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Properties of fluorine-doped tin oxide films prepared by an improved sol-gel process

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ABSTRACT

Fluorine-doped tin oxide (FTO) films were prepared by an improved sol-gel process, in which FTO films were deposited on glass substrates using evaporation method, with the precursors prepared by the conventional sol-gel method. The coating and sintering processes were combined in the evaporation method, with the advantage of reduced probability of films cracking and simplified preparation process. The effects of F-doping contents and structure of films on properties of films were analyzed. The results showed the performance index (Φ_{TC}=3.535×10^{-3} Ω^{-1} cm) of the film was maximum with surface resistance (R_{sh}) of 14.7 Ω cm^{-1}, average transmittance (T) of 74.4% when F/Sn=14 mol%, the reaction temperature of the sol was 50 °C, and the evaporation temperature was 600 °C in muffle furnace, and the film has densification pyramid morphology and $SnO_{2-x}F_x$ polycrystalline structure with tetragonal rutile phase. Compared with the commercial FTO films (Φ_{TC}=3.9×10^{-3} Ω^{-1} cm, R_{sh}=27.4 Ω cm^{-1}, T=80%) produced by chemical vapor deposition (CVD) method, the Φ_{TC} value of FTO films prepared by an improved sol-gel process is close to them, the electrical properties are higher, and the optical properties are lower.

1. Introduction

Since the appearance of transparent conductive oxide (TCO) film in the beginning of twentieth Century [1], two basic properties, transparency and electrical conductivity, have been the key factor to evaluate the film. There are currently three major categories of TCO films, SnO_2-based, In_2O_3-based, and ZnO-based film. The SnO_2-based film has a great potential in areas such as optoelectronic devices [2,3], transparent windows [4], due to the low electrical resistivity, high optical transmittance, high hardness, good electrochemical stability, and a rich source of tin. However, according to semiconductor theory [5], the natural semiconductor SnO_2 is not electrical conductive. With doping elements, such as Mn [6,7], Ta [8,9], Sb [10,11] and F [12,13], the electrical conductivity of TCO films has been improved. Moreover, because the ionic radius of F^- (R_F^-=1.33 Å) and O^{2-} (R_O^{2-}=1.32 Å) are similar in size, F-doping cannot significantly change the crystal structure of SnO_2 thin films and can be effective to adjust the band gap of SnO_2 via controlling the F-doping contents. Therefore, the fluorine-doped tin oxide (FTO) films have been the first choice and applied in industrial production [14].

The FTO films are prepared using a variety of coating techniques including spray pyrolysis [15], chemical vapor deposition (CVD) [16], sol-gel [17] methods. With these methods, the films were fabricated on suitable substrates by high temperature or vacuum technique, spin-coating or dip-coating. In the aspect of the simplifying preparation process and improving the photoelectric property, Chinnappaa et al. [15] reported that FTO films were deposited using a simplified spray technique, and suggested that the minimum sheet resistance is 42.59 Ω sq^{-1} and transmittance in the visible range is 80%. Shi et al. [18] and Wu et al. [19] prepared the FTO film with the minimum surface resistance of 35 Ω cm^{-1} and 110 Ω cm^{-1} by the sol-hydrothermal method, respectively. However, they both mainly reported the electrical properties of FTO films and did not analyze the influence of F concentration on optical performance. To the best of our knowledge, few works have been reported on the technique combined the merits of sol-gel and CVD.

In this study, we proposed a novel preparation process. The precursors of the FTO film were fabricated by sol-gel method and then deposited on glass substrates to obtain the FTO films by a evaporation method. Here, the evaporation process replaced a dip-coating or spin-coating process and a sintering process, which avoided the disadvantage of films cracking in sol-gel coating process [20]. Furthermore, the analyses of photoelectric properties of FTO films for various F-doping contents and structure of films were discussed.

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2. Experimental

2.1. Materials

Tin chloride pentahydrate ($SnCl_4{\cdot}5H_2O$) (AR, Tianjin Zhi Yuan Chemical Reagen Co., Ltd), Tin fluoride (SnF_2) (AR, Energy Chemical), Methanol (CH_3OH) (AR, Tianjin Zhi Yuan Chemical Reagen Co. Ltd), Monoethanolamine (MEA, C_2H_7NO) (AR, Tianjin Chemical Reagent Factory), and Ammonium hydroxide (NH_4OH) (purity 25–28%, Far Eastern Group), were used as tin source, fluoride source, solvent, stabilizer, catalyst, respectively. The glass (From bottom to top, 4 mm thick glass, 25 nm layer of SnO_2 and 25 nm layer of SiO_2 coated onto glass) provided by the Shandong jin jing group co., Ltd. was used as the substrate material to adjust the colour of the glass surface and prevent leaching of ionic impurities from the glass.

2.2. Synthesis of fluorine-doped tin dioxide precursor

The colourless transparent solution was obtained by stirring the mixed solution of CH_3OH, MEA, NH_4OH and $SnCl_4{\cdot}5H_2O$ with the molar ratio of 34:1:1.89:1 at 50 °C for 10 min. Added SnF_2 to the solution with the SnF_2 and $SnCl_4{\cdot}5H_2O$ molar ratios of 0–11 mol% (F/Sn=0–22 mol%) at 50 °C and kept stirring for 5 h, the gel was obtained by aging the transparent sol for 2 days at room temperature, and dried at 150 °C for 15 min in the Air-blower-driven Drying Closet. Then the precursor of fluorine-doped tin dioxide was obtained by the sol-gel method.

