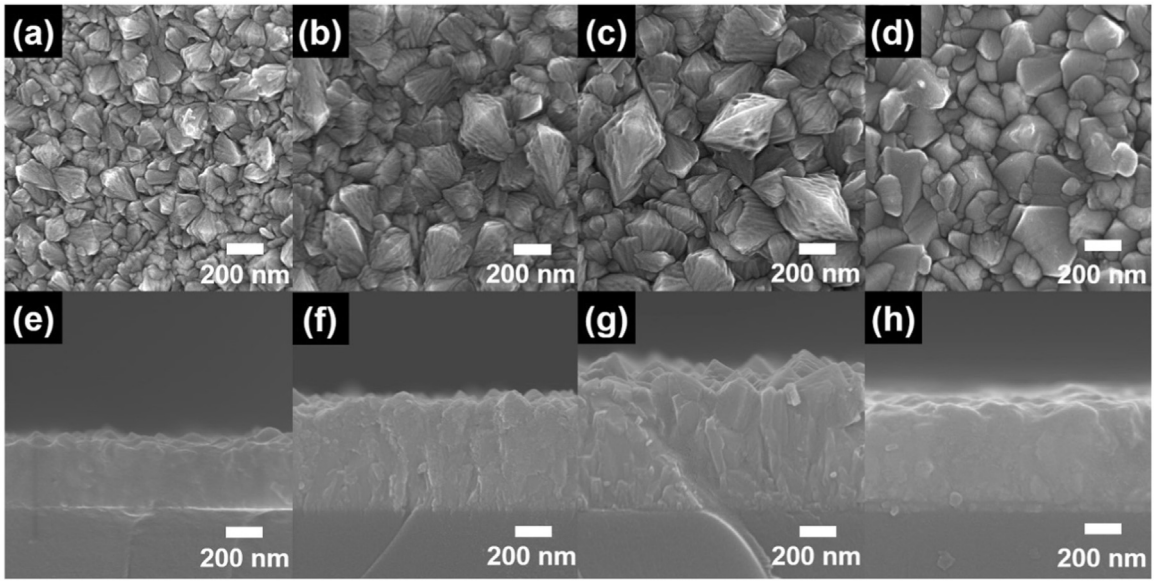

Fig. 1. Top-view and cross-view FESEM images of (a, e) FTO-10 Ω, (b, f) FTO-6 Ω, (c, g) FTO-3 Ω, and (d, h) commercial FTO, respectively.

example, Lin et al. controlled the deposition temperature of the FTO films using the USPD and showed the optimized performances at 400 °C with minimum resistivity of 6.20×10^{-4} Ω cm and maximum transmittance of 77.0% [13]. Furthermore, Moholkar et al. performed the FTO deposition by varying concentration of $SnCl_4$ solution, achieving the maximum values of transparent conducting performances (resistivity of 3.70×10^{-4} Ω cm and transmittance of 87.0%) at 0.81 M [14]. However, despite these efforts, convincing evidence on the relationship between the sheet resistance of the FTO films and EC performances has not been reported yet.

In the present study, we prepared the FTO films with three types of sheet resistance (~10 Ω/□, ~6 Ω/□, and ~3 Ω/□, where □ is cm^2) using horizontal ultrasonic spray pyrolysis deposition (HUSPD) and demonstrated the effect of their sheet resistances on the EC performances by investigating the morphological, structural, chemical, electrical, optical, and electrochemical properties.

2. Experimental details

2.1. Experimental

The FTO films with different sheet resistances were prepared by the HUSPD (Ceon, Nano SPD, TV500, Korea) on the glass substrate (Corning EAGLE XG™). For the preparation of the precursor solution for the FTO deposition, 0.68 M tin chloride pentahydrate ($SnCl_4{\cdot}5H_2O$, SAMCHUN) and ammonium fluoride (NH_4F, Aldrich) were dissolved into de-ionized (DI) water with 5 vol% ethyl alcohol (C_2H_5OH, Duksan); to obtain the optimum transparent conducting performance of the FTO films, the mole ratio of F/Sn was fixed at 1.765. After stirring, the resultant precursor solution was placed in a spray container and then the HUSPD was started after maintaining the substrate temperature at 420 °C by ultrasonic atomizer (1.6 MHz). All other deposition conditions during the HUSPD, such as flow rate (15 L/min) of the carrier gas (air), and rotation speed (5 rpm) of the substrate, were maintained constant. To adjust the sheet resistance of the FTO films, the deposition time of the HUSPD was controlled to be 18, 28, and 33 min, resulting in the FTO films with sheet resistance of ~10 Ω/□, ~6 Ω/□, and ~3 Ω/□, respectively (thereafter referred to as FTO-10 Ω, FTO-6 Ω, and FTO-3 Ω, respectively). To measure the EC performance of the FTO films as the transparent conducting electrode (TCE), WO_3 films were used as the working electrode. The WCl_6 sol solution for the preparation of the WO_3 films was obtained by mixing 10 wt% tungsten (VI) chloride (WCl_6, Aldrich) and 2-propanol ($(CH_3)_2CHOH$, Aldrich). The resultant sol solution was spin-coated at 2000 rpm for 30 s on all FTO films, which was repeated 2 times. Thereafter, the samples were annealed at 300 °C in air, finally obtaining the EC electrodes consisting of WO_3 films and FTO films (thereafter referred to as WO_3-FTO-10 Ω, WO_3-FTO-6 Ω, and WO_3-FTO-3 Ω, respectively). For comparison, the WO_3 film on the commercial FTO films (WO_3-commercial FTO) was also fabricated with the sample conditions.

2.2. Characterization

The surface morphology was characterized using field-emission scanning electron microscopy (FESEM, Hitachi S − 4800) and atomic force microscopy (AFM, diDimension™ 3100). The crystal structure and chemical state were evaluated using X-ray diffraction (XRD, Rigaku D/Max − 2500 diffractometer using Cu K_α radiation) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250 equipped with an Al K_α X-ray source), respectively. The electrical and optical properties were measured by a Hall-effect measurement system (Ecopia, HMS-3000) and ultraviolet-visible (UV − vis) spectroscopy (Perkim − Elmer, Lambda − 35), respectively. The electrochemical properties and EC performances were characterized using a potentiostat/galvanostat (PGSTAT302N, FRA32M, Metrohm Autolab B.V., Netherlands), which was performed in the three-electrode system with Ag wire as the reference electrode, Pt wire as the counter electrode, and 1 M $LiClO_4$ electrolyte at the scan rate of 20 mV/s from − 0.7–1.0 V. The measurement of *in situ* optical transmittances during coloration and bleaching processes was performed using ultraviolet-visible (UV − vis) spectroscopy (Perkim − Elmer, Lambda − 35) in the wavelength at 633 nm.

3. Results and discussion

Fig. 1 shows the top-view and cross-view FESEM images of (a, e) FTO-10 Ω, (b, f) FTO-6 Ω, and (c, g) FTO-3 Ω prepared by different deposition times of the HUSPD, respectively, and (d, h) commercial FTO. As can be seen in the top-view FESEM images (Fig. 1a–d), the FTO films fabricated by the HUSPD have the surface morphology with interlocked pyramid-shaped crystallites throughout the entire surface. Their crystallite sizes enhanced from 182.2–220.0 nm for FTO-10 Ω to 413.7–557.8 nm for FTO-3 Ω, which can be due to the crystallite growth by the increased deposition time of the HUSPD, leading to the