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Raman scattering, electrical and optical properties of fluorine-doped tin oxide thin films with (200) and (301) preferred orientation

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HIGHLIGHTS

- We coated fluorine-doped tin oxide thin films with preferred orientation of (200) and (301).
- We examine changes in the level of electrical and optical properties with the orientation.
- (200) preferred orientation showed lower electrical resistivity and optical transmittance.
- (200) oriented thin films have higher electron concentrations that are related with IR active modes.

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ABSTRACT

(200) and (301) preferred oriented fluorine-doped tin oxide (FTO) thin films were fabricated by spray pyrolysis of ethanol-added and water-based FTO precursor solutions, respectively. (200) oriented FTO thin film from ethanol-added solution shows the lower electrical resistivity and visible light transmission than (301) preferred thin film from water-based solution. It is due to the higher carrier concentration and electron mobility in (200) oriented crystals, that is, the lower ionized impurity scattering. The higher electron concentration is related to the higher optical band gap energy, the lower visible light transmission, and the higher IR reflection. For (301) preferred FTO thin films from water-based solution, the lower carrier concentration and electron mobility make the higher electrical resistivity and visible light transmission. Raman scattering analysis shows that IR active modes prominent in (200) oriented FTO thin film are related with the lower electrical resistivity.

1. Introduction

Transparent conducting oxide (TCO) is widely used for the application of flat panel display like liquid crystal displays and plasma display panel [1–5]. It is also applied in the field of touch panel, solar cell electrode, low-emissivity glass, defrost window, and anti-static material. Many researches about a crystal orientation of FTO thin film were published [6–9]. The texture of TCO is said to be better because the scattering and absorption of incident light in the interface is greater in the pn junction, the larger the texture structure of TCO.

SnO_2 thin film prepared from $SnCl_4$ precursor tends to show preferential growth along (200) direction, whereas the SnO_2 thin film deposited from $SnCl_2$ presents a disordered preferential growth along (101), (211) and (301) directions [6]. The electrical resistivity of SnO_2 thin film is dependent on the crystalline orientation. For example, the increase of (200) intensity leads to the decrease in the electrical resistivity. Chlorine or fluorine incorporation into SnO_2 thin film creates point defects by chlorine or fluorine substitution to oxygen and forms twin boundary planes (011) [7]. SnO_2 thin film deposited from $SnCl_2 \cdot 2H_2O$ consist of {101} crystallite faces with (110) preferred orientation, while the crystallites consist of {111} faces corresponding to a (200) preferred orientation for $SnCl_4$ [4]. The presence of (101) and (301) twin planes is used to explain the observations of (301), (211) and (101) preferred orientations, respectively. Water to propanol solvent ratio affects the texture coefficient along (200) orientation [9]. The increase of water ratio inhibits the crystal growth of (200) orientation. In our previous study [10], we investigated the effects of ethyl alcohol to the crystalline orientation and crystallite morphology of FTO thin film. FTO thin film deposited from water-solvent based solution showed the prismatic crystallites, corresponding to (301)

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preferential orientation, while the 5% ethyl alcohol addition to FTO solution changes the preferential orientation to (200) comprised of pyramidal crystallites.

Bruneaux et al. [11] studied of the structural and electrical relations of SnO_2 thin films formed by spray pyrolysis. They reached a conclusion that the grain resistivity is assumed to be the sum of two contributions: (1) that of neutral region characterized by a bulk mobility of about 25 cm^2V^{-1} s^{-1}, (2) that of the space charge region created by charge trapping at grain boundaries which is meaningful at low carrier density ($<5 \times 10^{-18}$ cm^{-3}). Haitjema et al. [12] also did their research about the electrical properties of pyrolytically sprayed FTO thin film. Their research results conclude that the electron mobility is mainly limited by ionized impurity scattering. Thangaruju [13] also reached the same conclusion that the ionized impurity scattering is the dominant mechanism limiting the mobility. Scattering mechanisms of charge carriers in transparent conducting oxide thin films show that grain boundary scattering is minimal due to the tunneling current for degenerate state [14–16]. In this research paper, we study the effects of crystal preferential orientations (200) and (301) to the electrical and optical properties. The preferential orientation of FTO thin films affects the electrical and optical properties.

