Low temperature synthesis of Ni-doped SnO_2 thin films by spin coating route

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Ni-doped thin films were prepared by sol-gel spin-coating method with thermal annealing in air atmosphere. In this study, Ni-doped tin (II) oxide (SnO_2) thin films were deposited by a simple spin coating method. The precursor solutions were deposited on the decontaminated glass substrate by sol-gel spin coating technique. Nickel (Ni) as impurities is chosen due to its corrosion resistance and its ductile properties. Precursor solution was prepared using a 0.05M Tin (II) Chloride ($SnCl_4.2H_2O$) in de-ionized water and then being added in 100 ml ethanol to get equal proportions or to obtain a consistent balance of water and ethanol, then soaked in an ultrasonic bath (300 W and 60 kHz) about 10 min. Followed by 1.5 wt% of nickel chloride 6-hydrate ($NiCl_2.6H_2O$) was added as a doped source into the solution and then soaked in an ultrasonic bath for another 5 min. The precursor solutions were deposited with 10 drops onto the substrate. The solutions were spin-coated on a glass slide substrates at 750 rpm speed. The spin coating duration for all samples were 2 minutes. Finally, the samples were annealed for 30 minutes at various temperature in air atmosphere. We prepared five kinds of samples annealed at 100 °C, 200 °C, 300 °C, 400 °C, and 500 °C, respectively. For comparison, we also prepared the as-deposited samples. Ni-doped thin films with wurtzite structure were synthesized in all the samples. The morphology of the Ni-doped SnO_2 thin films was studied by scanning electron microscopy (SEM). The sample annealed at low temperature showed the smooth surface morphology, and it gradually became rough with increase in annealing temperature. On the other hands, optical properties were studied using UV-visible spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy.

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1. Introduction

Tin oxide is well known as an inorganic compound with a wide direct band gap (3.6 eV) semiconductor at room temperature [1-2]. Therefore, it has been used as transparant electrodes, gas sensing, ceramics, biomedicine and heat insulators. It has a tetragonal arrangement of the atoms and that is one of the reason it receive the names of rutile or cassiterite. Customarily, tin oxide thin films have been prepared by various methods for example RF magnetron sputtering, metal organic chemical vapour deposition, solvothermal, gel-combustion, and splaying [3-7]. Nonetheless, it is not easy to prepare large, strong and homogeneous tin oxide monoliths by these methods. For this reason, it seems attractive to prepare tin oxide films by the sol-gel process. Present time, spreading interest towards sol-gel synthesis of the SnO_2 thin films has been observed because of the environmentally-friendly, convenient, do not need high vacuum equipments.

Doping SnO_2 with metal cations has been attempted for photo catalytic utilizations by shifting the threshold for photonic excitation of the tin oxide towards the visible [8]. To date, gently Ta-doped SnO_2 nanowires were applied to yield fully transparent FET type devices. According to Yadav et al., they studied electrical, structural and optical properties of Fluorine doped tin oxide thin films and described that at lower substrate temperature amorphous films are obtained. On the other hand, crystalline F-doped tin oxide films with special growth parallel with (2 0 0) plane have been perceived at higher temperature [9]. However, as far as we know, there is rare information on preparing Ni-doped SnO_2 thin films by spray pyrolysis method. In this study, we prepared the Ni-doped SnO_2 thin films by sol-gel spin-coating route at comparatively lower temperature (100 - 500°C), characterized them with emphasis on the sample quality.

2. Experimental

In this work, Ni-doped tin (II) oxide (SnO_2) thin films were deposited by spin coating method. The precursor solutions were deposited on the slide glass substrates by sol-gel spin coating technique. Precursor solution was prepared using a 0.05M Tin (II) Chloride ($SnCl_4.2H_2O$) in de-ionized water and then being added in 100 ml ethanol to get equal proportions or to obtain a consistent balance of water and ethanol, then soaked in an ultrasonic bath (300 W and 60 kHz) about 10 min. Followed by 1.5 wt% of nickel chloride 6-hydrate ($NiCl_2.6H_2O$) was added as a doped source into the solution and then soaked in an ultrasonic bath for another 5 min.

