Int. J. Electrochem. Sci., 11 **(2016)** 5395 – 5402, doi: 10.20964/2016.07.45

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Preparation of Large-scale SnO_2:F Transparent Conductive Film by Atmospheric Spray Pyrolysis Deposition and The Effect of Fluorine-doping

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Received: 5 April 2016 / *Accepted:* 7 May 2016 / *Published:* 4 June 2016

High-quality SnO_2:F films with an area of 15×15 cm^2 were prepared from stannic chloride ($SnCl_4$) solution via a house-made ultrasonic spray pyrolysis instrument. The focus of this investigation was on the volatilization of solution and doping process of fluorine, the main influencing factors on F doping content, and the effects of F doping content on the crystal structure, surface morphology, electrical, and optical properties. The results indicated that the crystallinity was enhanced with increasing doping concentration; the films exhibited (101) oriented growth and the resistivity decreased at first and then increased. During the preparation route, the droplet momentum and the temperature field above the hot plate demonstrate the most dominate influence on the film's properties. The spray droplet gradually hydrolyzed during the moving process from sprinkler to substrate while the F doping content decreased with the increasing distance between the sprinkler and the substrate. By controlling the doping of F, high-quality and large area SnO_2:F films with a resistivity of 1.2×10^{-3} Ω·cm and a visible light transmittance of 82% were prepared, demonstrating a promising application for organic solar cells and low emissivity glass.

Keywords: transparent conductive films; low emissivity glass; SnO_2:F; ultrasonic spray pyrolysis

1. INTRODUCTION

Transparent conductive oxide (TCO) films demonstrate an irreplaceable function in touch displays, solar cells, electromagnetic shielding systems, electrochromism glass, low emissivity glass, etc. [1-3]. Indium tin oxide (ITO) has become one of the most applied TCO materials because of its superior conductivity, transmittance and stable physicochemical properties. However, the storage of In, the major metal component of ITO, is very limited in the earth, hence, people have focused great

efforts of dining a substitute for ITO [3, 4], which have included SnO_2:F (FTO), Al:ZnO (AZO), graphene, Ag nanowire film and conductive polymers, etc. Because most substitute materials for ITO possess self-defects, such as the chemical stability of AZO, higher productivity cost of graphene and low uniformity of Ag nanowire film, are not capable of perfectly replacing ITO products.

The greatest advantage of FTO as a TCO material is its wide material sources, making it feasible for large scale applications, especially suitable in building glass and solar cells. High-quality FTO could be prepared via physical vapor deposition (PVD) [5] and chemical vapor deposition (CVD) [6] while it was more attractive to prepare the film via non-vacuum spray pyrolysis deposition (SPD) [3, 7, 8], which significantly reduces the cost of production. Despite this phenomenon, the current SPD technology has not yet matured. CVD pyrolysis furnace is the most commonly implemented instrument for film deposition in reported literature [9], which could prepare FTO films possessing enhanced electrical properties; however, the instrument demonstrates a turbulence effect of spray on the boundaries of the substrate that make it difficult to produce high uniformity while large-area rainbow patterns easily appears on the film. Therefore, in order to realize more extensive application of FTO, it is crucial to solve this problem in order to prepare large area uniform films.

According to the current defects in non-vacuum film deposition technology, this paper designed a set of ultrasonic spray system suitable for large area film deposition [10, 11]. Biaxial program-controlled moving hot plate was applied as the substrate carrier ensuring the substrate to move back and forth towards the sprinkler during the film deposition, preparing uniform FTO films of large area and conductivity. Compared with the conventional method in which there is relative no movement between the substrate and sprinkler, the process of the spray being delivered to the substrate and the deposition were transformed into a dynamic procedure. The surface temperature and deposition rate of every small region on substrate varies with time so that the control of processing parameters is different from the traditional control. During the preparation process of large area FTO via SPD technology in ambient conditions, the effects of key processing parameters on F doping, the appearance quality and electrical properties of FTO films were investigated, establishing a foundation to realize the scale productivity and extensive application of FTO-coated glass.

