Optical Properties of Pure and Erbium-doped Tin Dioxide Thin Films Fabricated by Sol-gel Technique

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ABSTRACT

In this study, the pure tin oxide (SnO_2) and erbium doped tin dioxide thin films have been prepared on glass substrate using sol-gel technique. The surface morphology, microstructure and properties of the films are characterized by using Field Emission Scanning Electron Microscope, X-ray diffraction and Photoluminescence. It was found that the particles in the SnO_2 thin films have the diameter ranging from 20 to 44 nm with spherical morphology. SnO_2 thin films have tetragonal structure with prominent peaks corresponding to (1 1 0), (1 0 1) and (2 1 1) crystal lattice planes. The photoluminescence (PL) emission peaks of SnO_2:Er^{3+} corresponding to the characteristic H → I transitions between the energy levels of Er^{3+} ion.

Keywords: *sol-gel, tin oxide (SnO_2), erbium doped SnO_2*

Introduction

Tin dioxide (SnO_2) has a wide bandgap semiconductor (3.5–4 eV) which possesses rutile (tetragonal) crystal structure (Sekhar *et al.*, 1998). Tin dioxide presents high transparency in the visibility above 90 %, low electrical resistance associated with high reflectivity in the infrared region (Marco *et al.*, 2008). Tin dioxide becomes an attractive matrix for electrically activated emission because a wide bandgap semiconductor has higher excitonic ionization energy. The wide band gap decreases the luminescence quenching effects, allowing the doping emission and the material can be applied at room temperature Thus, the new devices such as electroluminescent thin films can be fabricated by using rare-earth (RE) doped semiconductors (Evandro., et al.,). Rare-earth ions present radiative transitions in a large wavelength range, covering from the ultraviolet to the infrared. Tin dioxide has a potential applications in opto-electronic devices, gas sensors and solar collectors (Viviany *et al.*, 2003).

The sol–gel technique offers many advantages over other methods such as sol gel is a relatively simple way of preparing chemically homogeneous (Feng *et al.*, 2003a) and low cost method (Daoli *et al.*, 2006). The desired properties of the coatings can be adjusted with various dopants at various concentrations of this solution method (Yi and Hou, 2004). Thus, it is easy to control the doping level (Jing *et al.*, 2009) but strictly controlled amount of dopant. Even small quantities of dopants, such as organic dyes and rare earth elements, can be introduced in the sol and end up uniformly dispersed in the final product.

A metal oxide film is produced by depositing the precursor non-alkoxide sol such as chlorides, acetates, nitrates and carbonates on a substrate using spin coating technique. The film is dried in oven and calcined at a high temperature in furnace (Sekhar *et al.*, 1998). The calcination is needed to complete decomposition of $SnO_2.nH_2O$ in greater than 400 °C and ensure the reliable adherence of SnO_2 film to substrate. Generally, sol–gel derived precipitates are amorphous in nature. The complete transformation from amorphous to rutile phase can also be achieved through calcination in air. However, high annealing temperature generally lead the particles joined in agglomerates, grain growth and produce a small total surface area (Horvath *et al.*, 2005).

Experimental

An amount of 7.898 g tin (II) dichloride dihydrate ($SnCl_2{\cdot}2H_2O$) was dissolved in 100 mL anhydrous ethanol (C_2H_5OH). The mixture was stirred with a magnetic stirrer for 30 minutes in a closed three-necked flask vessel. After that, a complexing agent, Acetylacetone (AcAc) was added to stabilize the hydrolysis of $SnCl_2$. After

another 30 minute, the solution was continuously refluxed at 80 °C for 5 hours to form the SnO_2 sol. About 1 mL of polyethylene glycol (PEG) was added in pure SnO_2 sol and the sol was aged for 72 hours at 30 °C before coating. For doped samples, the solution was doped with erbium (III) nitrate pentahydrate ($Er(NO_3)_3.5H_2O$) to the SnO_2 sol. The concentration of Er^{3+} was estimated to be 5% in relation with the tin content in the sol. About 1 mL of PEG was added into the pure SnO_2: Er^{3+} sol and the sol was aged for 48 hours at 30 °C before coating.

All the samples were fabricated by spin-coating sol-gel technique on pyrex glass substrates at room temperature with a subsequent annealing process. Coated layers of thin films were formed in a two-stage spinning process on the substrates: 5 s at 1500 rpm and 30 s at 3000 rpm. Each deposited layer was dried at 100 °C for 15 min before deposition of the next layer. The final films were annealed at 600 °C for 1 hour.

