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Characterization of nanostructured Nd-doped TiO_2 thin film synthesized by spray pyrolysis method: Structural, optical and magneto-optical properties

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Abstract

Neodymium doped titanium oxide thin films with mole ratio Nd/Ti = 0, 6, 10, 15, 20, 25% were deposited on glass substrate by spray pyrolysis technique. The structural properties, surface morphology and absorption spectra of thin films have been obtained using X-ray diffraction (XRD), scanning electron microscope (SEM) and UV-Vis spectrophotometer, respectively. The XRD patterns show formation of unique phases of brookite, orthorhombic, hexagonal. Thin films were amorphous for 25% dopant. The optical band gap has been increased with increasing of dopant. The presence of Nd in the TiO_2 lattice causes a weak ferro-magnetism in the thin films at room temperature.

Keywords: Titanium oxide, Photo catalyst, Brookite, Room temperature ferromagnetism, Spray pyrolysis.

Introduction

After discovering the Honda-Fujishima's work, titanium oxide's thin layers attracted the attentions of many scientists and researchers because of its antibiotic and cleaning usages; it was also a replaced case for photo catalyst surfaces (Mori, 2005; Peng *et al.*, 2004; Matsushima *et al.*, 2007).

It also uses in different industries such as color, dentists and automobile industries. Using the nanotechnology and gap engineering, recently researchers and scientists decided to enhanced the thin films gap properties by taking various dopant such as Al, Li, Nb and some methods like chemical vapour deposition (CVD) (Nolan *et al.*, 2006), physical vapour deposition (PVD), pulsed laser deposition (PLD) (Suda *et al.*, 2005), sol-gel (Que *et al.*, 2006); so make it appropriate for photo catalysis applications.

In this research, neodymium doped titanium oxide thin films prepared on amorphous substrate by spray pyrolysis method and structural, optical and magneto-optical properties were investigated.

Experimental procedure and details

Primary solution for spray, gained from diluted 10 cc titanium isopropoxide (TTIP) in 30 cc pure ethanol (99.9%) that was fixed in all steps. Dopant solution gain with respect to the mole ratio of Nd/Ti in each step, and by solving neodymium chloride in ethanol appropriately; then it adds to primary solution to making the spray solution. Other parameters likewise carrier gas pressure and rate of spray were fixed at 2.5 atm and 5 cc/min, respectively. The worthwhile point here is the deposition temperature, since the phase formation of Nd in the structure of TiO_2 occurs at 575 ^oC, it was the best choice for substrate temperature. [Nd] concentration was changed from 0-25% to be able to investigate the effect of doping in TiO_2 properties.

Discussion

Structural properties

Fig.1 shows the X-Ray diffraction patterns of the films with different Nd value. Increasing dopant ratio has led to increasing amorphous structure in 25% prepared sample. The noticeable point is that making brookite phase occurs here in low temperature that happens because of neodymium in structure of titanium oxide. Also, tensity in structure has led to shape the hexagonal phase in some layers.

Microscopic properties

In order to obtain more quantitative information about the surface morphology, SEM images are presented in Fig. 2 which confirms the existence of particles in nanometric scale. It has been observed that film without dopant has uniform topology and increasing in dopant ratio lead to increasing in particle size and roughness. The average size of the agglomerated particles was measured to increase from 25 to 200 nm with dopant ratio from 6% to 25%. It is evident at the higher concentrations the agglomeration occurred more often, which probably leads to the sharp increase of the surface roughness.

Optical and magneto-optical properties

Fig. 3 shows the optical transmission spectrum for the samples. The optical band gap E_g was calculated using Tauc's plot (Tauc, 1966; Sarhaddi *et al.*, 2010) ($(\alpha h\nu)^{1/2}$ vs. $h\nu$), as shown in Fig. 4. The value of α is determined from transmission spectra. The photon energy at the point where $(\alpha h\nu)^{1/2}$ is zero represents E_g. It shows increasing of energy gap by increasing in dopant ratio in the samples; this is because of increasing of tension in structure and shift in valence and conductant bands towards each other. Moreover, the case of 25% has energy gap of 3.03 eV for amorphous certain structure.

