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Optimization and Characterization of Niobium Doped TiO₂ Nanostructured Thin Films

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Abstract: Niobium (Nb) doped TiO₂ nanostructure thin films were characterized by simple Chemical Bath Deposition method (CBD). The different characterization of Nb doped Nano structural, thin film studied by X-ray diffraction (XRD), UV-Vis Spectra, photoluminescence (PL). X-ray diffraction results showed that anatase phase is formed for both pure and Nb (5 wt%). Atomic Force Microscopy (AFM) is used to find the surface roughness it has been found to decrease with the increase of the Niobium doping concentration. Optical studies showed that the energy band gap of the films was lowered from 3.31 eV to 3.07 eV on Niobium (Nb) doping. PL emission intensity was decrease with Nb doped samples, which confirm the Nb doping in to TiO₂ host lattice site. The electrical resistivity was found to be 1.71 Ω.cm and 1.01Ω.cm for pure and Nb doped TiO₂ films for 500°C. This result confirmed that Nb doping has strong influence in the electrical properties of pure TiO₂.

Keywords: Transparent Conducting oxides, TiO₂ thin films, Nb doping, Optical property, Resistivity.

I. INTRODUCTION

Transparent conducting oxides (TCOs) are a different type of materials that combine electrical conductivity and optical transparency with a wide range of applications e.g. Displays, low emissive (low-e) windows, thin film photovoltaic (PV) and smart devices [1]. Titanium dioxide (TiO₂) belongs to the family of transition metal oxides. In nature, TiO₂ is known to occur in the structures of rutile, anatase, and brookite (brookite is a minority product of most synthesis). TiO₂ is a wide band gap semiconductor material which has been under extensive investigations due to its applications in a variety of fields such as dye-sensitized solar cell [2], gas sensors [3], photo catalysts [4-5], wave guiding [6], antireflective coatings [7], dielectric [8], etc. Tin-doped indium oxide (ITO) is a widely used material for TCO applications due to its high transmittance to visible light and high conductivity, but it is so important to find a substitute for it because of indium natural resources rarity. Although in recent years aluminium-doped zinc oxide (ZAO) [9] and fluorine-doped tin oxide (FTO) [10] are presented as new TCOs but the hardship in large area preparation of ZAO films with smooth surface morphology and easily etched ZAO films in both acid and alkaline environment and also relatively low electrical conductivity of FTO and its difficulty to pattern via wet etching as compared to ITO [11] Furubayashi et al. [12] prepared the Nb-doped TiO₂ (TNO) thin film by pulsed laser deposition (PLD) method and reported it as a novel TCO material with minimum resistivity of 2.3×10^{-4} Ω.cm and the transparency of higher than 95% in the visible range. Yamada et al. [13] also fabricated highly conductive polycrystalline TNO film on glass substrate by sputtering method so that resistivity of the film was measured 3×10^{-4} Ω.cm at room temperature and optical transmittance was achieved 75% in the visible range. Although highly conductive and transparent TNO thin films can be obtained by above methods, but industrial productions are limited by the expensive vacuum technique. Furthermore, the homogeneous and large-area films preparation is also an upfront challenge yet. A chemical bath deposition method has several advantages including simplicity, low cost, easily controlled doping levels and feasible preparation of large area films. Moreover the method is simple, less time consuming and cost effective compared to other methods. In the present work consist of synthesis and systemic investigation of structural, optical and electrical properties of Nb doped TiO₂ thin films by using simple chemical bath deposition method.

