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A study on the electrical properties of fluorine doped direct-patternable SnO_2 thin films

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Abstract

Direct-patternable fluorine doped SnO_2 (FTO) thin films were fabricated by a photochemical solution deposition method. The electrical properties and crystallinity of FTO thin films were slightly enhanced relative to undoped SnO_2 films and the improvement of electrical conduction was found to be due to an increase of carrier concentration. Direct-patterning of FTO thin films was performed without using photoresist or dry etching. These results suggest that a micro-patterned system can be simply fabricated at low cost, and the electrical properties of direct-patternable SnO_2 films can be improved by fluorine doping.

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1. Introduction

Indium tin oxide (ITO) is widely used as a transparent electrode for solar cells and optoelectronic devices [1]. However, there are many disadvantages of ITO including the fact that it is rare, and may eventually be exhausted, and its instability in hydrogen plasma [2]. SnO_2 thin films have been increasingly studied years as transparent electrode materials due to the high optical transparency, high chemical durability, and low cost [3]. However, for electrical device applications, improvement of the electrical properties is absolutely required.

For the fabrication of electronic circuits, a micro-patterning process is commonly used. However, the conventional etching process is accompanied by the generation of physical defects and the resulting degradation of properties, and pollution from hazardous materials. By using photochemical solution deposition, photoresist and dry etching are not necessary, as the coated films behave like the negative photoresist. In doing so, damage and problems from etching were avoided [4].

Among the various doped SnO_2 films, fluorine doped SnO_2 (FTO) thin films are the lowest resistive materials. Normally, FTO thin films are fabricated using spray pyrolysis [5]. In this method, in situ annealing of the film is possible during film deposition. However, fluorine does vaporize during drying or annealing fabrication steps, and the films have to be patterned after formation for device fabrication. So, in this study, we adopt a photochemical solution deposition (PSD) method for direct-patterning of the film.

In this work, the effects of fluorine on the properties of direct-patternable SnO_2 thin films prepared by PSD were investigated. Furthermore, direct-patterning of FTO thin films using a photosensitive solution and UV light exposure was performed to avoid damage from etching and to simplify the micron-scale patterning procedure.

2. Experimental

SnO_2 thin films were prepared by PSD. The tin source, solvent and fluorine source were tin chloride pentahydrate ($SnCl_4{\cdot}5H_2O$), methanol (CH_3OH) and tin fluoride (SnF_2), respectively. $SnCl_4{\cdot}5H_2O$ was dissolved in CH_3OH to a final concentration of 0.3 M and 2-nitrobenzaldehyde (NBAL) was introduced as a photosensitive additive. SnF_2 was only slightly soluble in CH_3OH, and formed a cloudy solution. By using $SnCl_4{\cdot}5H_2O$ and SnF_2, we obtained a clear solution for FTO thin film fabrication containing various F/Sn atomic ratios of 0 to 1.2 [6]. The dissolved photosensitive solution was stirred at room temperature for 3 h. Small amounts of solution were spin-

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coated at 2000 rpm for 20 s on Corning 1737 glass substrates. The spin-coated film was dried on a hot plate at 60 °C and the dried film was exposed to UV light of 365 nm. Then, the UV exposed film was washed by CH_3OH to remove the unexposed area. Films were then dried at 150 °C for 10 min and annealed at 500 °C for 1 h in a tubular furnace under a N_2 atmosphere [7]. Thicknesses of the films were obtained using scanning electron microscopy (SEM, Hitachi Model S-4200). Crystallinity was analyzed by using an X-ray diffractometer (XRD, D/MAX-2000, Rigaku) with Cu Kα radiation. The electrical properties of the film were measured using Hall Effect measurements (HMS-3000, Ecopia). Optical transmittance measurements were carried out using a UV–VIS–NIR spectrophotometer (V-570, Jasco). To investigate the surface chemical bonding state, X-ray photoelectron spectroscopy (XPS, ESCALAB 220i-XL, VG Scientific) was used with an Al Kα source.

