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Effect of Substrate Temperature on Nitrogen Doped Titanium Oxide Thin Films

B.V. Krishna Reddy[1], A. Sivasankar Reddy[1*], V. Sravanthi[1], T. Srikanth[1], R. Subba Reddy[1], P. Sreedhara Reddy[2], S. Uthanna[2], B.Radha Krishna[3], Ch. Seshendra Reddy[4]

[1]Department of Physics, VikramaSimhapuri University P.G. Centre, Kavali -524201, A.P., India
[2]Department of Physics, Sri Venkateswara University, Tirupati- 517502, A.P., India
[3]Department of Physics, NBKR Institute of Science& Technology, Vidyanagar-524413, India
[4]Department of Polymer science and engineering, Korea National University of Transportation, Chungju, Republic of Korea.
**Corresponding author: A. Sivasankar Reddy*

Abstract: *Nitrogen doped titanium dioxide (NTiO_2) thin films were prepared on glass substrates at different substrate temperatures by dc reactive magnetron sputtering technique and study the compositional, structural, surface morphology and optical properties. The composition of Ti and nitrogen increased with increasing the substrate temperature.The crystallinity of films started at 623K and increases with increasing the substrate temperature. From the Raman studies, the films deposited at substrate temperature of 623K, two broad peaks are appeared at 395 and 640 cm^{-1} are from TiO_2anatase phase. The absorption edge of the films shifted towards the visible light region by increasing the substrate temperature from 303 to 698K. The films surface changed from hydrophobic to hydrophilic nature by increasing the substrate temperature.*

Keywords:_Titanium dioxide, Nitrogen doped, Thin films, Sputtering, Substrate temperature_

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I. Introduction

Titanium dioxide (TiO_2) has found many industrial applications such as self-cleaning, energy conversion, antibacterial, surfaces with antifogging due its unique properties like non-toxicity, biologically and chemically inert, stable to corrosion, photocatalytic and hydrophilic[1-3]. Among these one particulararea of interest for TiO_2 is its photocatalytic activity forenvironmental protection[4]. However, undoped TiO_2 is most effectivephotocatalysis only in the ultraviolet (UV) region due to its large band gap of 3.2and 3.0 eV for anatase and rutile respectively [5-6]. In order to extend this photocatalysis behavior into the visible light region, it is necessary to reduce the band gap and this can be achieved by proper doping of TiO_2 with metals (e.g. Fe, Cu, Ag, Ni) or non-metals (e.g. N, F, C, S, P)[7]. However, metal-doped into TiO_2 suffer from thermal instabilities[2]. Among non-metals, nitrogen (N) is one of the most promising dopant material for TiO_2 films which narrowing the band gap effectively and it enriched the photoactivity of the TiO_2 under visible light region without reduction of the UV photoactivity. Various thin films deposition methods like sputtering [8-9], laser ablation [10], aerosol-assistedchemical vapor deposition [11] and sol-gel [12] have been used to prepare the N doped TiO_2 films. Among these techniques, dc magnetron sputtering is one of best technique due to its good adherent to substrate, no direct heating, uniformity, high deposition rates and easy to control the chemical composition of the film. In this work, we investigated the effect of substrate temperature on the compositional, structural, microstructural, morphological and optical properties of dc magnetron sputtered NTiO_2 films.

II. Experimental

N doped TiO_2(hereinafter denoted as NTiO_2) thin filmswere deposited on glass substrates at different substrate temperatures ranging from 303 to 698K by using dc magnetron sputtering. A high purity (99.99%) Ti target with 3mm thick and 100mm dia was used as sputtering target. The distance between target to substrate was 65mm and the substrate rotation was fixed at10rpm. Before deposition, the vacuum chamber was evacuated to a base pressure of $5x10^{-4}$ Pa by the combination of a rotary pump and diffusion pump. Sputtering was performed in pure argon (Ar), oxygen and nitrogen ambient through a mass flow controller. The target was pre-sputtered for 15min in Ar environment to remove contaminants on the target. The deposition pressure was 2.5 Pa. The films thickness was about 200nm and was measured with step method. The chemical composition of the films was analyzed by energy dispersive spectroscopy (EDS).The structural analysis of deposited films was carried out by X-ray diffractometer. The microstructure and surface morphology of the films were observed using a scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. Optical transmittance spectra in the UV-Visible range were measured by double-beam UV-Vis-NIR spectrophotometer.

