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Physical properties of nitrogen doped titanium dioxide thin films prepared by dc magnetron sputtering

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Abstract: In this study, nitrogen doped titanium dioxide (NTiO$_2$) thin films were deposited by dc reactive magnetron sputtering technique on glass substrates at different nitrogen partial pressures and studied the chemical composition, crystalline structure, surface morphology and optical properties. The composition of Ti and nitrogen increased with increasing the nitrogen partial pressures.The films exhibited anatase phase and crystallinity of films increases with increasing the nitrogen partial pressuresupto6x10^{-3} mbar. The films deposited at nitrogen partial pressure of 6x10^{-3} mbar two broad peaks are appeared at 395 and 644 cm^{-1}in Raman spectra and are from TiO$_2$anatase phase.The optical band gap of the films was calculated and a narrowing of the band gap from 3.11 eV to 2.98 eV was observed by increasing the nitrogen partial pressure.

Keywords:*Titanium dioxide, Nitrogen doped, Thin films, Sputtering, Nitrogen content*

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I. INTRODUCTION

Titanium dioxide (TiO$_2$) is most suitable for industrial and environment applications such as energy conversion, self-cleaning, air purification, destruction of microorganisms, etc., after discovery of photocatalytic and hydrophilic properties[1-2]. However, pristine TiO$_2$ is most effectivephotocatalysisunderultraviolet (UV) region only due to its wide band gap of 3.2- 3.0 eV [3-4]. In order to extend photocatalysis behavior into the visible light region, it is necessary to narrowing the band gap and this can be achieved by proper doping of TiO$_2$ with metalsor non-metals[5].Nitrogen (N) is one of the most promising dopant material for TiO$_2$among non-metals tonarrowing the band gap effectively and enriched the photoactivity of the TiO$_2$ under visible light region without reduction of the UV photoactivity. Various thin films deposition methods like sputtering [6], micro-arc oxidation [7], plasma enhancedchemical vapor deposition [8] and sol-gel [9] have been used to prepare the N doped TiO$_2$ films. Among these techniques, dc magnetron sputtering is an industrial scalable technique due to its good adherent to substrate, no direct heating, reproducibility, uniformity over large surface area, and easy to control the process parameters. In this study, we investigated the effect of nitrogen partial pressures on the compositional, structural, microstructural, morphological and optical properties of dc magnetron sputtered N doped TiO$_2$ films.

II. EXPERIMENTAL

N doped TiO$_2$(hereinafter denoted as NTiO$_2$) thin filmswere deposited on glass substrates by using dc reactive magnetron sputtering at different nitrogen partial pressures ranging from 3x10^{-3} to 9x10^{-3}mbar. 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^{-6} mbar 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 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

The films thickness was measured with step method andmaintained around 200nm by adjusting the deposition time. The deposition rate of the films decreases with increasing the nitrogen partial pressures. As increasing the nitrogen partial pressure, the elastic atomic collision frequency of target particles with gas particles increases, consequently the kinetic energy of target particlesreduced and less number of target particles are reached the substrate [10].

3.1. Structural and compositional properties

Fig.1. shows the XRD patterns of $NTiO_2$ films deposited at variousnitrogen partial pressures. The films show the amorphous structure at nitrogen partial pressure of $3x10^{-3}$mbar and as increasing the nitrogen partial pressure to $6x10^{-3}$mbar, the films exhibited (101) of anatase phase with low intensity.Beyond this nitrogen partial pressure, the films crystallinity is decreased. The TiNphase or any other nitrogen containing structures were not identified in the films regardless of the nitrogen partial pressures due to low chemical activity of N_2 compared to O_2 with Ti. The more nitrogen incorporation in the films reduces the crystallinity of the films which is may be due to reduction of the crystallite size or strain development in the films. Peng et al.[10] observed that crystallization quality of the films becomes deteriorated with increasing of N_2 flow rate in N doped TiO_2 films due to thedistortion of TiO_2 lattice.

