Effect of Spray Directions on the Crystal Growth of Fluorine-Doped Tin Oxide One-dimensional nanostructured Thin Films

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ABSTRACT

In this study the novel spray pyrolysis technique, known as rotational, pulsed and atomized spray deposition method was used to fabricate vertically aligned and well separated FTO One-dimensional nanostructures on glass substrate. It was confirmed that spraying at low angle to the substrate is mandatory for the crystal growth of vertically aligned nanorods. The preferential orientation of nanorods crystallites along the (101) direction and prepared nanorods thin film showed an excellent transparency of 84.8% and a low resistance of 26.7 Ω/sq.

Indexing terms/Keywords

FTO thin films; Wide bandgap semiconductors; One-dimensional nanostructure; Vertically align nanorods; Advanced SPD technique

Academic Discipline And Sub-Disciplines

Materials Science

SUBJECT CLASSIFICATION

Nanoscale science, Solid State Physics

TYPE (METHOD/APPROACH)

Experimental study

1.   INTRODUCTION

Transparent conducting oxides (TCOs) have become a technologically very important class of material due to the good optical transmittance while at the same time good electrical conductivity. These TCO thin films with wide bandgap (3 eV) semiconductor materials are used in many devices such as flat panel displays [1], low emissivity windows [2], electrochromic windows [3], light-emitting diodes [4], gas sensors [5], electromagnetic shielding and front-surface electrodes for solar cells [6]. Currently, TCO thin films with low-dimensional metal oxide nanostructured such as nanoparticles,nanotubes,nanorods,nanowires, nanosheets and so on are getting attractive components in a wide variety of technological applications in different fields due to their high surface-to-volume ratio, enhanced material characteristics because of quantum confinement effects and the high fraction of chemically similar surface sites [7].

There are several steps have already been studied to enhance the performance of dye-sensitized solar cells (DSSCs). Recently, control of material morphology such as nanotube (NT) and nanorod (NR) arrays of transparent front electrode has been employed to improve the DSSCs performance [8]. Such One-dimensional (1D) nanostructured metal oxide thin films use to improve interfacial surface area, light transmittance and high light trapping by scattering. This provides a direct scheme to higher light absorption by photoactive layer to enhance the power conversion efficiency of solar cells [9]. Among the different TCO's , Fluorine doped tin oxide (FTO) has become the more considerable thin films because they show quite stable toward atmospheric conditions, mechanically hard, chemically inert, low cost and ability to withstand high temperatures. Despite the increasing extensive use of FTO thin films in device applications, there are only few publications on 1D nanostructured FTO thin film and it has not been well explained the formation mechanism and required growth conditions for 1D nanostructured FTO thin films. For the first time, Russo and Cao fabricated FTO nanorods (FTO NR) with aid of the alumina template [10] and Cho et al. synthesized the FTO NR for gas sensing applications [11]. Recently, D.Liyanage et al. fabricated Ethylene Glycol assisted FTO NR using improved spray pyrolysis deposition method [12].

Herein, we investigated the effects of spray direction on the formation of the vertically aligned FTO 1D nanostructured thin films using a in house developed novel spray technique, known as rotational, pulsed and atomized spray deposition (RPASP). This technique is versatile and several spraying parameters can be controlled.

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2. MATERIAL AND METHODS

Firstly, tin (IV) chloride penta-hydrate ($SnCl_4 \cdot 5H_2O$ 98%, Wako Chemicals) and Ammonium fluoride (NH_4F 98%, Aldrich Chemicals) were dissolved in deionized water with addition of 8% propanone. The concentration of $SnCl_4 \cdot 5H_2O$ was fixed at 0.20M and NH_4F was controlled to be 0.80M. Rotational, pulsed and atomized spray pyrolysis deposition technique use to deposit FTO precursor solution on pre cleaned soda lime glass substrate (50mm * 50mm size) kept in a spray chamber with normal atmosphere at 470 °C as shown in Fig.1. The spray pressure was fixed in 0.20MPa with 2 s on and 13 s off spray pulses in order to maintain the substrate temperature. The distance from the nozzle exit to the substrate was 1 cm. We fabricated three types of FTO samples by precisely controlling the spray direction of the nozzle with the substrate, which is below 15°, about 30° and above 45°. Each sample was prepared with total spray time (including both on and off time) of 60min (effective 8 min spray on). After each deposition, the hotplate was switched off to cool the substrate containing samples to room temperature and the samples were retrieved and characterized.

