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FABRICATION OF FLUORINE DOPED TIN OXIDE (FTO) THIN FILMSUSING SPRAY PYROLYSIS DEPOSITION METHODFOR TRANSPARENT CONDUCTING OXIDE

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ABSTRACT

Fluorine doped tin oxide (FTO) thin films were prepared by using Ammonium Fluoride (NH_4F) and DBTDA. These two solutions were mixed and finally get the Fluorine doped with tin oxide. The solution then proceeds to spray pyrolysis process to produce the FTO substrate. This works is focused on producing high transparency materials above 85% which allows more sunlight absorption by the inner part of solar cell. Besides, the fabrication of thin film with low sheet resistance is investigated for enhancing the conductivity. The sample then anneal with different annealed temperature. Surface Morphology of FESEM show the particle distribution and size of FTO of all the annealed temperatures used in this research. From this method, by adjusting the anneal temperature the best film obtained is at 150°C anneal temperature which has the sheet resistance of $5.11x10^8\Omega$/sq and highest percentage of transmittance.

Keywords: spray pyrolysis deposition, flourine doped tin oxide, glass, FESEM.

INTRODUCTION

Solar cells or photovoltaic cell are made of a special material which named as semiconductors such as silicon or metal oxide. Basically, when light hit the cell, a certain portion of its energy is absorbed within the semiconductor material. The energy knocks electrons loose, allowing them to flow freely. Fundamentally, the device needs to fulfill only two functions: photogeneration of charge carriers which are electrons and holes in the material, and the separation of the charge carriers to a conductive contact that will transmit the electricity.

Tin oxide (SnO_2) is an n-type semiconductor with band-gap energy of 3.6eV. A thin film of SnO_2 is transparent in the visible region and reflecting in the high infrared region Kong, Deng *et al.* (2009). The conductivity of the material is mainly attributed due to the oxygen vacancies in the lattice whose structure is tetragonal and is similiar to the rutile structure (Moholkar, Pawar *et al.* 2008). Conductivity of SnO_2 can further be increased by doping it with group III, V, VI and VII elements of the periodic table; some of which are Tl, Sb, Te and F. Among these elements, the most widely used dopant is flourine because of the fact that the resultant flourine doped tin oxide (FTO) film is highly stable both chemically and thermally (Yadav, Masumdar *et al.* 2009, Ghafouri, Shariati *et al.* 2012). SnO_2 is a transparent material in the visible wavelength, reflecting in the infrared region and low sensitivity towards UV makes them stable for a long time. It is a n-type semiconductor with widely band gap energy which is 3.62eV (Kong, Deng *et al.* 2009, Pari, Chidambaram *et al.* 2014). The conductivity of SnO_2 can be enhanced by introduced dopant on it. The elements from group III, V, VI and VII periodic table can be use as dopant. Flourine element is most preferred to be doped to SnO_2 because the resultant fact that it will produce highly stable both chemically and thermally (Yadav, Masumdar *et al.* 2009). Furthermore, Flourine is an ideal substitution for oxygen because the anionic sizes are rather similar (R_O^{2-} = 1.32Å and R_F^{-} = 1.33Å) (Russo and Cao 2008).

FTO thin film has been used mainly for electronics devices. The performance of FTO films can be increased with highly crystalline and large surface area (Nazeeruddin, Baranoff *et al.* 2011). According to above concept, FTO film with 1-dimensional nanoparticle size could give high surface areas for better electron mobility and less electron recombination. It is known in the realm of nanoscience and nanotechnology that nanorods, nanowires and nanotubes play special roles because of their one dimensionality. When the diameter of the nanorods, nanowires and nanotubes become small, the physical and chemical properties of the one-dimensional nanostructure are clearly different from those of crystalline solids or even two-dimensional system.