2. EXPERIMENTAL

To improve the solubility of the solution, 0.04mol $SnCl_4 \cdot 5H_2O$ (Aladdin, 99.95%) was firstly dissolved in 8 mL concentrated hydrochloric acid (36.5%) with magnetic stirring, and then 142 mL deionized water was slowly added. Subsequently, 0-0.06mol NH_4F (Aladdin ，99.95%) was added and then 50 mL methanol was added to form the precursor solution with a $SnCl_4$ concentration of 0.2 mol/L and NH_4F concentration of 0-0.3 mol/L.

The substrate for FTO film deposition is soda-lime glass, the substrate was washed with detergent, acetone, deionized water and ethanol successively in ultrasonic cleaner, each cleaning lasted for 10 min, and the substrate was dried under vacuum at 80 °C.

The SPD instrument for film deposition is including one ultrasonic atomization cavity, one biaxial linear module, one constant temperature hot plate, one drop-proof quartz sprinkler with Φ15 mm and corresponding pipelines. The sprinkler was fixed above the hot plate by a shelf. During the film deposition process, compressed air was supplied as carrier gas at a flow rate of 10 L/min, the distance between sprinkler and substrate could be adjusted within the range of 0-50 mm, the temperature of film deposition was 450 °C, and the film thickness was about 150-200 nm.

In order to investigate the effect of processing conditions on the structure, morphology and properties of FTO films were implemented by investigation of the crystal structure and crystallinity via X-ray diffractometer (XRD, PANalytical X'Pert PRO), surface morphology was observed via scanning electron microscope (SEM , Hitachi S-4800), the film transmittance was measured by an ultraviolet and visible spectrophotometer (Hitachi U-3900). The electrical properties of films were tested by Hall instrument in which the samples were treated with vacuum evaporation before the test. An Ag electrode (width = 150 nm) was prepared on the film surface by means of evaporation coating. All of the film thicknesses were measured via Alpha-Step D-100.

3. RESULTS AND DISCUSSION

In terms of TCO films, its most advantageous property is its visible light transmittance and resistivity [12], therefore, the main influencing factors on the resistance and visible light transmittance of FTO films were investigated, such as the solution composition, substrate temperature, moving pattern of hot plate, and sprinkler shape and height, etc. The influence of substrate temperature on TCO films mainly focuses on its influence on crystal structure, in which literature has established precedence for a relationship [13, 14]. Additionally, the F doping content has a relatively larger influence on the optical and electrical properties of films [15]. In this paper, results suggest that not only the NH4F concentration in solution has a key effect on the F doping content, but also the delivery and spraying process should be considered.

The effects of F doping content on the structure, morphology and electrical properties and optical properties of FTO films were first investigated in this paper as the F doping content is controlled by adjusting NH_4F in the precursor solution. The surface morphology of FTO films prepared from precursor solution with different NH_4F concentrations are shown in Fig. 1. The SEM images verify that when the F doping content decreases, the film is constituted by rough surface particles with Φ20-50nm and the grain does not completely grow. As the F doping content increases, the grain size increases and it shows a fusiform shape; the films demonstrate few holes and the density is relatively higher; when NH_4F concentration is 0.2 mol/L, the grain size increases to about 200-300 nm, the surface roughness and number of stress cracks increases, and the density tends to decrease. The F doping content has a strong influence on the crystal structure, as shown by the XRD spectra of TFO films prepared at identical sprinkler height of varying NH_4F concentrations nd identical NH_4F concentration with varying sprinkler heights presented in Fig. 2. It can be seen that the as-prepared FTO films are tetragonal polycrystalline thin films, which is in agreement with PDF card (NO.411445). Pure SnO_2 films and low-doped FTO have diffraction peaks of lower density, indicating

lower crystallinity. As the NH_4F concentration increases, the films exhibit a distinct orientation, the diffracted intensity of (101) and (200) significantly increases; when NH_4F concentration is higher than 0.133 mol/L , the film orientation along the (101) crystal face direction is the most obvious.

