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Surface morphology and topographical studies of fluorine doped tin oxide as transparent conducting film

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ABSTRACT

Purpose: This paper deals about the preparation and characterization of transparent conducting metal oxide doped with fluorine for superhydrophobic applications.

Design/methodology/approach: Fluorine doped tin oxide(FTO) have been deposited on glass substrate employing an inexpensive spray pyrolysis route. Uniform coating of thin film was controlled by the parameters like flow rate, exposure duration, temperature of pyrolysis process etc.

Findings: Fluorine doped SnO_2 was confirmed from FTIR studies. Transparent nature of the coating was evaluated through UV-vis. spectroscopy. Electrical resistivity of the deposited film measured using source meter showed a least resistance of 13 Ω. AFM & SEM analysis revealed the texture of nano SnO_2 in the range of 100-300 nm. Unevenness is one of the prerequisite for achieving superhydrophobic nature, which has been explored through AFM results.

Practical implications: An attempt has been done to fabricate fluorine doped tin oxide thin film using spray pyrolysis technique may be used for developing super hydrophobic coating application.

Originality/value: This study aims to reduce the cost of forming superhydrophobic surfaces on comparison with the process like plasma etching and sensitizing with nanoparticles, etc.

Keywords: Transparent Conducting Oxides; Super-hydrophobicity; Spray pyrolysis; Transparency

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MATERIALS

1. Introduction

Transparent Conducting Oxide (TCO) films have a wide range of applications especially in OLED, solar cells, sensors and in thin film transistor's etc. Most of the transparent conducting materials reported so far are made up of indium doped tin oxide is one of the electronic products including smartphone's touch screens, solar panels layer etc. [1]. The fabrication cost of this TCO film is much higher [2], successful alternatives for fabricating the thin film have been identified by various researchers recently. Varieties of techniques like sputtering, CVD, etc., were adopted to fabricate the transparent conducting film [3]. Rather using such risky, expensive methods, spray pyrolysis is a facile method can produces an efficient film [4]. Super-hydrophobicity is a phenomenon normally found on lotus leaves and some other plants was reported by Barlhott and Ehler in the year of 1977 [5]. This property is implied by numerous researchers for many applications like self-cleaning, separation of oil from sea water and anti-corrosion etc. [6] Superhydrophobic character naturally found on lotus leaves was explained by many postulates [7,8]. It basically behaves like a water repellent surface owing to the presence of 500-600 nm rough structures covered with a material possessing low surface energy coating. Transparent films possess crystal clear nature due to three important physics lying on them, low light scattering [9] and larger band gap [10]. However, for a surface to behave superhydrophobic, logically needs roughness over the surface [11]. Research all over the universe resulted that nano level roughness will behave transparent also aid in superhydrophobicity [12]. This study aims to reduce the cost of forming superhydrophobic surfaces on comparison with the process like plasma etching and sensitizing with nanoparticles, etc. An attempt has been done to fabricate fluorine doped tin oxide thin film using spray pyrolysis technique may be used for developing super hydrophobic coating application.

2. Materials and methods

Stannic Chloride pentahydrate (97.5%, CDH Laboratory Reagent), Ammonium Fluoride (96%, NICE Laboratory Reagent) and 2-Propanol (Merck) were used as the starting materials. A homemade setup comprising air compressor, aero mist nebulizer, 'U' shaped glass tube and a hot plate was used for the spray pyrolysis process. 0.098 M $SnCl_4.5H_2O$ and 0.002 M of NH_4F in a solution of 3:1 isopropyl alcohol and water was taken as the precursor solution. The distance between the spraying nozzle and the glass slides was kept at 0.5 cm. The air pressure in the compressor output was set at 4.1 psi. The coating was done for a solution of 10 mL volume. The temperature at the glass slides surface was monitored though a temperature indicating setup present in the coating unit. SEM micrographs were obtained using SEM-SU150-HITACHI, Japan. AFM images were recorded from Scanning Probe Microscope (XE-70)-Park Systems, South Korea. Conductivity measurements were done using Agilent B2901A Precision source/measure unit-Keithley, USA. FTIR analysis was done using FTIR spectrometer (ALPHA-E)-Bruker Optics, Germany. UV-vis transmittance spectrum was recorded using UV/vis Spectrometer (Lambda 25)-Perkin Elmer, USA.

3. Results and discussion

3.1. FTIR analysis

FTIR spectra of F doped SnO_2 deposited over glass substrate was recorded in the range of 400-1000 cm^{-1} in Bruker Optics, Germany is shown in Fig. 1.

