The Synthesis, Characterizations and Application of One-Dimensional Nanostructured Fluorine Doped Tin Oxide Thin Films

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Doctoral Thesis

The Synthesis, Characterizations and Application of One-Dimensional Nanostructured Fluorine Doped Tin Oxide Thin Films

This thesis is submitted in partial fulfillment of the requirements for

the Degree of Doctor of Philosophy in Engineering

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I, Ajith Bandara, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

This thesis is dedicated to my son "Sayul".

Abstract

Transparent conducting oxides (TCO) materials have become technologically very important class of materials due to optically transparent and electrical conducting properties at the same time. An advanced version of spray pyrolysis technique which is known as rotational, pulsed and atomized spray pyrolysis (RPASP) was developed and deployed to fabricate One-dimensional (1-D) nanostructured fluorine doped tin oxides (FTO) thin films. This technique is versatile and deployed to prepare thin films of various nanotechnological architectures of fluorine-doped tin (IV) oxide (FTO) layers on glass surfaces. The different spray parameters have been controlled in order to fabricate FTO nanoparticles, cross-link nanorods, vertically aligned nanorods, hollow nanorods and needle type 1D nanostructured thin films on glass substrate.

RPASP was shown as a viable, and attractive, deposition technique for the synthesis of fluorine doped tin oxides one- dimensional nanostructured thin films, which allows for the perfect controllable spray directions for the fabricate vertically aligned FTO nanorods. Spraying at low angle to the substrate is mandatory for the growth of of vertically aligned nanorods. Spraying at low angle or horizontal to the substrate facilitate to sweep the aerosol spray of the fine atomized particles on the glass substrate and as a result density between the particles become high. Therefore, FTO crystal tends to grow along vertical direction with the pyrolysis process at higher substrate temperature. But, vertical or higher angle spraying of the SPD technique only facilitate to synthesize thin films consist with FTO nanoparticles. 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.

This technique allows for the perfect control of morphology of nanotechnological architectures of FTO, which can be achieved simply by controlling spray duration. As such, 0-D nanocrystallites, 1-D uncapped nanorods and 1-D capped nanorods; all in 2-D thin layers, and extensively cross-linked 3-D nanotechnological architectures of FTO can be prepared, on soda lime glass surfaces. This is the first time study on kinetically-controlled growth of different nanotechnological architectures of FTO, using the same technique.

X-Ray Diffraction (XRD), Scanning Electron Microscopic (SEM) and X-Ray Spectroscopic (XPS) data show excellent correlations. Photoelectron The one-dimensional FTO thin films are crystallized in the tetragonal rutile structure, with a preferential orientation of their crystal along the (101) direction. They exhibit an excellent transparency in the visible range of the electromagnetic spectrum. As evident from XPS data, FTO uncapped nanorods were found to contain more Sn²⁺ sites on their surfaces when compared to those of other nanotechnological architectures. ATR-FT-IR spectrum shows F-Sn-F and F-Sn stretching vibrations in all forms of FTO nanostructures. Thin layers have optical transmissions in the range 70% to 85%, in the visible range of the electromagnetic spectrum. This technique is versatile and is not limited only to fabricate FTO nanostructures, but, it can also be used to fabricate thin layers of nanotechnological structures of different dimensionalities of various materials on various substrates, which is capable to withstand required pyrolytic temperatures.

The effect of the fluorine concentration to the growth of FTO hollow nanorods at higher spray direction to the substrate was also investigated. The experiment was conducted at higher spray angle to the substrate while controlling the fluorine concentration of the spray precursor solution.

The incorporation of fluorine to tin dioxide has resulted to enhance the grain size of FTO thin films and hollow nanorods could be obtained with higher fluorine concentration. The fluorine ions substitute to the oxygen vacancies in the proper lattice position of tin oxide in the initial stage and the crystal size increased with the pyrolysis process. However, high concentration of fluorine affects as the impurities to the crystal structure and it restricted the growth of FTO crystal in horizontal direction but allowing to grow in the vertical direction. As a result, FTO hollow type nanorods has formed with the spray time duration. The fabricated nanorods show cubic structure of the tin dioxide with (111) direction as the preferred orientation. The deposition of sufficient amount of fine atomized FTO particles at fast rate with low spray nozzle distance has coursed to the growth of cubic crystal of tin oxide as it makes high pressure on the substrate. The film morphology, texture and transmittance properties of the thin films are show good interaction with each other.

The effect of the different additives for the crystal growth of FTO 1-D nanostructured thin films was investigated. It clearly shows that the different additives in the precursor solution are effected to improve both verticality and dimension of the FTO nanorods.

Vertically align and well separated nanotubes easily fabricate with propanone and ethanol as additives. We suggest that propanone addition plays a role to form vertically align nanorods with (101) preferential orientation while (110) face was the predominant plane of well separated nanorods with ethanol added solution.

The thin films prepared by using only water based solution was unable to grow separated 1-D nanostructures and growth of vertically aligned FTO nanorods could not be able to obtained with isopropanol as additives in the spray precursor solution. The conductivity of the 1-D nanostructured thin films also enhanced with commercial FTO glasses as the substrate. However, the preferred crystal growth orientation of the nanorods on commercial FTO glass substrate was along (200) direction due to the effect of the main FTO conducting layer.

The performance of the dye-sensitized solar cells was compared by assembling DSSCs with our 1-D nanostructured FTO thin films and commercially available FTO glasses. It clearly showed that the fill factor and open circuit voltage enhanced with FTO nanorods thin films as the front electrode of the DSSCs. However, the efficiency of the DSSCs with 1-D nanostructures was comparatively low due to the low film thickness of the photoactive electrode,

And further development of the DSSCs fabrication technique with FTO nanorods need to be studied.

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....."Learn from yesterday, live for today, hope for tomorrow. The important thing is not to stop questioning." Albert Einstein.

... "There are plenty of the rooms at the bottoms".... Rechard Feneman.

List of Analytical Techniques:

Scanning Electron Microscopy: SEM was performed using a JEOL

JSM-6320F Field Emission SEM at an accelerating voltage of 5 keV.

- X-ray Diffraction measurements: To analyze crystallinity and orientation of the samples, were completed using a Rigaku RINT Ultima-III X-ray diffractometer with Cu Kα, λ = 1.541836 Å voltage of 40 kV and current of 40 mA were used. The diffraction pattern was taken over 10-70° 20. The data were analyzed using PDXL and PCPDFWIN XRD analysis software
- UV/Visible Transmission Spectroscopy: was performed using a JASCO
 V-630 spectrometer in the wavelength range from 200nm to 800nm.
- X-ray Photo electronics Spectroscopy: was studied using a Shimadzu, ESCA-3400.

- Fourier Transform Infrared Spectroscopy: 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.
- Sheet Resistance: measurements were obtained using an 'in house set-up' linear four point probe Hewlett Packard 34401 a multimeter.

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CHAPTER 01 Introduction

The following research work describes the results obtained from a laboratory experiment about the fluorine- doped tin oxide semiconductor material to fabricate onedimensional nanostructured thin films for dye-sensitized solar cells application. The novel spray pyrolysis deposition technique which is known as "Rotational, Pulsed and Atomized Spray Pyrolysis Deposition" was designed and developed to synthesize fluorine-doped tin oxide nanorods thin films on glass substrate. Different spray conditions and parameters were controlled to obtained FTO nanostructures as required.

1.1 Thesis Overview

The first introductory chapter gives the details about transparent conducting oxide (TCO) materials and their application as thin films. It covers the basic techniques for the growth of transparent conducting oxides thin films. Also explain the parameters to select transparent conducting oxide materials for different applications and the reasons for selecting fluorine-doped tin oxide (FTO) as our semiconductor material. Finally, this introductory chapter describe the advantages of one-dimensional nanostructured thin films and their application as a working electrode of the dye-sensitized solar cells.

Chapter 2 describe the design and development of our advanced spray pyrolysis deposition technique which is known as Rotational, Pulsed and Atomized SPD (RPASP) for the thin films fabrication. The working mechanisms, process parameters, advantages and disadvantages of the RPASP technique discuss with respect to the conventional SPD. We have investigated the proper method to grow one-dimensional nanostructured FTO thin films by controlling the spray directions and their characterization discuss in details.

Chapter 3 details the effect of spray duration for the crystal growth of onedimensional nanostructured FTO thin films. The surface morphology and other characterizations technique presented in details.

Chapter 4 reports another method to fabricate FTO nanorods by controlling the fluorine doping concentrations of the precursor solution. The effect of higher fluorine concentration for the crystal growth of FTO nanorods explore and results discuss with experimental details.

Chapter 5 describe the formation of one-dimensional nanostructured FTO thin films with the improvement of conductivity. The effect of the different additives (propanone, ethanol and isopropanol) for the crystal growth of vertical aligned and well separated FTO nanorods are investigated. Finally, we review the performance of the dyesensitized solar cells with our FTO nanorods as the front electrode.

Chapter 6 state the final conclusion of the results presented in this thesis with developmental implications and future perspective of the current research.

1.2 Transparent Conducting Oxide materials

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 are semiconductor materials with wide bandgap (3 eV) structure. Therefore, thin layers are used in versatile electronic and opto-electronic applications including, but not limited to, flat panel displays [1], frost-resistant surfaces[2], aircraft windshields[3], gas-sensors[4], infraredreflective coatings[5], energy-efficient windows[6], photovoltaic solar cells[7, 8] and electrochromic[9], electroluminescent[10], liquid crystal[11], plasma, field emission *etc*. display devices.

The first evidence of the TCO material thin film was published in 1907 by K. Badeker. He has used cadmium metal to coat thin film by using a sputter technology [12]. There are two types of TCO materials namely, n-type and p-type. One way of developing n-type TCO materials is to dope semiconducting solids by other cations of approximately the same size, but with a higher valence; usually +1 higher than that of its own cation. In this way, n-type, wide band-gap semiconducting oxides, such as In₂O₃, ZnO, CdO, TiO₂ etc., have been doped with cations of valences +1 higher than that of the cation of the respective solid. Sn⁴⁺-doped In₂O₃ (Indiumtin oxide, ITO)[13,14], Al³⁺-doped ZnO (AZO)[15], B³⁺⁻doped ZnO (BZO)[16], Ga³⁺-doped ZnO (GZO)[17], In³⁺-doped CdO (ICO)[18] and Nb⁵⁺-doped TiO₂ (titaniumniobium oxide, TNO)[19] are typical examples for such n-type TCO materials[20]. TCO materials can also be prepared from n-type, large band-gap, semiconducting oxides by substituting some O²⁻ ions by anions of similar size but lesser charge, such as F⁻, as in the cases of FTO and F⁻-doped ZnO[21].

There are some binary TCO materials which were developed aiming at enhancing both optical and electrical properties though their performances are inferior. Some examples for such binary TCOs are phase-segregated ZnO-SnO₂, CdO-SnO₂, and ZnO-In₂O₃.[22] Some ternary compounds tested for TCOs include Zn₂SnO₄, ZnSnO₃, Zn₂In₂O₅, Zn₃In₂O₆, In₂SnO₄ and CdSnO₃.[23,24] Some other novel TCOs include GaInO₃ doped with Ge or Sn,[25] AgInO₂ doped with Sn[26], MgIn₂O₄, CdSb₂O₆ doped with Y[27], Ga₂O₄, In₄Sn₃O₁₂ and CdIn₂O₄ doped with Sn[28].

While all of the TCO materials, which are mentioned above, are n-type materials, p-type TCO materials have also been developed, though they are yet to be applied in industrial use. The first p-type TCO material reported was CuAlO₂ which was synthesized by Kawazoe et al. in 1997[29] [30]. CuBO₂ and CuGaO₂ are other such p-type TCO materials [31, 32]. Recent advances in computational chemistry also enabled the design of Li⁺-doped Cr₂MnO₄ as such a novel, p-type, TCO material[33].

1.3 Thin film Deposition Techniques

Basically, there are two ways to produce thin films, which in their broadest senses, can be categorized as chemical depositions and physical depositions [34, 35, 36]. In chemical deposition processes, the precursor in a fluidic form, usually as a solution, is brought to the surface of the solid, on which the thin layer is to be deposited, for the desired chemical reaction to take place at the surface, and hence to deposit the required material on the solid surface. There are several chemical deposition techniques which include electroless plating and electroplating, chemical bath deposition (CBD) [37], spin coating [38], chemical vapor deposition (CVD) [39], plasma-enhanced chemical vapor deposition (PCVD), atomic layer deposition (ALD) and spray pyrolytic deposition (SPD) [40]. In the physical deposition, precursor in solid phase is evaporated either by heating under vacuum or by using a focused electron beam or a focused ion beam and subsequently deposited from the vapor phase, onto the substrate surface, the processes of which are commonly known as physical vapor depositions (PVDs). Molecular beam epitaxy, pulsed laser deposition, cathodic arc deposition and electrospray deposition are some other physical deposition techniques [41, 42, 43, 44]. Out of these processes, SPD techniques are versatile yet very simple.

In our study, we have designed and developed cost effective advance version of SPD technique to fabricate TCO thin films. This technique known as Rotational, Pulsed and Atomized SPD and detail information about the instrument is discuss in the chapter 2.

1.4 Metal Oxide Selection for TCO materials

Thin films are used in a wide range of technological applications which include fabrication of electronic, optoelectronic, photoelectrochemical, photochromic, electrochromic, thermochromics, mechanochromic, and so on, devices. Even though, there are many types of TCO materials in the research field, the performance of the applications depend on the materials to materials. Therefore, the selection of transparent conducting oxide material for any particular application is very important. However, a number of chemical and physical features are correlated to the performance of a TCO in any technological application.

The properties such as figure of merit, conductivity, optical performance, plasma frequency, work function, physical, chemical and thermal stability, minimum

deposition temperature, etchability and toxicity, stability in hydrogen plasmas, mechanical hardness and production cost are the very important factors need to consider for the better selection of TCOs. Anyway, no one TCO material is well applicable for all applications and that depend on which properties of material is most important [45].

Despite the discoveries of a large number of TCO materials, the work horse in the TCO film technology is still ITO. This is due to its impressive optical and electronic properties, though, these properties may depend on the extent of substitution, grain size, number of grain boundaries, film thickness, preferred orientation of particles, and so on[13]. Thin films of ITO used in technological applications have electronic conductivity of over 10⁴ S cm⁻¹, and optical transmission of over 80% in the visible range, with carrier density exceeding 10^{20} cm⁻³ [46]. However, ITO is associated with some drawbacks, such as low natural abundance of indium and fast depletion of indium due to its current extensive use as ITO. These factors contribute to higher costs for ITO glasses. Also, ITO has a lesser stability in reducing environment [13]. Therefore, we have to think about a good TCO material to replace with ITO in industrial applicatins. Together with higher natural abundance of the constituent elements of FTO and similar electronic and optical properties, and also due to its astounding ability to withstand harsh conditions, such as,

acidic, basic, reducing and oxidizing and high-temperature, FTO stands out to be the best TCO material to replace ITO in future technological applications. FTO has already been successfully utilized in some devices such as dye-sensitized solar cells. Table 1 shows the some important criteria of the TCO materials and that may greatly help to select the appropriate materials for the particular application.