The morphologies of the FTO thin films were investigated by Scanning Electron Microscopic (JEOL JSM-6320F). The structural properties of the thin films were determined by X-Ray Diffraction (XRD, Rigaku RINT Ultima-III, Cu Kα, λ = 1.541836 Å) and the data were analyzed using PDXL XRD analysis software. The FTIR spectra were recorded on JASCO FT/IR 6300 Fourier Transformed Spectrometer at a resolution of 4 cm^{-1} with a spectral range of 400cm^{-1} -700cm^{-1}. The all IR spectra were the result of the average of 64 scans and were recorded at room temperature.   UV-Visible Transmission spectra were recorded on JASCO V-630 spectrometer in the wavelength range from 200nm to 800nm and sheet resistances were obtained by Hewlett Packard 34401 A multimeter.
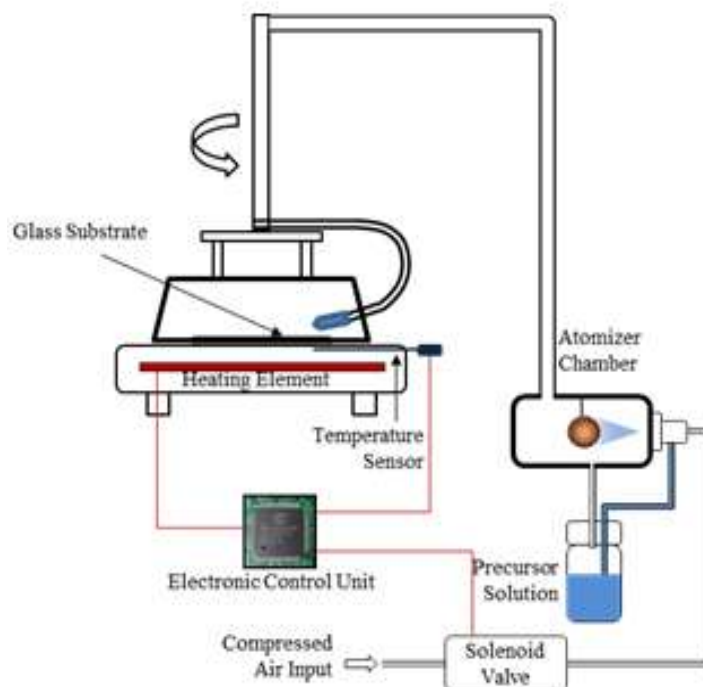

Fig.1. Basic setup of RPASP deposition method.

3. RESULTS AND DISCUSSION

The morphology of the prepared FTO thin film at higher spray angle to the substrate (above 45°) is shown in Fig.2. That SEM image clearly shows FTO nanoparticles (FTO NP) are formed with 50 to 120 nm in size range and 220 nm in film thickness. The rotational nozzle part of this new ASP technique is very important to fabricate homogeneous thin films. The fine aerosol droplets of the precursor solution are deposited on the hot glass substrate and then undergo pyrolysis to form nucleated FTO species.

This will then grow into FTO particles [13].The vertical spraying technique has already been used by many researchers to synthesize TCOs thin films. Vertical or higher angle spraying to the substrate facilitates to deposit precursor solution with lesser density due to scatter of the fine particles throughout the substrate surface. Hence, it provides more space for FTO grains to grow along horizontal directions, as a result the thin film consists of pyramidal and prismatic crystallites [14].