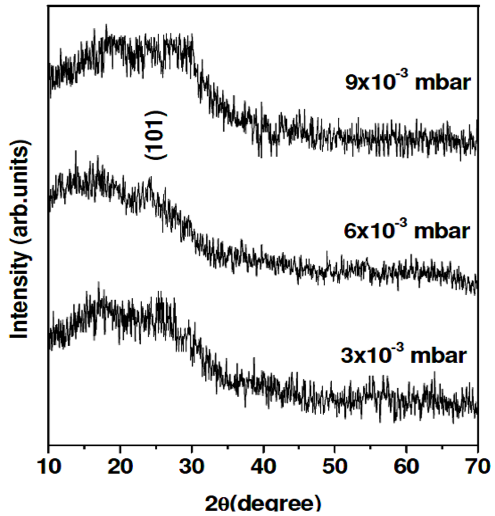

Fig.1. XRD patterns of $NTiO_2$ films at various nitrogen partial pressures.

It is difficult to dope the nitrogen into the TiO_2 lattice and oxygen defects are necessary to prepare N-doped TiO_2 films by the magnetron sputtering method[11]. EDS spectra of $NTiO_2$ films at various nitrogen partial pressures are shown in Fig.2. The atomic percentage of N and Ti increased with increasing of nitrogen partial pressure, whereas, atomic percentage of oxygen decreased. The elemental composition of N, O_2 and Ti in $NTiO_2$ films at various nitrogen partial pressures are listed in Table 1. The oxygen defects concentrationis more in the films deposited at nitrogen partial pressure of $9x10^{-3}$mbar compare to 3 $x10^{-3}$ and $6x10^{-3}$mbar deposited films.

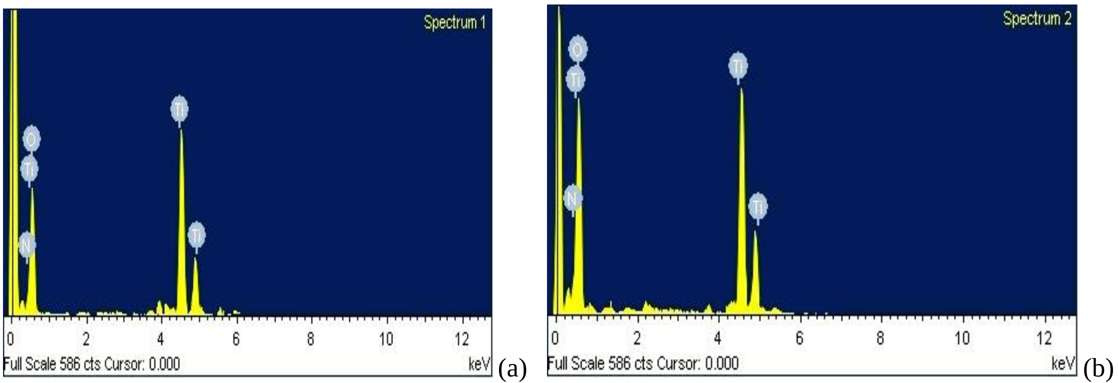

Fig.2. EDS spectra of $NTiO_2$ films at various nitrogen partial pressures (a) $3x10^{-3}$mbar and (b) $6x10^{-3}$mbar.

Table 1. Elemental composition of $NTiO_2$ films at various nitrogen partial pressures.

Nitrogen partial pressure	Elemental composition		
	Ti (at%)	O (at%)	N (at%)
$3x10^{-3}$ mbar	22.18	73.96	3.86
$6x10^{-3}$ mbar	23.27	68.19	8.54
$9x10^{-3}$ mbar	24.96	62.84	12.2

3.2. Raman studies

Raman spectroscopy is one of the best technique for qualitative and quantitative analysis of compounds. Fig.3. shows the Raman spectra of $NTiO_2$ films at various nitrogen partial pressures. From the Raman spectra, there is no significant peak appeared in the films deposited at nitrogen partial pressure of $3x10^{-3}$mbar and it indicates that films are amorphous. As increasing the nitrogen partial pressure from $3x10^{-3}$ to $6x10^{-3}$mbar two broad peaks are appeared at 395 and 644 cm^{-1} are from TiO_2anatase phase [4]. Beyond this nitrogen partial pressure, the peaks intensity decreased and broadness was increased. It deduced that the more nitrogen doping has reduced crystallinity of the films. There are no peaks related to rutile phase of TiO_2 and/or TiN phase were observed. This results are good consistent with obtained XRD results.