II. EXPERIMENTAL PROCEDURE

A. Preparation of Nb-TiO₂ thin films

Nb-TiO₂ thin films were prepared on carefully cleaned (in an ultrasonic water bath and then in absolute ethanol) quartz glass substrates by chemical bath deposition technique. The starting solution was prepared by mixing of titanium isopropoxide, niobium (V) chloride (NbCl₅), ethyl alcohol in molar ratio 5:50, in a closed beaker stirred for 30 min pH of the sol was adjusted to 8 with the addition of 2 ml of NH₄OH. Distilled water (1.5 mol) was added and the solution was refluxed under dry atmosphere for 2 h at 60

°C. For completion of the hydrolysis process, the solution was kept stirred at room temperature for overnight. The substrate was suspended vertically in the reaction bath after stirring the solution properly for homogeneity. The thin film samples were deposited at room temperature for 1 h. The as-deposited thin films were annealed at 500 °C for 2 h in muffle furnace, in order to improve the crystallinity. Pure TiO₂ thin films were prepared in a similar manner without the use of niobium source.

B. Characterization Techniques

The prepared samples (annealed) were successfully characterized by the following techniques. Structural properties of the Nb-TiO₂ thin films are analysed using X-ray diffraction (XRD, JEOL diffract meter) with mono chromatized Cu K α radiation ($\lambda=1.54056 \text{ \AA}$) in range of 10-80° with step size of 0.1° and the Fourier transform infrared (FT-IR) spectra are recorded on a Shimadzu-8400S spectrometer in range of 400 - 4000 cm⁻¹ using KBr pellets. The optical transmittance is measured by UV-Vis spectrophotometer (JASCO V-500) in the wavelength range of 300 - 900 nm. For electrical conductivity, the sheet resistance values of the films are recorded by a Jandel four point surface resistivity meter (RM3-AR) at room temperature. The morphology of the Nb-TiO₂ thin films is observed by scanning electronic microscope (JEOL Model JSM – 6390LV). Photoluminescence spectra of the samples were recorded using PerkinElmer LS 55 Spectrometer equipped with a 40 W Xenon lamp, Excitation length used was 325 nm.

III. RESULTS AND DISCUSSION

A. XRD analysis

Non-destructive X ray diffraction technique was used to determine the phase crystallinity and structural analysis of the pure and Nb doped TiO₂ thin films as shown in figure 1. It can be seen that the diffraction peaks of both samples are ascribed to the peaks of anatase phase. The observations indicate that there is no phase change in TiO₂ during the doping process. It was also noted that the XRD peak intensity decreases for Nb doped TiO₂, which indicating the growth is suppressed due to Nb doping. The lattice parameters of pristine TiO₂ were estimated as a = b = 4.6941 (Å) and c = 3.1851 (Å). These values decrease to a = b = 4.6745 (Å) and c = 3.1767 (Å) after Nb (5wt %) doping (Table 1). The observed variation in lattice parameters is consistent with the smaller radius of the Nb⁵⁺ ion (0.64 Å) with respect to the Ti⁴⁺ ion radius (0.68 Å) and with the small amount of Nb concentration used for doping.

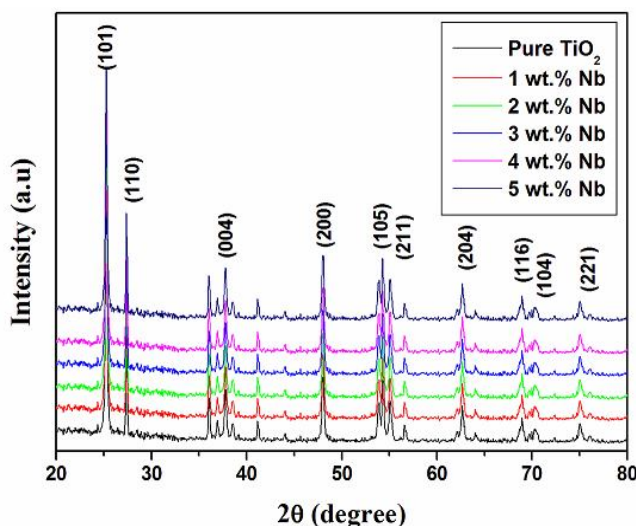


Fig. 1. XRD pattern of pure and Nb (5 wt.%) doped TiO₂ thin films.