The surface morphology was detected by Field Emission Scanning Electron Microscope (FESEM) Zeiss Supra TM 35VP. The microstructures of the films were determined by X-ray diffraction (XRD) Bruker AXS D8 Advance. The optical properties were investigated via photoluminescence (PL) of Perkin Elmer Luminescence Spectrometer LS50B.

Results and discussion

FESEM analysis

Figure 1 shows the FESEM images of the (a) pure SnO_2 and (b) SnO_2: Er^{3+} films. The surface of the films is smooth and transparent with a small crack appearance in all scanned areas of the sample. The surface of the undoped SnO_2 thin film consists of uniform spherical particles with average grain size of about 23.3 nm. The surface of the film in Figure 1(b) shows the irregular spherical particles with average grain size of about 43.7 nm. This irregular particles size is due to the uneven distribution of temperature and mass flow during the synthesis (Sandipan et al., 2010). The particles size of SnO_2 doped Er^{3+} thin films is larger than undoped once which indicates the influence of dopant atoms on the morphology. The addition of rare earth ion (Er^{3+}) caused particle size to increase. This is due to the ionic radius of Er^{3+} ion (0.088 nm) is larger than Sn^{4+} (0.071 nm) (Peng et al., 2005).

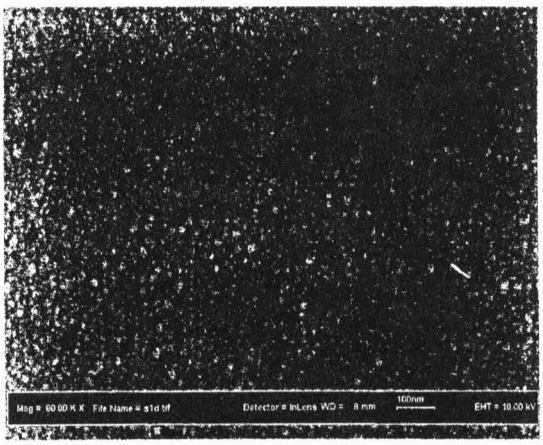

Figure 1(a): FESEM images for the pure SnO_2 thin film

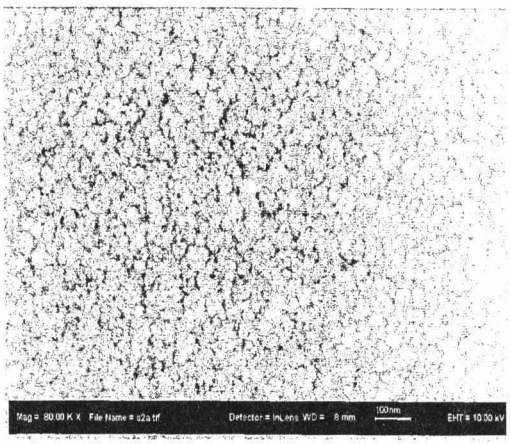

Figure 1(b): FESEM images for the SnO_2:Er^{3+} thin film

XRD analysis

Figure 2 shows the X-ray diffraction (XRD) patterns of the SnO_2: Er^{3+} thin film (a) and (b) pure SnO_2 thin film. All the diffraction lines were assigned to tetragonal crystalline structure of SnO_2. The XRD patterns with a

reference pattern (JCPDS No. 41-1445) of tin oxide show that the prominent orientation of the films are (1 1 0), (1 0 1) and (2 1 1). The (1 0 1) plane has the highest intensity peak as expected for a cassiterite crystal structure. Other small peaks observed are (2 0 0), (2 2 0), (3 1 0), (1 1 2) and (3 0 1). Compared to Figure 2(a), the peak positions of SnO_2: Er^{3+} thin film was increased slightly and their relative intensities change higher than pure SnO_2 thin film. It is suggested that SnO_2: Er^{3+} thin films have large crystallite size compared to pure SnO_2 thin films.