Figure 3 shows the SEM image of the cross-link FTO 1D nanostructure formed at middle spray angle (about 30°) to the substrate. It clearly shows that the morphology of the FTO thin film has changed to cross link nanorods. So it indicates

that this spray angle is sufficient to sweep the precursor solution along the substrate to form 1D nanostructure, but the density of the precursor particles is still not enough to improve verticality of nanostructure.
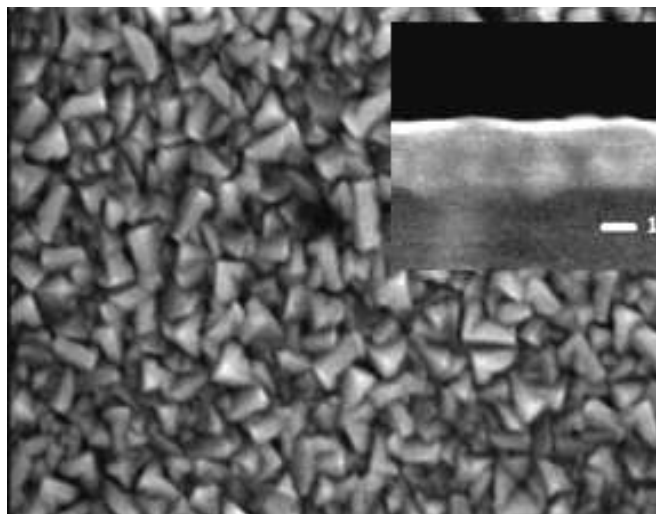

Fig.2. FTO nanoparticles grown at higher spray angle to the substrate (above 45°)

Figure 4 shows the morphology of the vertically align FTO 1D nanostructure prepared at low spray angle (below 15°). The kinetic phenomena of the formation of vertically align nanorods can simply be explained as follows. Horizontal or low angle spray technique facilitates to sweep the atomized fine particles along the hot substrate. As a result density of the particles become high and it direct to grow FTO particles along vertical direction while restricting in to other directions [15]. Vertically align niddle like structures form at the initial stage of the spray and it will then convert in to hollow nanorods with the spray amount.
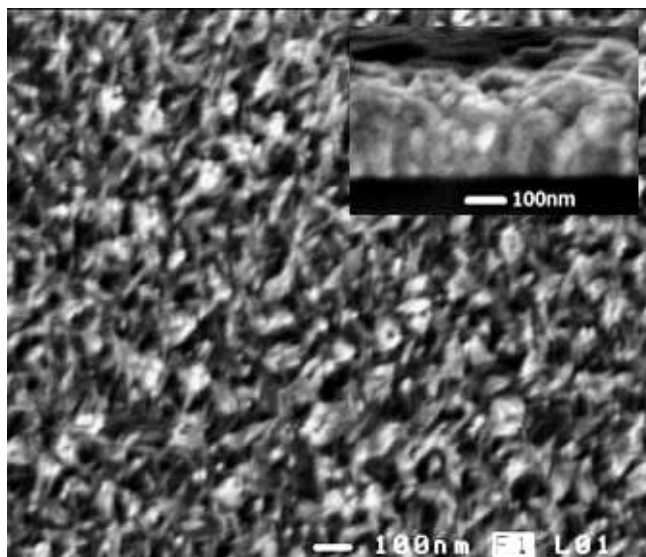