The average crystalline sizes of the Nb-TiO₂ thin films were calculated by using Scherrer's equation [14].

$$d = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where d is the mean crystallite size, K is the shape factor taken as 0.89, λ is the wavelength of the incident beam, β is the full width at half maximum and θ is the Bragg angle. The average crystalline size of TiO₂ was found to be 25 nm and it was further decrease to 18 nm for 5 wt % Nb doped TiO₂ thin films. This decrease in grain size of TiO₂ suggests that the growth is concealed due to doping of Nb into Ti-site.

TABLE.1
LATTICE PARAMETER AND CRYSTALLITE SIZE OF PURE AND NB DOPED TiO₂ THIN FILMS.

Nb Concentration Wt %	Crystallite size (nm)	Lattice Parameters		Cell Volume (Å ³)
		a(Å)	c(Å)	
0	25	4.694 1	3.185 1	70.18
1	23	4.684 1	3.182 1	69.81
2	22	4.680 1	3.180 1	69.65
3	21	4.679 8	3.179 8	69.63
4	19	4.678 9	3.178 5	69.58
5	18	4.674 5	3.176 7	69.41

B. AFM analysis

Atomic force microscopy (AFM) is a useful technique to determine the surface morphology and particle size of the samples. Figs. 2 shows the 2D and 3D AFM image of pure and Nb doped TiO₂ thin films.. The particles distribution is uniform and also particle size reduces for Nb doped samples when compared to pure TiO₂.. A systematic description of various analytical method used for roughness characterization can be found in ref [15].

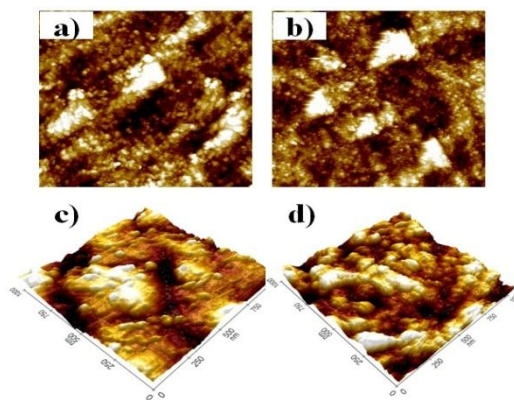


Fig.2. AFM 2D image of a) Pure TiO₂ b) Nb (5 wt.%) doped TiO₂, 3D image of c) Pure TiO₂ d) Nb (5 wt.%) doped TiO₂ thin films.

The Rrms values of pure and Nb doped TiO₂ were found to be 31, 22 nm respectively. These values are good in agreement with the crystalline size calculated from XRD results.

C. UV-Vis spectra analysis

In order to confirm the optical property and substitution of Nb in to TiO₂ site, the films were characterized by UV-Vis transmission spectra analysis. Fig. 3 a) show the UV-Vis transmission spectra analysis of pure and Nb doped TiO₂ films. Both the films are highly transparent in the visible region and a sharp fall in transmission is observed below 400 nm region. It is found that the absorption edge shifts toward longer wavelength (red shift) with doping of Nb ion. The observed red shift can be attributed to charge transfer transitions between localized d electrons of Nb ion and TiO₂ conduction band or valance band [16].