3. Results and discussion

Fig. 1 provides XRD patterns of SnO_2 thin films with various F/Sn atomic ratios after annealing at 500 °C. The diffraction peaks were indexed as (1 1 0), (1 0 1), (2 0 0), and (2 1 1) of the cassiterite SnO_2 crystalline phase (JCPDS 70-4177). Similar diffraction patterns were observed by the incorporation of SnF_2 as a fluorine dopant. With increasing F/Sn atomic ratio, the diffraction pattern intensity gradually increased. Normally, the ionic radius of F^- (1.33 Å) is close to that of O^{2-} (1.32 Å), so the doping process can take place easily, and the crystallinity of the films is not greatly affected [8]. The slight increase in the diffraction intensity with increasing F-content might be due to an increase in the thickness of FTO thin films. With increasing F/Sn atomic ratio, the thickness of FTO thin film was found to increase from 962 nm to 2.3 μm by SEM. This thickness increase with increasing F/Sn ratio was due to the use of a fixed molarity of 0.3 M. That is, the absolute amount of Sn increased in the coating solution with increasing F/Sn ratio because the molecular weight of SnF_2 (156.71 g/mole) was smaller than that of $SnCl_4{\cdot}5H_2O$ (350.58 g/mole).

The electrical properties of SnO_2 thin films with various F/Sn atomic ratios were investigated by Hall Effect measurements, and the results are given in Fig. 2. The values confirm that carrier concentration, mobility, and resistivity were affected by the F/Sn atomic ratio. Carrier concentration and mobility of SnO_2 thin films were 4.757×10^{14} cm^{-3} and 812.7 cm^2/Vs, respectively. The carrier concentration increased with increasing F/Sn ratio. Fluorine doping generated free electrons by F-substitution into O sites. Mobility decreased due to increased electron scattering by excess free electrons and ionized impurities [9]. Variation in the resistivity is proportional to the carrier concentration and mobility, and the resistivity of FTO thin films decreased with increasing F/Sn atomic ratio. The carrier concentration and mobility of FTO thin films with F/Sn atomic ratio of 0.75 were 5.599×10^{18} cm^{-3} and 16.1 cm^2/Vs, respectively. The resistivity of SnO_2 thin films increased above an F/Sn ratio of 0.75 due to the influence of decreased electron mobility.

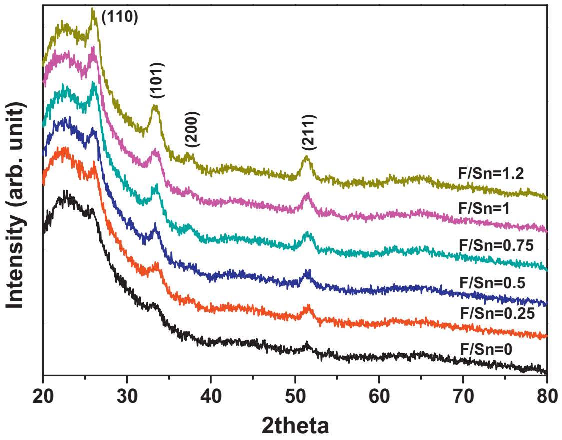

Fig. 1. XRD patterns of pure SnO_2 and F-doped SnO_2 thin films annealed at 500 °C with various F/Sn atomic ratios.

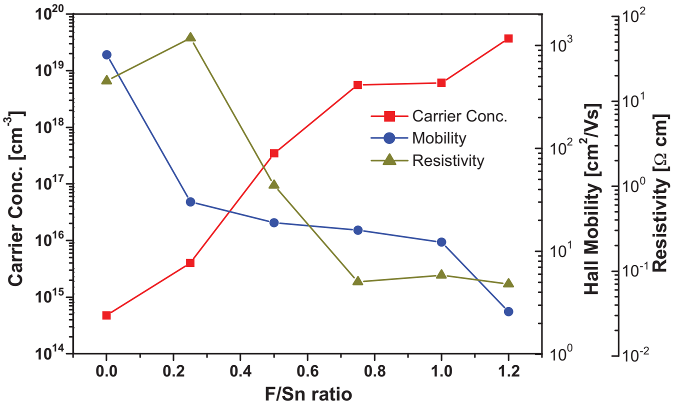

Fig. 2. Carrier concentration (■), mobility (●), resistivity (▲) of pure SnO_2 and F-doped SnO_2 thin films annealed at 500 °C with various F/Sn atomic ratios.

