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Influence of sol concentration on FTO nanopowders synthesized by co-precipitation method for solar cell applications

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Abstract

In the current research, Fluorine-doped tin oxide (FTO) nano-powders have been synthesized by the co-precipitation method. Stannous chloride pentahydrate, ammonium fluoride was used to synthesize FTO nano-powder, followed by calcination at 600 °C. The results showed that when the solution concentration value increased from 0.2 M to 1 M, the average crystallite size and particle size increased from 8 nm to 30 nm and 25 nm to 70 nm. By increasing sol concentration from 0.2 M to 1M, transmittance decreased. The bonding energy for fluorine is 684.7 eV Which corresponds to the peak of fluorine substitution in tin dioxide. The sample 0.2 M sol concentration would be a good candidate to achieve a high density and conductivity sputtering target.

Keywords: *fluorine-doped tin dioxide, co-precipitation, Nano powder, sol concentration*

1. Introduction

From the view of energy, one of the important applications of thin-film technology is solar cells that convert solar energy into electrical energy [1].
SnO_2 is an n-type semiconductor material with a wide bandgap (3.6 eV) with transparency in the visible region is about 80% due to oxygen vacancies. For its potential has found applications such as a transparent conductive electrode for solar cells, a gas sensing material for gas sensors devices, photochemical and photoconductive devices in liquid crystal display, gas discharge display, and lithium-ion batteries [2, 3].
Thin films of transparent conductive oxides such as fluorine-doped tin dioxide (FTO), due to the high carrier concentration (*N*d)
caused by the oxygen vacancies and the substitutional fluorine dopant [4] have high electrical conductivity, good transparency, thermal and chemical stability. They have found extensive applications in the industry and attracted the attention of many researchers [5]. Many processes have been developed for the synthesis of SnO_2 nanostructures such as co-precipitation, vapor-liquid-solid, sol-gel, emulsion, hydrothermal, ion-exchange, and sol-gel combustion.
chemical precipitation synthesis technique is a fast and facile method. Inexpensive precursors, the sample preparation technique, and consumes less material than other methods are the benefits of chemical precipitation [6].
Sol concentrations are one of the interesting factors that affect the optical properties of nanoparticles and were done by some researchers in different methods [7]. Particle size has a significant role in optical properties and its emission shift occurs due to the recombination of the electrons with holes in the valence band [6]. In the research was done by us recently [8] to achieve a high density and conductivity

sputtering target, FTO nanopowder with the smallest particle size is needed.

2. Experimental Procedure

All the raw materials and precursors used in the present research were of high purity grades. Stannous chloride pentahydride and ammonium fluoride were purchased from Aldrich and Merck, respectively, and used as the starting materials. Ammonium hydroxide (Merck) was used to adjust the pH and deionized water was used as the solvent. FTO nanopowder were synthesized by dissolving of 3.5 g. (0.2 M) $SnCl_4.5H_2O$ in 50 ml deionized water and a certain amount of NH_4F was added, so that the concentration of fluorine was set based on the mole ratio of [F]/[Sn]=0.2. Afterwards, NH_4OH aqueous solution was added with constant stirring to the mixture until it achieved the desired pH of 9. The precipitate was formed and the resulting mixture was filtered at room temperature and dried in oven at 80°C for 24 hours. Then the co-precipitation process was repeated for the 0.6 and 1 molar sol concentration respectively. The product was calcined for one hour at 600°C. To determine the phase structures of the FTO powder and the sintered ceramics, X-ray diffraction (XRD, Scifert, model 3003PTS) was applied using Cu Kα radiation (λ=1.542 A°). The sample was scanned from 20° to 70° (2θ) with a 0.02 step size. The microstructures of the FTO powder were observed using a field emission scanning electron microscope (FE-SEM, MIRA3TESCAN-XMU) and the grain size was estimated with Image J software. To investigate the optical properties of FTO powders, 1 g of the FTO powder was dissolved in 50 ml of distilled water and the solution was put in ultrasonic for 2 minutes. Then the sample was put in Spectrometry. The surface composition was
examined by X-ray photoelectron spectroscopy (XPS, Bestec, ESCA system) with Al K radiation.Fluorine content in tin dioxide was studied byelectrochemical measurement technologies by a PF-4C (204) fluoride ion electrode instrument.