III. Results and Discussion

To prepare $NTiO_2$ films, oxygen defects are necessary and these vacancies are act as the photocatalytic centers [13-14]. The elemental composition of N, O_2 and Ti in $NTiO_2$ films at different substrate temperature was determined by EDS and are listed in Table 1. The atomic percentage of N and Ti increased with increasing of substrate temperature, whereas, atomic percentage of oxygen decreased. EDS spectra of $NTiO_2$ films at different substrate temperatures is shown in Fig.1.

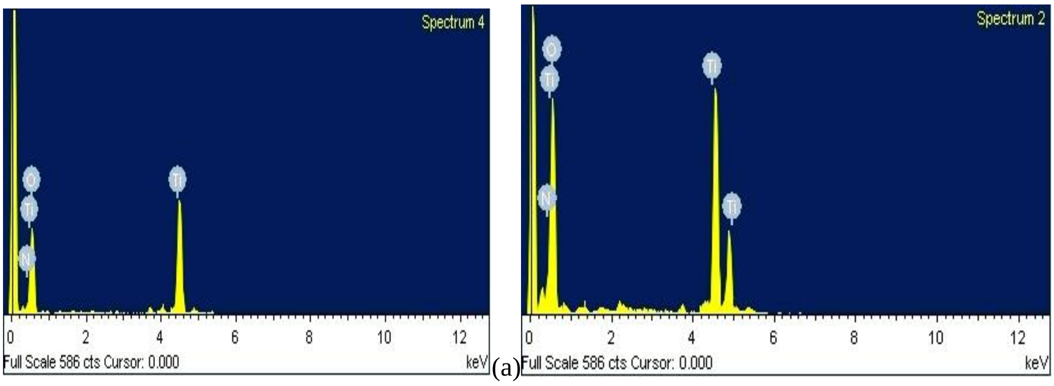

Fig.1. EDS spectra of $NTiO_2$ films at different substrate temperatures (a) 303K and (b) 623K.

Table 1. Elemental composition of $NTiO_2$ films at different substrate temperatures

Sample history	Elemental composition		
	Ti (at%)	O (at%)	N (at%)
303K	21.67	72.23	6.10
623K	23.27	68.19	8.54
698K	24.78	64.32	10.90

3.1. Structural properties

Fig.2. shows the XRD patterns of $NTiO_2$ films deposited at different substrate temperatures. The films deposited below the substrate temperature of 623K no diffraction peak is observed, which indicates the $NTiO_2$ film is in the amorphous state.When the films deposited at substrate temperature of 623K exhibited a broad peak with low intensity related to (101) of anatase phase, indicating the beginning of crystallinity of the films. On further increasing the substrate temperature to 698K the peak intensity increased slightly and no other phases like rutile are observed. In general, the crystallinity of TiO_2 films started at higher temperatures when it deposited on the amorphous substrates. Gibbs free energy of anatase phase is lower than that of rutile phase,hence, the TiO_2films exhibited anatase phase rather than rutile at this temperatures [15]. The TiN phases are not observed in this results due to low chemical acitivity of N_2 compared to O_2 with Ti. Wang et al. [4] observed that the crystallinity of N doped TiO_2 films increased after annealed the films at higher temperatures.