MRS BULLETIN/AUGUST 2000	Choice of Transparent Conducto	ors.
Property	Material	
Highest transparency	ZnO:F, Cd ₂ SnO ₄	
Highest conductivity	In ₂ O ₃ : Sn	
Lowest plasma frequency	SnO ₂ :F, ZnO:F	
Highest plasma frequency	Ag, TiN, In ₂ O ₃ :Sn	
Highest work function, best conta	SnO ₂ :F, ZnSnO ₃	
Lowest work function, best contain	ZnO:F	
Best thermal stability	SnO2:F, TiN, Cd2SnO4	
Best mechanical durability	TiN, SnO ₂ :F	
Best chemical durability	SnO ₂ :F	
Easiest to etch	ZnO:F, TiN	
Best resistance to H plasmas	ZnO:F	
Lowest deposition temperature	In ₂ O ₃ :Sn, ZnO:B, Ag	
Least toxic	ZnO:F, SnO ₂ :F	
Lowest cost	SnO ₂ :F	

Table 1: The important properties of the TCO materials for better selection.

As clearly state in the above table, FTO semiconductor material has tremendous properties as a TCO material. According to the Table 1, FTO has best chemical, mechanical durability, least toxic and lowest cost when compared with other transparent conducting oxide materials. Therefore, we have also selected FTO as our TCO material to fabricate 1-D nanostructured thin films. FTO has a tetragonal rutile crystal structure as shown Figure 1 (a) and commercially available FTO glasses are shown in Figure 1(b).



Figure 1: Fluorine-doped tin oxide (a) unit cell of the FTO, (b) commercial FTO glasses

1.5 Introduce One-Dimensional Nanostructured TCO Thin films

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 [47]. The Figure 2 shows the low-dimensional crystal structures of materials. Recently, onedimensional nanostructures such as nanorods, nanotubes and nanowires are getting more attractive in the research field to enhance the performance of device applications.



Figure 2: Low-dimensional nanostructures of materials

There are various TCO materials which are showing both good electrical conductivity and optical transparency together. The high band gap (>3.2 eV) semiconductor materials are very important to prevent absorption the light in the visible region of the electromagnetic spectrum. Hence, one-dimensional nanostructures of TiO₂, undoped, doped ZnO, and SnO₂ are mainly used in advanced industrial applications. The organic nanostructure material such as Carbon Nanotubes (CNTs) are widely used in many technological applications from the past resent years. This research field into

develop unique nanostructures of graphene based compounds are vastly improved after published first report about characterizations of CNTs in 1991 by Lijima et al at the NEC laboratory in Japan [48].

However, undoped and doped metal oxides semiconductor materials are yet stand along strongly for the applications in the field of optoelectronics and photovoltaics due to their stability in various way. Preparation, characterization and technological applications of FTO nanograins with average size of ~ 500 nm on glass surfaces is well known [49, 50-53] and in fact, FTO glasses with excellent electronic and optical properties are commercially available. Best properties can be achieved when the FTO layer is composed of a mixture of smaller and larger particles, where larger particles to give fewer grain boundaries to minimize the light scattering and to increase mobility of charge careers and smaller particles to give higher surface area to decrease sheet resistance [54].

Although, the synthesis of FTO nanograins is quite straightforward and has been well documented, there has been very little research reported on the one-dimensional nanostructured FTO thin films such as nanotubes and nanorods.to the best of our knowledge. For instance, b. russo and g.z. cao, have synthesized fluorine-doped thin oxide thin films and nanorod arrays via spray pyrolysis in 2008 [55]. They have used a template based method to fabricate FTO nanorods array as shown in Figure 3.



Figure 3: FTO nanorods array fabricated by B. russo and g.z. cao.

Then, in 2012, Cho et al. have synthesized vertically-aligned FTO nanorod array by SPD and used them as gas sensors [56]. By controlling spray time, they were able to produce 100 nm and 500 nm long FTO nanorods as shown Figure 4.





Figure 4: vertically-aligned FTO nanorods thin films by Cho et al.

Third work on FTO nanorod synthesis is by our group, in which we have used ethylene glycol to assist in forming vertically-aligned FTO nanorod arrays on glass surfaces which we have fabricated using atomized, SPD technique[57]. The fabricated nanostructures are shown in Figure 5.



Figure 5: Ethylene glycol assisted FTO nanorods.

In this research study, one-dimensional nanotechnological architectures of fluorine-doped tin oxide thin films synthesized by changing different spray conditions and parameters in order to enhance the performance of the dye-sensitized solar cells by applying as transparent and conducting working electrode.

1.5.1 One-dimensional nanostructured FTO thin films for DSSCs

The dye-sensitized solar cells (DSSCs) is a well-known photovoltaic device which can be simply used to convert sunlight into electricity [58]. This is a one of the most simple and cost effective technology in the research field to generate electricity and consisted with both organic and inorganic compounds.

The several factors may influence the performance of DSSCs. Hence, many scientists have been working on different sections of the DSSCs such as photo anode, dye, electrolyte and counter electrode to higher power conversion efficiency. In the working electrode of the DSSCs are consisted with TCOs glass substrate and photo active nanostructured layer of TiO_2 or ZnO. The schematic diagram of the DSSC is presented in the Figure 6.



Figure 7: The working principle of DSSCs

Basically, FTO thin films consisted with nanoparticles (nanograins) are used in working electrode of the DSSCs. The objective of our study is to introduce 1-D nanostructured FTO thin films for the front electrode of the DSSCs as illustrated in the Figure 8.



Figure 8: The propose 1-D nanostructured FTO thin film for the photo anode of 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 [59]. Such One-dimensional (1-D) 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 [60]. The fabrication of DSSCs with FTO nanorods thin films and their parameters such as fill factor (FF), open circuit voltage (Voc), current density (Jsc) and power conversion efficiency (η) are discussed in the chapter 4.

1.6 References

[1] Chae, G. S., Soh, H. S., Lee, W. H. & Lee, J. G. Self-passivated copper as a gate electrode in a poly-Si thin film transistor liquid crystal display. J. Appl. Phys. 90, (2001) 411–415.

[2] B. Russo, G.Z. Cao, Fabrication and characterization of fluorine-doped thin oxide thin films and nanorod arrays via spray pyrolysis, Appl. Phys. A, 90 (2008) 311-315.

[3] Z.M. Jarzebski, Preparation and physical properties of transparent conducting oxide films, physica status solidi (a), 71 (1982) 13-41.

[4] C.-W. Cho, J.-H. Lee, D.-H. Riu, C.-Y. Kim, Fast Responsive Gas Sensor of Vertically Aligned Fluorine-Doped Tin Oxide Nanorod Thin Film, Jpn. J. Appl. Phys., 51(2012) 045001.

[5] R.G. Gordon, Method of depositing electrically conductive, infra-red reflective, transparent coatings of stannic oxide, US Patent No. 4,146,657 (1979).

[6] I. Hamberg, C.G. Granqvist, Evaporated Sn - doped In2O3 films: Basic optical properties and applications to energy - efficient windows, J. Appl. Phys., 60 (1986) R123-R160.

[7] E. Fortunato, D. Ginley, H. Hosono, D.C. Paine, Transparent Conducting Oxides for Photovoltaics, MRS Bull., 32 (2007) 242-247.

[8] B. O'Regan, M. Gratzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films, Nature, 353 (1991) 737-740.

[9] C.G. Granqvist, Transparent conductive electrodes for electrochromic devices: A review, Appl. Phys. A, 57 (1993) 19-24.

[10] R. Tueta, M. Braguier, Fabrication and characterization of indium tin oxide thin films for electroluminescent applications, Thin Solid Films, 80 (1981) 143-148. [11] K. Jin-Yeol, K. Eung-Ryul, H. Yang-Kyoo, N. Kei-Hyun, I. Dae-Woo, Highly Transparent Tin Oxide Films Prepared by DC Magnetron Sputtering and Its Liquid Crystal Display Application, Jpn. J. Appl. Phys., 41 (2002) 237.

[12] K.Badeker, Annals of Physics 1907, (22), 749.

[13] R.B.H. Tahar, T. Ban, Y. Ohya, Y. Takahashi, Tin doped indium oxide thin films:Electrical properties, J. Appl. Phys., 83 (1998) 2631-2645.

[14] E. Benamar, M. Rami, C. Messaoudi, D. Sayah, A. Ennaoui, Structural, optical and electrical properties of indium tin oxide thin films prepared by spray pyrolysis, Sol. Energy Mater. Sol. Cells, 56 (1999) 125-139.

[15] S. Mridha, D. Basak, Aluminium doped ZnO films: electrical, optical and photoresponse studies, Journal of Physics D: Applied Physics, 40 (2007) 6902.

[16] B.J. Lokhande, P.S. Patil, M.D. Uplane, Studies on structural, optical and electrical properties of boron doped zinc oxide films prepared by spray pyrolysis technique, Physica B: Condensed Matter, 302–303 (2001) 59-63.

[17] V. Bhosle, A. Tiwari, J. Narayan, Electrical properties of transparent and conductingGa doped ZnO, J. Appl. Phys., 100 (2006) 033713.

[18] S. Kose, F. Atay, V. Bilgin, I. Akyuz, In doped CdO films: Electrical, optical, structural and surface properties, Int. J. Hydrog. Energy, 34 (2009) 5260-5266.

[19] Y. Furubayashi, T. Hitosugi, Y. Yamamoto, K. Inaba, G. Kinoda, Y. Hirose, T.
Shimada, T. Hasegawa, A transparent metal: Nb-doped anatase TiO2, Appl. Phys. Lett.,
86 (2005) 252101-252101-3.

[20] K. Ellmer, Past achievements and future challenges in the development of optically transparent electrodes, Nat Photon, 6 (2012) 809-817.

[21] J. Suffner, P. Ágoston, J. Kling, H. Hahn, Chemical vapor synthesis of fluorinedoped SnO2 (FTO) nanoparticles, J. Nanopart. Res., 12 (2010) 2579-2588.

[22] D.H. Lee, Y.J. Chang, G.S. Herman, C.H. Chang, A General Route to PrintableHigh-Mobility Transparent Amorphous Oxide Semiconductors, Adv. Mater., 19 (2007)843-847.

[23] T. Minami, T. Miyata, T. Yamamoto, Work function of transparent conducting multicomponent oxide thin films prepared by magnetron sputtering, Surface and Coatings Technology, 108–109 (1998) 583-587.
[24] T.J. Coutts, D.L. Young, X. Li, W.P. Mulligan, X. Wu, Search for improved transparent conducting oxides: A fundamental investigation of CdO, Cd2SnO4, and Zn2SnO4, J. Vacuum Sci.Technol. A, 18 (2000) 2646-2660.

[25] R.J. Cava, J.M. Phillips, J. Kwo, G.A. Thomas, R.B. van Dover, S.A. Carter, J.J. Krajewski, W.F. Peck, J.H. Marshall, D.H. Rapkine, GaInO3: A new transparent conducting oxide, Appl. Phys. Lett., 64 (1994) 2071-2072.

[26] S. Ibuki, H. Yanagi, K. Ueda, H. Kawazoe, H. Hosono, Preparation of n-type conductive transparent thin films of AgInO₂:Sn with delafossite-type structure by pulsed laser deposition, J. Appl. Phys., **88** (2000) 3067-3069.

[27] S.E. Dali, M. Jayachandran, M.J. Chockalingam, New transparent electronic conductor, MgIn₂O₄ spinel, Journal of Materials Science Letters, 18 (1999) 915-917.

[28] D.R. Kammler, T.O. Mason, K.R. Poeppelmeier, Bulk Phase Relations, Conductivity, and Transparency in Novel Bixbyite Transparent Conducting Oxide Solution in the Cadmium-Indium-Tin Oxide System, J. Am. Ceram. Soc., 84 (2001) 1004-1009.

[29] H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, H. Hosono, P-type electrical conduction in transparent thin films of CuAlO2, Nature, 389 (1997) 939-942.

[30] H. Kawazoe, H. Yanagi, K. Ueda, H. Hosono, Transparent p-Type ConductingOxides: Design and Fabrication of p-n Heterojunctions, MRS Bull., 25 (2000) 28-36.

[31] M. Snure, A. Tiwari, CuBO2: A p-type transparent oxide, Appl. Phys. Lett., 91 (2007) 092123.

[32] D.O. Scanlon, A. Walsh, G.W. Watson, Understanding the p-Type Conduction Properties of the Transparent Conducting Oxide CuBO2: A Density Functional Theory Analysis, Chem. Mat., 21 (2009) 4568-4576.

[33] A.R. Nagaraja, K.H. Stone, M.F. Toney, H. Peng, S. Lany, T.O. Mason, Experimental Characterization of a Theoretically Designed Candidate p-Type Transparent Conducting Oxide: Li-Doped Cr2MnO4, Chem. Mat., 26 (2014) 4598-4604.

[34] L. D. Smith, Thin-Film Deposition Principles & Practice. McGraw-Hill: New York, 1995, pp.1-7.

[35] M.L.Hitchman; K.F.Jenson, Chemical Vapor Deposition Principles and Applications. Academic Press Limited: Salt Lake City, 1993, pp.35-39.

[36] R.A.Stradling, Growth and Characterisation of Semiconductors. IOP Publishing Ltd: New York, 1990, 17-35. [37] M. A. Aegerter; J. Puetz; G. Gasparro; N. Al-Dahoudi, *Optical Materials* 2004, 26,
(2), 155-162.

[38] G. Srinivasan; N. Gopalakrishnan; Y. S. Yu; R. Kesavamoorthy; J. Kumar, *Superlattices and Microstructures* **2008**, 43, (2), 112-119.

[39] S. W. Rees, CVD of Nonmetals. VCH: Weinheim, 1996, pp.12-18.

[40] E.V.A. Premalal, N. Dematage, S. Kaneko, A. Konno, Preparation of high quality spray-deposited fluorine-doped tin oxide thin films using dilute di(n-butyl)tin(iv) diacetate precursor solutions, Thin Solid Films, 520 (2012) 6813-6817.

[41] L. I. Maissel; M. H. Francombe, An introduction to Thin films. Gordon and Breach: New York, 1973, pp.14-36.

[42] H. K. Pulker, Surface and Coatings Technology 1999, 112, (1-3), 250-256.

[43]. R. G. Sharafutdinov; S. Y. Khmel; V. G. Shchukin; M. V. Ponomarev; E. A. Baranov; A. V. Volkov; O. I. Semenova; L. I. Fedina; P. P. Dobrovolsky; B. A. Kolesov, Solar Energy Materials and Solar Cells 2005, 89, (2-3), 99-111.

[44] S.M.Park; T.Ikegami; K.Ebihara; P.K.Shin, Applied Surface Science 2006, 253, (3), 1522-1527. [45] R.G. Gordon, U.S. Patent No. 4,146,657 (1979).

[46] M. Mizuhashi, Electrical properties of vacuum-deposited indium oxide and indium tin oxide films, Thin Solid Films, 70 (1980) 91-100.

[47] D. Chen and L. Gao : Chemical Physics Letters 398 (2004) 201–206.

[48] S.Iijima, Nature 1991, 354, 56-58.

[49] A. N. Banerjee, et al., "Synthesis and characterization of nano-crystalline fluorinedoped tin oxide thin films by sol-gel method". Journal of Sol-Gel Science and Technology, vol. 28(1), pp. 105-110, 2003.

[50] S. G. Suh, et al., "Atmospheric-pressure chemical vapor deposition of fluorinedoped tin oxide thin films". Thin Solid Films, vol. 345(2), pp. 240-243, 1999.

[51] E. Elangovan and K. Ramamurthi, "Studies on micro-structural and electrical properties of spray-deposited fluorine-doped tin oxide thin films from low-cost precursor". Thin Solid Films, vol. 476(2), pp. 231-236, 2005.