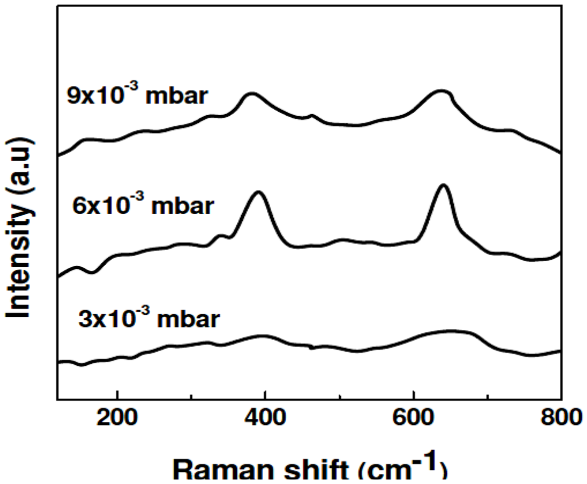

Fig.3. Raman spectra of $NTiO_2$ films at various nitrogen partial pressures.

3.3. Microstructure and surface morphology

The SEM images of $NTiO_2$ films at various nitrogen partial pressures are shown in Fig.4. The films exhibited irregular shape grains with patched type surface at nitrogen partial pressure of $3x10^{-3}$mbar.The films deposited at nitrogen partial pressure of $6x10^{-3}$mbar exhibited homogeneous surface with small grains without cracks and voids. The films deposited at higher nitrogen partial pressure of $9x10^{-3}$mbar islands of grains,voids and thick boundaries are appeared clearly.

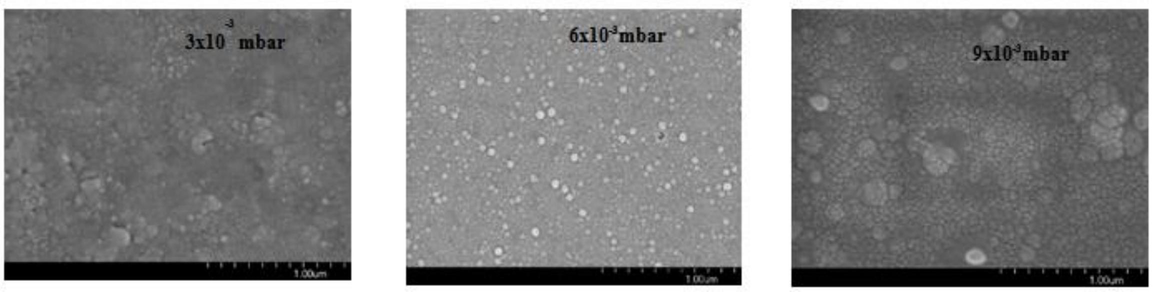

Fig.4. SEM images of $NTiO_2$films at various nitrogen partial pressures.

The surface morphology can influence the photocatalytic and wettability of the films. The AFM images of $NTiO_2$ films at various nitrogen partial pressures are shown in Fig.5. From the images, it can be seen clearly that surface morphology of films waschanges by varying the nitrogen partial pressures. The films deposited at nitrogen partial pressure of $3x10^{-3}$mbar shows the combination of small grains andislands with rough surface. When the films deposited at nitrogen partial pressure of $6x10^{-3}$mbar exhibited fine grains with smooth surface. On further increasing the nitrogen partial pressure to $9x10^{-3}$ mbar, films exhibited irregular shape grains and islands. The obtained RMS roughness values are 3.2, 1.1 and 2.4nm for nitrogen partial pressure of $3x10^{-3}$, $6x10^{-3}$ and $9x10^{-3}$mbar, respectively. The decreasing of the surface roughness with increasing ofnitrogen flux was observed by Grigorovet al.[12] in RF reactive magnetron sputtered nitrogen doped TiO_2 films.

