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Influence Of Substrate Bias Voltage On Physical Properties Of Nitrogen Doped Titanium Dioxide Thin Films Deposited By Dc Magnetron Sputtering

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ABSTRACT:*Nitrogen doped titanium dioxide ($NTiO_2$) thin films were deposited on glass substrates using dc reactive magnetron sputtering technique and their composition, crystalline structure, surface morphology and optical properties were studied as a function of substrate bias voltage. The films exhibited amorphous structure irrespective of the substrate bias voltage. From the SEM images, grain size of the films increases with increasing the substrate bias voltage. The optical band gap of the films was narrowing from 3.07 to 3.02 eV with increasing the substrate bias voltage. The wettability of the films increases with substrate bias voltage.*

KEYWORDS:*Titanium dioxide, Nitrogen doped, Thin films, Sputtering, Bias voltage*

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I. INTRODUCTION

Titanium dioxide (TiO_2) is one of best photocatalytic material due to its catalytic activity, anti-photocorrosion, non-toxicity, biologically and chemically inert [1-3]. However, because of its wide band gap 3.2eV makes itmost effective photocatalysis under ultraviolet (UV) region [4-5].Various methods such as doping of metals or non-metals have been used to extend photocatalysis behavior of TiO_2 into the visible light region by narrowing the band gap[6]. Nitrogen (N) is one of the best dopant material for TiO_2 among non-metals due to its high stability, comparable atomic size with oxygen and small ionization,and it enhance the photoactivity of the TiO_2 under visible light region without reduction of the UV photoactivityby narrowing the band gap [7]. Various thin films deposition methods have been used to prepare the N doped TiO_2 films like chemical vapor deposition [8], sol-gel [9], precipitation-peptization method [10], atomic layer deposition [7] and sputtering [11-12]. Among these techniques, dc magnetron sputtering is an industrial scalable technique. The films properties are highly influenced by deposition parameters such as, partial pressures of reactive gas, sputtering pressures, sputtering power, substrate temperature and substrate bias voltages.Among these deposition parameters, substrate bias voltage is most influenced parameter, becauseit allows controlling the energy of the ions bombardment on thegrowing film and can affect the proprieties of the deposited films [13]. In this work, we deposited nitrogen doped TiO_2 films at different substrate bias voltages and study the compositional, structural, microstructural, morphological and optical properties of the films.

II. EXPERIMENTAL

N doped TiO_2(hereinafter denoted as $NTiO_2$) thin films were deposited on glass substrates by using dc reactive magnetron sputtering at different substrate bias voltages ranging from 0 to -150V. 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 at 10rpm. 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. The films thickness was measured with step method and maintained around 200nm by varying the deposition time.

III. RESULTS AND DISCUSSION

In this work, deposition rate of the $NTiO_2$films is inversely propositional to substrate bias voltage. The decreasing of deposition rate with increasing of the substrate bias voltage was observed whichis due to re-sputtering caused by ion bombardment on the surface of the growing film.

3.1. Structural and compositional properties

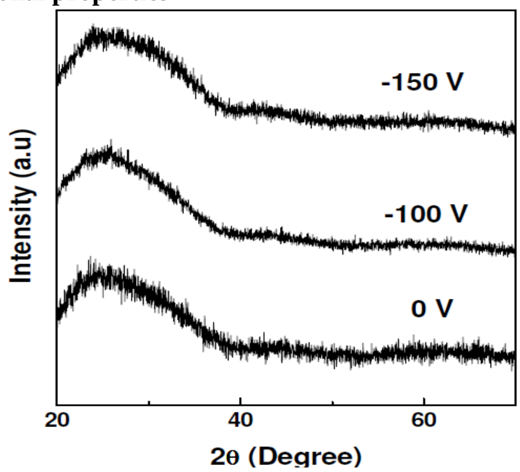

Fig.1. XRD patterns of $NTiO_2$ films at various substrate bias voltages.

Fig.1. shows the XRD patterns of $NTiO_2$ films deposited at various substrate bias voltages. The as deposited films at different substrate bias voltages are show the amorphous structure.It is known that crystallinity of TiO_2 films is started at higher temperatures when they deposited on amorphous substrates. Applying the bias to substrate is also provided thermal energy, however, it is not enough to growth the crystallinity of the $NTiO_2$ films. Additionally, no other phase of Ti or TiN are observed, though their crystalline growth is lower than of TiO_2. From this analysis, we believe that the films having TiO_2 structure but it is lower than the limit of diffractometer.