[52] M. Okuya, et al., "Low temperature deposition of SnO2 thin films as transparent electrodes by spray pyrolysis of tetra-n-butyltin(IV)". Journal of the European Ceramic Society, vol. 21(10-11), pp. 2099-2102, 2001.

[53] A. V. Moholkar, et al., "Properties of highly oriented spray-deposited fluorinedoped tin oxide thin films on glass substrates of different thickness". Journal of Physics and Chemistry of Solids, vol. 68(10), pp. 1981-1988, 2007.

[54] E. V. A. Premalal, et al., "Preparation of high quality spray-deposited fluorine-doped tin oxide thin films using dilute di(n-butyl)tin(iv) diacetate precursor solutions".
Thin Solid Films, vol. 520(22), pp. 6813-6817, 2012.

[55] B. Russo and G. Z. Cao: Appl. Phys. A 90 (2008) 311.

[56] C.-W. Cho, J.-H. Lee, D.-H. Riu, and C.-Y. Kim: Jpn. J. Appl. Phys. 51(2012) 045001.

[57] L. Devinda, B. Herath Mudiyanselage Navaratne, J. Viraj, M. Kenji, Ethylene Glycol Assisted Synthesis of Fluorine Doped Tin Oxide Nanorods Using Improved Spray Pyrolysis Deposition Method, Appl. Phys. Express, 6 (2013) 085501.

[58] Ma, W.L, Yang. C.Y, Gong. X, Lee. K, Heeger. A. J. (2005), Adv. Funct. Mater.

[59] F. Wang, N. K. Subbaiyan, Q. Wang, C. Rochford, G. Xu, R. Lu, A. Elliot, F.D'Souza, R. Hui, and J. Wu: ACS Appl.Mater. Interfaces 4 (2012)1565.

[60] Zhou, D.; Biswas, R. J. Appl. Phys.103 (2008) 093102-5.

CHAPTER 02

Fabrication of One-Dimensional FTO Thin Films

The following work presents the details of the design and development about the advanced version of SPD technique to fabricate one-dimensional nanostructured FTO thin films. The features and advantages of this technique has discussed by comparing with conventional techniques. The effect of the spray conditions for the crystal growth of 1-D nanostructured FTO thin films has investigated. The results obtained from an experiment into the use of FTO precursor solution for the growth of one-dimensional nanostructured thin films has also discussed in details.

2.1. Design and Development of advance version of SPD technique

Among the diverse techniques for thin film fabrication, spray pyrolysis (SP) stands out as a simple and versatile technique which can be used to fabricate practically any thin film on many substrate surfaces. These substrates include, but not limited to, ordinary glasses, electronically-conducting glasses such as fluoride-doped tin oxide-coated glasses (FTO), silicon wafers and even plastic substrates such as Teflon.

Spray-pyrolytic deposition also provides the flexibility to select required temperatures depending on the thermal stability of the substrates used and the required temperature for the pyrolysis of the precursor solution to form the desired thin layer material with required morphology on the substrate surface. As regard to thin films, they may be thin films of insulating materials such as hydroxyapatite nanoparticle modification of stainless steel or titanium prosthesis materials to introduce biocompatibility, osteo-integration, non-toxicity and corrosion resistance in aggressive body fluid environments or interconnected, Nanoparticulate semiconducting materials required for solar cell fabrications, and thin layers of semiconductors required for electronic and optoelectronic industries, transparent conducting oxide thin films, thin films of 1-D nanomaterials such as nanotubes and nanorods, 2-D nanomaterials such as nanosheets and 3-D nanomaterials such as stacks of thin layers on substrate surfaces, and many more.

Ordinary spray pyrolysis, which is used in many laboratories for the fabrication of thin films, is very simple but suffers from several drawbacks. In the fabrication of thin layers of nanoparticulate materials, care should be taken to ensure that the nanoparticles to deposit individually rather than in their agglomerated forms.

However, aggregation of nanoparticles, which are dispersed in a suspension, takes place spontaneously, and if there is no mechanism to separate these aggregated nanoparticles before deposition, that will result in the deposition of such lumps with inhomogeneous morphologies which can act as light scattering centers diminishing the transparency of the layer towards visible light and thereby limiting their applications in optoelectronic applications. A way round this problem is to apply ultrasound to the tip of the spray nozzle to enable the separation of individual particles from agglomerated lumps so as to result in homogenous thin films and the technique is commonly known as Ultrasonic Spray Pyrolysis (USP). These ultrasonic nebulizers used in USP generate fine aerosols of individually-dispersed particles though the technique demands power for ultrasound generation. As such, developing techniques which do not require additional power is an important task to prepare optically-transparent and homogeneous thin films. We have addressed this problem and improved the ordinary SPD technique to have a chamber to break agglomerated particles simply by allowing them to collide with the Teflon spherule placed in the aerosol stream of the aspirated solution. This process is termed atomization and hence the chamber is called atomizer. Such improved SDP technique is called Atomized Spray Pyrolysis (ASP). Figure 1 depicts schematic representations of SPD and ASP apparatus to distinguish between the two techniques.



Figure 1 (a): Schematic representation of the Spray Pyrolytic Deposition (SPD) and (b) Atomized Spray Pyrolysis (ASP) techniques.

Although, the use of ASP technique enables the preparation of versatile nanotechnological architectures, we found that during the continuous spray of aqueous solutions to the heated surfaces of substrates, the local temperature falls down giving an adverse effect on the adhesion of the thin layer on to the substrate surface and, sometimes, to the homogeneity of the thin layers produced. To eliminate this problem, we have introduced a pulse system using controlling electronics where the spraying is done for a shorter period and then spraying is turned off for a reasonable time to reach the temperature of the substrate surface back to its pre-set required value. In our experiments, we identified the best pulse sequence as 2 s on and 13 s off. When this improvement is made to ASP technique we call it Pulsed ASP or PASP.

Schematic representation of the process flow diagram of PASP is shown in Figure 2.



Figure 2: Schematic representation of the Pulsed, Atomized Spray Pyrolysis (PASP) apparatus.

In the preparation of thin films of 1-D nanotechnological architectures such as nanotubes, nanorods etc. of materials, such as transparent, conducting oxide thin films, sometimes, it is advantageous to allow films to deposit on static substrate surfaces rather than moving the substrates to enable the deposition of the thin layer over the entire surface. In order to form 1-D nanotechnological architectures, it is also of vital importance to allow the aerosol of fine particles to sweep along the substrate surface in the horizontal direction for 1-D materials grow in the vertical direction. If the substrate is kept static, in the pyrolysis chamber, the horizontal flow takes the shape of a flame when it is impinged from the nozzle. The resulting layer also then takes the same shape. To have a circular layer, it is important to rotate the spray flow about the vertical axis and to select proper pulses to make sure the deposition of the layer from all angles to happen. Such an improved version of the PASP has been constructed and termed rotating, pulsed, atomized spray pyrolysis (RPASP). Figure 3 shows 3D Computer-aided Design (CAD) of RPSAP equipment.





Figure 3: (a) Computer-aided Design of Rotating, Pulsed, and Atomized Spray Pyrolysis (RPASP) Setup. (b) A part of RPASP setup showing the rotation about the vertical axis around the vertical shaft to which spray nozzle is fixed and a part of the pyrolysis chamber.

As depicted in the flow diagram given in Figure 1(a), the SPD technique involves a precursor solution, a pressure pump to aspirate the precursor solution, tubing system, a nozzle at the end of the fluid flow and a pyrolysis chamber to hold the substrate surface at the required temperature and the materials in the aerosol spray to undergo pyrolysis to deposit required material on the substrate surface. These components can easily be bought and assembled *in situ* though ready-made instruments are commercially available.

As explained in the introduction section, one of the drawbacks of this technique is the possibility for the deposition of aggregated particles from aerosols containing particles in the nanorange, if the particles have undergone spontaneous aggregation. Such aggregated particles may exceed the size of the wavelengths of the visible range of the electromagnetic spectrum thus not allowing visible light to pass through the layer. If this happens, that limits the applicability of such thin layers in opto-electronic applications.

In order to circumvent this problem, we have introduced an atomizer chamber between the precursor solution and the pyrolysis chamber. Precursor solution aspirated by a pressurized air flow is first directed to the atomizer chamber where it hits with the Teflon spherule present in the atomizer chamber. Due to momentum transfer, these aggregated particles are then separated to individual ones and the aerosol containing only these discrete particles are directed through the tubing system towards the pyrolytic chamber for pyrolytic deposition of discrete nanoparticles on the hot substrate surface in order to form required thin films [Figure 1 (b)]. Discrete nanoparticles (Particles with at least one dimension in the "nanorange", i.e., 1-100 nm, usually 0-D nanoparticles have their diameter in this range.) allow visible light to transmit through the layer thus making the layer transparent to visible light. We have utilized this technique to make a variety of thin films including optically-transparent thin films of interconnected discretely deposited nanoparticles on FTO surfaces for dye-sensitized solar cell (DSC) applications to obtained higher performance.

In the PASP technique, we have introduced a sequence of spray pulses of 2 s on and 13 s off by introducing controlling electronics and this enables us to allow the substrate surface to return back to the pre-set value during the spray off period so that spraying is done only when the substrate surface is at the required temperature.

We illustrate the synthesis of different nanotechnological architectures of transparent, conducting FTO on glass surfaces as an example for the applications of PASP. Components of RPASP contains essentially the same components of PASP with an additional component of a rotating vertical steel bar to hold the spray nozzle and controlling electronics to control rotation speed and the alignment of the spray nozzle against the substrate surface. This advanced version of SPD technique is versatile and can be used to prepared different nanostructured thin films. The rotational speed, spray angle, spray time, spray interval time and spraying pressure of the precursor solution can be controlled. The FTO solution is converted into a fine mist using the apparatus and the generated mist is allowed to deposit on the glass substrate kept in a spray chamber at higher temperature

2.2 Effect of the spray direction to the crystal growth of 1-D FTO

We have investigated the proper method to grow one-dimensional nanostructured FTO thin films by using RPASP technique. Specifically, the effect of spray direction for the thin films fabrication has studied in details. The film morphology, texture, conductivity and transmittance data has discussed in details in following sections.

2.3 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. 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 [1].

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.

2.4 Experimental

Firstly, tin (IV) chloride penta-hydrate (SnCl₄·5H₂O 98%, Wako Chemicals) and Ammonium fluoride (NH₄F 98%, Aldrich Chemicals) were dissolved in deionized water with addition of 8% propanone. The concentration of SnCl₄·5H₂O was fixed at 0.20M and NH₄F 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 K α , $\lambda = 1.541836$ 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.

2.5 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 [2]. 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 [3]. 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.

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

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 SnO₂ 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.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°)



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 [3]. 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 [5]. 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 [6] also asserted that the preferred direction of SnO₂ 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 SnO₂ crystal structure due to the lowest surface energy [7].

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, O²⁻ :0.132 nm) and comparable energy of bond with tin (Sn-F bond: 26.75 D⁰/KJmol⁻¹, Sn-O bond 31.05D⁰/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 O²⁻ [8].

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 SnO₂ lattice due to the different bond length of O-Sn-O group (O-Sn-O: 2.597 Å, Sn-O: 2.053 Å) [9]. 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 [10].



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 make the nanorods interconnect from the bottom. The sheet resistance of the nanorods was around 6.74 M Ω /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.

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

Table 1. Sheet resistances of FTO thin films.

2.6 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.

2.7 References

1) D. Chen and L. Gao : Chemical Physics Letters 398 (2004) 201–206.

Kumara, G.R.A, C.S.K. Ranasinghe, E.N. Jayaweera, H.M.N. Bandara, M.Okuya and R.M.G.
 Rajapakse, Preparation of Fluoride-Doped Tin Oxide Films on Soda–Lime Glass Substrates by
 Atomized Spray Pyrolysis Technique and Their Subsequent Use in Dye-Sensitized Solar Cells.
 The Journal of Physical Chemistry C, 118[30] (2014) 16479-16485.

3) C. Y. Kim and D. H. Riu, Thin Solid Films, 519 (2011) 3081-3085.

4) Effect of spray conditions on formation of one-dimensional fluorine-doped tin oxide thin films. A. Bandara, R. M. G. Rajapakse, M. Okuya, M. Shimomura, K. Murakami, JJAP Conf. Proc. 4, 011102 (2016).

5) Kim, C.-Y. and D.-H. Riu, Raman scattering, electrical and optical properties of fluorinedoped tin oxide thin films with (200) and (301) preferred orientation. Materials Chemistry and Physics, 148(3) (2014) 810-817.

 L. Devinda, B. Herath Mudiyanselage Navaratne, J. Viraj, M. Kenji, Ethylene Glycol Assisted Synthesis of Fluorine Doped Tin Oxide Nanorods Using Improved Spray Pyrolysis Deposition Method, Appl. Phys. Express, 6 (2013) 085501.

Floriano, Emerson Aparecido, Scalvi, Luis Vicente de Andrade, Sambrano, Julio Ricardo, &
 Geraldo, Viviany. Evaluation of bulk and surfaces absorption edge energy of sol-gel-dip-coating
 SnO2 thin films. Materials Research, 13[4] (2010) 437-443.

B. Zhang, Y. Tian, J.X. Zhang, W. Cai, The role of oxygen vacancy in fluorine-doped SnO2
 films, Physica B: Condensed Matter, Volume 406, Issue 9, 15 April 2011, Pages 1822-1826.

 B. Zhang, Y. Tian, J.X. Zhang, W. Cai, The characterization of fluorine doped tin oxide films by Fourier Transformation Infrared spectrum, Materials Letters, Volume 64, Issue 24, 31 December 2010, Pages 2707-2709.

10) Khan, A.F.; Mehmood, M.; Aslam, M.; Ashraf, M. Characteristics of electron beam evaporated nanocrystalline SnO2 thin films annealed in air. Appl. Surf. Sci. 2010, 256, 2252-2258.

CHAPTER 03

Growth of 1-D Nanostructured FTO Thin Films

The following chapter describes the use of Rotational Pulsed and Atomized Spray Pyrolysis deposition Technique to fabricate one-dimensional nanostructured FTO thin films with different spray time durations. The crystal growth of 1-D nanostructured FTO thin films on normal glass substrate was studied in details. The resultant films were analyzed with various analytical techniques. The surface morphology, texture of thin films, fluorine doping to the tin oxide structure and transmittance properties of one-dimensional FTO thin films have presented throughout the below study.

3.1 Effect of spray duration for the growth of 1-D FTO

A novel Spray Pyrolysis (SP) technique, known as Rotational, Pulsed and Atomized Spray Pyrolysis (RPASP), was developed and deployed to prepare thin films of various nanotechnological architectures of fluorine-doped tin (IV) oxide (FTO) layers on glass surfaces.

This technique allows for the perfect control of morphology of nanotechnological architectures of FTO, which can be achieved simply by controlling spray duration. As such, 0-D nanocrystallites, 1-D uncapped nanorods and 1-D capped nanorods; all in 2-D thin layers, and extensively cross-linked 3-D nanotechnological architectures of FTO can be prepared, on soda lime glass surfaces. This is the first time report on kinetically-controlled growth of different nanotechnological architectures of FTO, using the same technique. X-Ray Diffraction (XRD), Scanning Electron Microscopic (SEM) and X-Ray Photoelectron Spectroscopic (XPS) data show excellent correlations. As evident from XPS data, FTO uncapped nanorods were found to contain more Sn²⁺ sites on their surfaces when compared to those of other nanotechnological architectures. ATR-FT-IR spectrum shows F-Sn-F and F-Sn stretching vibrations in all forms of FTO nanostructures. Thin layers have optical transmissions in the range 70% to 85%, in the visible range of the electromagnetic spectrum. This technique is versatile and is not limited only to fabricate FTO nanostructures, but, it can also be used to fabricate thin layers of nanotechnological structures of different dimensionalities of various materials on various substrates, which is capable to withstand required pyrolytic temperatures.

