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Improving the performance of fluorine-doped tin oxide by adding salt

Agus Purwanto [a,*], Hendri Widiyandari [b], Risa Suryana [c], Arif Jumari [a]

[a] Department of Chemical Engineering, Faculty of Engineering, Sebelas Maret University, Jl. Ir. Sutami 36 A, Surakarta, Central Java 57126, Indonesia
[b] Department of Physics, Faculty of Sciences and Mathematics, Diponegoro University, Jl. Prof. Dr. Soedarto, Tembalang, Semarang 50275, Indonesia
[c] Department of Physics, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Jl. Ir. Sutami 36 A, Surakarta, Central Java 57126, Indonesia

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ABSTRACT

High-performance fluorine-doped tin oxide (FTO) films were fabricated via a spray deposition technique with salt added to the precursor. The addition of NaCl in the precursor improved the conductivity of the FTO films. Increasing the NaCl concentration to its optimal concentration reduced the sheet resistance of the FTO film. The optimal values for the addition of a NaCl were 0.5, 0.5, 1.5, and 1.5 at.% for the FTO film prepared using NH_4F concentration of 4, 10, 16, and 22 at.%, respectively. The lowest sheet resistance of the salt-added FTO film was 4.8 Ω/□. The FTO film averaged a transmittance of more than 80% in the visible range region ($\lambda = 400$–800 nm). XRD diffractograms confirmed that the crystal structure of the as-grown FTO film was that of a tetragonal SnO_2 and that the addition of salt improved its crystallinity. This film has the potential for use as an electrode for dye-sensitized solar cells (DSSCs).

1. Introduction

Fluorine-doped tin oxide (FTO) film has the potential for application in displays, solar cells, LEDs, smart windows, etc. [1]. In the case of solar cells, FTO film is the primary material that is used for working and counter electrodes for dye-sensitized solar cells (DSSCs). FTO serves as a conductive substrate to transport the electrons from/to solar cells. The ability to resist the high corrosiveness of electrolyte solutions is the main advantage of using FTO films in DSSCs.

FTO film can be produced using many techniques such as spray pyrolysis deposition (SPD) [2–6], sputtering [7], and chemical vapor deposition [8]. SPD offers many advantages: simple processing, low cost, atmospheric operation, and ease of scale-up [2–6,9–17]. To improve the performance of FTO films, many physical modifications have been reported for the SPD technique. These include the application of lamp radiation [14], electric field induction [18], and ultrasonic nebulizer [16,19]. These modifications have improved the production of FTO films.

In this paper, we report an enhancement of FTO performance via chemical modification using a salt. NaCl addition to the precursor and its effect on FTO performance were investigated systematically. The addition of NaCl improved the electrical conductivity of FTO films. This improvement gave these films the potential for DSSC applications that require films with low resistivity and high transmittance. Also, the addition of NaCl improved the film morphology of FTO films by eliminating spot holes and enhancing the crystallinity. In this investigation, high-performance FTO films were produced using a simple SPD technique with a chemical modification that involved the addition of NaCl.

2. Experimental

A schematic diagram of the SPD system is shown in Fig. 1. In this method, the substrate (soda lime glass) was placed on a hot plate heater and heated to a temperature of 500 °C. The precursor was made up of 0.7 M of an ethanolic (96%) solution of $SnCl_2 \cdot 2H_2O$ (98%, Merck Ltd., Germany), and NH_4F (98%, Merck Ltd., Germany). The concentrations of the NH_4F were 4, 10, 16, and 22 at.% of the $SnCl_2$ concentration. To evaluate the effect of salt addition, the NaCl (98%, Merck Ltd., Germany) was added to the precursor in concentrations of 0 to 4 at.%. The precursor solution was then added to the sprayer tank and transported to the glass surface using a flowing rate of 1 L/min with argon gas. The deposition process was conducted for 13 min.