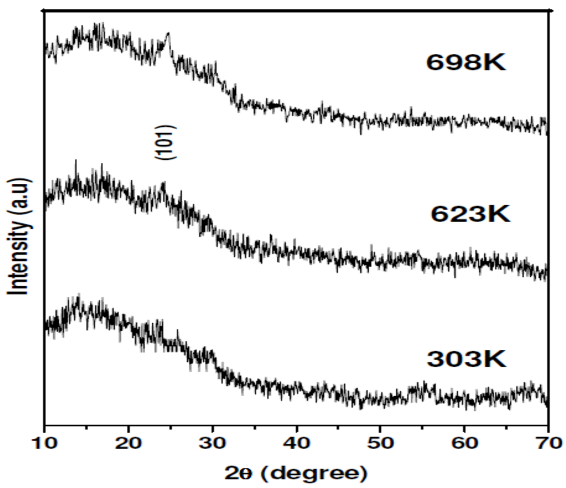

Fig.2. XRD patterns of $NTiO_2$ films at different substrate temperatures.

3.2. Microstructure and surface morphology properties

The SEM images of $NTiO_2$ films at different substrate temperatures are shown in Fig.3. The films exhibited very fine grains with dense structure at substrate temperature of 303K.The films deposited at substrate temperature of 623K exhibited small grains without cracks and voids. Beyond this substrate temperaturegrainsize increased due to improvement of crystallinity of the films.Chunyu et al. [16] observed that the grain size of the films increased with increasing the annealing temperature in rf magnetron sputtered N doped TiO_x films.

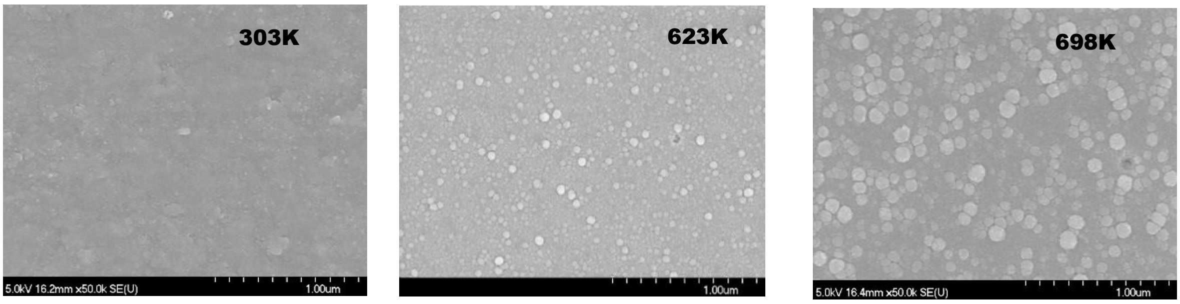

Fig.3. SEM images of $NTiO_2$ films at different substrate temperatures.

The AFM analysis shows that surface morphology and RMS roughness of $NTiO_2$ films. The AFM images of $NTiO_2$ films at different substrate temperatures are shown in Fig.4. The surface morphology of films was strongly influenced by the substrate temperature. The films deposited at substrate temperature of 303K shows islands with rough surface. When the films deposited at substrate temperature of 623K exhibited fine grains with smooth surface. On further increasing the substrate temperature to 698K, films show bigger grains with irregular shape and high surface roughness. The obtained RMS roughness values are 3.8, 1.1 and 2nm for substrate temperature of 303, 623 and 698K, respectively.

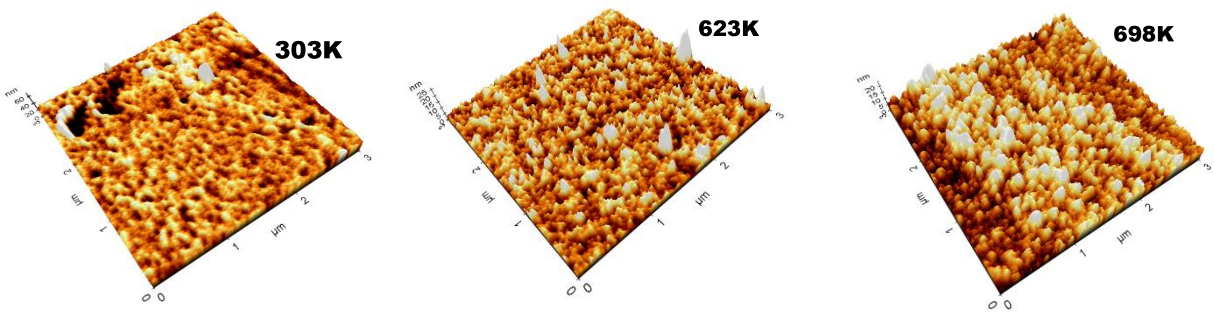

Fig.4. AFM images of $NTiO_2$ films at different substrate temperatures.