3.2 Introduction

To the best of our knowledge, no literature is available for the preparation of kinetically-controlled growth of different nanotechnological architectures of FTO. Herein, we, therefore, report the first time study on the development of a low-cost, Rotational, Pulsed and Atomized Spray Pyrolytic (RPASP) method to fabricate thin films containing grains of FTO as well as those of well-defined 1-D architectures of both uncapped and capped nanorods of FTO on soda lime glass surfaces. The desired shape of the nanostructures can be achieved simply by controlling the spray time. The work described here, therefore, is concerned not only with just the synthesis of FTO nanorods arrays, but also preparation of various nanotechnological architectures of FTO, simply by controlling the kinetics of deposition, to result in well-defined architectures, such as nanoparticles, almost vertically-aligned uncapped nanorods, almost vertically-aligned capped nanorods and extensively cross-linked nanotechnological architectures of FTO on soda lime glass surfaces and characterizations of the materials prepared . The technique can be extended to synthesize versatile architectures of nanomaterial thin films on various substrate surfaces.

3.3 Experimental

A precursor solution containing 3.50 g SnCl₄.5H₂O (98%, Wako Chemicals), 1.50 g NH₄F (98%, Wako Chemicals), 46.0 mL of distilled and de-ionized water, 4.0 mL of acetone and 10.0 mL of 0.10 M HCl was withdrawn, at 0.20 MPa pressure, using a pressurized air flow, with the help of a sequence of pulses of 2 s on and 13 s off. This pulse program was so chosen as to maintain the same temperature of the substrate surface throughout spray pyrolytic deposition. When the spray of aqueous aerosol onto hot glass is carried out, continuously, then the local temperature of the substrate surface was found to decrease slightly, after a few seconds. By carrying out several pulse programs we found that the sequence of 2 s on and 13 s off is the best one that gives constant temperature during SP. The withdrawn aerosol was then directed to an atomizing chamber containing a Teflon spherule and allowed to collide on the spherule in order to breakdown any agglomerated particles, if any. A fine aerosol spray of non-agglomerated particles was then directed horizontally to the pre-heated glass substrate, placed on a pre-heated (e.g., 480 °C) hotplate, present in the pyrolytic chamber.

The materials present in the spray solution were then subjected to pyrolysis and the desired material was then deposited on the heated glass surface producing a thin film. Figure 1 depicts the schematic representation of the non-rotational mode of the PASP set up which was purpose-built in situ.



Figure 1: Schematic representation of the process flow diagram of the Pulsed, Atomized Spray Pyrolysis Equipment.
The precursor solution was sprayed for total spray times (including both on and off times) of 30 min (effective 4 min spray on), 45 min (effective 6 min spray on), 60 min (effective 8 min spray on), 90 min (effective 12 min spray on), 120 min (effective 16 min spray on) and 180 min (effective 24 min spray on). At the end of each spray time, the electronic controller of the spray pulses and the hotplate were turned off, and the deposited glass plate was allowed to cool down to ~ 200 °C, and then it was removed. Samples prepared at the above spray durations are abbreviated to Sample 1, Sample 2, Sample 3, Sample 4, Sample 5 and Sample 6, respectively.

XRDs of the substances, which were formed at different spray durations, were recorded on Rigaku RINT Ultima-III XR Diffractometer, using Cu Kα radiation of wavelength 1.541836 Å and the data were analyzed using PCPDFWIN program. XPS studies of the samples were done on Shimadzu, ESCA-3400. SEM studies were carried out using JEOL JSM-7001F Field-emission SEM, at 3 or 5 kV acceleration voltages. UV-visible Transmittance Spectra were recorded on JASCO V-630 Spectrometer, in the wavelength range from 200 nm to 800 nm. FT-IR spectra were recorded on JASCO FT/IR 6300 Fourier Transformed Spectrometer.

3.4 Results and Discussion

3.4.1 Sample 1 Prepared at 4 min spray over 30 min

Figure 2(a) shows X-Ray Diffractogram of sample 1, which was prepared at 4 min spray, over 30 min. The XRD consists of peaks located at $2\theta = 26.57^{\circ}$, 33.93° , 38.02° , 51.81° 54.85°, 61.87° and 65.96° which can be assigned, respectively, to the diffractions from (110), (101), (200), (211), (220), (310) and (301) basal planes (JCPDS Card No. 77-0452). The diffractogram corresponds to that of the Cassiterit form of SnO₂ in its tetragonal rutile structure (PDF# 770448, PCPDFWIN software). Major peak which is appearing at $2\theta = 26.57$ °, which corresponds to diffraction from (110) plane is characteristic of the preferred plane of crystallite growth in SnO₂, as reported earlier by Zhang et al. As opposed to preferred (110) of SnO₂ nanoparticles, without F⁻ doping, they have also shown that the preferred growth plane of FTO to be (200) and the latter was shown to be independent from the amount of F^- used in the precursor solution [1]. However, we believe that the preferred plane of crystallite growth, in the SP techniques, may depend on many physical parameters, such as, pyrolytic temperature, angle of spray, seed particle alignment, type of the crystalline form and so on and also on the shapes of nanomaterials obtained; the latter will be explained from the results obtained for different Dimensionalities of FTO <u>NR</u>s prepared in this work (vide infra). In fact, there are reports to show other preferred planes such as (211) in high-quality FTO nanoparticles produced by some of the co-authors of this paper where they have shown that the preferred plane also depends on annealing of the samples[38]. $\frac{I_{(200)}}{I_{(110)}}$ ratio of the XRD peaks, where I indicates intensity of the peak, is 0.17. This may be due to low F⁻-doping. Since all other minor diffraction peaks can also be assigned to this crystalline form of SnO₂, it can be concluded that there are no other crystalline materials present in the sample, even as impurities, indicating very high purity of Sample 1. Also, there are no peaks due to SiO₂ and hence it can be concluded that the glass surface has not undergone crystallization, as a result of 30 min heat-treatment at 480 °C.

SEM image, shown in Figure 2(b-i) clearly indicates the presence of grains typical of commercial FTO, though the grain sizes are somewhat smaller and of ~150 nm in size. The cross-sectional view of this sample, depicted in Figure 2(b-ii), shows that the average thickness of the layer to be ~ 170 nm.



Figure 2 (a) X-Ray Diffractogram, (b-i) SEM front view (b-ii) SEM cross-section (c) XPS of (c-i) Sn_{3d} (c-ii) O_{2p} (c-iii) F_{1s} (c-iv) Na_{1s} (c-v) C_{1s} and (d) ATR-FT-IR Spectrum and (e) UV-visible transmission spectrum of FTO sample 1 prepared at 4 min spray, over 30 min.

Figure 2 c shows the XP spectra of Sn_{3d} [Figure 2(c-i)], O_{2p} [Figure 2(c-ii)] and F_{1s} [Figure 2 (c-iii)] of Sample 1. As Figure 2(c-i) reveals, the peaks at 486.9 eV and 495.2 eV represent the $\ Sn_{3d_{5/2}} and \ Sn_{3d_{3/2}},$ respectively, indicating that Sn in its $\ Sn^{4+}$ state [2, 3]. The O spectrum [Figure 2(c-ii)] shows a main peak at 531.8 eV, which may be assigned to be due to lattice oxygen of SnO₂. A small peak appearing at 533.5 eV may be assigned to be due to OH groups present on the FTO surfaces. However, O_{1s} spectrum of FTO nanoparticles on glass can be complicated due to the presence of non-bridging (Si-O⁻ Na⁺) and bridging (Si-O-Si) O atoms of exposed glass surfaces. Mekki et al. have studied XPS of same soda lime glass and assigned the peak at ~530 eV to bridging O and that at ~532 eV to non-bridging O of the soda lime glass[4]. As such, in our case, O peaks could have been originated from both FTO and glass making the resolution of peaks to exact atoms very difficult. The F_{1s} spectrum for this sample is weak since F atomic percentage is low though a peak at ~ 686.0 eV can be traced which can be assigned to Sn-F bonding, which provides evidence as to the presence of F in O sites[5-7].

Analysis of the XPS data reveals the presence of Sn, O, Na, C, F and Si, in this sample, with atomic percentages of 16.58%, 39.09%, 3.78%, 34.81%, 0.18% and 5.46%, respectively. Since the F% is very low, the XPS peak is only barely visible. These data give evidence for the presence of F^- ions in the lattice sites of O^{2-} where 0.4% of O^{2-} sites have been replaced by F⁻ ions. From the Sn to Si peak heights, the ratio of FTO to void on the surface of glass can be calculated to be 3:1, and hence it can be concluded that only 3/4th of the glass surface has been covered by the FTO seed particles. In order to further ascertain the presence of F in the thin film of Sample 1, its' ATR-FT-IR spectrum was recorded after drying the sample at 150 °C for 45 min. The spectrum consists of features only in the wave number range 400 to 750 cm⁻¹ (Figure 2 d) and the spectrum is flat without any bands from 750 cm⁻¹ to 4000 cm⁻¹. As shown in the figure, the bands centered at 413, 430, 463, 604 and 731 cm⁻¹ can be assigned to be due to stretching vibrations of F-Sn-F, F-Sn, O-Sn-O, Sn-O and Sn-O-Sn, respectively[8]. The absence of any feature after 750 cm⁻¹ indicates the absence of adsorbed water, O-H groups or any other functional groups[7]. There are no any bands around 3500 cm⁻¹. In fact, the spectrum is featureless in this range. This proves that these samples do not contain any adsorbed water molecules, O-H groups or any other functional groups except those given above.

Depicted in Figure 2 (d) is the UV-Visible Transmittance spectrum of Sample 1. It provides good evidence to show that the sample is highly transparent in the entire visible region with percentage transmission of over 80%. UV-visible absorption spectrum (Given in Supplementary Figure S1 (a)) reveals that the band gap of FTO Nanoparticles (NPs) in Sample 1 to be 3.62 eV. This is typical of the band gap of around 3.60 eV of FTO NPs as reported by Wu et al. though the band gap shifts to higher values due to confinement effect as the particle size is decreased[3]. As such, three independent analytical techniques, namely, XRD, XPS and FT-IR provide evidence to the presence of SnO₂ and F⁻doping, thus demonstrating excellent correlations and mutual agreements of the results obtained by different analytical methods.

3.4.2 Sample 2: Prepared by spraying for 6 min over 45 min periods

Thin film, prepared at spray for 6 min over 45 min period, i.e., Sample 2, has an XRD spectrum, as depicted in Figure 3 (a), which is quite similar to that of Sample 1 though the relative intensities of the peaks have been drastically decreased. XRD spectrum still shows diffractions from (110), (101), (200), (211), (310) and (301) with (110) as the dominant diffraction plane as in FTO grains.

However, $\frac{I_{200}}{I_{110}}$ ratio has now increased to 0.74 which is 3.36 times increase from that of typical FTO nanoparticles of Sample 1 indicating a significant increase in F⁻doping. SEM image shown in Figure 3(b) gives evidence as to the change of the crystallite shape from that typical of FTO grains, as observed for Sample 1, to a kind of tetragonal shape with a small reduction in grain size also (~ 80 nm), with an increased film thickness of 200 nm. The increase in sample height is readily understood since more materials are deposited due to increased spray duration. The sample is still transparent with percentage transmission in the entire visible range exceeding 80% [Figure 3(d)].

The XPS peaks of different elements are very much similar in shapes to those of the sample 1 but their positions have been shifted to slightly higher binding energies. Now, the F_{1s} spectrum is much improved giving a peak at around 686.9 eV as opposed to typical 686.0 eV for Sn-F bonding in FTO. This small shift in peak position may be due to the broadness of the peak. F% has also been increased significantly from to 0.27% which is a 50.0% increase from the first value.



Figure 3: (a) X-Ray Diffractogram, (b-i) SEM front view (b-ii) SEM cross-section (c) XPS of (c-i) Sn_{3d} (c-ii) O_{2p} (c-iii) F_{1s} (c-iv) Na_{1s} (c-v) C_{1s} and (d) UV-visible transmission spectrum of FTO sample 2 prepared at 6 min spray, over 45 min.

3.4.3 Sample 3: Prepared by spraying 8 min over 60 min periods

Further increase in the spray time, for 8 min, over 60 min, results in the formation of FTO nanorods with the small depression at the top of the structures which we call as uncapped nanorods clearly revealed by their SEM images which are shown in Figure 4 (b-i and b-ii). Shape of these uncapped nanorods shows a tetragonal cross-section, the shape of which are quite similar to the shape of the crystallites obtained in Sample 2. Since the top view only shows small depression, it is possible that the nanorods are at least almost vertically-aligned. The average diameter of the cross-section is ~80 nm and the wall thickness is 18 nm. The cross-sectional image gives the thickness of the layer to be around 350 nm. This suggests that the uncapped nanorods have been formed by erecting from the atoms/ions on the edges of the tetragons. Since the atoms/ions on the edges have no valency satisfaction, it is quite likely that these species are more energetic than those in the interior of the tetragons, and hence the erection from the edge atoms/ions is energetically more favorable to form such nanorods with a tetragonal cross-section.

The cross-sectional view of this layer reveals that the height of the FTO uncapped nanorods formed is ~ 350 nm [Figure 4 (a-ii)]. XRD spectrum of sample 3 is shown in Figure 4(b). The XRD spectrum is distinctly different in this case and the peak corresponding to diffraction from (101) plane is quite distinct and other peaks are either absent or too small to distinguish between actual peaks and noise though those due to 2θ = 26.57° (101), 51.81° (211) and 65.96° (301) are still noticeable. This suggests that most of the rods are aligned alone (101) plane in FTO uncapped nanorods as opposed to preferred (110) plane of 0-D FTO particles. Since there are no peaks due to SiO₂, it is clear that the glass surface has not undergone any crystallization.

As depicted from Figure 4, XPS F_{1s} peak appears at 686.0 eV, which is typical of fluorine substitution in oxygen vacancies of SnO₂, as revealed by many authors for FTO NPs with high F⁻ substitution of typically over 1%[9]. However, there is also another broad feature around 680 eV though an actual XPS peak is difficult to distinguish from the noise level. If there were a peak around this value, that would be due to interstitial fluoride ions. A distinct feature to note in the XPS studies of FTO uncapped nanorods is that the spectrum of Sn_{3d} is now consist of four peaks centered at 487.27, 488.79, 495.46 and 496.97 eV, respectively.