The reason of nitrogen incorporation into TiO_2 is to extend the light absorption edge from ultraviolet to visible light region. However, to prepare the N-doped TiO_2 films by magnetron sputtering method,oxygen defects are necessary [11]. Fig.2. shows the EDS spectra of $NTiO_2$ films at various substrate bias voltages. The atomic percentage of N and Ti increased and O_2 decreased with increasing the substrate bias voltages from 0 to -100V. Beyond, this substrate bias voltage the atomic percentage of O_2 and Ti increased, whereas N is decreased. The elemental composition of N, O_2 and Ti in $NTiO_2$ films at various substrate bias voltages are listed in Table 1.

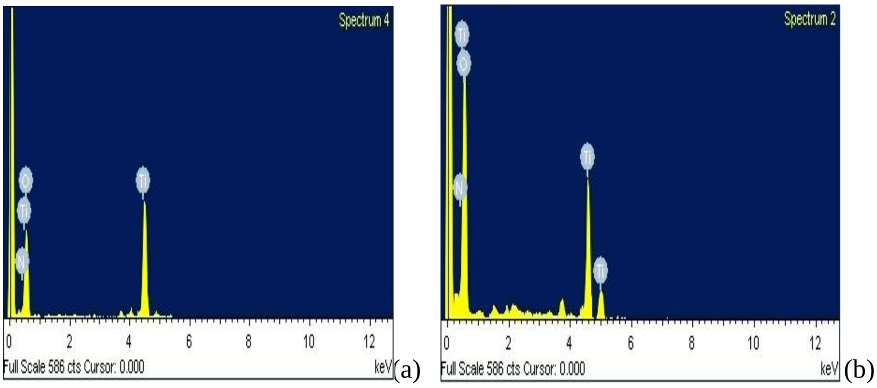

Fig.2. EDS spectra of $NTiO_2$ films at various substrate bias voltages (a) 0V and (b) -100V.

Table 1. Elemental composition of $NTiO_2$ films at various substrate bias voltages.

Substrate bias voltage	Elemental composition		
	Ti (at%)	O2 (at%)	N2 (at%)
0V	21.67	72.23	6.10
-100V	22.31	70.67	7.02
-150V	23.19	71.08	5.73

3.2. Raman studies

Raman spectroscopy is one of the best technique for qualitative and quantitative analysis of compounds. The obtained results of Raman spectroscopy of $NTiO_2$ films at various substrate bias voltages are shown in Fig.3. From the Raman spectra, there is no significant peak observed in the films deposited at substrate bias voltage of 0V, and it indicates that films are amorphous. The films deposited at substrate bias voltage of -100V exhibited two broad peaks at 391 and 635 cm^{-1} are from TiO_2anatase phase.Anatase phase shows six Raman active modes at: 144 [Eg(1)], 197 [Eg(2)], 399 [B1g(1)], 519 [A1g+B1g(2)] and 639 [Eg(3)] [14].On further increasing the substrate bias voltage to -150V, the intensity of the peaks decreased and slightly shifted towards higher wavelength sides. There are no other phases of TiO_2 and/or TiN phase were observed, because, higher temperatures are required to growth rutile phase of TiO_2, and oxygen has a stronger reactivity than nitrogen thus the TiN phases are absence in the present results [15].From the Raman studies, it is confirmed that the anatase phase is predominant in the films.

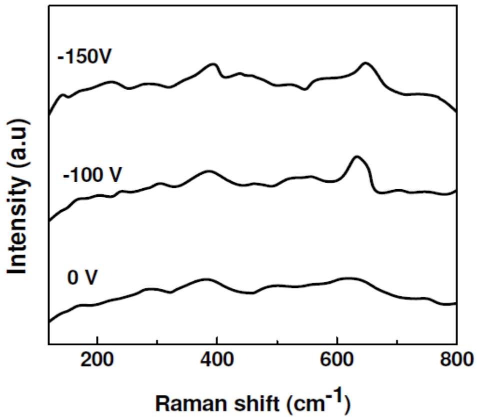

Fig.3. Raman spectra of $NTiO_2$ films at various substrate bias voltages.