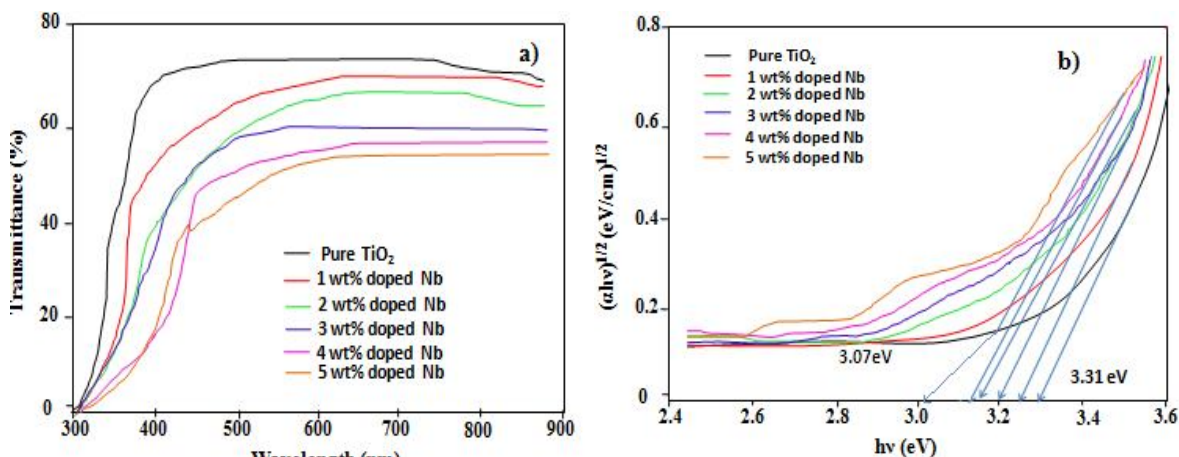


Fig 3. UV-Vis spectra of a) Pure TiO₂ and Nb (1,2,3,4 and 5 wt.%) doped TiO₂ thin films. b) Band gap of Pure TiO₂ and Nb (1,2,3,4 and 5 wt.%) doped TiO₂ thin films.

The absorption coefficient (α) was calculated from the transmission spectra using equation [17],

$$\alpha = 1/t \ln(1/T) \quad \text{----- (2)}$$

Where T is the optical transmission and t is the film thickness. The direct band gap of thin films were calculated from figures 4 b) using the formula [18],

$$\alpha h\nu = A(h\nu - E_g)^m \quad \text{----- (3)}$$

Where α is the absorption coefficient, h is the Planck's constant, ν is the frequency of incident light, E_g is the energy band gap of material and m is the factor governing the direct/indirect, etc.. The band gap energy was calculated as 3.32 eV and 3.07 eV for pure and Nb doped TiO₂ films. The observed decrease in band gap energy confirms that Nb⁵⁺ ion substituted in TiO₂ host lattice. Similar findings were observed in Fe doped TiO₂ thin films [19].

D. Photoluminescence spectra analysis

PL emission spectra have been widely used to investigate the efficiency of charge carrier trapping, migration and transfer, and to understand the fate of electron hole pairs in the semiconducting oxide materials [19]. Fig.5 shows the PL emission spectra of both pure and Nb doped TiO₂ films measured from 300 to 600 nm using a 325 nm He–Cd laser. The pure TiO₂ samples show UV emission (395 nm), blue-green (425, 467 nm) and green emissions (490 nm) were observed at 415 and 490 nm respectively.

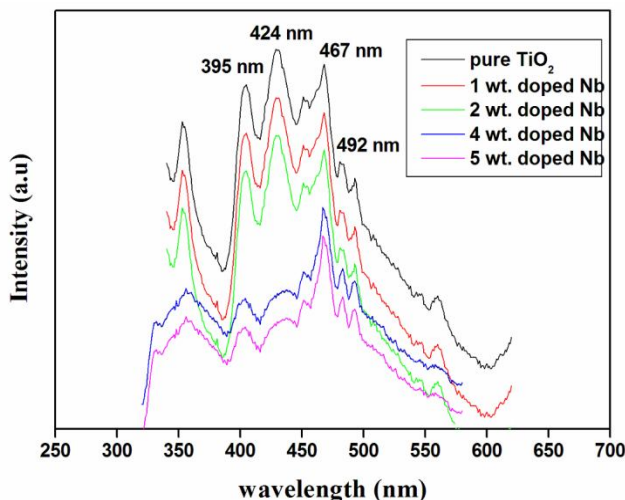


Fig. 4. Photoluminescence spectra of Pure and Nb (1,2,4 and 5 wt.%) doped TiO₂ thin films.