This suggests that both Sn(IV) and Sn(II) exist on the surface. The peak height ratios are $Sn(II)_{3d_{5/2}}$: $Sn(IV)_{3d_{5/2}}$: $Sn(II)_{3d_{3/2}}$: $Sn(IV)_{3d_{3/2}} = 1 : 0.707 : 0.667 : 0.667$ 0.471. It is surprising to see such high percentile of Sn(II) at such low F⁻ incorporation. This is because XPS is a surface analytical technique which explores only 2 nm depth from the surface, and hence what it measures is Sn(II) ions that are present on the surface. Since uncapped nanorods are 350 nm long and 80 nm wide with 18 nm walls each side, both inside and outside surfaces are exposed for XPS analysis. Hence, in the case of FTO uncapped NRs, almost all Sn(II) ions are detected by the XPS. This accounts for Sn(IV) : Sn(II) ratio of 0.7 but this is only at the vicinity of surfaces. This means that the almost all of the bulk tin ions are composed of Sn(IV) only. As such, surface states of FTO are Sn(II) ions present on the surface whereas bulk tin ions are exclusively Sn(IV). The presence of Sn(II) on the surface is observed in the Sample 4 also where there are more capped FTO NRs and some uncapped FTO NRs present in this sample. However, in that case the Sn(IV) : Sn(II) is much less than 1 (vide infra). The Sn(II) amount in FTO nanoparticles is hardly measurable from XPS due to two reasons: (i) the F⁻ substitution is much less than that in FTO NRs and (ii) the surface area of nanoparticles are significantly less than that of NRs, which accounts for the perfectly symmetrical two peaks obtained for Sn_{3d} of FTO NPs.

XPS data of this sample show the presence of Sn, O, Na, C, F and Si with atomic percentages of 16.14%, 39.75%, 8.97%, 29.29%, 0.59% and 5.48%, respectively. Fortuitously, the atomic percentages of Sn, O, Si have not changed from those in the FTO grains of the Sample 2, suggesting that the numbers of surface atoms/ions of these elements have not changed as a result of increased SP. As such, the FTO:void ratio also remains at 3:1 as observed in the previous case. This brings us to the point that, upon prolonged SP, initially formed crystallites act as seeds for vertical growth of 1-D nanostructured architectures and there is no more seed particle formation due to continued spray. The 1-D nanomaterials are grown only by initiating from these seed crystallites. There is no further growth of seed crystallites across the surface of the glass also. One distinct result is the decrease in C atomic percentage and increase in F atomic percentage in the XPS data of FTO uncapped nanorods when compared to those of FTO nanocrystallites. Since there is no change in the O atomic percentage, which is remaining around 39%, in both cases, but increase in F atomic percentage by 2.18 times, suggest that the additional F⁻ ions are occupying in interstitial positions rather than as substitutes for O^{2-} sites. The decrease in C% is due to increased mineralization of acetone to CO_2 and H₂O. FT-IR spectrum (Figure 4 (d)) is very similar to that of FTO NPs showing all the vibrations shown in FTO NPs.



Figure 4: (a) X-Ray Diffractogram, (b-i) SEM front view (b-ii) SEM cross-section (c) XPS of (c-i) Sn_{3d} (c-ii) O_{2p} (c-iii) F_{1s} (c-iv) Na_{1s} and (c-v) C_{1s} and (d) ATR-FT-IR Spectrum and (e) UV-visible transmission spectrum of FTO sample 3 prepared at 8 min spray, over 60 min.

FTO uncapped NRs have optical transmissions (Figure 4(e)) of over 80% in the entire visible range. UV-visible absorption spectrum given in S1 (b) can be used to estimate band gap to be same as that of FTO NPs (3.62 eV).

3.4.4 Sample 4: Prepared by spraying 12 min over 90 min periods

SEM images of Sample 4 are depicted in Figure 5 (a i-ii). Careful examination of the front view reveals that there are both uncapped and capped nanorods of FTO are present in this sample but mostly capped ones. This is because as the nanorods with small depression at the top grow in the vertical direction from the surface their growth rate is progressively decreased and the materials formed afterword deposits on the top surface of the uncapped nanorods capping them. Such capped nanorods formation has been observed in many cases including carbon nanotubes. This time of spray is insufficient to cap all the NRs and hence some uncapped NRs are still visible. Capping has hardly affected the optical transmission of the thin layer and the transmission spectrum has hardly changed from that of FTO uncapped nanorods.



Figure 5: (a) Front view SEM image and (b) XPS Sn_{3d} spectrum of Sample 4 prepared at spraying 12 min over 90 min period.

3.4.5 Sample 5: Prepared by spraying 16 min over 120 min periods

Sixteen min spray, over 120 min, gives the materials as shown in Figure 6(b). This SEM image clearly shows the end capped FTO nanorods rather than further increasing the length of the uncapped nanorods. XRD shown in Figure 5(a) reveals that the capped nanorods are also aligned in the (101) as in the case of uncapped ones. This is because capping has taken place on top of the uncapped nanorods. Crosssectional SEM images show that capped nanorods are slightly tilted from surface normal possibly due to high weight on their top part. These capped nanorods have dimensions of 60 - 70 nm cross-sections and 500 nm heights.

Note now that the XPS spectra are quite similar to those of FTO nanoparticles. Splitting observed in Sn_{3d} for FTO NTs is no longer there since the total surface area now available for XPS measurements is limited due to unexposed interior of the uncapped nanorods. The composition of the sample as determined by XPS is Sn 16.41%, O 39.53%, Na 8.97%, C 29.29%, F 0.59%, Si 5.48%. FT-IR spectrum (Figure 6 (d)) is very similar to that of FTO NPs and uncapped NRs showing all the vibrations shown in these structures.

FTO capped NRs have slightly lower optical transmissions (Figure 6(e)) between 70- 80% in the entire visible range. UV-visible absorption spectrum given in S1 (b) can be used to estimate band gap to be same as that of FTO NPs (3.62 eV).



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Figure 6: (a) X-Ray Diffractogram, (b-i) SEM front view (b-ii) SEM cross-section (c) XPS of (c-i) Sn_{3d} (c-ii) O_{2p} (c-iii) F_{1s} (c-iv) Na_{1s} and (c-v) C_{1s} and (d) ATR-FT-IR Spectrum and (e) UV-visible transmission spectrum of FTO sample 5 prepared at 120 min (effective 16 min spray on).

3.4.6 Sample 6: Prepared by spraying 24 min over 180 min periods

Further increase in the SP duration, to 24 min spray, over 180 min, gives the front SEM view characteristic of extensively cross-linked nano-needles on the top surface of these materials as shown in Fig.7. This indicates that when the hollow type nanorods are capped completely, there is no further growth of these 1-D nanomaterials of FTO, and subsequently formed materials deposit on the top surface as extensively cross-linked nano-needles to an appreciable thickness of nearly 100 nm since the layer thickness of this final product is around 520 nm as shown in their cross-sectional view of SEM images. XPS data gives atomic percentages of Sn, O, Na, C, F and Si of 21.67%, 42.84%, 5.27%, 27.31%, 0.56% and 2.35%, respectively. Comparison of these data with those obtained in previous samples, clearly shows that the increase in the FTO coverage on the glass surface is due to prolonged exposure.



Figure 7: (a) X-Ray Diffractogram, (b) SEM front view (c) XPS of (c-i) Sn_{3d} (c-ii) O_{2p} (c-iii) F_{1s} (c-iv) Na_{1s} and (c-v) C_{1s} and (d) UV-visible transmission spectrum of FTO sample 6 prepared by spraying 24 min over 180 min period.

The FTO: void ratio is now 9:1, which means 9/10th of the glass surface is covered by FTO when compared to 3/4th surface coverage in the previous cases. This is understandable and the result agrees well with the morphologies shown in the respective SEM images. In the present case, there is an over layer of extensively cross-linked FTO nano-needles on approximately vertically-aligned FTO nano-needles. As such, most of the glass surface is covered by the FTO nano-needles without allowing X-rays to penetrate to the glass surface. Interestingly, the F⁻ ion percentage has not been changed from that is present in capped FTO nanorods. As such, this F atomic percentage may be the highest that can be obtained in 1-D nanoarchitectures of FTO. The optical transparency of thin layers lie within 70% to 80% in the visible range of the electromagnetic spectrum.

This technique is versatile and can be used to prepare nanomaterials of various substances on substrate surfaces that can withstand required temperatures.

G. R. Asoka Kumara et.al have prepared interconnected FTO nanoparticles by spraying vertically on to soda lime glass surfaces and used these transparent conducting glasses in dye-sensitized solar cell (DSC) applications (10). K.A.T. Amalka Perera et.al have also prepared various nanotechnological architectures of ZnO using Atomized Spray Pyrolysis method. Interestingly, we were able to prepare a very thin layer (~1 nm thick) of CaCO₃ coating on interconnected SnO₂ particles to suppress recombination in SnO₂-based DSCs (11).

3.5. Propose crystal growth mechanism of the 1-D nanostructures

We would like to propose a crystal growth mechanism for the above 1-D nanostructured FTO thin films by using some images as shown in the figure 8. In the initial stage of the horizontal spray process, arriving fine droplets of the FTO precursor solution sweep along the glass substrate and vertically-oriented FTO Nano species are formed. These vertically-oriented FTO nanostructures have highly reactive polar crystal surfaces such as (111) and (101). Hence, these unsaturated K faces are highly reactive and easily interact with arriving growth atoms to form 1-D structure with the increment of spray time duration as shown in the figure 8(b). In this case, we can see the hollow-type structure due to the small depression of top of the FTO nanostructure. This would be due to the higher growth rate of the corner atoms of vertically-oriented 1-D FTO structure.



Figure 8: Schematic diagram for the crystal growth of FTO 1-D nanostructures.

Further increase of the spray time duration has facilitated to fill the inner reactive planes and formed FTO nanorods appeared as shown in the figure 8(c). However, fine droplets of the atomized FTO solution react further with 1-D nanostructure and result to formed needle-type 1-D structure as shown in the figure 8(d) and finally, these onedimensional nanostructures grow and tends to cross-link with spray time duration. This may be due to the mass effect of the deposited FTO droplets.

3.6. Conclusion

A versatile method has been developed to prepare various nanotechnological structures of fluoride-doped tin oxide transparent conducting thin layers on ordinary soda lime glass surfaces. Different architectures can be obtained simply by controlling only the deposition time. The method developed is called PASP where a stream of fine droplets of precursor solution is sprayed horizontally for 2 s on and 13 s off pulse program onto glass substrate surface resting on a hotplate placed in the pyrolytic chamber, which is preheated to 500 °C. Materials present in the precursor solution then undergo pyrolysis to form FTO 0-D seed particles at the shortest time scale of spray,

Which follows the erection of seed particles from their corners to result in approximately vertically-aligned uncapped nanorods with depression at the top of the structure. Further spray gives almost vertically-aligned capped nanorods. Finally, the top surface of the capped nanorods is covered by extensively cross-linked nano-needles. Conversion of 0-D nanoarchitectures to 1-d materials results in the decrease in crystallinity as shown by XRD results. XPS results reveal that the initially formed FTO seed particles have 0.8% fluoride doping with FTO coverage of 75% on the glass surface. The surface coverage by FTO does not change due to the formation of uncapped nanorods and capped nanorods.

However, when there are extensively cross-linked nanorod architectures are formed surface coverage increases to 90% since this cross-linked layer has been formed in the horizontal plane on top of the vertically-aligned nanorods. These thin layers have optical transmission in the range from 80% to 70% as more and more complicated structures are formed due to prolonged spray pyrolytic deposition. The versatility of this technique is not limited to FTO layers but it can also be used to fabricate any other thin layers on various substrate surfaces.

3.7. References

[1] B. Zhang, Y. Tian, J. Zhang, W. Cai, The FTIR studies on the structural and electrical properties of SnO₂:F films as a function of hydrofluoric acid concentration, Optoelectronics and Advanced Materials – Rapid Communications, 4 (2010) 1158-1162. [2] H.-J. Ahn, H.-C. Choi, K.-W. Park, S.-B. Kim, Y.-E. Sung, Investigation of the Structural and Electrochemical Properties of Size-Controlled SnO2 Nanoparticles, The Journal of Physical Chemistry B, 108 (2004) 9815-9820.

[3] S. Wu, S. Yuan, L. Shi, Y. Zhao, J. Fang, Preparation, characterization and electrical properties of fluorine-doped tin dioxide nanocrystals, J. Colloid Interface Sci., 346 (2010) 12-16.

[4] A. Mekki, D. Holland, C.F. McConville, M. Salim, An XPS study of iron sodium silicate glass surfaces, J. Non-Cryst. Solids, 208 (1996) 267-276.

[5] N.S. Ramgir, I.S. Mulla, K.P. Vijayamohanan, Effect of RuO2 in the Shape Selectivity of Submicron-Sized SnO2 Structures, The Journal of Physical Chemistry B, 109 (2005) 12297-12303.

[6] W.S. Epling, C.K. Mount, G.B. Hoflund, Surface characterization study of the chemical alteration of an air-exposed polycrystalline tin foil during H-atom exposures, Appl. Surf. Sci., 134 (1998) 187-193.

[7] T. Moon, S.-T. Hwang, D.-R. Jung, D. Son, C. Kim, J. Kim, M. Kang, B. Park, Hydroxyl-Quenching Effects on the Photoluminescence Properties of SnO2:Eu3+ Nanoparticles, The Journal of Physical Chemistry C, 111 (2007) 4164-4167.

[8] S. Chaisitsak, Nanocrystalline SnO2:F thin films for liquid petroleum gas sensors, Sensors (Basel), 11 (2011) 7127-7140.

[9] A.A. Shaltout, H.H. Afify, S.A. Ali, Elucidation of fluorine in SnO₂:F sprayed films by different spectroscopic techniques, Journal of Electron Spectroscopy and Related Phenomena, 185 (2012) 140-145.

[10] G. R. Asoka Kumara, C. S. Kumara Ranasinghe, E. Nirmada Jayaweera, H. M. Navaratne Bandara, Masayuki Okuya and R. M. Gamini Rajapakse, "Preparation of Fluoride-Doped Tin Oxide Films on Soda–Lime Glass Substrates by Atomized Spray Pyrolysis Technique and Their Subsequent Use in Dye-Sensitized Solar Cells", J. Physical Chemistry C, 03/2014; DOI:DOI: 10.1021/jp411354b.

[11] K.A.T. Amalka Perera, G. Anuradha Sepalage, G.R. Asoka Kumara, M. Lal Paranawitharana, R.M. Gamini Rajapakse, H.M.N. Bandara, "The Interconnected, CaCO₃ coated SnO₂ Nanocrystalline Dye-sensitized Solar Cell with Superior Performance", Electrochimica acta, 56 (2011) 4135-4138.

CHAPTER 04

Synthesis of 1-D nanostructured FTO Thin Films at Higher Fluorine Concentration

The following chapter describes the use of Rotational Pulsed and Atomized Spray Pyrolysis Deposition Technique to fabricate FTO nanostructured thin films with different fluorine concentrations. The higher fluorine concentration shows a great influence to crystal growth of 1-D nanostructured FTO thin films even at a large angle of the spray direction of RPASP technique. The prepared FTO nanorods show cubic structure of the tin dioxide. The pressure effect for the growth of cubic FTO nanostructure has explained in details and electrical properties of the thin films has also presented.

4.1 Introduction

The transparent conducting oxides (TCOs) materials have become more attractive topic in the technological fields due to its advance properties for device performance [1]. The different film morphologies such as 1-D and 3-D nanostructures have getting more advantage to enhance the performance of the applications in industrial sectors [2-6]. In the previous chapters, we introduced the simple and cost effective SPD technique, which can be used to prepared 1-D nanostructured FTO thin films. Also, we have studied the effect of the spray direction for the crystals growth of FTO nanostructured thin films by using that RPASP [7]. Moreover, the effect of the spray time durations for the 1-D nanostructured FTO thin films have also studied with more analytical details. In this section, we are going to introduce another method to grow one-dimensional nanostructured FTO thin films by using different molar ratios of fluorine even at higher spray angle to the substrate. The prepared FTO nanorods show cubic structure of tin dioxide with (111) direction as the predominant plane.