3. Results and Discussion

Figure 1 shows the XRD patterns of the FTO powder at different concentrations of sol. The XRD results showed that the characteristic peaks of the cassiterite structure of SnO_2 crystals could be obtained by varying sol concentration without any significant structural changes. No obvious reflection peaks were detected as a result of impurities. It was also observed that by increasing the sol concentration from 0.2 to 1, the intensity of the XRD peaks increased, where as the width of the diffraction peaks were reduced. The peak broadenings decrease and the intensities of the peaks are gradually sharper with increasing sol concentrayion led to nanopowders with average crystallite sizes varying from 8 to 30 nm. This implies that crystallinity of the FTO powders increased by sol concentration [9]. The mean crystallite size of the FTO powders, measured by the Scherer's technique, is reported in Table 1.

Table1: Crystallite size and particle size of the samples

Sol Concentration	Crystallite Size (nm)	Particle Size (nm)
0.2	8	25
0.6	18	48
1	30	70

The results obtained for the lattice parameters of the samples are summarized in Table 2. As can be seen, as the sol concentration increase from 0.2 to 1, it leads to an increasing in the SnO_2lattice parameters.

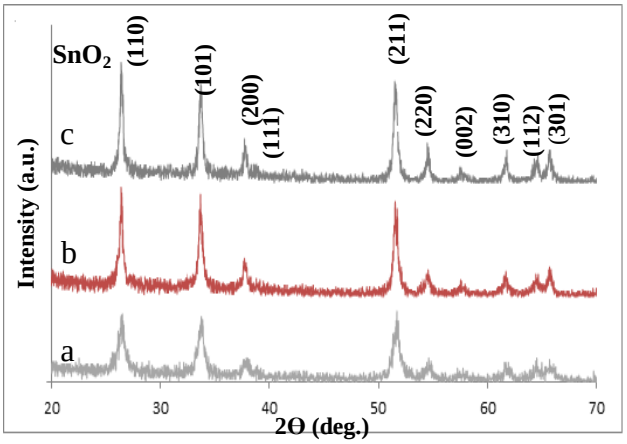

Figure1. XRD patterns of the FTO powders in different sol concentration (a) 0.2, (b) 0.6, (C) 1

This is because the radius of the fluorine ion is (0.133 nm) and the radius of the oxygen ion is (0.132 nm), and the substitution of the fluorine ion by the oxygen ion lead to expansion in the lattice parameters.

The results of the FESEM photograpgh FTO powders are shown in Figure 2. particle size and morphology of the synthesized FTO powders rely on the sol concentration of the solution. The average particle size of the FTO powders, as measured by Image J software, was listed in table 1

Table 2: Lattice parameters of the samples

Sol Concentration	Lattice parameter $a = b$ (Å)	Lattice parameter c (Å)
0.2	4.72	3.17
0.6	4.74	3.2
1	4.76	3.22

From the observation of XRD and FESEM, it is find out that, when the sol concentration Increase from 0.2 to 1, in addition to a color change of the primary solution, crystallite size and particle size of the FTO powders increase.

Not only does the variation of concentrations of sol lead to grain growth but morphological transformation too. FTO particles transformed from regular sphere to irregular sphere and subsequently to polyhedron shape with an increase in sol concentration.

This clearly shows sol concentration plays a role in the growing mechanism of SnO_2 particles.

However FTO powders were produced by co-precipitation method relatively bigger than those of by sol-gel combustion process [10].

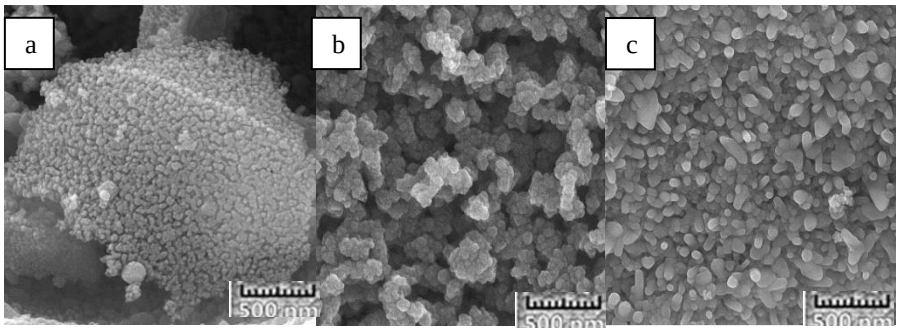

Figure 2. FESEM images of FTO powders in different sol concentration (a) 0.2, (b) 0.6, (C) 1

The optical properties were measured by UV-Vis spectrophotometer in the range of 300-900 nm. Fig. 3 shows the optical transmittance spectra of FTO powders with two sol concentrations (0.2 M and 1 M). The spectra shows FTO powders with 0.2 M solconcentration have high transmittance in the visible region.