We attributed the UV emission to dangling bond and structural defects. The broad blue emission to electron transition mediated by defect levels in the band gap, such as oxygen vacancies, Ti interstitials. After substitution of Nb⁵⁺ ion all the emission peak shifts a little to lower energy with decreased intensity. The incorporation Nb⁵⁺ ion in TiO₂ host lattice and decreasing the optical band gap energy was also confirmed by UV-VIS absorption spectroscopy. The green emission peak (490 nm) was related to V⁺_O oxygen vacancies.

F. Electrical measurements

The electrical resistivity of the annealed films of both pure and Nb doped TiO₂ was determined in the temperature range from room temperature to 500°C by using four probe method (Scientific equipment, Roorkee, India) with ± 0.5 accuracy.

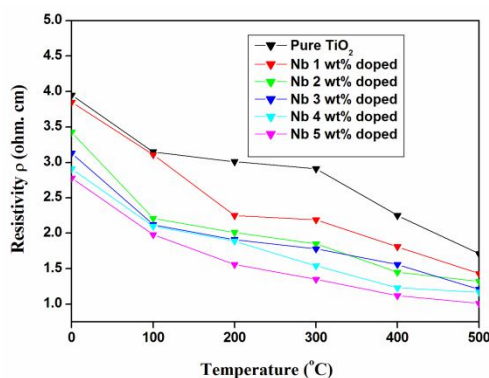


Fig. 5. Electrical Resistivity measurements of Pure and Nb (1.2.3.4 and5 wt.%) doped TiO₂ thin films.

Fig.5 shows the electrical resistivity measurement of pure and Nb doped TiO₂ films as a function of temperature. The resistivity of pure TiO₂ was found to be 1.71Ω.cm and 1.01Ω.cm for pure and Nb doped at 500°C respectively. The observed decrease in resistivity due to Ti⁴⁺ ions have more concentration in films obtained with high annealing temperature regarding the O²⁻ ions, which results in an increase in the free electron concentration there after there is a decrease in film's resistivity. The resistivity drastically decreased for Nb doped TiO₂ films, because Nb-doped TiO₂ could exhibit a stronger n-type character and a higher electronic conductivity than undoped TiO₂ as the electron concentration in the titania lattice might increase and the Fermi level might be shifted closer to the conduction band level. The extracted band gap values of the annealed Tio2 films slightly decreases from 3.32 eV to 3.07eV. The results, suggested that the n-type semiconducting behaviour of Nb-doped TiO₂ is enhanced by inducing oxygen deficiency related to Nb⁵⁺ states, which additionally donate of free electrons to the formation of d-orbital conduction paths. The preliminary results obtain from the electrical measurements confirm that Nb doping has strong influence in the electrical properties of TiO₂ thin films and these films are more suitable for high performance gas sensor device.

IV. CONCLUSIONS

In summary, we have successfully synthesized Nb doped TiO₂ thin films by chemical bath deposition method. The diffraction peaks of both samples are ascribed to the tetragonal anatase phase of TiO₂. The average crystalline size of TiO₂ was found to be 25 nm and it was further decrease to 18 nm for 5 wt % Nb doped TiO₂ thin films.. The surface of the films is very smooth and the uniform crystalline size. The surface roughness has been found to decrease with the increase of the dopant concentration as investigated by atomic force microscopy. A considerable red shift in the absorption edge was found to be Nb doped TiO₂ by UV-Vis absorption spectra. The defect in band gap energy and oxygen vacancy was analysed by using PL emission spectra. The drastic decrease of resistivity or increase the conductivity of Nb doped TiO₂ confirm the Nb doping has significant improvement in the electrical properties of TiO₂ films. So these types of materials are preferable of photo catalytic and gas sensing applications.

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