Fig.3. FTO cross link nanotubes grown at middle spray angle to the substrate (about 30°)
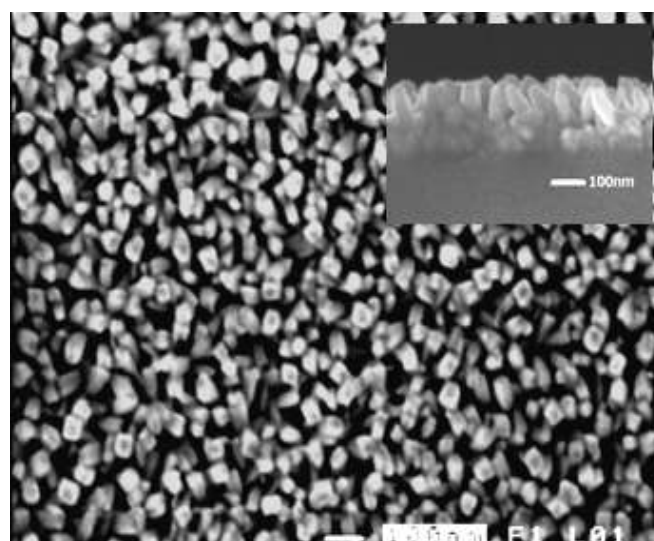

Fig.4. FTO nanotubes grown at low spray angle to the substrate (below 15°)

Figure 5 illustrate the X-ray diffraction (XRD) pattern for three FTO samples prepared at different spray directions. All the diffraction peaks can be readily indexed to the cassiterite type of tetragonal SnO_2 phase (PDF card no 01-070-4175 of PDXL XRD analysis software). Other peaks were not observed, indicating the high purity of obtained product.
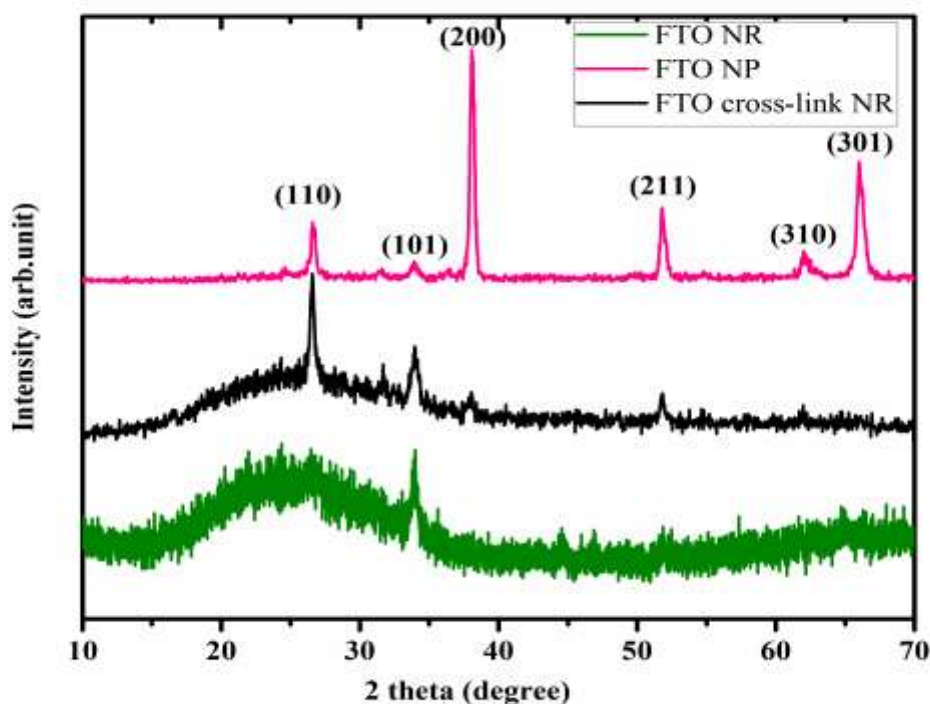
Fig.5. XRD patterns of FTO thin films prepared at different spray angle to the substrate