It is observed the transmittance in the visible region decreased with increasing the concentration of the sol from 0.2 M to 1 M because decreasing the sol concentration will cause the absorption edge to shift to the shorter wavelengths.

Figure 4 shows XPS of the sample 0.2 M sol concentration.

Photoelectron peaks for F 1s, Sn $3d_{5/2}$, $3d_{3/2}$, O 1s and C 1s were detected for the sample in the binding energy range of 0–1200 eV as shown in figure 4.

The binding energies of the F 1s, $3d_{5/2}$, $3d_{3/2}$, and O 1s photoelectron peak are at 684.7, 487.16, 495.58 and 530.80 eV, respectively. It should be noted that the rest of the unnamed peaks are related to tin. A C 1s peak at a binding energy of 290 eV is also observed in the sample. The bonding energy for fluorine is 684.7 eV Which corresponds to the peak of fluorine substitution in tin dioxide [11] as shown in figure 5. It seems that the sample 0.2 M sol concentration would be a good candidate to achieve a high density and conductivity sputtering target.

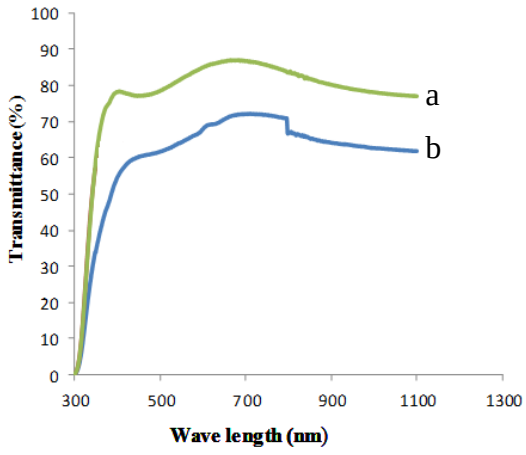

Figure 3. The UV-Vis Transmittance spectra of FTO powders for (a) 0.2 M and (b) 1 M

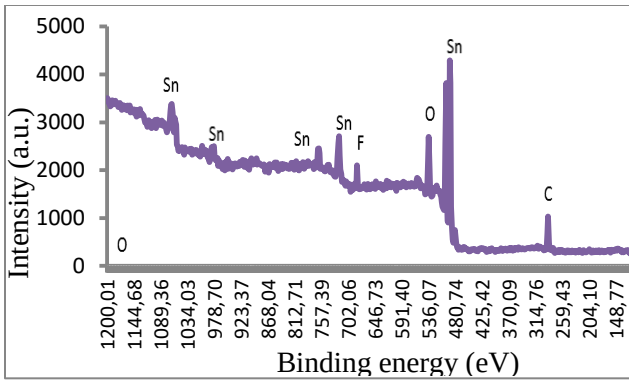

Figure 4. X-ray photoelectron spectroscopy FTO powders for 0.2 M sample

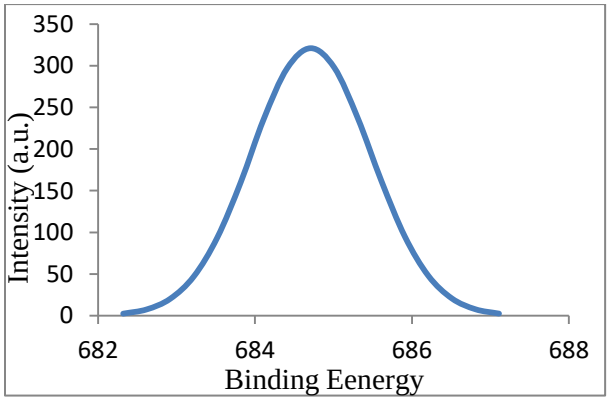

Figure 5. X-ray photoelectron spectroscopy of fluorine for 0.2 M sample

4. Conclusion

In summary, FTO powders were synthesized by co-precipitation method obtained at 80°C. The XRD patterns confirmed that SnO_2 nanocrystalline powders possess a tetragonal rutile structure. The average crystallite size of the nanopowders are in the nanometer range. variation of the sol concentration led to grain growth and morphological change. When sol concentration increased from 0.2 to 1, the average particle size increased from 25 to 70 nm and the morphology of the particles changed from spherical to polyhedral in shape. The optical transmittance spectra for 0.1 M sol concentration showed a high transmittance in the visible region and transmittance decreased by increasing the concentration.

The presence of fluorine additives in the FTO nano powder was determined by XPS method and the bonding energy for fluorine is 684.7 eV Which is related to the peak of fluorine substitution in tin dioxide.

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