The sheet resistance (R_s) of the FTO films was evaluated using four-probe measurements (Jandel Engineering, Bedfordshire, UK). The optical properties of the FTO films were evaluated using a UV–Vis spectrophotometer (UV 2450, Shimadzu, Kyoto, Japan). To evaluate the crystal structure, the films were characterized using an X-ray diffractometer (XRD, RINT 2200 V, Rigaku-Denki Corp., Tokyo, Japan). The XRD measurements were carried out using nickel-filtered CuKα radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA. The morphology of the FTO

* Corresponding author. Tel./fax: +62 271 632112.
E-mail address: Aguspur@uns.ac.id (A. Purwanto).

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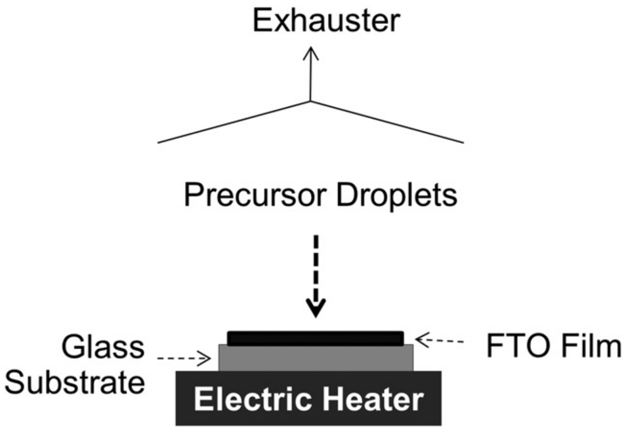

Fig. 1. Schematic diagram of the spray pyrolysis deposition (SPD) technique.

films was evaluated using FE-SEM observations with an S-5000 at 20 kV (Hitachi Ltd., Tokyo, Japan).

3. Results and discussion

The preparation of FTO films using a PSD method started with an evaluation of the effect of the NH_4F addition on sheet resistance. In our previous studies using a flame-assisted spray deposition (FASD) process, the optimal conditions for the addition of NH_4F concentration were 8 at.% [13]. When using PSD, we found that 10 at.% was the optimum concentration of NH_4F for FTO fabrication while maintaining a substrate temperature of 500 °C, as shown in Fig. 2. Such a small increase in NH_4F concentration may have been the result of the different temperature distribution of a hot plate heater in the PSD process compared with that of a flame burner. The conductivity of the FTO film originated from the substitution of fluorine atoms in the SnO_2 lattice. The substitution of oxygen ions with fluorine ions left an oxygen vacancy that suggested the conduction of electrons by the SnO_2 film [4,13]. When doping concentrations exceeded the optimal level (10 at.%), the Rs (sheet resistance) increased. The high Rs originated from an accumulation of fluorine in the grain boundaries [4]. When using the PSD technique, the thickness of the film can be controlled via the deposition time. Prolonging the deposition time increases the thickness of the FTO film. As a result, the sheet resistance of the FTO film will be reduced.

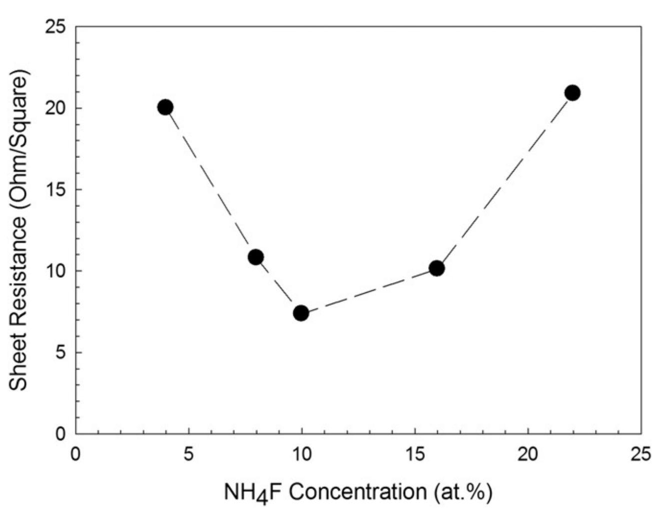

Fig. 2. Sheet resistance of FTO film as a function of NH_4F concentration.