3.3. Microstructure and surface morphology

The SEM images of $NTiO_2$ films at various substrate bias voltages are shown in Fig.4. The substrate bias voltage is highly influenced the microstructure of the films. The films deposited at unbiased conditions exhibited fine grains with patched type surface. After applying the bias voltage(-100V) to substrate the film surface is changed and fine grains with homogeneous surface appeared. As increasing the substrate bias voltage to -150V, grains size is increased, islands of grains formed and thick boundaries are appeared on the films surface.

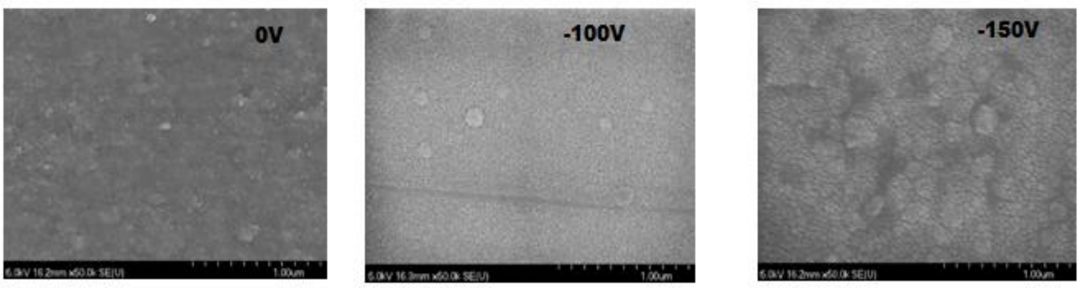

Fig.4. SEM images of $NTiO_2$ films at various substrate bias voltages.

It is known that wettability is improved by fine roughness. Therefore, to enhance the wettability of films a precise control of surface microstructure is need [16]. The AFM images of $NTiO_2$ films at various substrate bias voltages are shown in Fig.5. From the images, the surface morphology of films was changes by varying the substrate bias voltages. The films exhibited pours surface at substrate bias voltage of 0V, whereas, the films deposited at -100V sharp flakes with few clustersare appeared on the films surface. On further increasing the substrate bias voltage, the flakes size decreased and clusters are increased slightly. The obtained RMS roughness values are 3.8, 2.5 and 2.9nm for substrate bias voltage of 0, -100 and -150V, respectively.

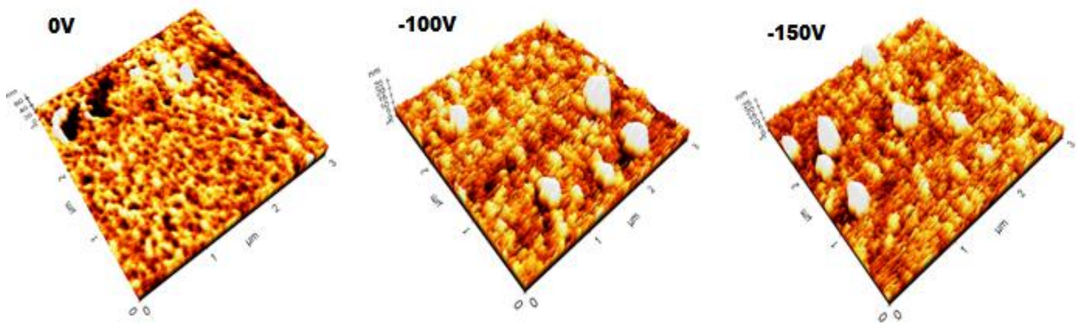

Fig.5. AFM images of $NTiO_2$ films at various substrate bias voltages.

3.4. Optical properties

The visible light absorption of N-doped TiO_2 was due to incorporation of nitrogen and oxygen defects. Fig.6. shows the absorption spectra of the $NTiO_2$ films at various substrate bias voltages. The absorption edge of the films shifted towards into visible region as increasing the substrate bias voltage which is evidence of nitrogen incorporated into TiO_2, consequently narrowing the band gap of $NTiO_2$ films. This results indicates the enhancement of visible light induced photocatalytic ability of $NTiO_2$ films with substrate bias voltages.