These XRD data clearly shows us the texture of the thin films has changed with spray directions. However, the preferred orientation can be controlled by varying different spray parameters such as precursor source, gas flow rate, deposition time, and deposition temperature [14]. As shown in Fig.5. FTO nanoparticles prepared at higher angle to the substrate shows (200) plane as the preferred orientation. The intensity of (301) crystal orientation was also comparably high in nanoparticles thin film. In Chang-Yeoul Kim et al. also reported that preferred orientation of FTO crystallites along the (200) and (301) plane [16]. FTO nanorods prepared at low angle to the substrate grow preferably in the (101) direction as shown in Fig.5. It is also confirmed that the nanorods are vertically aligned along the (101) direction. This is in accordance with previously published works. Devinda et al [12] also asserted that the preferred direction of SnO_2 nanorods occurs along the (101) plane. As shown in Fig.5. The dominant peak of the cross-linked nanorods was along (110) direction, which clearly indicates that the nanorods are not vertically aligned and side walls of the nanorods are more exposed to the XRD. The (110) plane is the thermodynamically most stable plane of SnO_2 crystal structure due to the lowest surface energy [17].

The FTIR spectrum contains the resonance of tin oxide stretching vibration modes and substitution of fluorine ion to oxygen ion in SnO_2 lattice of the thin films are shown in Fig.6. The oxygen and fluorine vacancies have been considered to be the donors and the substituted oxygen ion provides one more free electron to enhance the carrier concentration in the FTO thin films. In this thin film, the fluorine ions are supposed to occupy the position of oxygen due to the similar ionic size (F^- : 0.133nm, O^{2-} :0.132 nm) and comparable energy of bond with tin (Sn-F bond: 26.75 D^0/KJmol^{-1}, Sn-O bond 31.05D^0/KJmol^{-1}). Also, the Coulomb forces that bind the lattice together are reduced since the charge on F^- is only half of the charge on O^{2-} [18]. The stretching vibrations of Sn-O and O-Sn-O are found at 612cm^{-1} and 473cm^{-1} , respectively for the all nanostructured thin films. The oxygen vacancy occurs in the SnO_2 lattice due to the different bond length of O-Sn-O group (O-Sn-O: 2.597 Å, Sn-O: 2.053 Å) [19]. As shown in FTIR, the substitution of F^- ions are well confirmed by the features of Sn-F and F-Sn-F bands at 420 cm^{-1} and 406 cm^{-1} respectively on the FTO NR thin film. These values have slightly changed from FTO NP and FTO cross-link NR thin films. This supposed to be due the change of morphology of 1-D nanostructured thin film. Also, the FTIR spectra show comparatively broader features due to nanocrystalline nature of FTO thin films [20].
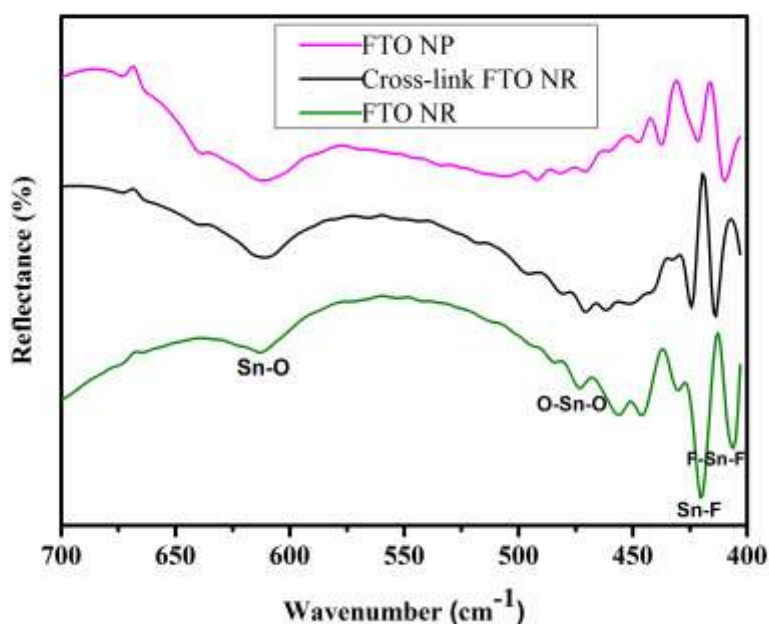
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Fig.6. FTIR spectrum of FTO thin films.