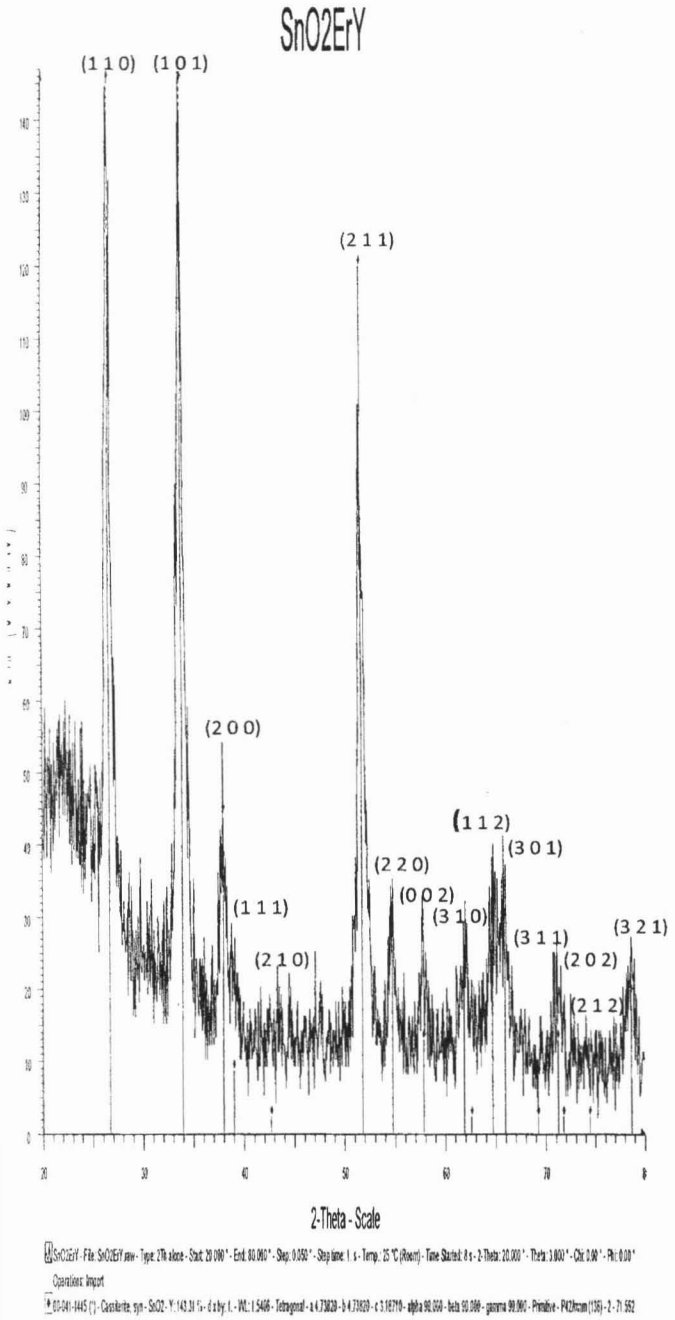

Figure 2(a): XRD patterns of SnO_2:Er^{3+} thin film
Reference pattern (JCPDS No. 41-1445)

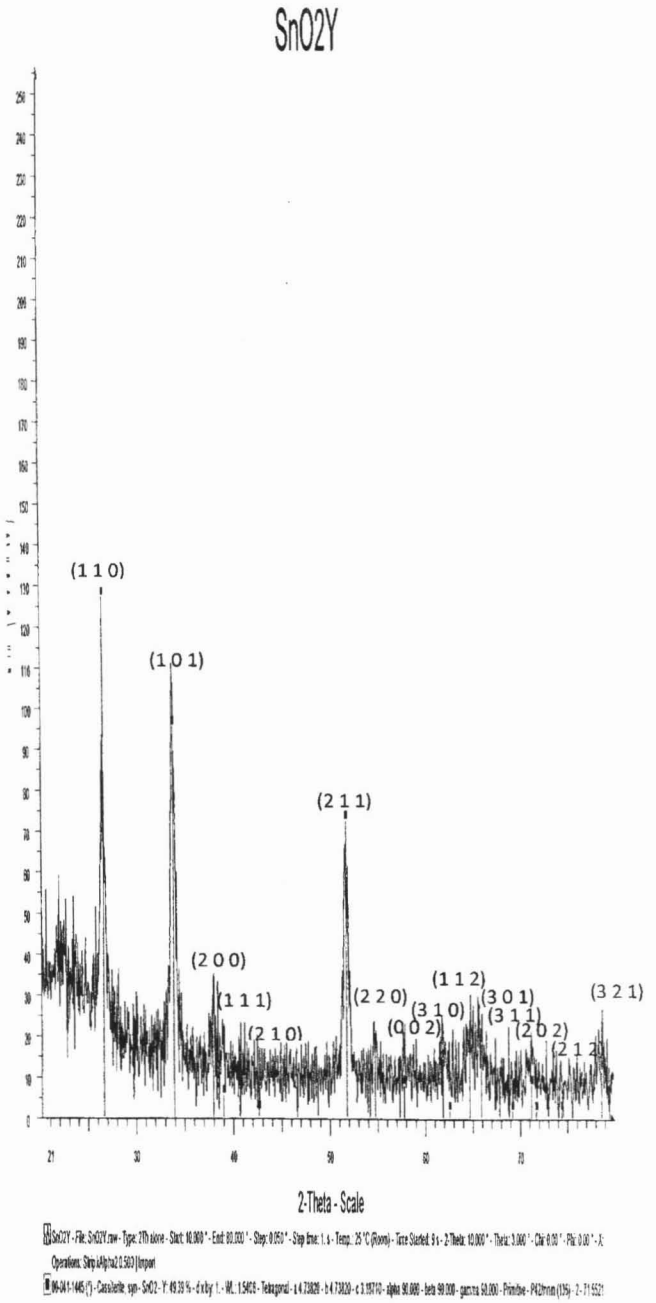

Figure 2(b): XRD patterns of pure SnO_2 thin film
Reference pattern (JCPDS No. 41-1445)