For investigation on effect of neodymium presence in magnetic properties of titanium oxide thin films, Kerr-Faraday effect at room temperature were measured, then

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Fig. 1. X-Ray Diffraction patterns of the films prepared with different [Nd]/[Ti] mole ratio.

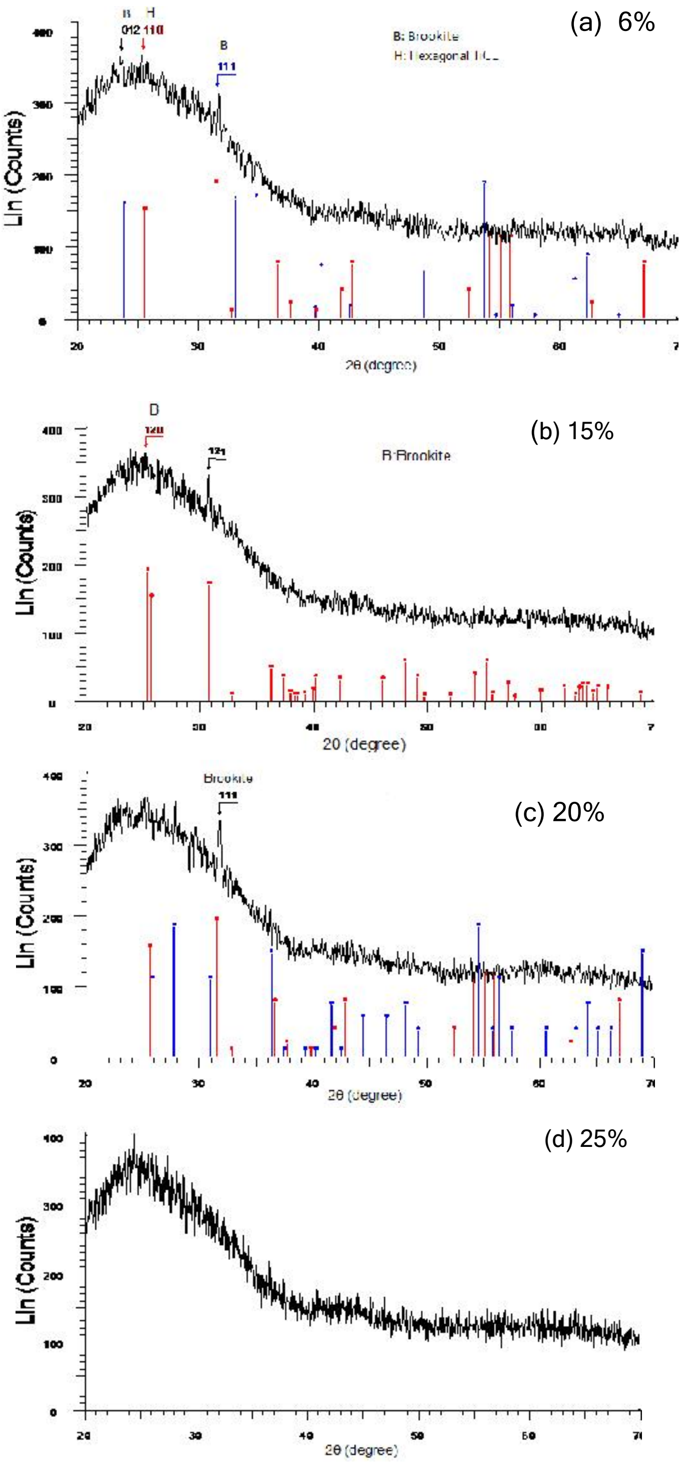

Fig. 2. SEM micrographs of thin films with different [Nd]/[Ti] mole ratio.