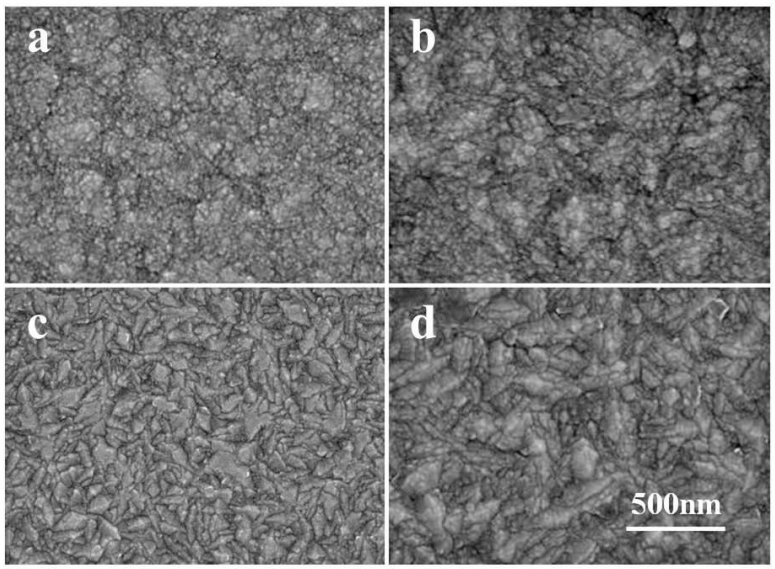

Figure 1. Effects of NH_4F concentration on surface morphology of FTO films: (a) 0 mol/L, (b) 0.067 mol/L, (c) 0.133 mol/L, (d) 0.2 mol/L

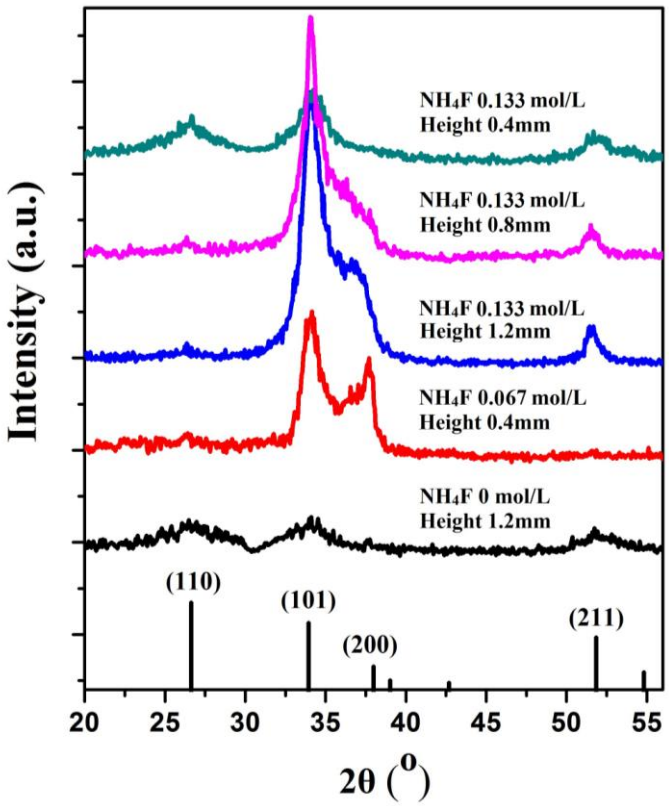

Figure 2. XRD spectra of as-prepared films with different NH_4F concentrations and sprinkler heights