FTO thin films is widely used in various fields of device making technologies such as window layers in solar cells (Chae, Kim *et al.* 2010), gas sensor devices (Hossein-Babaei and Amini 2012), substrates for electrodeposition (Khelladi, Mentar *et al.* 2010) and transparent contact in optoelectronic and so on. Solar cell that using FTO thin films is DSSC. FTO film is used to collect electron from the sensitized dye. Enhancement in surface area of FTO film will improve the electron collection of DSSC and the efficiency of DSSC is also improved (Nazeeruddin, Baranoff *et al.* 2011).The usage of FTO in various field of the technology is due to its chemical and thermal stability along with the high optical transparency in the visible range and high electrical conductivity (Nazeeruddin, Baranoff *et al.* 2011). FTO has

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been prepared by various methods including chemical vapor deposition (CVD) (Fang and Chang 2003), pulsed laser deposition (Chen, Lai *et al.* 2005), rf sputtering, sol-gel and spray pyrolysis deposition (SPD) (Moholkar, Pawar *et al.* 2007). Spray pyrolysis is widely used to prepare FTO films, owing to its simplicity, low cost experimental apparatus set up, ready incorporatability of various dopants, high growth rate and high mass production capability for large area coatings (Aouaj, Diaz *et al.* 2009). Spray pyrolysis is a process in which a thin film of a required material is deposited on to a hot surface by spraying a precursor solution on to it.

Several tin compounds such as tin (II) chloride dihydrate (Purushothaman, Dhanashankar *et al.* 2009), tin (IV) chloride pentahydrate (Fang and Chang 2003), tetra(n-butyll)tin and di(n-butyl)tin(iv)diacetate (DBTDA) (Fang and Chang 2003) have been used as a tin element in the precursor solution for preparing FTO films using SPD technique.

Their preferred crystal growth orientation and crystal size differ with the nature of the compounds used which in turn affect the optical and electrical properties of resulting thin films of FTO. Kaneko *et al.* has used DBTDA as tin compound for preparing the SnO_2 film and they have studied the initial growth mechanism of SnO_2 formed and the thermal decomposition of DBTDA (Kaneko, Yagi *et al.* 2001, Murakami, Nakajima *et al.* 2007).

In this work, we investigated the growth of FTO on glass substrates with varying the anneal temperature in constant reaction time and concentration of precursor solution. The surface morphology, electrical and optical has been studied and discussed.

EXPERIMENTAL DETAIL

Solution preparation

The complete solution is a mixture of two different precursors. For the first solution, a 3.0 ML of 0.1M DBTDA is mixed with 15ML 2-propanol into a beaker then the solution is left stirred for 15 minutes until the solution is completely dilute. The solution is labeled as solution A. The other solution is a mixture of 1g of NH4F and 2ML DI water. The solution also left stirred for 15 minutes until the reaction between NH4F solid crystal and DI water homogeneous. Then the solution is set as solution B. Both of the solution A and B was mixed into a beaker and left for stirred for 30 minutes until the clear solution was obtained.

Spray Pyrolysis Deposition

To prepare the tin oxide thin films, the final precursor was sprayed through the airbrush spray nozzle with uniform air pressure. When the precursor sprayed out from the nozzle, it will separate into tin oxide particles. These particles are push out from nozzle and hit the surface of the substrate that placed onto the hot plate. The hot plate temperature is kept constant at 150°C. Low temperature was used to produce crack-free glass substrate. The distance between substrate on hot plate and airbrush spray assumed to be 20cm to make sure that only the fine spherical droplets hits on the glass substrate.

The process was take place in the fume chamber to produce a uniform area coating of thin films. This spray process is determined by kept the time interval of 10s stop between 1 minute spray times due to make sure that the droplets on the glass substrate dried completely before applied another coating of thin films. This also avoids wet surface substrate produced. The multiple layers of thin films will lead to a wet surface of glass substrate. The wet surface of the glass substrate will produce cracked after anneal process.

The deposited thin film are characterized to study their surface, electrical and optical properties. The surface morphology of FTO films are studied using field emission scanning electron microscopy (FESEM) to identify the distribution of grain, grain size and the growth of nanostructured with preferred orientation. The thickness of thin film we obtain from surface profiler. The electrical properties of sample are analyzed by using four point probe method. The optical properties are studied using UV-ViS spectrophotometer (UV-ViS) to investigate the visible transmittance in 300-1000nm wavelength.