2.3. Preparation of fluorine-doped tin dioxide film

The $Sn(OH)_{4-x}F_x$ xerogel was placed at the bottom of the large crucible, and a glass substrate was positioned at the 3.5 ± 0.5 mm point above the xerogel source, and the sample of the FTO film was evaporated at 600 ℃ for 2 h in a muffle furnace. The specific process was shown in Fig. 1.

For the convenience of the research, the products made in Shandong jin jing group by CVD method were used as the contrast samples.

2.4. Characterization of performances

The sheet resistance was measured by the four-point probe method using a KDY-1 four-point probe meter. The UV–visible transmittance spectra were observed by a TU-1901 spectrophotometer. The phase and crystallinity of the FTO films were analyzed by a D8 ADVANCE X-ray diffraction (XRD). The surface morphology of films was observed by a Sirion200 scanning electron microscopy (SEM). The morphologies, particles sizes and the structures of the samples were investigated by a FEI-TECNAI G^2 high resolution transmission electron microscopy (HRTEM). Diffraction patterns and lattice fringes were obtained by

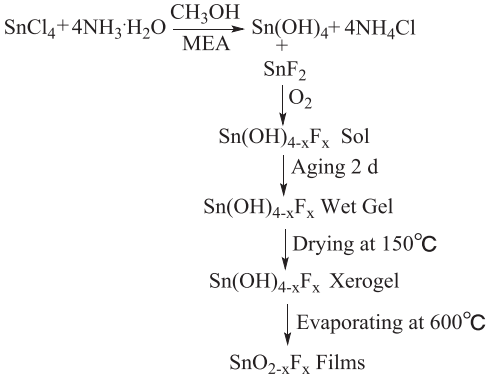

Fig. 1. Preparation processes of the $SnO_{2-x}F_x$ films.

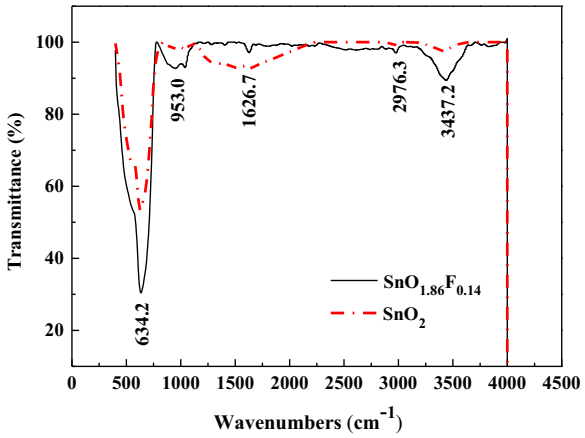

Fig. 2. FT-IR curve of $SnO_{2-x}F_x$.

TEM images in the Gatan Digital Micrograph software by the Fast Fourier transform (FFT) and Inverse Fast Fourier transform (IFFT). The elements and functional groups of the samples were characterized by Nicolet 5700 Fourier transform infrared (FT-IR) spectrometer.

The TEM observation was prepared by ultra-sonicating 0.01 mg mL^{-1} powder samples of FTO thin films in alcohol, then dipping a TEM sample grid into the dispersion.

Transparency and electric conductivity are the two basic characteristics of FTO thin films, and they are a contradiction. To evaluate the comprehensive performance of FTO thin films, Fraser et al. [21] defined the performance index F_{TC}, and Haacke et al. [22] modified it as $\Phi_{TC}=T^{10}/R_{sh}$, where T is the transmittance, and R_{sh} is the sheet resistance. The larger the value of Φ_{TC}, the better the comprehensive photoelectric properties of FTO films.

3. Results and discussion

3.1. The formation of $SnO_{2-x}F_x$

The FT-IR spectra of $SnO_{2-x}F_x$ samples heat-treated at 600 °C are shown in Fig. 2. The main absorption peak at 634.2 cm^{-1} is corresponding to the SnO_3^{2-} group, which indicates that groups of Sn-O and Sn-O-Sn or SnO_2 are generated. And the increase of absorption peak intensity of 634.2 cm^{-1} for 14 mol% F doped SnO_2 may be attributed to the incorporation of fluorine ions. The Sn-OH group [23] peak at 1626.7 cm^{-1} is weak for $SnO_{1.86}F_{0.14}$. This result shows the fluorine can promote the reaction of Sn-OH. The absorption peak of –OH group presented at 3437.2 cm^{-1} get much strong at 14 mol% F doping. This may be due to the residue of –OH originated from solvents such as CH_3OH or $HO(CH_2)_2NH_2$.

3.2. Effects of F content and structure of films on properties of films

3.2.1. Structure

The XRD patterns of FTO films with various F concentrations are presented in Fig. 3. The XRD results reveal that the $SnO_{2-x}F_x$ crystals are polycrystalline with tetragonal rutile phase (JCPDS card no. 41-1445). All the samples contain the SnO_2 characteristic peaks along (110), (101) and (211) planes, and the diffraction of (110) plane is dominant. Obviously, the intensity of peak (110) increases with F concentrations in 6–14 mol% and gradually decreases with the further increase of F contents in 14–22 mol%, which indicates the $SnO_{2-x}F_x$ crystalline is the best at 14 mol%. However, Wang et al. [24] and Shi et al. [25] reported that (200) (110) or (211) planes were the preferential orientation for the FTO films. They analyzed the reason of different preferred orientation and found that the peak intensities changed for different solvents. In present work, as expected, the (110) plane is obtained as the preferential orientation in methanol solvent.