Fig. 3 shows UV–Vis transmittance spectra of SnO_2 thin films with various F/Sn atomic ratios. The transmittance of SnO_2 films slightly decreased in the visible light region by incorporation of fluorine dopant. The values of average transmittance in the visible region for F/Sn atomic ratios from 0 to 1.2 were 92.6, 91.0, 90.7, 88.2, 90.0, and 89.7% with increasing F/Sn ratio. A slight decrease in the optical transmittance with F/Sn ratio could be attributed to an increase in the film thickness and excess free electrons in the films [10].

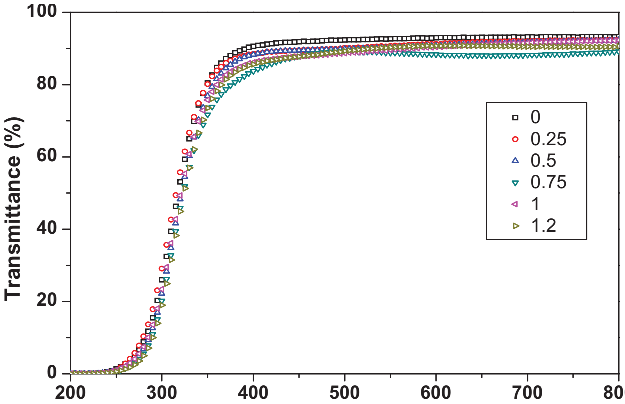

Fig. 3. Optical transmittance of pure SnO_2 and F-doped SnO_2 thin films annealed at 500 °C with various F/Sn atomic ratios.

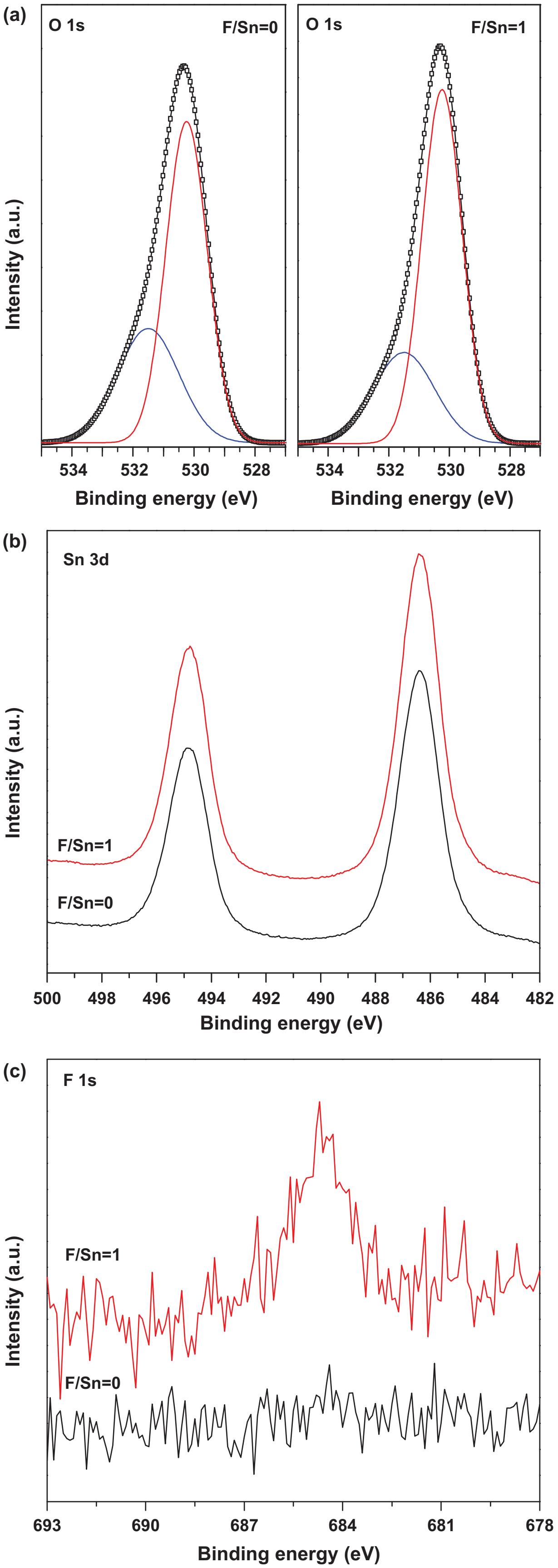

Fig. 4. XPS core level spectra of (a) O 1s, (b) Sn 3d, and (c) F 1s at the surface of pure SnO_2 and F-doped SnO_2 films with a F/Sn atomic ratio of 1 after annealing at 500 °C for 1 h.