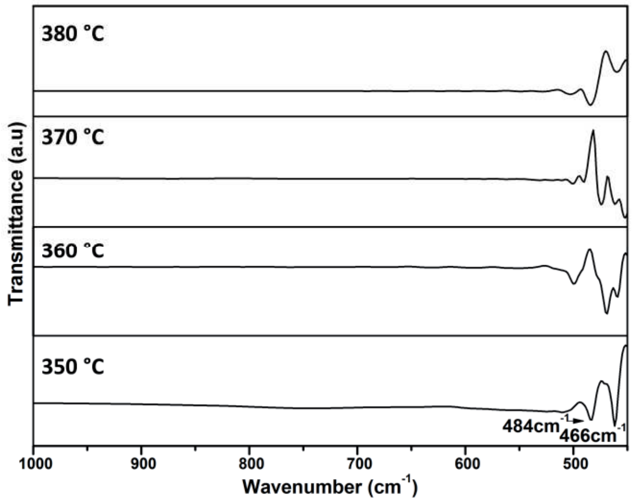

Fig. 1. FTIR spectra of FTO coated glass slides

It exhibit two prominent bands at 466 cm^{-1} and 484 cm^{-1}. The band at 466 cm^{-1} is a characteristic peak attributable to the vibrational frequency of O-Sn-O stretching [13]. The peak at 484 cm^{-1} ascribed to the formation of Sn-F bond exist in the surface [13]. Peaks other than the Sn-O and Sn-F vibration bands were observed due to the constituents of glass matrix over which FTO was coated. Thus, crystallization of Sn-O over glass surface and doping of fluorine on the SnO_2 lattice is confirmed through FTIR analysis.

3.2. Scanning electron microscopic analysis

SEM images (Fig. 2) were recorded with an applied voltage of 10 kV. This analysis helps in revealing the surface morphology of the spray coated samples.

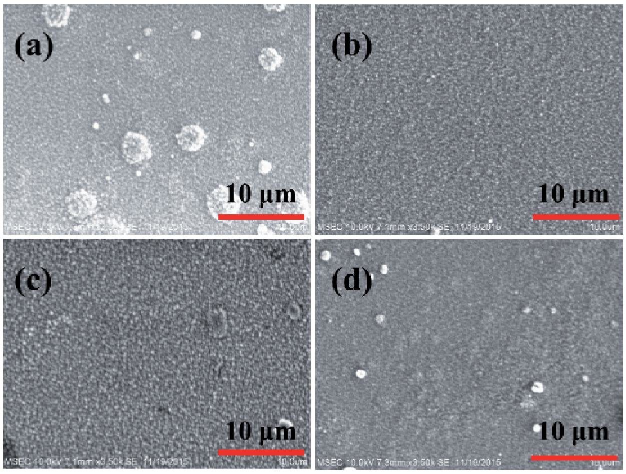

Fig. 2. SEM images of F doped SnO_2 thin films coated at (a) 350 °C, (b) 360 °C, (c) 370 °C and (d) 380 °C

Thin films coated at a substrate temperature of 350°C shows uniform sized particles of ~100 nm. Nevertheless, some irregular size particles were also observed over the surface. This is due to the accumulation of mist at some spots due to insufficient temperature for crystallization of the thin films leads to the formation of unevenness. These droplets in turn crystallized out and developed into a 5 µm sized particles. Film coated at a substrate temperature of 360°C appears as a uniform coated without any abnormal structures over the surface with the size of ~100 nm. The film coated at 370°C was also without any abnormal nucleation and growth, but the grown spots were nucleation sites for another compound. The size of the particles gets increased to 200 nm at this temperature. At 380°C the uniformity of the coating gets improved much, but inter-particle distance also increased due to the nucleation and growth with a size of ~ 300 nm. Such larger particles obviously enhances the roughness in nano scale, and thus generating superhydrophobic behaviour over it. Further, increasing the temperature and coating time developed a film with higher roughness (> 500 nm). However, the transparency was observed to be lost. Based on these results, we had optimized that, the coating that provides both transparency and adequate amount of roughness is 360°C in the spray coating process.

3.3. AFM studies

AFM analysis was done to study about the unevenness/roughness of the fabricated film obtained by spray coating process at various temperatures (Fig. 3). The scan area was fixed at a distance of 10 µm x 10 µm. As the scan was started, the cantilever tip moves in ‘x’ direction to and fro and by varying its position in ‘y’ direction each time when it completes a line in ‘x’ direction. The different topographical structures were drawn using XEI software, which is inbuilt with the PARK XE-70 system. This software converts the change in position of the tip into ‘z’ axis heights. At last, each of the scanning line is added to get the image of the surface in 3D.