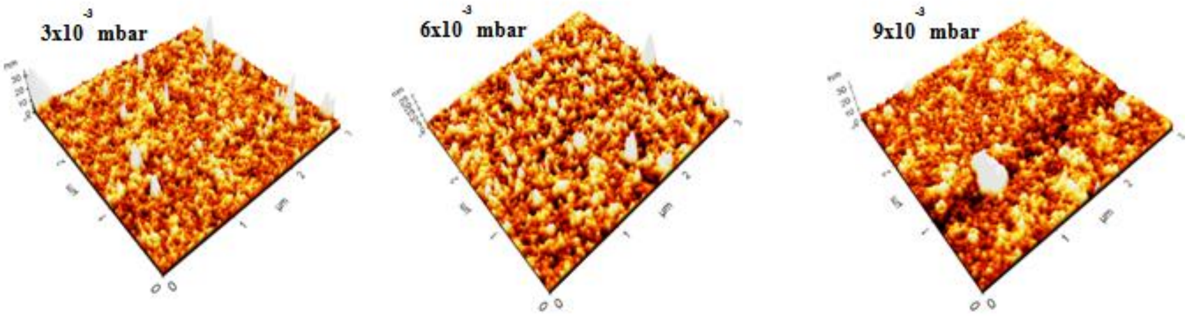

Fig.5. AFM images of $NTiO_2$films at various nitrogen partial pressures.

3.4. Optical properties

The main purpose of nitrogen incorporation into TiO_2 is to extend the light absorption edge from ultraviolet to visible light region in order to make use of the majority of the ambient light spectrum. Fig.6. shows the absorption spectra of the $NTiO_2$ films at various nitrogen partial pressures. As increasing the nitrogen partial pressures, the absorption edge shifted towards the higherwavelength side(visible region), which is evidence of narrowing the band gap of $NTiO_2$ films.As a result, the visible light induced photocatalytic ability of $NTiO_2$ films increases.The visible light absorption of N-doped TiO_2 arises from the nitrogen incorporation and oxygen defects. The N-induced mid-gap levels formed slightly above the top of valance band and shift the valance band edge, and additionally the oxygen defects form defect energy levels in the TiO_2 forbidden band, and also pulldown the conduction band of TiO_2 [11]. Mohamed et al. [13] observed the improving of the absorption capabilities in the visible light in nitrogen doped in TiO_2nanorods due to introduce of localized N 2p states above the valance band.

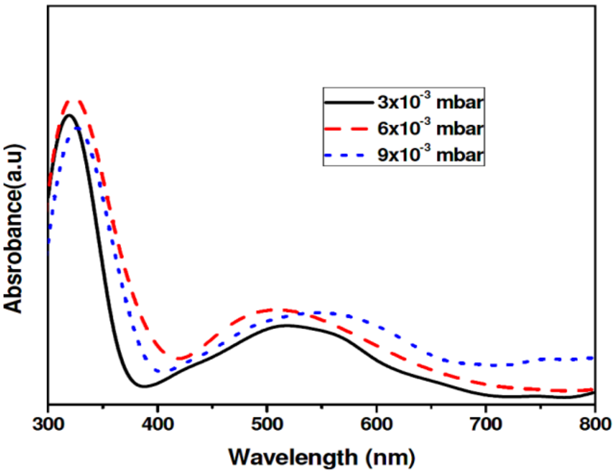

Fig.6. Absorption spectra of the $NTiO_2$ films at various nitrogen partial pressures.