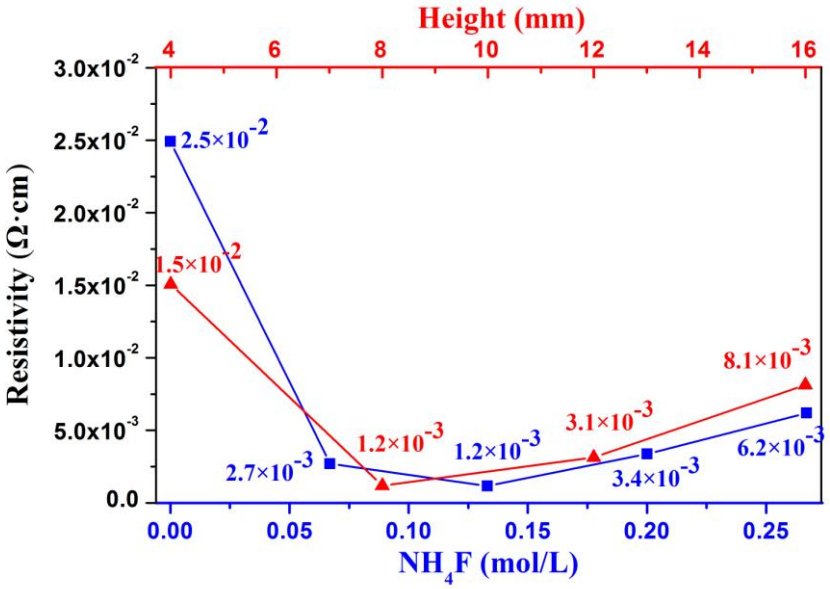

Figure 3. Effects of NH_4F concentration and sprinkler height on conductive properties of films

The electrical properties of films have a strong correlation with the F doping content, and the relation between film resistivity and NH_4F concentration is described as the blue broken line in Fig. 3. When the sprinkler height is fixed at 8 mm, the conductive properties of undoped SnO_2 films decreases with a resistivity of 2.5×10^{-2} Ω·cm. As the content of NH_4F increases, the sheet resistance rapidly decreases; when NH_4F concentration is 0.133 mol/L, the resistivity decreases to the minimum of 1.2×10^{-3}Ω·cm, which indicates that F^- doping content with in the form of displacement in the SnO_2 crystal is crystallized and saturated [8]. As the NH_4F concentration continues to increase, the sheet resistance shows a proportional increasing trend. The excessive F^- enters the lattice space or concentrates on the grain boundaries creating an excessive quantity of electron scattering centers, which not only impedes the generation of more carriers, but also strengthens the scattering degree of carriers, thus resulting in a gradual increase in film resistivity. Due to the experiment being carried out in an open atmosphere, during the process of the droplet approaching the substrate, elements F and Cl continue to volatilize in the form of HF and HCl until the raw compound transforms into SnO_2; meanwhile, a small quantity of F and Cl remains [16]. The amount of F entering the lattice is not only related to the solution concentration, but also directly correlates with the momentum of the droplet and the temperature field distribution above the hot plate. The relation between film resistivity and sprinkler height is described by the red curve in Fig. 3. When the flow rate of carrier air is maintained at 10 L/min and the content of NH_4F concentration is 0.133 mol/L, the resistivity of FTO films initially increases and then gradually decreases as the height ascends, demonstrating a similar behavior of resistivity with NH_4F concentration.

The mechanism of spray arriving at the substrate is analyzed in accordance to the chemical properties of substance in the precursor solution and the process of spray pyrolysis. As presented in Fig. 4, the temperature of droplet increases when it is approaching the substrate, signifying the volatilization of substance in solution proceeds step by step. If the distance between sprinkler and substrate is too far, the moving distance of droplet in the process is so large that the air resistance

results in a high momentum loss of the droplet. The drastically low speed results in the excessive long standing time in the high temperature stage, therefore, there is large volatilization loss of element F and the actual doping content is lower. Meanwhile, the precursor prematurely crystallizes and it is transformed into smoke particles and dissipated by air flow before getting to the substrate, causing a decrease in the film deposition rate. Inversely, if the sprinkler is excessively low relative to the substrate, the volatilization content of element F is lower and the actual doping content is larger. However, the lower distance between sprinkler and substrate results in a more concentrated spray, the air flow rate is excessively high, regional hypothermia of the substrate occurs too rapidly, which does not allow for a high enough driving force for the precursor to take part in pyrolysis and the film crystallinity worsens. It can be seen from the XRD spectra in Fig. 2 that when the sprinkler height is 4 mm and NH_4F concentration is 0.133 mol/L, the film shows obvious amorphous characteristics.

