Optical and Photoluminescence Studies of Tb Doped TiO_2 Thin Films Deposited By RF Magnetron Sputtering

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Abstract:- **Undoped and Tb doped TiO_2 thin films (0.2, 0.3, 0.4 at%) were deposited onto quartz substrates by RF magnetron sputtering. The optical and photoluminescence (PL) properties of the films, post-annealed at 873 K were examined using UV-vis optical transmission spectra and PL spectra. Tb doping caused a blue shift of the absorption edge which indicates an increase in optical band gap. An increase in refractive index was also observed with increasing Tb content. Two main PL emission peaks at 475.80 and 573.53 nm corresponding to intra 4f $^5D_3 \rightarrow {}^7F_3$ and $^5D_4 \rightarrow {}^7F_4$ transitions respectively of Tb^{3+} ions were observed in all the Tb doped films. PL intensity was found to increase with increasing Tb content upto 0.3 at% after which it showed a decrease due to concentration quenching.**

Keywords: TiO_2: Tb thin films, RF magnetron sputtering, photoluminescence, concentration quenching

1. INTRODUCTION

Rare earth (RE) doped luminescent materials have wide industrial and technological applications in many advanced phosphor and photonic devices, light emitting diodes, solid state lasers, flat panel displays, high energy radiation detectors, fluorescent lamps, optical data storage and in medical diagnostic devices [1–3]. Among the various host matrices for RE ions, TiO_2 is an excellent candidate due to its outstanding mechanical, optical, thermal and anticorrosive properties.

Though Tb is a promising candidate for obtaining green emission (green phosphors), the reports in literature differ regarding the frequency of PL emission from Tb incorporated in TiO_2 host matrix. Frindell et al [4] has reported that energy levels of the $^5D_4$ emitting states of Tb^{3+} ions are higher than the defect (trap) states of TiO_2. Hence luminescence from Tb^{3+} embedded in TiO_2 matrix is not possible due to the inefficient energy transfer mechanism from conduction band (CB) of TiO_2 to luminescence excited states of Tb^{3+} through TiO_2 defects states. But there is no clear evidence in literature regarding how the phase of films and film deposition method influence the PL emission in TiO_2:Tb films. Since RF magnetron sputtering is a unique way to produce high quality, uniform and large area coatings on industrial basis for practical applications, we investigate the effect of Tb doping on TiO_2 thin films deposited by RF magnetron sputtering.

2. EXPERIMENTAL DETAILS

Pure TiO_2 and Tb_2O_3 (99.99% Sigma Aldrich) powders were used for target preparation. They were mixed together in the desired proportions and ball milled for 8 h using ball milling apparatus. The sputtering target was prepared by standard ceramic procedure [5]. Four different targets with Tb/Ti atomic ratio 0, 0.2, 0.3 and 0.4 at% were prepared. The substrate-target distance was 5 cm. Sputtering was carried out at sputtering pressure 0.015 mbar and RF power 120 W for 2 h in pure Ar atmosphere on quartz substrates maintained at room temperature. Post deposition thermal annealing of the 0, 0.2, 0.3 and 0.4 at% Tb doped films at 873 K was done in air for 2 h. The films thus obtained were coded TO[873], 0.1TTO[873], 0.2TTO[873], 0.3TTO[873] and 0.4TTO[873] respectively.

XRD patterns of the films were recorded using Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 0.15405 nm). SEM images were recorded using JEOL Model JSM-6390LV microscope. UV–vis transmission spectra of the films were recorded using JASCO V-550 spectrophotometer. From the transmission spectra, Swanepoel's envelope method [6] was used to calculate the optical constants (film thickness, refractive index) and Tauc plot [7] was used to determine the optical band gap of the films. Photoluminescence spectra of the samples were recorded using Horiba Jobin Yvon Flourolog (III) spectrofluorometer equipped with 450 W Xenon lamp and Hamatsu R928-28 photomultiplier. Excitation wavelength used was 350 nm.

3. Results and discussions

3.1 XRD studies

XRD patterns of pure and TiO_2:Tb thin films annealed at 873K showed an amorphous nature (fig. not shown). It is seen from our previous studies [5] that post-deposition thermal annealing can induce crystallinity in TiO_2 thin films deposited at room temperature by sputtering method. Hence it is inferred that doping with Tb inhibits the crystallisation of TiO2 thin films.