Table 1
The atomic percentage of elements in the pure SnO_2 and F-doped SnO_2 thin films with a F/Sn atomic ratio of 1 after annealing at 500 °C for 1 h.

	C (%)	F (%)	O (%)	Sn (%)
Pure SnO_2	14.23	–	65.01	20.76
F-doped SnO_2	14.49	1.06	64.01	20.44

The electrical bonding states of pure SnO_2 and FTO thin films were analyzed using XPS, and the results are given in Fig. 4, which shows O 1s, Sn 3d, and F 1 s core level spectra of pure SnO_2 and FTO thin films of a F/Sn atomic ratio of 1. The binding energies were corrected using the referencing C 1s peak at 284.5 eV. In Fig. 4(a), O 1s peaks of pure SnO_2 and FTO thin films were fitted, and the fitted binding energies were located at 530.24 eV and 531.5 eV, respectively. The peak binding energy around 530.24 eV is attributed to oxygen in Sn–O–Sn bonds. The other peak, positioned at 531.5 eV, is ascribed to surface hydroxyl groups –OH [11]. The atomic ratio of O/Sn of pure SnO_2 and FTO thin films except –OH bonds were 1.16 and 1.21, respectively. Due to the highly hydrophobic nature of fluorine, surface –OH groups were minimized with FTO, so the apparent surface composition of O/Sn for FTO was found to be larger than that of pure SnO_2. As shown in Fig. 4(c), the F 1s peak of the FTO thin film was observed at 684.7 eV. The atomic percentage of fluorine was 1.06 at% and the F/Sn atomic ratio was 0.05. The atomic percentage of elements in the SnO_2 films is summarized in Table 1. These values were calculated from core level spectra by using atomic sensitivity factors [12]. The fluorine content on the films was very low because fluorine vaporized from the films during the drying and annealing process [13].

The possibility of direct-patterning of FTO thin films was examined by removing the area unexposed to UV using a methanol. An optical micrograph in Fig. 5 contains a relatively dark area (green-reddish) corresponding to the FTO thin film and a bright area (bluish area) corresponding to the glass substrate. As shown at the edge of the centered pattern,

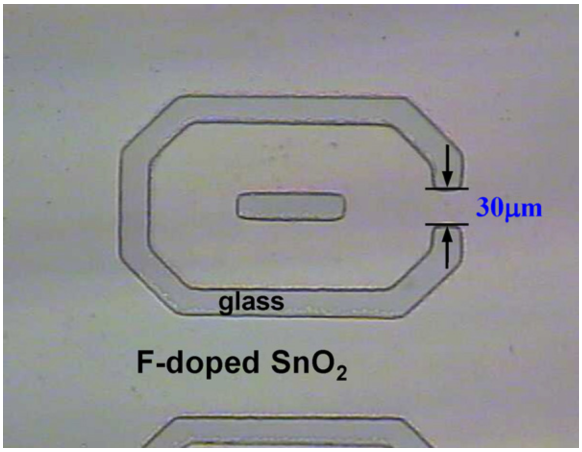

Fig. 5. Optical image of direct-patterned F-doped SnO_2 thin film after drying at 150 °C for 10 min.

micron-scaled patterning was successfully obtained by direct-patterning using photochemical solution deposition.

4. Conclusions

The crystallinity of the SnO_2 films was almost unaffected by the incorporation of fluorine dopant. With increasing incorporation content of fluorine in the SnO_2 film, the optical transmittance of the films slightly decreased and thickness increased. However, the resistivity of the FTO thin films was lower compared to pure SnO_2 film because the carrier concentration was increased due to free electron generation by fluorine substitution into O sites. Fluorine doping enhanced the electrical properties of direct-patternable SnO_2 thin films without significant degradation in the structural and optical properties. With direct-patterning of FTO thin films using PSD, a line-width of 30 μm was successfully performed without photoresists or dry etching.

Acknowledgements

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