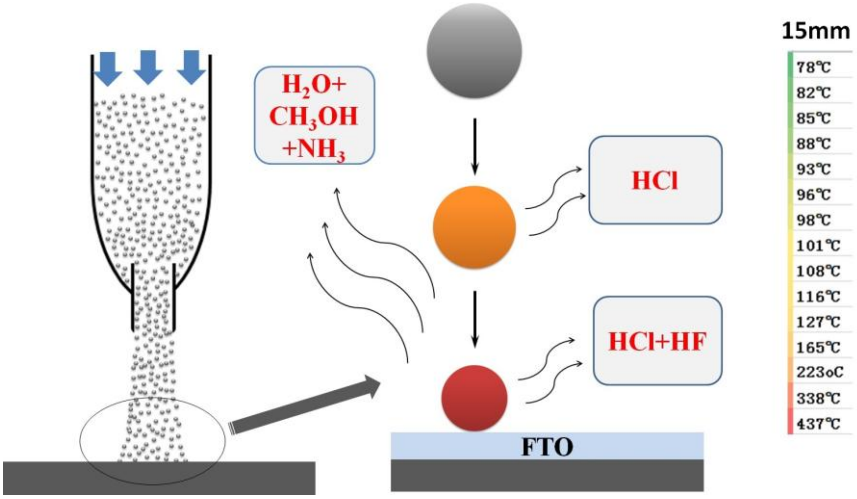

Figure 4. Schematic diagram of film deposition process

When F enters the lattice and the saturation point has not yet been reached, the free carriers result in the absorption and reflection to visible light, specifically causing a significant decrease in optical transmittance of the long wavelength band. In addition, when the sprinkler is too low or the heating temperature is too low, it will result in the insufficient driving force for decomposition of precursor causing the impurity in the films to produce electron scattering and lowering of the visible light transmittance [14, 15]. From the transmittance spectra of FTO films in Fig. 5, it can be seen that as the F doping content increases, the transmittance within long wave area slightly decreases due to the absorption of free carriers. When the sprinkler height is 8 mm and NH_4F concentration is 0.133 mol/L, the conductive property reaches an optimum and the average transmittance of FTO films is about 82%, which indicates that the as-prepared FTO film of this investigation demonstrates a higher transparency and enhanced electrical properties that make it suitable for applications in solar cells, low emissivity glass and touch displays, etc.

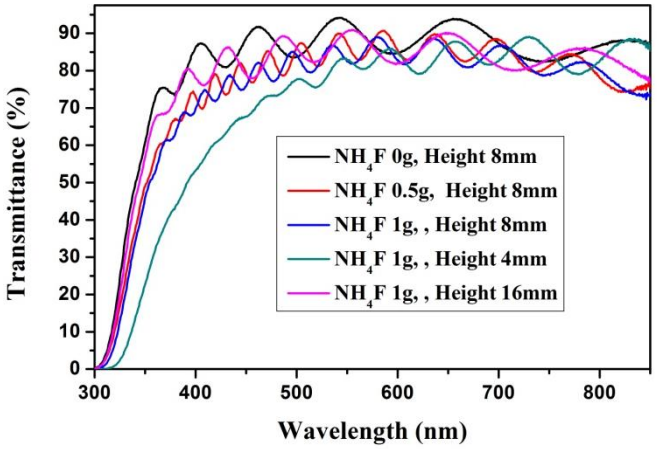

Figure 5. Visible light transmittance of films prepared with different NH_4F concentrations and sprinkler heights

4. CONCLUSIONS

The house-made ultrasonic spray system realizes the scalable preparation of large-area FTO films. The NH_4F concentration in the precursor solution and sprinkler height both have an effect on the F doping content, structure, surface morphology, optical and electrical properties. When 5 wt% of NH_4F versus $SnCl_4$ was utilized with a sprinkler height of about 8-12 mm, the films demonstrated improved quality, the transparency was 82-83% and the minimum resistivity was $1.2\times10^{-3}\Omega$ cm. This investigation reports a procedure that involves a non-vacuum coating technology with a simple device and low cost that benefited in the preparation of large area FTO films of high quality suited for the demand of scale –up production.

ACKNOWLEDGEMENTS
This work was supported by National Natural Science Foundation of China (Grant No. 61505018), Technology Project from Chongqing Education Committee (Grant No. KJ1401113), Chongqing Science & Technology Commission (Grant No. cstc2013jcyjys50001) and Chongqing University of Science and Arts (Grant No.R2012CJ18 & Z2013CJ02).

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