RESULT AND DISCUSSIONS

Surface morphology (FESEM)

The annealed temperature is set to 100 °C, 150 °C, 200 °C, 250 °C, and 300 °C. For temperature of 100°C, the grains deposited completely uniform on the glass substrate. The small particles of FTO are due to the low temperature applied to the substrate. For 150°C, the particle was larger than 100 °C.

The large particles deposited causes by the spraying stage process. This might be occurred because of the position of glass sample arranged on the hot plate. The over size of spherical particles was deposited on the glass sample of 150 °C, this lead to large particles deposited. For temperature of 200 °C, the particles deposited uniform on the glass substrate. The moderate temperature produces the best results. It will be discuss further on the characterization of the electrical properties of the glass using four point probe. For temperature of 250 °C, it produces crack structures on the sample. Refer to Table 4, the high temperature will causes the particles on the glass cracked and evaporated. This will lead to the production of low performance of FTO sample. So, the high temperature is not suitable for the precursors used.

The FTO layer thicknesses are measured by using surface profiler. The thickness of FTO thin film of each samples which are conducted at 100 °C, 150 °C, 200 °C, 250 °C and 300 °C anneal temperature are 227, 269, 321, 387 and 641nm. The overall thickness of FTO film that can be controlled by adjusting the anneal temperature. When the anneal temperature is used take higher degree Celsius so the thickness of FTO film will be increased because increase of anneal temperature will be supplied more energy for the growth of thin film.

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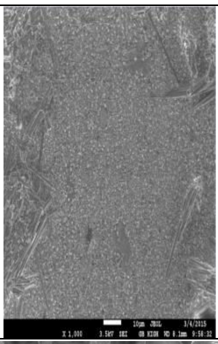
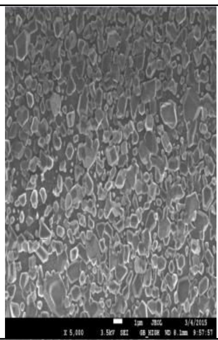
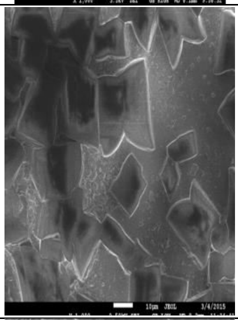
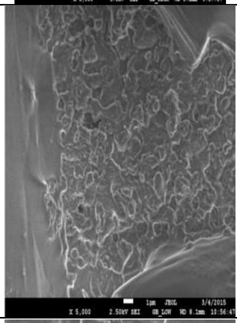
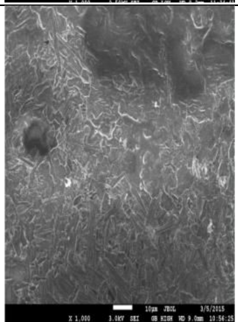
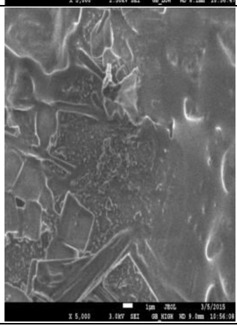
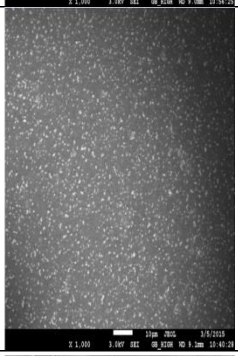
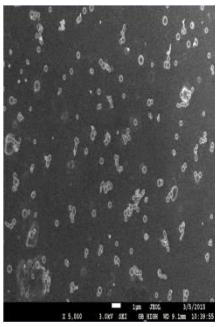
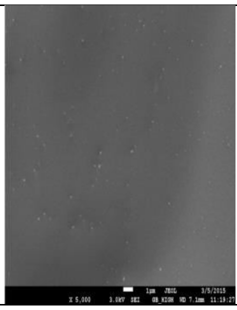
Table-1. Surface morphology of FTO with different annealed temperatures (a) 100 °C (b) 150 °C (c) 200 °C (d) 250 °C and (e) 300 °C.