3.3. Raman studies

Fig.5. shows the Raman spectra of $NTiO_2$ films at different substrate temperatures. The films deposited at 303K, there is no peak in the spectra and it implies that films are amorphous. When the films deposited at substrate temperature to 623K, two broad peaks are appeared at 395 and 640 cm^{-1} are from TiO_2anatase phase [4]. On further increasing the substrate temperature to 698K, the peaks intensity increased and broadness was decreased. The increases of the peak intensity with substrate temperature is due to increase in crystallinity of the films.There are no peaks related to rutile phase of TiO2 and/or TiN phase were observed. This results are good consistent with XRD results.

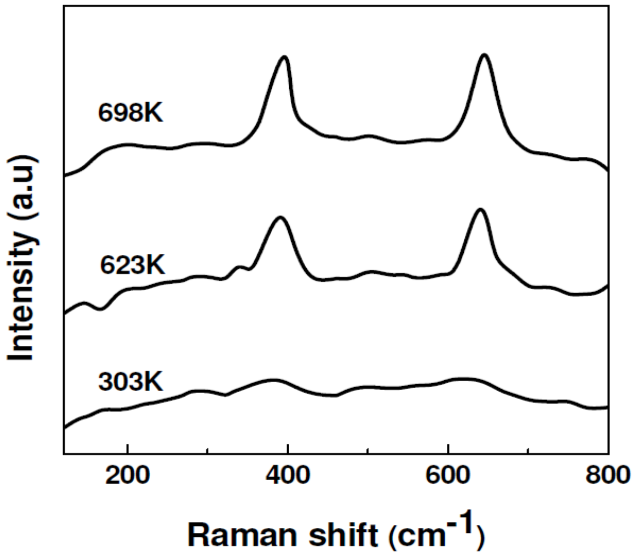

Fig.5. Raman spectra of $NTiO_2$ films at different substrate temperatures.

3.4. Optical properties

Fig.6. shows the absorption spectra of the $NTiO_2$ films at different substrate temperatures. The absorption edge of the films shifted towards the visible light region by increasing the substrate temperature from 303 to 698K, which is evidence of a narrowed band gap of the $NTiO_2$ films. The shifting of the absorption edge was due to increasing of the nitrogen incorporation and oxygen vacancies in the films with increasing the substrate temperature. The optical band gap (E_g) of the films was determined from the extrapolation of the linear portion of the plots of $(\alpha h\nu)^{1/2}$ versus (hν) (α is the absorption coefficient, hν is the photon energy). The variation of band gap of$NTiO_2$ films as a function of substrate temperature is presented in Fig.7. It is found that the band gap of the film decreasing from 3.07 to 2.89eV with increasing the substrate temperaturefrom 303 to 698K.

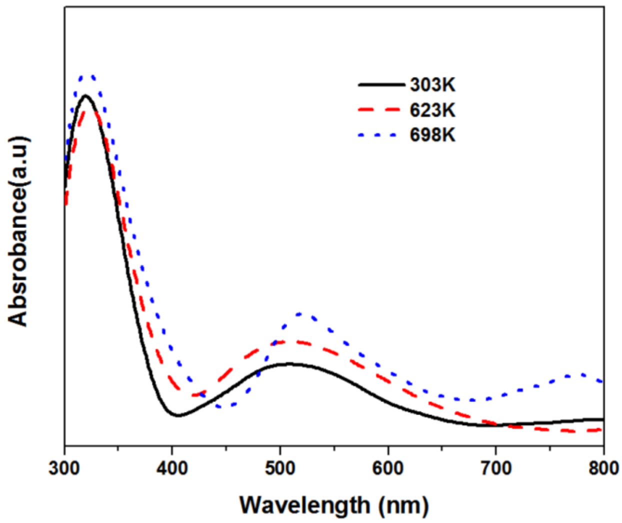

Fig.6. Absorption spectra of the $NTiO_2$ films at different substrate temperatures.