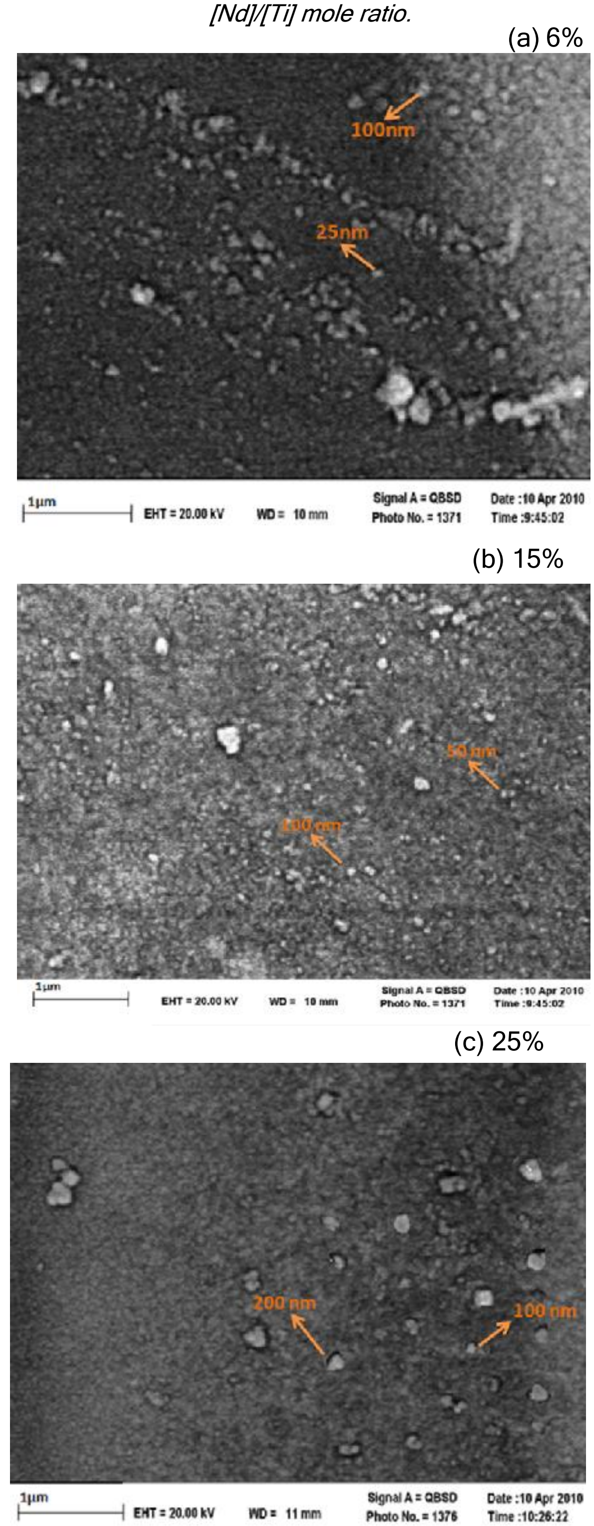

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Fig. 3. Transmission spectra of the layers for different dopant ratio

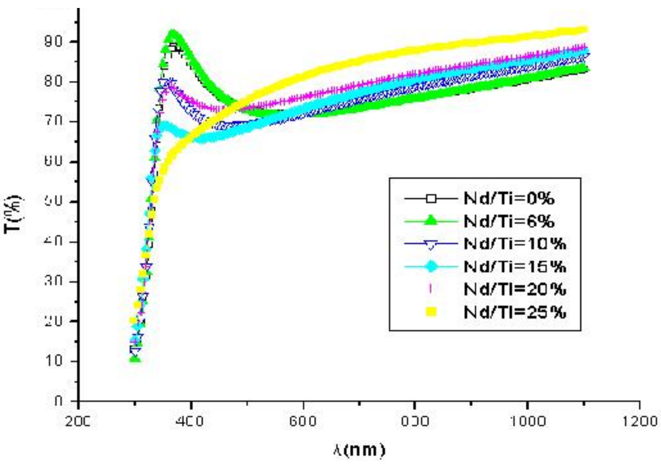


Fig. 4. Absorption spectra, the energy gap obtained by extrapolating the linear absorption edge part.