4.2 Experimental

4.2.1 FTO thin films fabrication

Tin (IV) chloride pentahydrate [SnCl₄.5H₂O 98%, Wako Chemicals], ammonium fluoride (NH₄F 98%, Aldrich Chemicals) and propanone used were purchased and used without further purification. Soda lime glasses were cleaned thoroughly with deionized distilled water using a textran first and then they were ultrasonically cleaned in 1:1 v/v mixture of ethanol: acetone in an ultrasonic bath. FTO precursor solution was prepared by mixing SnCl₄.5H₂O and NH₄F in deionized water with addition of propanone. The concentration of SnCl₄.5H₂O was fixed at 0.20 M and Mass of theNH₄F was changed in order to control the Sn: F molar ratios as shown in the Table 1.

FTO precursor solution was sprayed on to the soda lime glass substrate with 50 mm x 50 mm size by using the RPASP technique and air as a carrier gas. The glass substrate was put onto the hot plate and preheated at 470°C for 10 minutes. The spray pressure of precursor solution was 0.20 MPa and the nozzle distance from the glass substrate was around 0.5 cm. The spray angle was kept at higher angle to the substrate which was around 45⁰ with the substrate surface. The each FTO thin films with different Sn: F molar ratio was prepared by using 2s on and 13s off spray pulses. This was helped to maintain the substrate temperature constant during the spray time period. The 50ml volume of the precursor solution used to fabricate each FTO thin film. The thin films formed through each precursor solutions with different molar ratios were subjected to Scanning Electron Microscopy (SEM, JEOL JSM-6320F), X-Ray Diffractometer (XRD, Rigaku RINT Ultima-III, CuK \Box , \Box =1.541836 Å) and UV-Visible spectroscopy (JASCO V630). The sheet resistance of the thin films measured by using linear 4 probe system.

Sample No	SnCl4. 5H2O(g)	NH4F (g)	Molar Ratios
1	3.50	0	Un-doped
2	3.50	0.37	1:1
3	3.50	0.75	1:2
4	3.50	1.11	1:3
5	3.50	1.50	1:4
6	3.50	1.85	1:5
7	3.50	2.22	1 :6

Table 1: FTO thin films with various Sn: F molar ratios.

4.3 Results and Discussion

4.3.1 Morphological properties

The morphology of the thin films prepared with different Sn: F molar ratios are shown in the Figure 2. These SEM images clearly show us crystal structure of the FTO thin films has changed with fluorine incorporation to the lattice structure of Tin dioxide. Vertically oriented small nanograins has formed with undopped tin dioxide. Then the size of the nanocrystals has slightly enhanced with fluorine doping. Sample with 1: 3 molar ratio shows large nanoparticles due to substitute of Fluorine ions in to the proper lattice positions in the tin dioxide and growth the crystals with pyrolysis process of the reaction.





Figure 1: SEM images of FTO thin films deposited with different Sn: F molar ratios (a) undopped, (b) 1: 1, (c) 1: 2, (d) 1: 3, (e) 1: 4, (f) 1: 5 and (g) 1: 6 of the precursor solution.

Then the grain size of the FTO nanoparticles has reduce with the increase of fluorine doping amount and lot of irregular grains can be seen the sample prepared with 1: 5 molar ratios. However, we observed the compact structure with lot of smaller grains between larger grains. So, density of smaller grains increased at doping level of 1:5. Finally, vertically aligned one-dimensional nanostructured FTO thin films could be able to synthesized with 1: 6 molar (Sn: F) ratios. The phenomena of the formation of FTO nanorods can be explain as follows. In the initial stage, doping of smaller amount of fluorine substitute to the proper lattice position and cause for the increment of grain size, but higher amount of fluorine doping increase the amount of fluorine ions without substitute to the oxygen in the lattice structure. This may act as the impurities to the system and it can restrict the growth of FTO crystals in horizontal directions and provide rooms to grow in vertical direction. As the result, crystal grow in the vertical directions and formed nanorods with sufficient amount of precursor and spray rate. A.V. Moholkar et.al have also studied about the effect of the fluorine doping for FTO thin films by using SPD technique and they also reported that dramatic change of morphology of FTO microstructure occurred with fluorine doping concentration [8].

4.3.2 Structural studies

Figure 2 shows the XRD patterns of FTO thin films prepared by the precursor solutions with various Sn: F molar ratios. The results clearly shows that the some strange peaks are appeared as the preferred orientation for the doped nanostructured thin films.





Figure 2: X-ray diffractograms of the FTO thin films deposited with different fluorine molar ratios.
These peaks are identify as the (111) and (222) plane of the cubic structure of tin dioxide according to the PDF card no 00-050-1429 of PDXL XRD analysis software. Other peaks can be assigned to the tetragonal structures of tin dioxide based on the PDF card no 00-041-1445 of PDXL XRD analysis software. Therefore, both cubic and tetragonal structure of tin dioxide present for the FTO thin films and only (111) plane of the cubic tin dioxide was exist as the preferred orientation for the FTO 1-dimensional nanostructured thin films prepared at higher fluorine concentration. Normally, cubic structure of tin dioxide is unstable and synthesize under higher pressure such as 48 GPa [9]. However, obtain of the cubic structure of FTO nanorods thin film can be explain as below. In this experiment, we use atomizer to break large particle of precursor solution and as a result fine atomized mist like solution allow to deposit on hot glass substrate at very low distance of the nozzle. So, these conditions may provide the well enough pressure for the fine atomized droplets to deposit on the glass substrate, though we have used around 0.20 MPa pressure during the experiment. Also, low nozzle distance (0.5 cm) facilitate to deposit large amount of aerosol spray of the precursor solutions on the substrate at fast rate with specific time duration. Therefore, both cubic and tetragonal phase of tin dioxide formed in the initial stage of the reaction. Normally, (111) planes are polar and highly reactive because there are plenty of unsaturated bonds cutting their

surfaces [10].

Therefore, arriving atoms of the precursor solution react with the (111) plan at fast rate and crystals have grown along that plane. The sample synthesized at the highest fluorine molar ratio (1:6), excess fluorine ions suppress the growth of crystals in horizontal directions and allow to grow in vertical direction to formed FTO nanorods with cubic (111) plane as the preferred crystal growth orientation due to its highly reactive feature. Jian Tao Wang et.al have also reported that cubic tin oxide crystal structure can be synthesis at fast rate as long as sufficient growth atoms are provided and it can't be changed by even high fluorine doping [11].

The lattice parameters show the physical dimension of unit cells in a crystal lattice. Hence, we have calculated the lattice parameters of both cubic and tetragonal structures by using cellcalc software. The data of the thin film prepared at 1:4 mole ratio was used for the calculation. Table 2 shows the values of lattice parameters with their reference values.

Crystal Structure		Reference		
	a	b	с	Kelelence
Cubic (111),(222)	4.88882	4.88882	4.88882	a=b=c=4.88830
Tetragonal (110), (200)	4.75424	4.75424	3.16571	a=b=4.73700 c=3.18500

Table 2: Lattice parameters of the FTO thin film prepared at 1:4 molar ratio.

These data confirmed us lattice parameters of (111) and (222) are matching with the cubic structure of tin dioxide and values of tetragonal structures have been deviated from their reference data. This may be due to the nanocrystalline nature of FTO and present of both cubic and tetragonal structures in the thin film.

4.3.3 **Optical and Electrical properties**

The 1-D nanostructured FTO thin film synthesis at high fluorine concentration show good optical transparent in the entire visible range with percentage of maximum transmittance value around 74.6% as depicted in Figure 3. However, transmittance has little bit reduced when compare with tetragonal FTO nanorods which I have presented in the previous chapters. This may be due to the effect of excess fluorine impurities in the film. The electrical conductivities of the thin films are shown in the Table 3.



Figure 3: The optical transmittance of the FTO nanorods thin film.

We did not focus to enhance the conductivity of the FTO thin films with this experiment. But, these values would be very useful to identify the proper amount of doping level of the fluorine to enhance the electrical conductivity. The high sheet resistant values may be due to the low films thickness and lack of contact between the nanorods prepared on normal glass substrate. However, thin film prepared at 1: 3 mole ratio shows the lowest sheet resistance value for the FTO thin film. This is due to the large crystal size of the FTO nanoparticles as fluorine substitute to the proper lattice positions of the oxygen vacancies and hence increase the crystal size with pyrolysis process. Also, fluorine substitution may enhance the effective free carrier charge density of the thin film.

Sample No	Molar Ratios	Sheet Resistance
1	Un-doped	13.73 ΜΩ
2	1:1	1.870 MΩ
3	1:2	329.20 ΚΩ
4	1:3	20.30 ΚΩ
5	1 :4	48.20 ΚΩ
6	1:5	3.46 MΩ
7	1 :6	7.62 ΜΩ

Table 3: Sheet resistance of the FTO thin films.

4.4 Annealed Testing

In order to confirm the synthesized FTO thin films consist with both cubic and tetragonal structure of tin dioxide, annealing testing was carried out. Cubic structure of tin dioxide is not stable when compare with the tetragonal structure. We used a FTO thin film prepared at 400 °C with 1:4 mole ratio for the test. Then the FTO thin film was annealed at 600 °C for 1 h in an electrical furnace. The interesting results have been observed as shown in the Figure 4. The XRD data clearly shows us both (111) and (222) peaks are disappeared after annealed test.



Figure 4: SEM and XRD data of FTO thin film before annealed and after annealed test, (a),(c) before annealed test and (b),(d) after annealed test.

Therefore, we can conformed that the both (111) and (222) peaks are belonging to the cubic structure of tin dioxide and the conditions used in the RPASP techniques are well enough for synthesize cubic structure of tin dioxide in normal atmospheric environment. Also, we have carried out additional experiments by changing spray parameters such as spraying pressure and nozzle distances. Though, we did not report those results here, low nozzle distance from the substrate and high spraying pressure of atomized spray pyrolysis technique was well enough to provide sufficient growth atoms at fast rate for the formation of cubic structure of tin dioxide.

4.5 Conclusion

Advance version of SPD technique, known as RPASP technique was used to synthesize the one-dimensional nanostructures of FTO thin film on glass surfaces. Though, spraying at low angle to the substrate is very important to the formation of FTO 1-D nanostructures, we can produce FTO nanorods even at large angle spraying with high fluorine concentration of the precursor solution. Fluorine substitute for the oxygen vacancies in the tin oxide lattice structure and enhance the size of the crystal with pyrolysis process up to 1:3 mole ratio and crystal size decreased thereafter due to effect of the fluorine ions which are not substitute for the proper lattice positions of the tin dioxide.. Finally, the FTO thin film prepared at 1:6 mole ratio facilitate eradiate crystals in vertical direction to form vertically aligned FTO nanorods with small depression at the top. The formed FTO nanarods show (111) direction as the preferred crystal growth orientation of the cubic tin dioxide. This was due to the effect of low nozzle distance of the RPASP technique. The fabricated 1-D nanostructured FTO thin film show good optical transparency in the visible range and low electrical conductivity due to the lack of interconnectivity of nanorods on normal glass substrate.

4.6 References

- [1] R.G. Gordon, Criteria for choosing transparent conductors, MRS Bulletin, 2000.
- [2] Z.W.Chen, J.K.L.Lai, C.H.Shek, Phys.Rev.B70 (2004)165314.

[3] Z.Dai, J.L.Gole, J.D.Stout, Z.L.Wang, Phys.Chem.B106 (2002)1274.

[4] G.Gao, Nanostruct.Nanomater. ImperialCollegePress, London, 2004.

[5] P.Yang, H.Yan, S.Mao, R.Russo, J.Johnson, R.Saykally, etal., Adv.Funct. Mater. 12(2002)719.

[6] O.Lupan, G.Chai, L.Chow, Microelectron.J.38 (12)(2007)1211.

[7] Ajith Bandara, Masayuki Okuya, Masaru Shimomura, Kenji Murakami and Rajapakse M.G. Rajapakse, Effect of Spray Directions on the Crystal Growth of Fluorine-Doped Tin Oxide One-dimensional nanostructured Thin Films, Journal of Advances in Physics, 12[1](2016) 2347-3487.

[8] A.V.Moholkar et al, Applied surface science 255(2009) 9358-9364.

[9] Haines, J., C.N.R.S., Laboratoire de Physico-Chimie des Materiaux, Meudon, France.,

Private Communication, (1998).

[10] Smith, A., Laurent, J. M., Smith, D. S., Bonnet, J.-P. & Clemente, R. R. Relation between solution chemistry and morphology of SnO2-based thin films deposited by a pyrosol process. Thin Solid Films 266, 20–30 (1995).

[11] Wang, Jian Tao et al. "Influence of Preferred Orientation on the Electrical Conductivity of Fluorine-Doped Tin Oxide Films." Scientific Reports 4 (2014).

CHAPTER 05

Improving the performance of 1-D nanostructured FTO thin films and application

The following chapter describes the use of Rotational Pulsed and Atomized Spray Pyrolysis Deposition Technique to fabricate one-dimensional nanostructured FTO thin films with different additives such as propanone, ethyl alcohol and iso-propanol. The purpose of the use of different additives is to study the effect of their chemical features for the growth of FTO nanostructure. The crystal growth of 1-D nanostructured FTO thin films with these additives have showed interesting features and properties of the films morphology and texture discussed in details. The conductivity of the FTO nanorods has improved with commercial FTO glass as the substrate and finally, performance of the dye-sensitized solar cells was studied with 1-D nanostructured FTO thin films as the transparent front electrode of DSSCs.

5.1 Introduction

This section describes preparation and characterization of the opticallytransparent and electrically conducting thin films of fluoride-doped tin dioxide (FTO) one-dimensional nanostructures and features of the purpose-built, novel and advanced version of spray pyrolysis technique, known as Rotational, Pulsed and Atomized Spray Pyrolysis. This technique allows perfect and simple control of morphology of the nanostructures of FTO layer by adjusting the spray conditions. Effect of the different additives on crystal morphology, size and texture of the 1-dimensional (1-D) nanostructured FTO thin films is studied. Vertically aligned and well separated nanotubes are easily fabricated using propanone and ethanol as additives. We suggest that propanone additive plays a role to form vertically aligned nanotubes with (101) preferential orientation while (110) face is the predominant plane of well separated nanotubes with ethanol additive. The conductivity of the 1-D nanostructured thin films are also enhanced using the commercial FTO glasses as a substrate.

5.2 Experimental

5.2.1 Formation of FTO thin Films

Tin (IV) chloride pentahydrate [SnCl4.5H2O 98%, Wako Chemicals], ammonium fluoride (NH4F 98%, Aldrich Chemicals), propanone, ethanol and isopropanol used were purchased and used without further purification. Soda lime glasses were cleaned thoroughly with Deionized distilled water using a textran first and then they were ultrasonically cleaned in 1:1 v/v mixture of ethanol: acetone in an ultrasonic bath. FTO precursor solution was prepared by mixing SnCl4.5H2O and NH4F in deionized water with addition of different additives (propanone, ethanol and isopropanol). The concentration of SnCl4.5H2O was fixed at 0.20 M and NH4F was controlled to be 0.80 M.