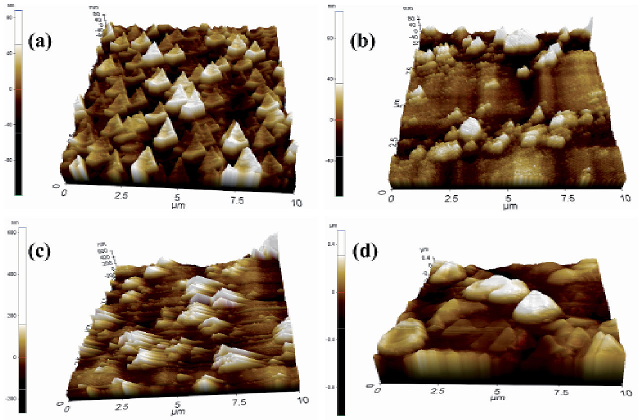

Fig. 3. AFM images of F doped SnO_2 thin films coated at (a) 350 °C, (b) 360 °C, (c) 370 °C and (d) 380 °C

AFM images reveal that the thin films fabricated at 350°C have particle heights of ~100 nm. These particles are highly concentrated in the specific area. At 360°C, the particle heights were also in the range of ~100 nm. Film deposited at 370°C showing the height of the particles around ~200 nm. At 380°C, the formed film exhibits the height of about ~300 nm. Thus, roughness of the fluorine doped tin oxide films were achieved by spraying the precursor at various temperatures.

3.4. UV-vis characterization

UV-vis transmittance spectra of the FTO coated glass slides were recorded to evaluate the transparent nature of the spray coated metal oxide film (Fig. 4).

The samples coated below 360°C results in higher transmittance values of >75% in the visible region. But, the coating fabricated above the substrate temperature of 360°C results in poor transmittance value of about >58% whereas the film formed at 370°C exhibits >45% transmittance in the visible region. Hence, the coating obtained at 360°C possesses good transparency with optimum roughness suitable for transparent superhydrophobic films. If the substrate temperature is higher, the micron sized particles agglomerated over the surface scatters the light passing through the glass slides throughout all directions. So, a large amount of visible light was found lost thereby decrease in transmittance was noticed.

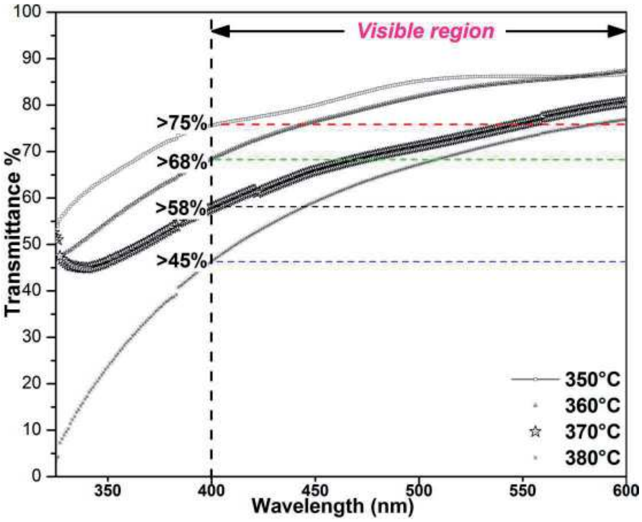

Fig. 4. UV-vis transmittance spectrum of FTO coated at different temperatures

3.5. Electrical resistance measurements

A source meter was connected to two probes providing positive and negative potential over them. The probe terminals were separated by a distance of ~ 10 mm. Resistance values were measured over the areas of the film with this arrangement. Resistance of the 350°C coated film was about 300 Ω while coating FTO at 360°C exhibit lower resistance of 13 Ω, indicates about the enhanced conductivity. However, the film fabricated at 370°C & 380°C display higher resistance values of 123 Ω and 243 Ω respectively. This is attributable to the film fabricated other than the temperature of 360°C have discontinuous nature of SnO_2 particles which do not favours the conductivity. This is also evidenced from the SEM images that the particles found on the film were isolated as discontinuous.

4. Conclusion

Successful fabrication of highly conducting thin film by cost efficient method has been reported. FTIR studies have confirmed the presence of Sn-O bonds and Sn-F bonds. UV-vis spectra confirm the transmittance nature of F doped SnO_2. Resistance studies with a source meter displayed at least value of 13 Ω for the thin film coated at substrate temperature of 360°C. SEM micrograph revealed about the particles and their agglomerated nature distributed over the surface of the film fabricated at lower temperatures. AFM studies confirmed the size of particles found on the coating was about 100-300 nm. At higher temperatures, the particles located in the thin film were well separated and constitute for lower conductivity. Optimum temperature for high uniformity with low resistance nature was about 360°C. We conclude that FTO films developed at this temperature possess suitable roughness and transparency to behave as a transparent superhydrophobic surface.

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