	1k Magnification	5k Magnification
(a)		
(b)		
(c)		
(d)		
(e)		

Electrical properties

Refer to Table-2 below; there is an increment in the value of sheet resistance. The sheet resistance increase directly to the increment of annealed temperature. For the optimum performance of thin films, it must have low sheet resistance and high conductivity. For the optimum performance of FTO glass, it can be conclude that the high annealed temperature will produce low resistivity because there are plenty of conducted deposited particles on the glass substrate after an annealed process. For this research, it can be shown that lower annealed temperatures have high conductivity.

Table-2. Sheet resistance of different annealed temperature.

Temperature(°C)	**Rs**(Ohm/Sq)
100	$4.45x10^8$
150	$5.11x10^8$
200	$5.75x10^8$
250	$6.89x10^8$
300	$7.70x10^8$

Optical properties (UV-Vis)

Figure-2 shows variation of transmittance versus wavelength for spray deposited F: SnO_2 thin films deposited by using different annealed temperature. It can be seen that number of maximum and minimum wavelength within 300–800 nm which are the frequency of visible light range. These data shows that all annealed temperature used, 100 °C, 150 °C, 200 °C, 250 °C and 300 °C can be used for producing a high transparency transparent conductive oxide (TCO).

The FTO thin films of 100 °C, 150 °C and 300 °C achieved transmittance more than 70 % which showed a high transparency as it is a TCO properties. Unfortunately the transmittances for 200 °C and 250 °C have low transmittance. This occurs because of the thin doped precursors does not annealed perfectly. Therefore the milky white structure deposited on the glass substrate. This can be shown that at temperature of 200 °C and 250 °C, the structure growth imperfectly on the glass substrate during annealed process.

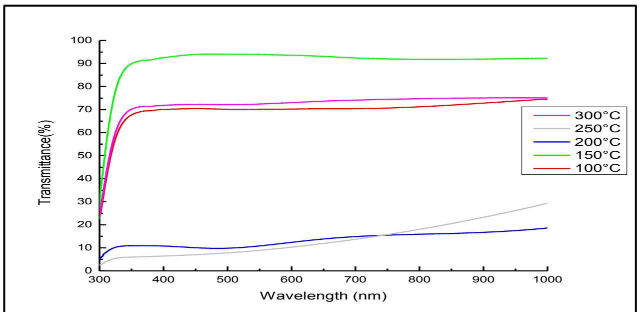


Figure-1. The transmittance spectra of FTO films recorded in the spectral wavelength 300-1000nm for different annealed temperature.

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High transparency of thin films is needed for the window layer which is light can be passing through to absorbance layer. Therefore, all of these annealed temperatures can be considered. The color of the undoped tin oxide precursors is milky white, which becomes colorless after doping with fluorine which formed fluorine doped tin oxide. For higher Fluorine concentration, the milky color structure will produce on the FTO thin films. This will decrease the transmittance of the thin films. The transmittance variation is attributed to the variation in free-carrier concentration.

CONCLUSIONS

Transparent conducting oxide (TCO) film has been widely used as electrode in many electronic devices, mainly for solar cells and sensors. The performance for these electronic devices could be increased with high surface area of TCO film. In this research, the growth of nanostructures FTO (n-FTO) on top of FTO layer substrate using hydrothermal method will be discussed. By increasing the surface area, the electron collection by the TCO film will be increased, thus the efficiency of solar cell are also increased. There are two kind of TCO films which are widely used nowdays; Indium-doped Tin Oxide (ITO) and Flourine-doped Tin Oxide (FTO). FTO film is more preferable than ITO due to stability in chemical and thermal.

The n-FTO will be prepared using spray pyrolysis method. The glass as substrate and the FTO will be prepared using dilute precursor solution of di (n-butyl) tin (iv) diacetate (DBTDA). The spray process will be performed to optimize the nanostructures based on the parameters as anneal temperature.

The FTO films were prepared on the glass substrates by spray pyrolysis method. By varying the anneal temperature, we get the nanostructure of FTO on glass substrates. From this method, by adjusting the anneal temperature the best film obtained is at 150^{o}C anneal temperature which has the sheet resistance of $5.11x10^8\Omega$/sq and highest percentage of transmittance.

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