The precursor solutions were deposited with 10 drops onto the substrate. The solutions were spin-coated on a glass slide substrates at 750 rpm speed. The spin coating duration for all samples were 2 minutes. Finally, the samples were annealed for 30 minutes at various temperature in air atmosphere.

We prepared five kinds of samples annealed at 100 °C, 200 °C, 300 °C, 400 °C, and 500 °C, respectively, in an electrically heated furnace (Fig. 1). For comparison, we

also prepared the as-deposited samples. The surface morphology and crystallinity of the samples were observed by scanning electron microscopy (SEM). Optical transmission measurement was also conducted at room temperature using a UV-visible spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy.

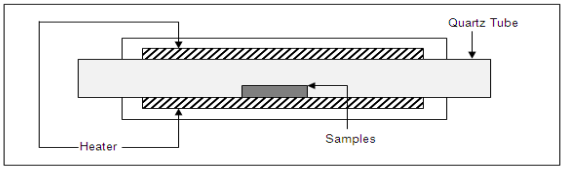


Fig. 1. Samples are positioned at the center of the tube furnace for thermal annealing.

3. Results and discussions

Fig. 2 shows the UV-VIR patterns of the Ni-doped SnO_2 and the samples heat-treated from 100 °C to 500 °C for 30 min. The figure shows the optical transmittance spectra of the Ni-doped SnO_2 films as a function of wavelength. The transmittance of these films stays high over a wide range in the visible region. The optical band gap of the films deposited does not vary much with the annealed temperature. The average transmission of the Ni-doped SnO_2 films deposited on glass substrates is more than 80% over the range 400 nm to 800 nm.

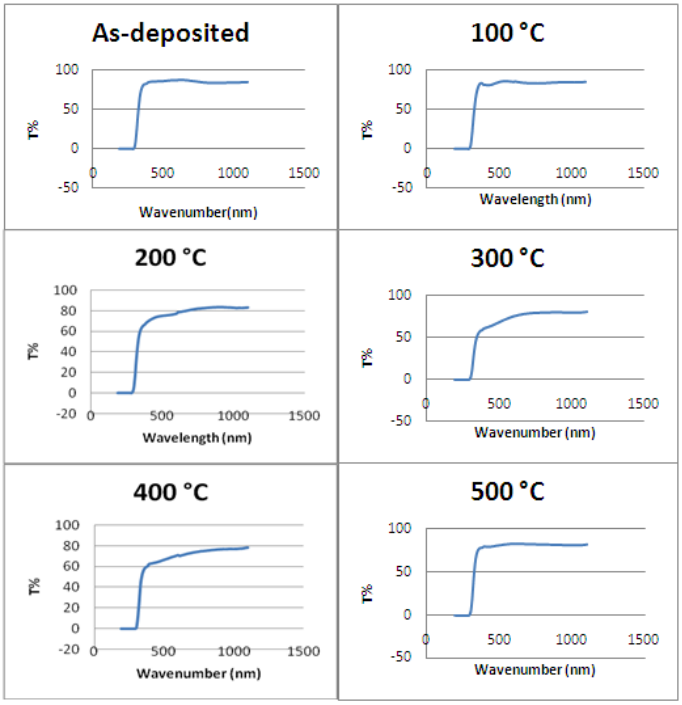
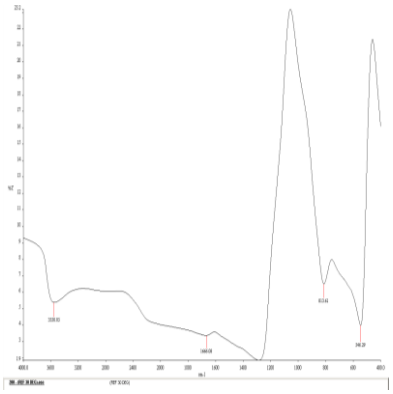


Fig. 2. Set 1 UV-Visible transmittance spectra of the Ni-doped SnO_2 films prepared at different annealing temperatures.