It is well known that the transmittance and conductivity of the FTO thin films is very important to the performance of the DSSCs. The development of suitable TCO substrates, which have high electrical conductivity and high optical transmittance, could be one of the most vital factors for the performance of DSSCs. As shown in Fig.7.optical transmittance of FTO nanoparticles, cross link nanorods and vertically align nanorods are observed to be 89.9%, 70.8% and 84.8% respectively. However, the transmittance of the cross linked nanorods is lower than for the other thin films due to the light scattering by the non-aligned nanorods and nanorods tips.
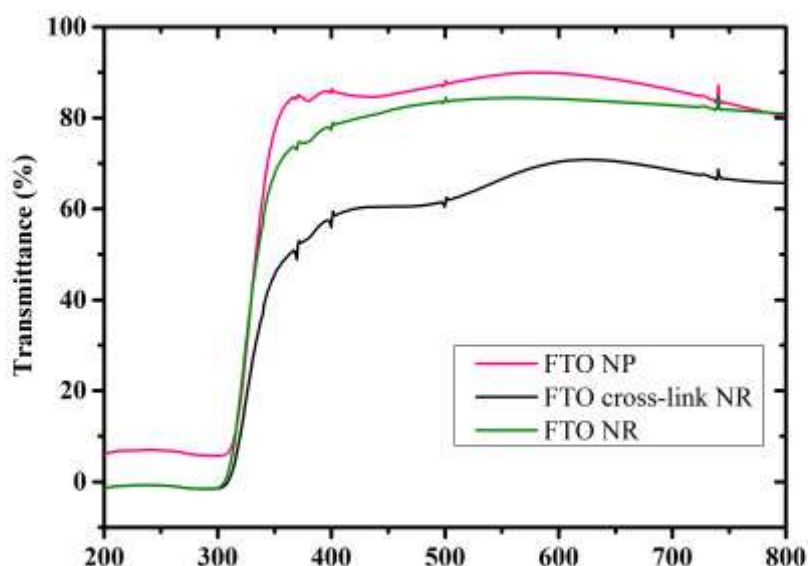

Fig.7. Transmittance spectrum of FTO thin films.

The thin films prepared on normal glass substrate show high sheet resistances. The high surface resistance of the FTO nanorods is due to the gap between the rods and low thickness of the thin film. As presented in Table 1. Conductivity of the nanorods was enhanced with commercial FTO glasses as the substrate. In this case, conducting glass facilitate to

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make the nanorods interconnect from the bottom. The sheet resistance of the nanorods was around 6.74 MΩ/sq on normal glass substrate and 26.7 Ω/sq on commercial FTO substrate. It clearly indicates the significant increase of the conductivity of FTO nanorods with conducting glass as the substrate.

Table 1. Sheet resistances of FTO thin films.

Sample Name	Sheet resistances on surface
FTO NP on normal glass	56.8 Ω/sq
FTO cross-link NR on normal glass	4.62 MΩ/sq
FTO NR on normal glass	6.74 MΩ/sq
Commercial FTO	14.3 Ω/sq
FTO NR on commercial FTO	26.7 Ω/sq

4. CONCLUSION

The improved version of spray pyrolysis deposition technique, known as, rotational, pulsed and atomized SPD can successfully be used to fabricate 1D nanostructured FTO thin films. The spraying at low angle to the substrate is mandatory to grow well separated and vertically aligned 1D nanostructure. The preferred growth orientation of the nanorods was along (101). The FTIR spectra of FTO thin films provide experimental evidence of oxygen vacancy and fluorine substitution for oxygen. The conductivity of the nanorods has also improved with commercial FTO glass as the substrate.

ACKNOWLEDGMENTS

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