As shown in Fig 1, the FTO precursor solution was sprayed on to the soda lime glass substrate with 50 mm x 50 mm size by using the RPASPD technique and air as a carrier gas. The glass substrate was put onto the hot plate and heated at 470°C. The materials in precursor solution are transferred to the glass substrate by atomizing the solution and form the required nanostructures after evaporation of the solvent. The spray pressure of precursor solution was 0.15 MPa and the spray angle was kept at low angle to the substrate. Distance between the spray nozzle and the substrate surface is fixed to be 1 cm. Also we sprayed only for 2 s with an interval of 13 s and repeat the cycle (2s on and 13a off pulse) to keep the substrate temperature. The spray duration is controlled by total amount of the precursor solution.



Figure 1: Basic setup of RPASPD method

5.2.2 Characterization

The thin films formed through each precursor solutions were subjected to Scanning Electron Microscopy (SEM, JEOL JSM-6320F), X-Ray Diffractometer (XRD, Rigaku RINT Ultima-III, CuK \Box , \Box =1.541836 Å) and UV-Visible spectroscopy (JASCO V630).

5.3 Results and Discussion

5.3.1 Film morphology

Figure 2 shows the SEM images corresponding to the FTO thin films with different additives, where 100 ml of the precursor solution is sprayed on the soda lime glass, respectively. These images clearly show that the morphology of one-dimensional (nanotubes) nanostructured thin films has changed with the different additives. Also the SEM images confirm that the prepared thin films are crack-free and uniform. It was really difficult to prepare clearly visible and well separated 1-D FTO nanotubes only using water based solution, which could be attributed to a poor pyrolytic reaction of the water based solution. As a result, generated tiny nanotubes have fused together and finally formed grains.



(a)



(b)



(c)



(d)

Figure 2: SEM images of FTO thin films deposited with (a) water, (b) propanone, (c) ethanol and (d) isopropanol of the precursor solution.

Figure 2 (b) clearly shows that the vertically aligned and separated FTO nanotubes are synthesized with propanone as an additive in the precursor solution. Propanone has an ability to break the relatively strong bonds between water molecules by making hydrogen bonds between slightly positive hydrogen of water molecule and a lone pair on the oxygen in the carbonyl group [1]. This may facilitate to increase the pyrolysis reaction of atomized FTO solution to synthesize the 1-D nanostructured thin films. As shown in the Fig. 2 (c), almost vertically aligned and well separated nanotubes are also easily fabricated with ethanol as an additive. The size of the nanotubes increases with an addition of ethanol and it varies from 50 nm to 100 nm in the range. The formation of FTO nanotubes in the presence of ethanol can be explained in the following way. It is expected that ethanol react with in SnCl₄ and cuts the periodic bond chains of Sn(OH)₄ which is formed by the reaction of $SnCl_4$ with H_2O . Then water molecules in the solution react with the Sn-(OCH₂CH₃) molecules to form Sn(OH)₂ leading to the well separated SnO₂ nanotubes. It was really difficult again to prepare the vertically aligned FTO nanotubes with isopropanol as an additive. As shown in Fig. 2 (d), most of the 1-D nanostructures have grown along horizontal directions as well. This phenomenon can also be explained by using the properties of isopropanol in the precursor solution. Wang et al, has also reported that the morphology of FTO thin films changed with the addition of different additives [2].

5.3.2 XRD analysis

Figure 3 shows the XRD patterns of FTO thin films prepared by the precursor solution with the different additives. The results confirm that the nanostructured thin films belong to the cassiterite types with tetragonal rutile structure (PDF card no 01-077-0447 of PDXL XRD analysis software). Peaks for SnO or Sn phases are not detected, which indicates that the films are fully oxidized. The occurrence of a specific growth direction depends on many parameters. Specially, the precursor materials used for deposition and the thermodynamics of deposition conditions are important parameters. In this study, the low angle spraying to substrate is mandatory in order to fabricate the 1-D nanostructures.







(b)









Figure 3: XRD profiles of the FTO thin films prepared with (a) water, (b) propanone, (c) ethanol or (d) isopropanol as an additive in the precursor solution.

Figure 3 (a) clearly indicates that the 1-D nanostructures tends to grow along (101) direction. But, as shown in the SEM image, it was difficult to grow well separated nanotubes. Therefore, several peaks such as (110), (200), (211) and (301) also presence with the (101) preferred orientation. As shown in Fig. 3 (b), the predominant peak for FTO nanotubes grown with propanone is also (101) direction. Preferred orientation of the film, implying an enhancement in the number of grains of 1-D nanostructures along the (101) plane.

XRD data also confirm that the well vertically aligned nanotubes can be fabricated with propanone as an additive. FTO nanotubes with ethanol show the (110) as the predominant plane as shown in Fig. 3 (b). The (110) crystal faces are the side planes of FTO nanotubes, and due to large gaps among nanotubes (as shown in Fig. 2 (b)) these planes can be easily detected by XRD. Also, the (110) plane is the thermodynamically most stable plane due to the lowest surface energy [3,4].

5.3.3 Optical and Electrical measurements

All 1-D nanostructured FTO thin films are highly transparent in the entire visible range with percentage of transmittance values of 85.0%, 84.0%, 83 % and 76.0%, respectively. Although the visible light transmission of all prepared FTO thin films show high values, the conductivities are not seemed to be good in the nanostructured thin films due to a lack of contact among nanostructures. Therefore, the 1-D nanostructured FTO thin films were prepared on a commercial FTO glass in order to enhance a conductivity of the thin films.

Vertically aligned 1-D nanostructures are successfully fabricated on the commercial FTO glass surface as shown in Fig. 4 (a). In this case, total amount of spraying precursor solution was 50 ml.

The thin film shows a high transmittance value over 85% in the visible range as shown in Fig. 4 (c) and a good electrical conductivity (surface resistance is 25.6 Ω) at the same time. As shown in Fig. 4 (b), preferred orientation of the 1-D nanostructured thin films on commercial FTO has changed to the (200) direction.

This is due to the substrate effect of the commercial FTO. For tetragonal rutile SnO₂, [200] orientation has a low atomic density and a minimum interfacial energy [5, 6, 7]. Here, the commercial FTO layer serves as both a nucleation source for determining the predominate orientation of over layer and a barrier layer against Na diffusion from the glass [3].



(a)



(b)



(c)

Figure 4: 1-D FTO thin films fabricated on the commercial FTO with ethanol as an additive: (a) SEM image, (b) XRD profile and (c) UV-Vis spectrum.

5.4 Application of 1-D nanostructured FTO thin film

The prepared one-dimensional (nanorods) nanostructured FTO thin films on commercial FTO glass substrate was applied to the front electrode of the dye-sensitized solar cells (DSSCs) in order to compare the performance of DSSCs with 1-D nanostructured FTO thin films and commercial FTO.

DSSCs have become one of the most attractive and promising device to get electrical energy from freely available sun light. Also, this is a cost effective, simple and environmental friendly method to generate electricity and many researchers have been working on this field to enhance the power conversion efficiency of the device.

In this study first, we have assembled DSSCs with commercially available glass substrate as the working electrode to get higher efficiency. After that, DSSCs assembled with 1-D nanostructured FTO thin films in order to compare the performance between them. The fill factor (FF), open circuit voltage (Voc), current density (Jsc) and power conversion efficiency (Eff) of the solar cells will be discussed in the following section. Anyway, the DSSCs with FTO nanorods was showed higher FF and Voc values than that of with commercial FTO glasses. However, power conversion efficiency was quit low due to less film thickness of the photo anode of DSSCs with FTO nanorods. Therefore, further research work need to be carried out in order to improve the performance of DSSCs.

5.5 Experimental

5.5.1 Materials

Ethanol, TiO₂ powder (Degussa 25), Acetic acid, Triton-X-100, iodine, lithium iodide, 4-tert-butyl-pyridine, 1-Butyl-3-Methylimidazoliumiodide, 3methoxypropionitrile and N-719 dye were purchased and used without further purification. The commercial FTO glass substrates ($12 \Omega/cm^2$) purchased from SPD ink laboratory of Japan.

5.5.2 Nanocrystalline TiO₂ film preparation

The TiO₂ electrodes were prepared by spray pyrolysis deposition technique using mixture of TiO₂ colloid at 160 °C. TiO₂ (P25) powder was preheated at 400 °C for 30

minutes and allowed cool into room temperature before use it. Then the different combinations of TiO₂ colloid solutions were prepared by mixing TiO₂ powder (0.2g, 0.3g, and 0.4g), ethanol (20ml, 30ml, and 40ml), acetic acid (3drops, 4drops and 6drops) and Triton-x-100 (5drops, 7drops and 10drops) respectively. Each photo anode thin films prepared by spraying above solutions and plates were sintered at 500 °C for 30 minutes in an electric furnace. Then allowed the TiO₂ plates to cool down to the temperature around 70 °C and plates were dipped in 3×10^{-4} M ethanol solution of the N-719 for 12h to adequately absorb the dye.

5.5.3 Assemblage of the DSSCs

The each TiO₂ photo anode plates were cleaned with acetonitrile and dry with air gun. Then DSSCs were assembled by filling the electrolyte included with 0.6 M 1-Butyl-3-Methylimidazolium iodide,0.1 M LiI,0.1 M I₂, 0.5 M *tert*-butylpyridine in 3methoxypropionitrile aperture between the TiO₂ working electrode and Pt-coated FTO counter electrode. The two electrodes of each cells were clipped together and the I-V characteristics was carried out using a calibrated solar simulator under incident light intensity 1.5 AM, 100 mWcm⁻². The exposed active area of the each cell is 0.25 cm².

5.6 **Results and Discussion**

The performance of the each solar cells with commercial FTO glass substrate as the working electrode were listed and photovoltaic parameters such as fill factor (FF), open circuit voltage (Voc), current density (Jsc) and overall power conversion efficiency (η) [8] are shown in the Table 1.

Sample	Ethanol (ml)	P25 (g)	Voc (V)	Jsc (mA/cm ²)	FF	η (%)
1	20	0.2	0.379	7.934	0.678	3.651
2	20	0.3	0.710	14.910	0.610	6.450
3	20	0.4	0.731	10.650	0.661	5.141
4	30	0.2	0.715	9.372	0.671	4.050
5	30	0.3	0.669	11.560	0.699	5.404
6	30	0.4	0.707	10.690	0.667	5.036
7	40	0.2	0.732	9.351	0.702	4.806
8	40	0.3	0.705	10.210	0.691	4.968
9	40	0.4	0.682	11.250	0.597	4.588

Table 1: IV parameters of DSSCs fabricated from commercial FTO.

The parameters of the nine DSSCs samples are presented in the Table 1. According to that, the best power conversion efficiency was obtained for the sample fabricated with 20 ml of ethanol and 0.3 g of TiO₂ (P25). The SEM images of the TiO₂ photo anode thin films with top 3 DSSCs efficiency on commercial FTO glass substrates are shown on Figure 5.



(a)



(b)





Figure 5: The SEM images of the TiO_2 photo anode thin films of commercial FTO glasses with best three DSSCs efficiency (a) 6.450 %, (b) 5.404 %, (c) 5.141 %.

As shown in Figure 5 (a), the SEM image of the photo anode thin film with the best power conversion efficiency is consisted with crack free and interconnected TiO_2 particles when compared to the other samples. Hence, it provides better path for the charge carrier mobility and as a result current density has increased. These results we have confirmed at several time by repeating the DSSCs with same procedure. Hence, these DSSCs results are reproducible with above fabricate conditions.

We used the same procedure to fabricate DSSCs using our 1-D nanostructured FTO thin films as working electrode. The performance comparison of DSSCs with commercial FTO glass and FTO nanorods thin films as the front electrode are shown in the Table 2.

Table 2: The parameters of DSSCs fabricated with commercial FTO substrate and FTO nanorods

thin films.

No	Sample	Voc	FF	Jsc	η (%)	Thickness (TiO ₂ Film)
1	Commercial FTO	0.710	0.610	14.910	6.450	10 µm
2	FTO nanorods	0.720	0.730	5.490	2.900	6 µm

As clearly shown in the above table, the DSSCs fabricated with FTO nanorods as the front electrode has higher Voc and FF values than that of with commercial FTO glass. But, the current density and power conversion efficiency show low values than DSSCs with commercial FTO. This may be due to the less film thickness of the TiO₂ photo anode with FTO nanorods array. Hence, dye loading and absorbance of light has decreased. The images of the both commercial and nanorods FTO photo anode after N 719 dye attached are shown in Figure 6.





(b)

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Figure 6: Photographs of the TiO₂ electrode after N 719 dye attached. (a) Commercial FTO, (b) FTO nanorods

It also confirmed that the low dye attachment for the thin films consisted with FTO nanorods and has resulted to generate less free charge carriers. When we are spraying the TiO₂ solution on the FTO nanorods thin films, large portion of the solution can be go out without deposit on it due to hydrophobic effect of the nanostructures. Therefore, further research need to be carried out in order to improve the TiO₂ film thickness of the DSSCs with FTO nanorods. Specifically, preparation method of TiO₂ colloidal precursor solution should be changed by introducing TiO₂ fine particles mixture such as Tayca.

5.7 Conclusion

A novel and improved SPD technique, known as RPASPD technique has been developed to prepare the different nanostructures of FTO thin film on glass surfaces. Low angle spraying to the substrate is very important to grow the 1-D nanostructured thin films. FTO nanostructured thin films were prepared with the addition of different additives, H₂O, propanone, ethanol or isopropanol in the precursor solution. Prepared thin films were characterized for investigating an effect of the additive on the 1-D nanostructured morphology and texture. Vertically aligned and well separated nanotubes were fabricated with propanone or ethanol as an additive. The preferred orientation of nanotubes with propanone was along (101) direction while it was along (110) plane with ethanol as an additive. It was difficult to grow vertically aligned nanotubes with water or isopropanol. Prepared 1-D nanostructured FTO thin films had excellent optical transparency in the visible range. Conductivity of the thin films was improved by using commercial FTO glass as the substrate. The rotational mode of this technique was important to enhance the homogeneity of FTO thin films. Open circuit voltage and fill factor of the DSSCs with 1-D nanostructured FTO thin films were enhanced when compared with commercial FTO substrate as the working electrode.

5.8 References

- [1] <u>http://www.chemguide.co.uk/organicprops/carbonyls/background.html</u>.
- [2] Wang JT, Shi XL, Liu WW, Zhong XH, Wang JN, Pyrah L, Sanderson KD, Ramsey PM, Hirata 3, Tsuri K, Influence of Preferred Orientation on the Electrical Conductivity of Fluorine-Doped Tin Oxide Films. Scientific Reports, 2014, 4: 3679.

[3] E.R. Leite, T.R. Giraldi, F.M. Pontes, E. Longo, A. Beltra'n, J. Andre's, Appl. Phys.Lett. 83 (2003) 1566.

[4] B. Cheng, J.M. Russell, W.S. Shi, L. Zhang, E.T. Samulski, J.Am. Chem. Soc. 126 (2004) 5972.

[5] Fantini, M., Torriani, I. L. & Constantino, C. J. Influence of the substrate on the crystalline properties of sprayed tin dioxide thin films. J. Cryst. Growth 74, 439–442 (1986).

- [6] Poate, J. M., Tu, K. N. & Mayer, J. W. Thin Films Inter-diffusion and Reactions [243–304] (Wiley, New York, 1978).
- [7] Korotkov, R. Y., Ricou, P. & Farran, A. J. E. Preferred orientations in polycrystalline SnO2 films grown by atmospheric pressure chemical vapor deposition. Thin Solid Films 502, 79–87 (2006).