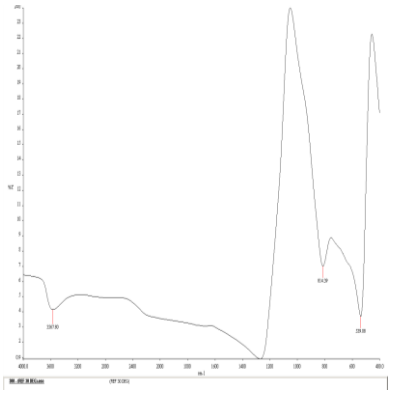
Fig. 3 shows the FTIR patterns of the Ni-doped SnO_2 and the samples heat-treated from 100 °C to 500 °C for 30 minutes. Tin oxide FTIR pattern generally shows the presence of stretching vibration bands at around 540 cm^{-1}. The peak at 800 cm^{-1} can be assigned to Sn-O-Sn stretching vibrations. The absorption band at 540 cm^{-1} was ascribed to the terminal oxygen vibration (Sn-OH). A broad band around 3500 cm^{-1}, coupled to that at about 1640 cm^{-1}, characteristic of water bending, is observed in the as-deposited, 100 °C and 200 °C sample.

For sample annealed at 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C, the absorption observed at 1640 cm^{-1} due to OH group is weak or absent. In all the samples, absorption peaks near 550 cm^{-1} corresponding to Sn-O vibrations, was observed.

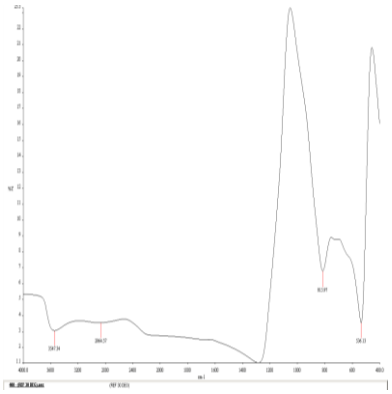
No additional absorption peaks were observed with Ni addition, indicating its homogeneous dispersion in the support material [10,11].