3.2 SEM analysis

SEM images of pure TiO_2 thin film and 0.4 at% TiO_2:Tb thin films, annealed at 873 K are shown in fig. 1. The films are crack free and showed good adherence to the substrate. Homogeneous surface morphology is observed in pure TiO_2 thin film. Narrow grains can be observed on the surface of Tb doped films.

3.3 Optical studies

UV-vis optical transmittance spectra of pure and Tb doped TiO_2 thin films annealed at 873 K are shown in fig.2. The films are transparent in the visible region with an average transmittance of >80%. The presence of interference fringes in the visible region of the spectra is an indication of the homogeneity of the films. A sharp fall in transmittance is observed in the UV region, which corresponds to the absorption edge. Tb doping introduces a slight blue shift of the fundamental absorption edge, which indicates an increase in optical band gap. The variation in optical band gap can be attributed to the following factors: (1) strain effect from lattice distortion (2) oxygen vacancies and (3) film optical density [8].

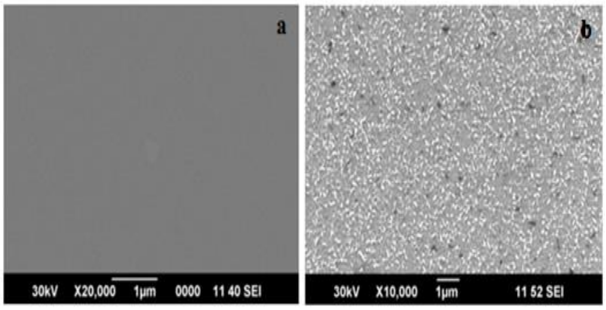

Fig 1: SEM images of (a) pure (b)0.4at% Tb doped TiO_2 thin film

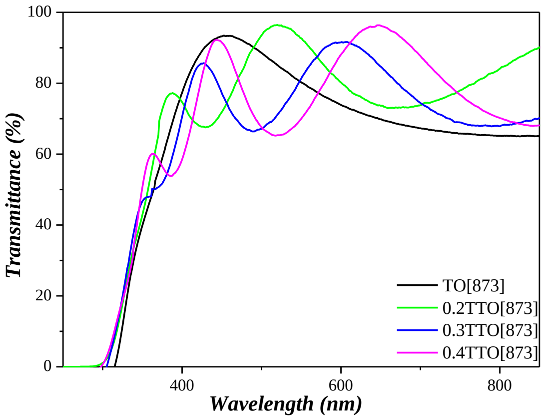

Fig 2: UV-vis transmittance spectra of pure and Tb doped TiO_2 thin films

The values of film thickness, direct optical band gap, refractive index (n) and porosity (P) are given in table 1. Post-depositional thermal annealing of the films along with increase in film thickness caused an increase in refractive index. Porosity was found to decrease with increase in Tb concentration.

Table 1: Variation of optical parameters (at λ=550 nm) with Tb doping

Sample	***E_g (eV)***		***t (nm)***	***n***	***P (%)***
TO[873]	3.70		-	-	-
0.1TTO[873]	3.71		167	2.22	24.76
0.2TTO[873]	3.72		228	2.23	24.09
0.3TTO[873]	3.72		275	2.25	22.37
0.4TTO[873]	3.71		294	2.48	1.16

3.4 Photoluminescence studies

Photoluminescence spectra of pure TiO_2 and TiO_2:Tb thin films excited using light of wavelength 350 nm is shown in fig.3.