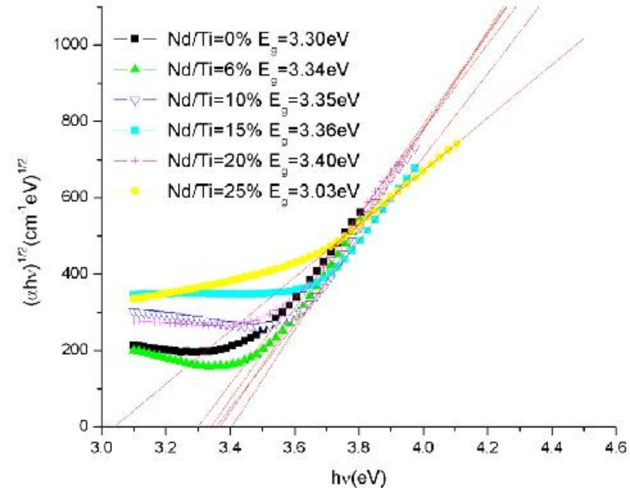
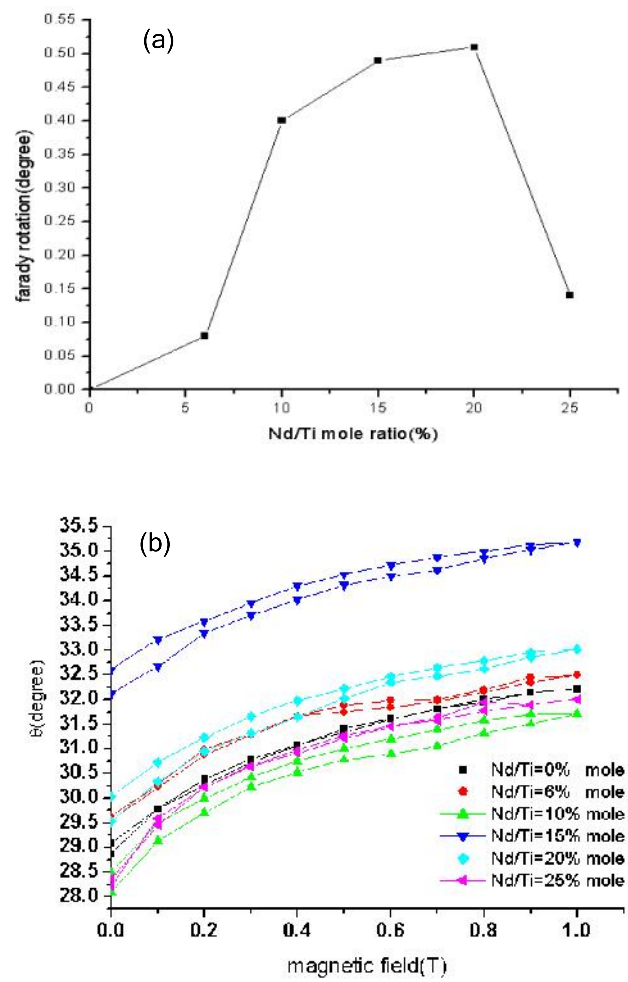


Fig. 5. Kerr-Faraday rotation in room temperature ($T=300^{o}K$) Vs.(a) dopant ratio (b) magnetic field



by using Malus law (Nolan *et al.*, 2006; Amrani *et al.*, 2009) the magnetization were calculated respect to angle of rotation and dopant ratio (Fig.5).

Since Nd^{3+} have radii bigger than Ti^{4+}, it is predictable the deposition of thin films directly related to the Nd/Ti mole ratio. The amorphous phase upper than 25% shows this and increasing of the band gap respect to mole ratio is another proof. It was discussed completely by Amrani *et al.* (2009). It shows week ferro-magnetism effect by increasing in dopant ratio in crystal lattice of titanium oxide. The reason is probably the produced donor and acceptor states at the gap edges and the carrier interaction in the levels with localized magnetic moments of neodymium "f orbital" under RKKY weak interaction (Yibing & Chunwei, 2004; Priour & Des Sarma, 2006). This effect disappeared for the sample with 25% dopant. It proves this process is strongly depended to band structure and localized states. The worthwhile point here is the presence of f-orbital of Nd which has localized electron and forms a spin interaction with the p-orbitals of oxygen and cause a weak ferromagnetism in the thin films.

Conclusion

Deposition of doped thin films by spray pyrolysis technique was successful. The neodymium doped titanium oxide (Nd: TiO_2) thin films with unique brookite and hexagonal phase were deposited on glass substrate. Optical studies show the increasing of band gap in neodymium presence. The films had high transmittance in visible spectra range. Kerr-Faraday effect measuring shows week ferro-magnetism in the layers, so it may be because of the presence of neodymium in RKKY interaction.

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