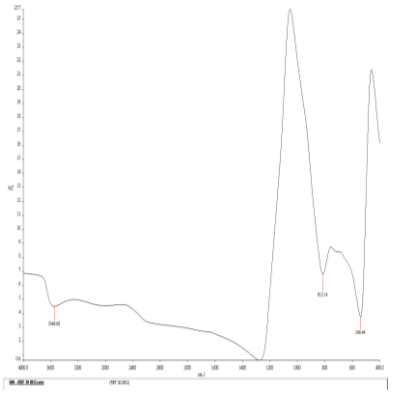
(a) As deposited Ni-doped SnO_2



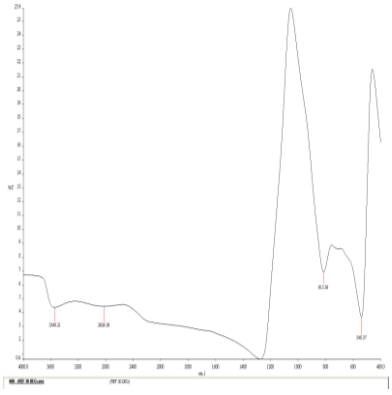
(b) 100 °C



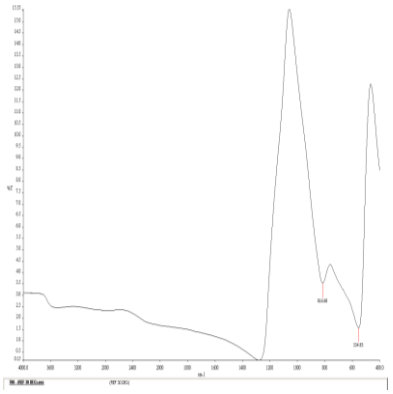
(c) 200 °C



(d) 300 °C



(e) 400 °C



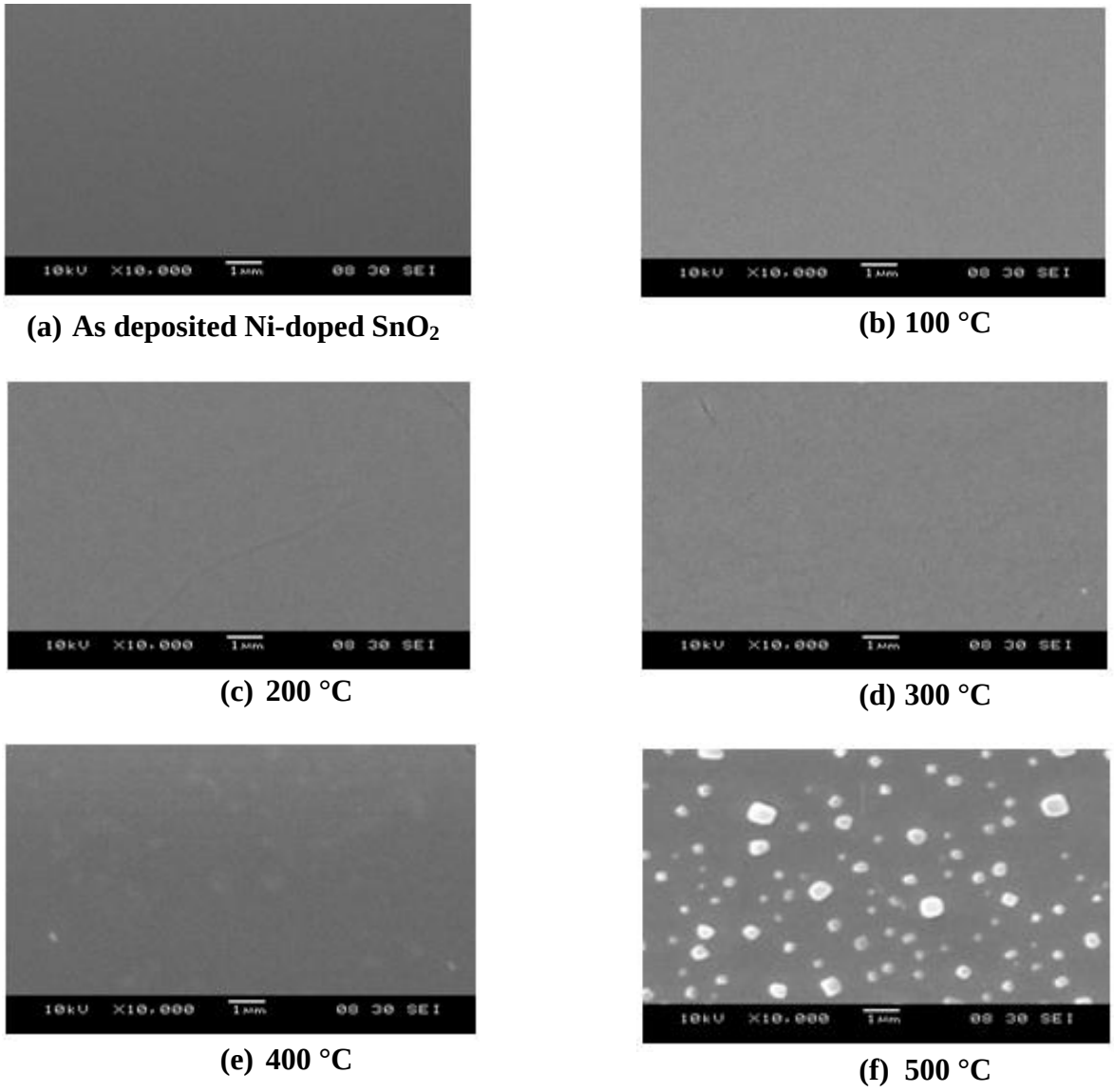
(f) 500 °C

Fig. 3. The FTIR patterns of the as-deposited specimen and the samples heat-treated from 100 °C to 500 °C for 30 min.