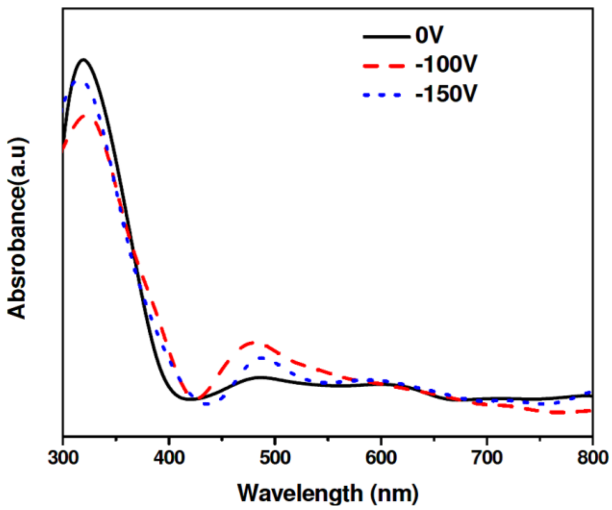

Fig.6. Absorption spectra of the $NTiO_2$ films at various substrate bias voltages.

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 substrate bias voltages. The band gap of the film decreasing from 3.07 to 3.02 eV with increasing substrate bias voltages from 0 to -100V, thereafter it increased slightly at higher substrate bias voltages. The proper incorporation of N into TiO_2 causes valance band edge is shift and form the defect energy levels and pulldown the conduction band, consequently the band gap is narrowing [17]

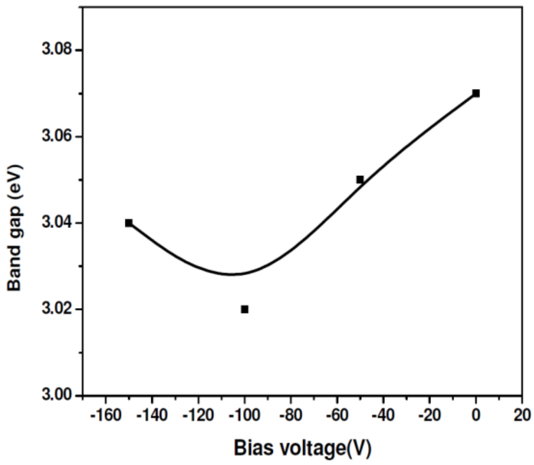

Fig.7. Optical band gap of $NTiO_2$ films as a function ofsubstrate bias voltages.

The wettability of the films is strongly influenced by the surface energy and particle size. Fig.8. shows the water drop contact angle on $NTiO_2$ films surface at various substrate bias voltages. The water droplet on the surface of the films appeared as spherical shape and it indicate that contact angle is very high due to low surface energy and poor microstructure of the films. When the films deposited at substrate bias voltage of -100V the shape of water droplet changed from spherical toburger bun shape due to increasing of the surface energy and particle size. Beyond this substrate bias voltage, the shape is not changed considerably. From this observation, the films deposited at substrate bias voltage of -100V shows good hydrophilic behavior.

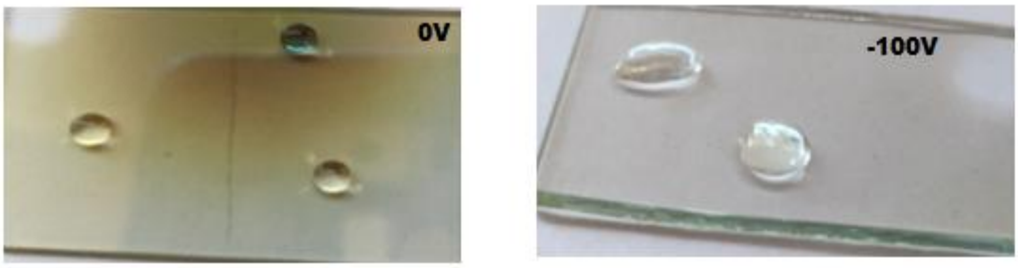

Fig.8. Water droplet on $NTiO_2$ films at various substrate bias voltages.

IV. CONCLUSIONS

$NTiO_2$ thin films were deposited by dc reactive magnetron sputtering onto glass substrates at various substrate bias voltages. The films exhibited amorphous nature irrespective of substrate bias voltage. The Raman results indicates the films grown anatase phase of TiO_2 only. The microstructure of the films increasing with increasing of substrate bias voltage. The more homogenous in films was observed at the substrate bias voltage of -100V.The contact angle of films decreasing with increasing the substrate bias voltage.

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