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 $(h\nu)$ (α is the absorption coefficient, $h\nu$ is the photon energy). Fig.7 shows the optical band gap of $NTiO_2$ films at various nitrogen partial pressures. It is found that the band gap of the film decreasing from 3.11 to 2.98eV with increasing the nitrogen partial pressure from $3x10^{-3}$ to $6x10^{-3}$ mbar. The band gap of the films increased slightly at higher nitrogen partial pressure of $9x10^{-3}$mbar. The narrowing of the band gap is due to nitrogen incorporation and oxygen defects which are great effect on the valence band and conduction band of TiO_2 [14].

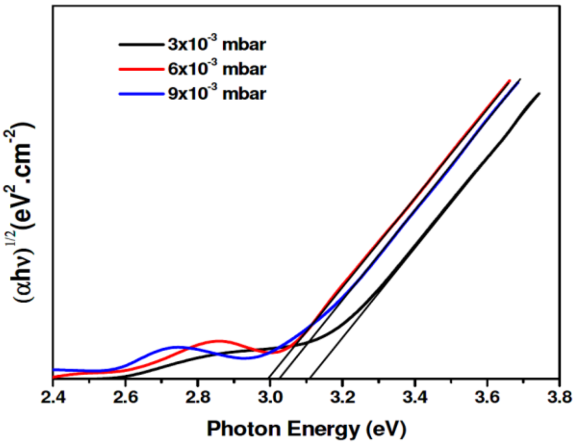

Fig.7. $(\alpha h\nu)^{1/2}$ versus (hν) for $NTiO_2$films at various nitrogen partial pressures.

Fig.8. shows the water drop contact angle (CA) on $NTiO_2$ films surface at variousnitrogen partial pressures. The films deposited at low nitrogen partial pressure of $3x10^{-3}$mbar, the water droplet CA is high andappeared as spherical shape. This indicate that films having hydrophobic nature due to low surface energy. The CA of water dropletdecreased effectively with increasing the nitrogen partial pressure to $6x10^{-3}$mbar due to decreasing the surface roughness and band gap,and increasing the surface energy of the films. This behavior suggests that films surface changed from hydrophobic to hydrophilic nature. However, the CA angle is increased again when the films deposited at higher nitrogen partial pressure of $9x10^{-3}$mbar(not shown here). From these results, one conclusion could be confirmed that the nitrogen partial pressure is one of the most important parameters to control the growth and properties of N doped TiO_2 films.

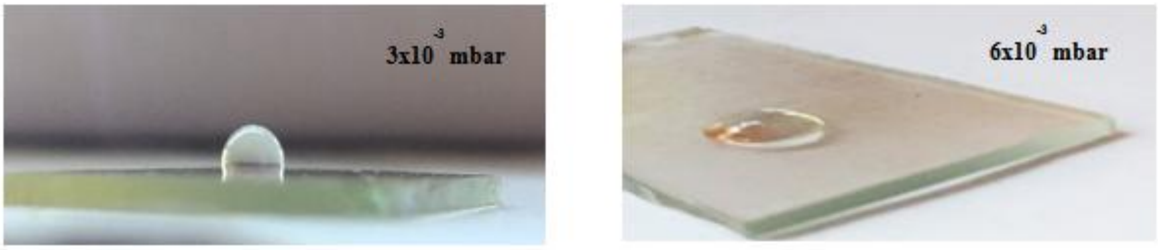

Fig.8. Water droplet on $NTiO_2$films at various nitrogen partial pressures.

IV. CONCLUSIONS

$NTiO_2$ thin films were successfully deposited by dc reactive magnetron sputtering onto glass substrates at various nitrogen partial pressures. The atomic percentage of oxygen decreased with increasing the nitrogen partial pressures. The films exhibited anatase phase at nitrogen partial pressure of $6x10^{-3}$mbar. There are no peaks related to rutile phase of TiO_2 and/or TiN phase were observed in Raman spectra. The decreasing of the surface roughness with increasing of nitrogen partial pressure was observed. As increasing the nitrogen partial pressures, the absorption edge shifted towards the visible region, and narrowing the band gap of $NTiO_2$ films. The contact angle of films decreasing with increasing the nitrogen partial pressure, which is a desirable feature when optical or self-cleaning antifogging materials properties are required.

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