According to Popescu and Verduraz et al. [12], they have observed these peaks for SnO_2 powder at 665 cm^{-1}, 770 cm^{-1} and 960 cm^{-1}, respectively; their peaks were correlatively narrower in comparison with this FTIR spectra. This could be because of the amorphous and nanocrystalline characteristics in these thin films. The appearance of the FTIR spectra and the points of the peaks have been presented to differ with the synthesis methods and particle size [13].

Figs. 4 show the SEM images results of 10k magnification for samples. During the lower temperature, 400 °C and below, not much alter in grain size for all sets of samples. The sample have the smooth surface morphology. On the other hand, with increase in annealing temperature, the surface morphology gradually became

rough, there are some formations of nanoclusters appeared on the surface of Ni-doped tin oxide films. These nanoclusters are suspected to be the grain of the Ni-doped tin oxide films. The average grain size for the 500°C image seen is around 0.1μm.



(a) As deposited Ni-doped SnO_2 **(b) 100 °C**

(c) 200 °C **(d) 300 °C**

(e) 400 °C **(f) 500 °C**

Fig. 4. The SEM patterns of the as-deposited specimen and the samples heat-treated from 100 °C to 500 °C for 30 min.

4. Conclusion

In conclusion, Ni-doped SnO_2 thin films have been successfully prepared by a simple sol–gel method. The FTIR spectrum shows the presence of stretching vibration bands at around 540 cm^{-1}. The peak at 800 cm^{-1} can be assigned to Sn-O-Sn stretching vibrations. In all the samples, absorption peaks near 550 cm^{-1} corresponding to Sn-O vibrations, was observed. Ordinarily, the starting material is low value and the synthesis processes are very easy, which should be a good choice instead of the sol–gel method. This technique can also be utilized to synthesize many other doped tin oxide nanocrystallites.

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References

[1] G. Cheng, K. Wu, P. Zhao, Y. Cheng, X. He, K. Huang, Journal of Crystal Growth **309**, 53 (2007).
[2] Y. Kobayashi, M. Okamoto, A. Tomita, Journal of Materials Science, **31**, 6125 (1996).
[3] L. Abello, B. Bochu, A. Gaskov, S. Koudryavtseva,

G. Lucazeau, M. Roumyantseva, Journal of Solid State Chemictry, **135**, 78 (1998).
[4] M. Ristic, M. Ivanda, S. Popovic, S. Music, J. Non-Crystal. Solids, **303**, 270 (2002).
[5] L. Fraigi, D. G. Lamas, N. E. W. Reca, Nanostruct. Mater., **11**, 311 (1999).
[6] M. Bhagwat, P. Shah, V. Ramaswamy, Mater. Lett., **57**, 1604 (2003).
[7] D. T. Martinez, R. C. Perez, G. T. Delgado, O. Z. Angel, Journal of Materials Science: Materials in Electronics, **22**, 684 (2011).
[8] E. Elangovan, K. Ramamurthi, Thin Solid Films, **476**, 231 (2005).
[9] H. K. Yadav, K. Sreenivas, V. Gupta, R. S. Katiyar, Journal Appl. Phys. **104**, 113523 (2008).
[10] L. S. Chuah, S. S. Tneh, Z. Hassan, Composite Interfaces Letters, **18**, 371 (2011).
[11] L. S. Chuah, M. Y. Yaacob, M. S. Fan, S. S. Tneh, Z. Hassan, Optoelectron. Adv. Mater.-Rapid Commun. **4**(10), 1542 (2010).
[12] D. A. Popescu, F. B. Verduraz, Catal. Today **70**, 139 (2001).
[13] M. Ristic, M. Ivanda, S. Popovic, S. Music, J. Non-Crystall. Solids **303**, 270 (2002).

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