2. Experimental method

2.1. Synthesis of FTO spray coating solution

FTO coating solution was synthesized by mixing tin (IV) chloride penta-hydrate ($SnCl_4 \cdot 5H_2O$, 98% Daejung, Korea) and ammonium fluoride (NH_4F, 98 +% Aldrich, USA) in deionized water (water-based solution) and deionized water with addition of 5% ethyl alcohol (5% EtOH-added solution). The concentration of $SnCl_4 \cdot 5H_2O$ was fixed at 0.68 M and NH_4F was controlled to be 1.765 M ratio of F/Sn. The F/Sn molar ratio was determined by our previous work, where FTO thin film showed the lowest electrical resistivity.

FTO coating solution was sprayed on to aluminoborosilicate glass substrate with 8 cm * 8 cm size by using nebulizer (1.2 MHz) and air as a carrier gas. The glass substrate was put on graphite plate and heated at 530 °C for 10 min before coating. The mist of coating solution was carried into coating chamber through an inlet along side wall of reactor chamber horizontally and the exhaust gases exited through an outlet of the other side wall. The spray speed of coating solution was 10 ml min^{-1} and the deposition time was varied from 2 to 20 min.

2.2. Characterization of FTO thin film

The crystal structure of FTO thin film was analyzed by X-ray diffractometer (Rigaku, 2311-B, Japan) at 50 kV and 100 mA and the microstructure evolutions and thickness changes were observed by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6700, Japan). Raman scattering spectroscopy of FTO films with thickness changes were analyzed by using 532 nm laser beam through 20 times objective lens and detecting scattering signals by thermoelectrically cooled charge coupled detector (JASCO, NRS3100, Japan). The electrical properties of FTO thin films were measured by Hall measurement system (HMS3000, Ecopia, Korea) under 0.5 T magnetic field. UV-vis-NIR spectra were also characterized by using UV-vis-NIR spectrophotometer (V4700, JASCO, Japan) in the range of 200–2500 nm.

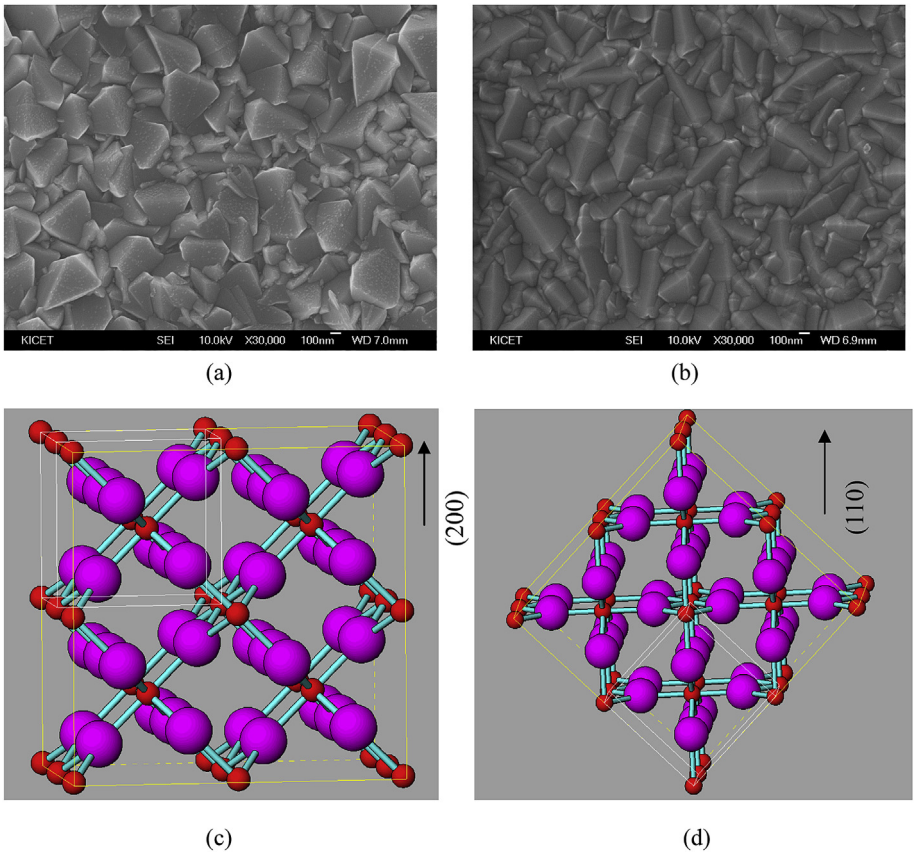

Fig. 1. FE-SEM images of FTO thin films from 5% ethanol-added solution (a) and water-based solution. The deposition time was 8 min at 500 °C.