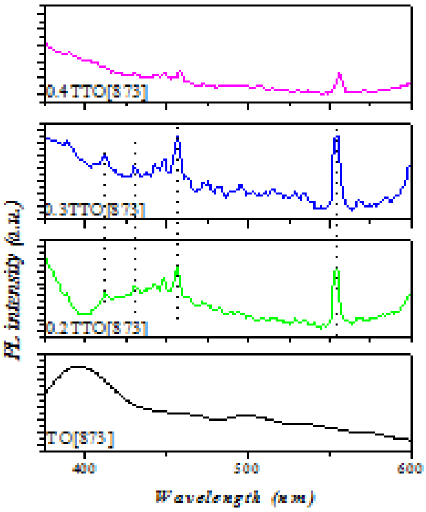

Fig 3: PL spectra of pure and Tb doped TiO_2 thin films

Pure TiO_2 thin film exhibits a broad emission band centred around 395.08 nm, which is the exciton band due to self trapped excitons in TiO_2. A weak broad emission peak at 497.73 nm due to transitions via oxygen defects are also observed in this film. In Tb doped films, the host matrix (TiO_2) absorbs energy of the incident photon and this energy is transferred to the RE ion resulting in PL emission. PL emission peak at 411.93 and 430.21 nm corresponding to $^5D_3 \rightarrow {}^7F_5$ and $^5D_3 \rightarrow {}^7F_4$ transitions respectively are observed in 0.2 and 0.3 at% Tb doped film. Two main peaks at 456.11 and 553.21 nm corresponding to intra 4f $^5D_3 \rightarrow {}^7F_3$ and $^5D_4 \rightarrow {}^7F_5$ transitions respectively of Tb^{3+} ions are observed in 0.2 and 0.3 at% Tb doped films. PL emission peaks of least intensity, corresponding to $^5D_3 \rightarrow {}^7F_3$ and $^5D_4 \rightarrow {}^7F_5$ transitions are observed at 456.11 and 555.80 nm respectively for 0.4 at% Tb doped film. The strongest peak corresponding to $^5D_4 \rightarrow {}^7F_4$ transition observed in all the Tb doped films represents green emission.

PL emission in Tb doped films in our studies, based on emission mechanism proposed by C.Jia et al [9] and Y.Sheng et al [10], can be interpreted as follows: The host matrix absorbs a photon and electrons are transferred from valence band to conduction band of TiO_2. This energy is non-radiatively transferred to $^5D_3$ level of Tb^{3+} ions. From this $^5D_3$ level, excited electrons can make transitions to lower energy state in four ways: (1) Radiative transition from $^5D_3 \rightarrow {}^7F_j$ level (2) Cross relaxation between $^5D_3 \rightarrow {}^5D_4$ and $^7F_6 \rightarrow {}^7F_1$due to similar energy gap of transitions (3) Inter ionic cross relaxation between $^5D_3 \rightarrow {}^7F_{0,1}$ and $^5D_4 \rightarrow {}^7F_6$ of two adjacent Tb^{3+} ions (4) Multi-phonon assisted non-radiative transition between $^5D_3 \rightarrow {}^5D_4$ level followed by radiative transition between $^5D_4 \rightarrow {}^5F_j$ levels.

Radiative transition from $^5D_3 \rightarrow {}^7F_{5,4,3}$ levels contributes to the emission peak at 411.93, 430.21 and 456.11 nm in our studies. Cross relaxation occurs due to similar energy gap of $^5D_3$ and $^5D_4$ (5761 cm^{-1}) and $^7F_6$ and $^7F_1$ (5623 cm^{-1}) levels. During inter ionic cross relaxation between adjacent Tb^{3+} ions, electrons of one activated Tb^{3+} level will release energy during $^5D_3 \rightarrow {}^7F_{0,1}$ transition and this energy is absorbed by the neighbouring unactivated Tb $^{3+}$ ions [11,12]. Cross depopulates the excited $^5D_3$ levels and populates $^5D_4$ levels. This accounts for the lower emission intensity from $^5D_3$ level than that from $^5D_4$ level. Radiative transition occurs from $^5D_4 \rightarrow {}^7F_5$ level contributes to emission peak at 553.21 nm in our studies. Characteristic green emission due to transition between $^5D_4 \rightarrow {}^7F_5$ levels is observed in all Tb doped films indicating the suitable use of these films in green phosphors.

PL intensity increases with increase in Tb content. But when Tb^{3+} content exceeds a certain limit, concentration quenching occurs. Co-operative up-conversion, energy migration and cross relaxation process results in quenching of luminescence [13]

4. Conclusions

Undoped and 0.2, 0.3 and 0.4 at% Tb doped TiO_2 thin films were deposited onto quartz substrates maintained at room temperature by RF magnetron sputtering. The films were thermally annealed at 873 K. No characteristic diffraction peak corresponding to anatase or rutile phase was observed in the XRD spectra revealing an amorphous nature of the films. The films were crack free and adhered well to the substrate. The films were transparent in the visible region and absorption edge showed a blue shift with increase in Tb content in films. An increase in refractive index was observed with increasing Tb concentration. A broad PL emission band due to self trapped excitons was observed in pure TiO_2 thin film along with a weak broad band in the visible region due to transitions via oxygen defects. But two main peaks at 456.11 and 553.21 nm corresponding to intra 4f $^5D_3 \rightarrow {}^7F_3$ and $^5D_4 \rightarrow {}^7F_5$ transitions respectively of Tb^{3+} ions are observed in all the Tb doped films. Intensity of PL emission peaks was found to increase upto a certain optimal Tb doping concentration (0.3 at%) after which it decreases. This decrease in PL intensity at higher doping concentration is attributed to concentration quenching.

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