Photoluminescence (PL) analysis

The photoluminescence (PL) emission spectra of undoped SnO_2 films shown in Figure 3(a). The undoped SnO_2 presents a broad PL peak at 382.76 nm. The emission at 382.76 nm is attributed to electron transition mediated by defect levels in the band gap such as oxygen vacancies. The peak at 558.25 nm also observed in undoped SnO_2 film. This peak has been assigned to metastable energy levels associated with oxygen vacancies. This peak which was attributed to the oxygen vacancies presents at a lower energy position with higher wavelength region than the green luminescence peak.

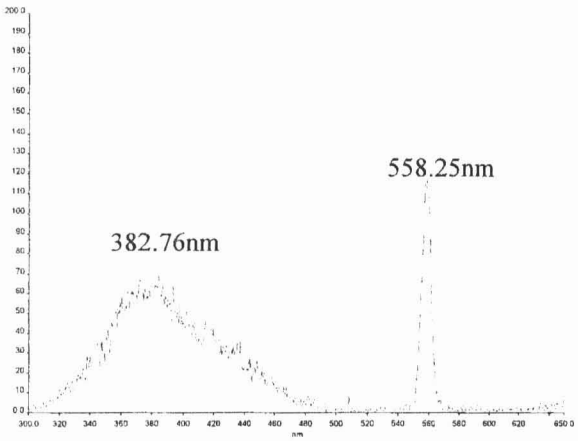

Figure 3(a) PL emission spectra of pure SnO_2

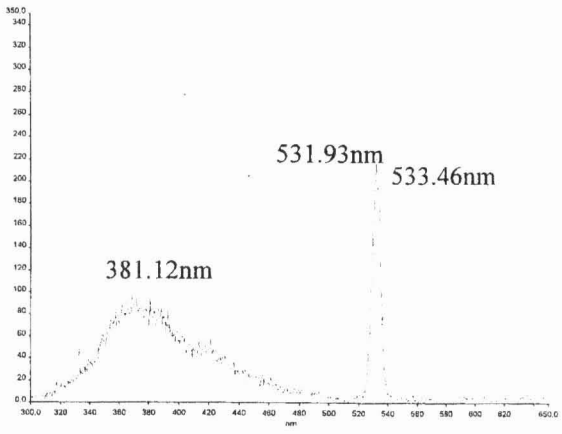

Figure 3(b) PL emission spectra of SnO_2:Er^{3+} thin film

The PL emission peak appear at 381.12 nm which attributed to singly charged oxygen vacancies in the SnO_2. The peak is about 531.93 nm and 533.46 nm in SnO_2:Er^{3+} thin films show green emission corresponds to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ radiative transition of Er^{3+} ion. The oxygen vacancies may be created by incorporation of Er^{3+} ion because the 1-charge of the ErSn ion has to be compensated somewhere in the lattice in the form of oxygen vacancy. The diffusion of Er^{3+} ions in SnO_2 may be accelerated by higher heat treatment. This induces the formation of more oxygen vacancy. The oxygen vacancies are known to be the most common defects and act as radiative centres in luminescence process. The oxygen vacancies also act as a sensitiser for the energy transfer to the Er^{3+} ion. The radiative recombination of the large amount of trapped carriers excited from SnO_2 host cause the Er^{3+} ion emission (Bouzidi *et al.*, 2009).

Conclusion

Tin oxide (SnO_2) and erbium doped tin oxide (SnO_2: Er^{3+}) thin films have been prepared by sol-gel technique with spin-coating process. The Er^{3+} dopant concentration was estimated to be 5 %. We investigated the films by SEM, XRD and photoluminescence (PL) measurement. It can be concluded that FESEM analysis shows the particle nano-sized of SnO_2 doped Er^{3+} ion thin films is increased compared to undoped SnO_2 thin films which indicate the influence of dopant atoms on the morphology of SnO_2 thin films. It has been determined by XRD that the obtained samples are tetragonal structure of pure SnO_2, with prominent peaks corresponding to (1 1 0), (1 0 1) and (2 1 1) crystal lattice planes. While instead of introducing a new phases, the addition of Er^{3+} causes the peak positions in XRD patterns to shift slightly and their relative intensities to change.

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