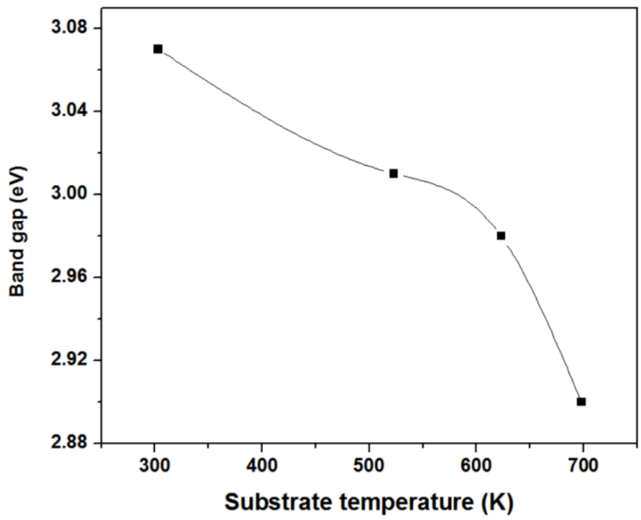

Fig.7. Variation of optical bang gap of $NTiO_2$ films as a function of substrate temperature.

Fig.8. shows the water contact angle (CA) on $NTiO_2$ films surface at different substrate temperatures. The water droplet on the films surface appeared as spherical shape and high CA at substrate temperature of 303K,which indicate that the films having hydrophobic nature due to low surface energy. The CA of water dropletdecreased effectively with increasing the substrate temperature from 303 to 623K, due to increasing the surface energy and decreasing surface roughness and band gap of the films. This behavior suggests that films surface changed from hydrophobic to hydrophilic nature. On further increasing the substrate temperature to 698K the CA is not decreased considerably.

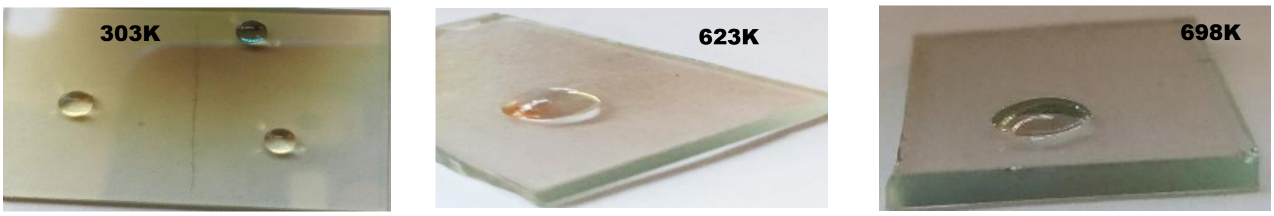

Fig.8. Water droplet on $NTiO_2$ film surface at different substrate temperatures.

IV. Conclusions

$NTiO_2$ thin films were deposited onto glass substrates by dc magnetron sputtering at different substrate temperatures. The atomic percentage of N and Ti increased with increasing of substrate temperature, whereas, atomic percentage of oxygen decreased. The films exhibited anatase phase and crystallinity of the films increased with substrate temperature. The grain size and RMS roughness of the films decreased with increasing the substrate temperatureupto 623K. The band gap of $NTiO_2$ thin films decreasing from 3.07 to 2.89eV with increasing the substrate temperature from 303 to 698K.The contact angle of films decreasing with increasing the substrate temperature from 303 to 623K.

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