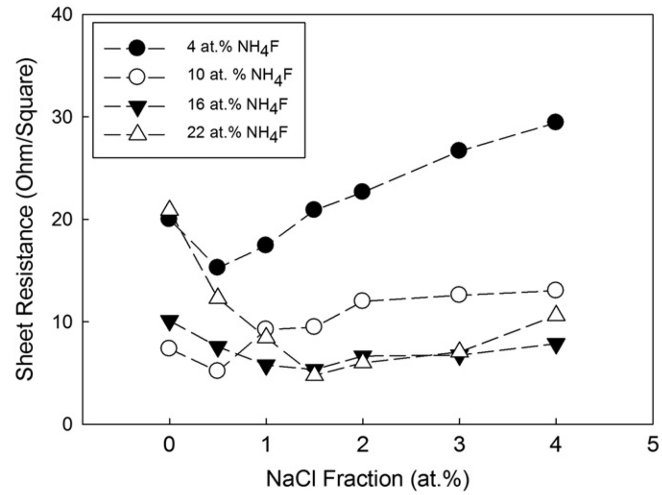

Fig. 3. Sheet resistance of FTO film as a function of NaCl addition with variations in NH_4F concentration.

However, the transmittance of the film decreases as the FTO film thickens [6,10,12,13].

In order to reduce the sheet resistance of an FTO film without reducing its transmittance, we experimented with an addition of NaCl to the precursor. Surprisingly, the addition of NaCl in the precursor improved FTO film conductivity, which was indicated by a lowering of the sheet resistance. Fig. 3 shows the sheet resistance of FTO films as a function of the addition of NaCl. Increasing the NaCl concentration to its optimal concentration reduced the sheet resistance of the FTO film. The optimal values for the addition of a NaCl were 0.5, 0.5, 1.5, and 1.5 at.% for the FTO film prepared using NH_4F addition of 4, 10, 16, and 22 at.%, respectively. NaCl addition at more than 4 at.% was also tested and the result indicated that the increasing of sheet resistance was consistent. The sheet resistance for 5 at.% NaCl addition in FTO prepared using NH_4F concentration 22 at.% was 14.52 Ω/□.

To clarify the effect of NaCl addition on the enhancement of FTO film conductivity, XRD analysis was conducted. Fig. 4 shows the XRD pattern on a FTO film prepared using the addition of NaCl. The crystalline structure of the FTO films was that of tetragonal SnO_2 (JCPDS no. 770451, and space group: F42/nm(136)) [13]. The addition of salt improves the crystallinity of the film as indicated in Fig. 4. The improvement in crystallinity originated from the enhancement of precursor mass transfer in the oxidation reaction due to the presence of

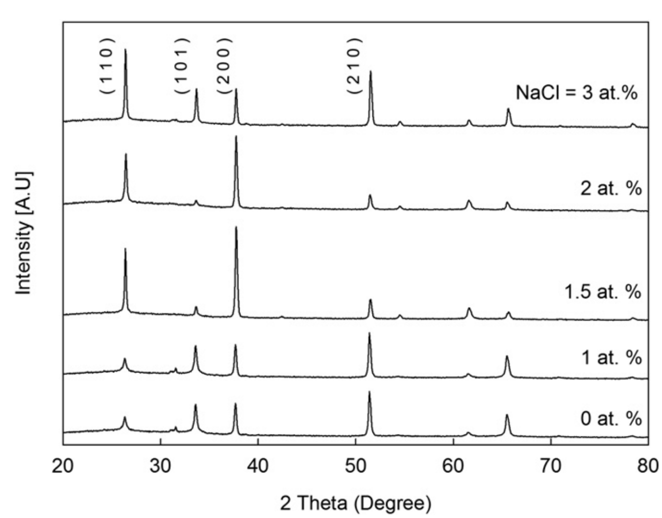

Fig. 4. XRD pattern of FTO film as a function of NaCl addition for a NH_4F concentration of 22 at.%.