[8] Michael Grätzel, Journal of photochemistry and photobiology, 2003

CHAPTER 06

Conclusion

6.1 Summary of Results

The experimental results presented and discussed in this research study mainly based on the synthesis, characterization and applications of fluorine doped tin oxide (FTO) one-dimensional nanostructured thin film. FTO is a one of most attractive metal oxide semiconductor material among wide variety of transparent conducting oxides (TCOs). FTO thin films show quite stable toward atmospheric conditions, mechanically hard, chemically inert, low cost and ability to withstand high temperatures.

One-dimensional nanostructures such as nanorods, nanotubes, nanowires and nanoneedles are have been vastly used in many advanced technological applications in recently. These nanostructured TCOs thin films are used to enhance the performance of many devices such as flat panel displays, low emissivity windows, electrochromic windows, light-emitting diodes, gas sensors, electromagnetic shielding and front-surface electrodes for solar cells. These low-dimensional nanostructures provide high surface area when compare with to their volume, high fraction of similar chemical surface and improved materials characteristics due to the quantum confinement effect of nanoscale. In our research work, we have developed one-dimensional nanostructured FTO thin films in order to apply for the working electrode of the dye-sensitized solar cells (DSSCs). Normally, these transparent and conducting oxides thin films consist with nanograins. However, when we introduce such FTO nanostructures to the front electrode, it help to improve the light transmittance, interfacial surface area and light scattering between photo anode and FTO electrode as these films are acting as brag reflectors. Hence, light trapping increase to provide higher light absorption by photo active layer to enhance the power conversion efficiency of the DSSCs.

FTO-coated glasses can be fabricated by various methods. These include Metal-Organic Vapor Phase Epitaxy, Molecular Beam Epitaxy, Vacuum Arc Plasma Evaporation, Magnetron Sputtering, Ultrasonic Spray Pyrolysis (USP) and Spray Pyrolysis. In USP, ultrasound is used to atomize the spray solution and special corrosion-resistant cobalt A12 series ultrasonic nozzles are used in the fabrication of thin films of TCO materials, on various substrates, such as glass. All these methods, however, produce FTO nanoparticle grains with zero-dimensional (0-D) morphologies. Among these techniques, spray pyrolysis deposition (SPD) is considered as quite simple and cost effective method to
synthesized TCOs thin films.

We have designed and developed low cost novel SPD technique which is known as Rotational, Pulsed and Atomized Spray Pyrolysis (RPASP) to fabricate onedimensional (1-D) nanostructured FTO thin films. This technique is versatile and several spray parameters can be controlled to achieve desire nanostructures. In the first stage of the research, we investigated the perfect method to fabricate FTO nanorods thin films. The 1-D nanostructured FTO films are formed on glass substrate by preciously controlling spray angle and other required parameters of RPASP. The spraying at low angle to the substrate is mandatory for the erection of FTO crystals along vertical direction. Therefore, vertically aligned and well separated FTO nanorods can easily be prepared with (101) direction as the predominant orientation. The fluorine substitution to the oxygen vacancies of the tin oxide lattice structures can be monitored with Fourier transformed infrared spectrometer. Though, FTO nanorods thin films show high transmittance in the visible region, conductivity of the thin films was low due to lack of contact of the under layer of nanostructures on normal glass substrate.

In the next step of the research study, various nanotechnological architectures of FTO thin films could be able to fabricate on soda lime glass substrate by controlling the deposition time of the RPASP technique. The fine atomized aerosol stream of the FTO precursor solution is sprayed horizontally to the glass substrate with 2 s on and 13 off pulse programmed in order to maintain the substrate temperature. The materials presents in the precursor solution undergo pyrolysis reaction at higher temperature of the substrate in order to form FTO seed particles at the shortest time of the spray. Then, these FTO particles grow along the vertical direction to result in almost vertically aligned uncapped nanorods and then convert into the capped nanorods with further increment of the spray time duration. Finally, extensively cross-linked nanoneedles formed due to prolonged of spray time duration. The optical transmittance of the prepared FTO nanostructured thin films was in the range from 70% to 80% in the visible region. XRD results confirmed that the from FTO nanostructures are belongs to the cassiterit mineral form of tin oxide in its tetragonal rutile crystal structure. XPS and FT-IR data clearly indicate the presence of oxygen vacancies, fluorine doping level of each thin films and possible chemical bond structures of the FTO lattice respectively. Hence, this section of the research work has proved us FTO nanostructures can be controlled kinetically simply by changing spray time duration of the RPASP.

The preparation of one-dimensional nanostructured FTO thin films using a higher spraying angle to the substrate could also be able to achieve with RPASP technique. In this section, we investigate the effect of fluorine concentration for the crystal growth of FTO nanorods thin films. The obtained results are confirmed us FTO naorods thin films. can simply be synthesized with high fluorine concentration in the precursor solution. The fluorine ions substitute for the proper lattice positions of tin oxide crystal structure at the initial stage and crystal size enhanced with the pyrolysis process. However, crystal morphology was disordered with the increment of fluorine molar ratio as higher amount of fluorine act as impurities to the system without substitute for the proper lattice position. Hence, crystals grow along vertical direction and finally formed FTO nanorods at high fluorine concentration. The preferred orientation of the nanorods on normal glass substrate was along (111) direction of the cubic tin dioxide. The cubic crystal structure of tin dioxide formed due to the pressure effect of fine atomized precursor particles of the RPASP technique.

In the last chapter, our novel SPD technique which is known as RPASP deposition was used synthesized fluorine-doped tin oxide one-dimensional nanostructured thin films with different additives such as H₂O, propanone, ethanol and

isopropanol in the precursor solution. Spraying at low angle to the substrate was used to prepare these nanostructured thin films. The effect of the additives for morphology and textures of the one-dimensional nanostructured FTO thin films were investigated with detailed discussion. Propanone as an additive was facilitate to produce vertically aligned and separated hollow type nanorods with (111) direction as the predominant orientation while well-separated and higher dimensions hollow type nanorods was obtained with ethanol as an additives. These nanorods were grown along the (110) plane of the tetragonal rutile structure of tin dioxide. However, vertically aligned one-dimensional nanostructured thin films was difficult to obtain with water and isopropanol as additives. The rotational mode of the SPD technique is very useful to fabricate large area and well homogeneity FTO thin films on glass substrate. The prepared one-dimensional nanostructured FTO thin films show excellent optical transparency in the visible region of the electromagnetic spectrum and conductivity of the thin films was able to enhance by using commercial FTO as the substrate. Finally, Dye-sensitized solar cells (DSSCs) were assembled to compare the performance by using commercial FTO glasses and our 1-D nanostructured FTO thin films as the working electrodes. The results clearly shows that value of fill factor and open circuit voltage was improved with 1-D nanostructured FTO thin films and further research study is required to conduct in order

to increase the films thickness of photo anode. Then power conversion efficiency of the DSSCs with FTO nanorods will be enhanced tremendansly.

6.2 Future Developmental and Perspectives

The experimental results outlined in this study provide benefit to the various advanced technological industries. Such as functional added glass manufacturing industry, photovoltaics, thermoelectric, gas sensing and other industries which are required transparent and conducting oxides interface as well as one-dimensional nanostructures. Hence, development and further research about these nanostructured thin films are required.

We are considering to fabricate one-dimensional nanostructured thin films by using various transparent conducting oxides materials such as doped ZnO and TiO_2 as well as technologically most attractive organic material such as graphene. Graphene is most viable material in the modern technology. Therefore, development of conducting and transparent graphene nanostructured thin films are essential. We are looking forward to enhance the conductivity, transmittance and dimensions of the one-dimensional nanostructured thin films by using different spray parameters and conditions of the RPASP technique.

In first step of the development of research, we have been fabricating FTO onedimensional nanostructured thin films by using various tin oxide precursor solutions. As such, di(n-butyl)tin(iv) diacetate (DBTDA) was used to fabricated FTO thin films with NH₄F as fluorine source. In this, needle shape FTO Nano network thin film could be able to synthesize as shown in the SEM image of Figure 1. Therefore, optical and electrical properties of the thin films will be altered.

Also, we are planning to improve our present SPD technique by introducing more spray parameters as well as additional automated functions. Anyway, we have already designed and developed our new RPASP machine with controllable spraying speed as required. As an example, 2s spray on means it rotates only one round to spray the solution in our previous SPD technique, But this new machine has a function to change the number of rotation circles within 2s on spray time. Hence, it is possible to change the speed of the spray with the new RPASP machine. This will be benefited to change the morphology and texture of the particular TCOs thin film.



Figure 1: FTO nanostructured thin films with DBTDA as the Tin oxide precursor.

Finally, our present study was based on the synthesis, characterization and applications of FTO one-dimensional nanostructured thin films. In the future development, we planned to conduct more research studies base on this technique to enhance the performance and also hope to find more suitable industrial applications which can be develop by using our nanostructured thin films.

7 List of publications

Accepted Papers

- Ajith Bandara, R.M.G. Rajapakse, Masayuki Okuya, Masaru Shimomura and Kenji Murakami, Effect of Spray Conditions on Formation of One-Dimensional Fluorine-Doped Tin Oxide Thin Films, JJAP Conf. Proc. 4, 011102 (2016).
- Ajith Bandara, Masayuki Okuya, Masaru Shimomura, Kenji Murakami and Rajapakse M.G. Rajapakse, Effect of Spray Directions on the Crystal Growth of Fluorine-Doped Tin Oxide One-dimensional nanostructured Thin Films, Journal of Advances in Physics, 12[1](2016) 2347-3487.
- 3. Ajith Bandara, Kenji Murakami, Rajapakse M. G. Rajapakse, Piyankarage V. V. Jayaweera, Masaru Shimomura, Herath M. N. Bandara, D. Liyanage, Edirisinghege V. A. Premalal, Versatile Synthesis of Fluorine-doped Tin (IV) Oxide Nanotubes on Glass, Journal of Thin Solid Films. (Just Accepted)
- 4. Kenji Murakami, Ajith Bandara, Masayuki Okuya, Masaru Shimomura, and R.M.G. Rajapakse, Synthesis and Characterization of One-dimensional Nanostructured Florine-doped Tin Dioxide Thin Films, Nanostructured Thin Films IX, Proc. of SPIE Vol. 9929 99290X-1, doi: 10.1117/12.2237522, (2016).

Conference Presentation

- The 2nd International Conference on Nano Electronics Research and Education (ICNERE 2014), Development of Uniformly Distributing Fluorine Doped Tin Oxide Nanostructures by Advanced Rotational Spray Pyrolysis Deposition Method, Ajith Bandara, Naoki Matsuzaki, Keita Yamamoto, R.M. Gamini Rajapakse and Kenji Murakami, November 2014.Shizuoka University, Hamamatsu Campus, Japan
- The 3rd International Conference on Nanoscience and Nanotechnology (ICONN 2015), Formation of nanostructured fluorine-doped tin oxide by using advanced rotational spray pyrolysis deposition technique, Ajith Bandara, Naoki Matsuzaki, Keita Yamamoto, R.M. G. Rajapakse and Kenji Murakami, February 4-6, 2015, SRM University, Chennai, India.
- 3. The International Integrated Engineering Summit (IIES 2014), Versatile Formation of Fluorine Doped SnO₂ Nanostructures on Glass Substrate, Kenji Murakami, R.M.G.Rajapakse, P.V.V.Jayaweera, Masaru Shimomura, H.M.N.Bandara, Devinda Liyanage, E.V.A.Premalal, Ajith Bandara and Varichetti Madu Mohan, 1-4 December 2014, University Tun Hussein Onn Malaysia.

- The 62nd Japan Society of Applied Physics(JSAP), Fluorine-Doped Tin Oxide Nanostructured Thin Films by using Horizontally Spraying Technique, Ajith Bandara, K.Murakami and R.M.G. Rajapakse, Spring Meeting, March 11-14, 2015, Tokai University, Japan.
- 5. The Annual Meeting of the Materials Science Society of Japan 2015, Synthesis of transparent and conducting fluorine-doped tin oxide thin films based on 1-D nanostructures, Ajith Bandara, R.M.G. Rajapakse and K.Murakami, Kogakuin University, Shinjuku Campus, Tokyo, Japan (Juny 2015)
- The 14th International Conference on Quality in Research (QiR 2015), Application of New Spray Pyrolysis Technique to formation of Transparent Conducting Oxides Layer, Ajith Bandara and Kenji Murakami, August 10-13, 2015, Lombok, Indonesia.
- The Inter-Academia 2015, Effect of spray conditions on formation of onedimensional fluorine-doped tin oxide thin films, Ajith Bandara, R.M.G. Rajapakse and K.Murakami, Congress Center in Hamamatsu ACT CITY, 28-30 September, 2015 Japan
- The 76th JSAP Autumn Meeting 2015, Formation of 1-D Nanostructured Fluorine-Doped Tin Oxide Thin Films, Ajith Bandara, M. Okuya, M. Shimomura, K. Murakami and R.M.G. Rajapakse, September 13(sun)-16(wed),Nagoya Congress Center, Japan.

- Ajith Bandara, Naoki Matsuzaki, Keita Yamamoto, R.M. Gamini Rajapakse and Kenji Murakami, Synthesis of Fluorine Doped Tin Oxide Nanstructures using Rotational Spray Pyrolysis Deposition Method, The 7th International Symposium on Surface Science, November 2 (Sun) - 6 (Thu), 2014 Matsue, Japan.
- 10. Ajith Bandara, Kenji Murakami, R.M. Gamini Rajapakse, P.V.V Jayaweera and Devinda Liyanage, Versatile Synthesis of Fluoride-doped Tin(IV) oxide Nanoarchitectures on Glass, 2015 International Symposium Toward the Future of Advanced Researches in Shizuoka University, January 27- 28, 2015, Shizuoka University, Japan.
- 11. The 9th International Symposium on Transparent Oxide and Related Materials for Electronics and Optics (TOEO-9), The Effects of Fluorine Concentration on 1-D nanostructured Fluorine Doped Tin Oxide Thin Films, Ajith Bandara, Kenji Murakami and M. Okuya, Oct. 19-21, 2015 at Tsukuba (Ibaraki), Japan.
- 12. The 63rd JSAP Spring Meeting, 2016, Effect of additives on the 1-D Nanostructured Fluorine-Doped Tin Oxide Thin Films, Ajith Bandara, M. Okuya, M. Shimomura, K. Murakami and R.M.G. Rajapakse, March 19(Sat)-22(Tue), Tokyo Inst. of Tech.Ookayama Campus, Japan.

- The 17th Takayanagi Kenjiro Memorial Symposium, Control of Nanostructure of Fluorine-doped Tin Oxide Thin films by Spray Pyrolysis Deposition, Ajith Bandara, M. Okuya, M. Shimomura, R.M.G. Rajapakse and K. Murakami, November 17-18, 2015, Sanaru Hall, Hamamatsu Campus, Shizuoka University.
- 14. The International conference of Nanostructured Thin Films IX-SPIE, Synthesis and characterization of one-dimensional nanostructured fluorine –doped tin oxide thin films, Kenji Murakami, Ajith Bandara, M. Okuya, M. Shimomura, and R.M.G. Rajapakse, Tuesday -Thursday 30 August - 1 September 2016, San Diego Convention Center, San Diego, California, United States
- 15. The 77th JSAP Autumn Meeting, 2016, Effect of Different Precursor Solutions for the growth of Fluorine-Doped Tin Oxide 1-D Nanostructured Thin Films, Ajith Bandara, M. Okuya, M. Shimomura, K. Murakami and R.M.G. Rajapakse, September 13(tue)-16(fri),TOKI MESSE, Niigata City, Japan.