Correlation of structural, optical and surface morphological properties of N-doped TiO$_2$ thin films prepared by facing targets sputtering technique

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Abstract. In this study, N-doped TiO$_2$ films were prepared by facing targets sputtering technique without substrate heating. Nitrogen partial pressure (P$_N$) was varied from 0 Pa to 0.08 Pa to vary the amount of nitrogen doping in TiO$_2$ thin film. The X-ray diffraction study indicates that increase of nitrogen partial pressure increases replacement of oxygen by nitrogen in TiO$_2$ crystal. An abrupt change of crystal structure, crystallinity, porosity and surface morphological property of N-doped TiO$_2$ thin films is observed for the samples, prepared over nitrogen partial pressure 0.05 Pa.

1. Introduction

Titanium dioxide (TiO$_2$) is a well known semiconductor for various photodriven applications i.e. photocatalytic, photovoltaics and photochromic applications etc [1]. However, its technological application seems to be limited by the need of using an ultraviolet (UV) excitation source. In order to extend absorbance into the visible region, band gap engineering of TiO$_2$ by anionic doping has been receiving huge attention, in which nitrogen doped TiO$_2$ is a prime representative. The substitutional doping of N atom is most effective because its $p$ states contribute to the band-gap narrowing by mixing with O 2$p$ [2]. On the other hand, Irie et al. suggested that the isolated N 2$p$ narrow band formed above the O 2$p$ valence band is responsible for the visible light absorption [3].

A variety of techniques have been employed to prepare N-doped TiO$_2$ in immobilized form and it is revealed that a slight change in preparation approach and synthesis parameters would lead to significant variation in measured property [4]. Among the different preparation techniques, conventional single target dc reactive magnetron sputtering has also been used for the preparation of N-doped TiO$_2$ [5, 6]. However, conventional magnetron sputtering has certain limitations, i.e., high substrate temperature is necessary for achieving good crystallinity etc, which can be overcome by facing targets sputtering (FTS) technique [7]. FTS is an effective technique for the deposition of high quality thin film. Because of its total plasma confinement, the system can achieve deposition, free from the damage, caused by $\gamma$ electrons, O$^-$ ions and high atomic mobility at the surface of the substrate. Although FTS is very popular for the preparation of magnetic and transparent conducting oxide thin films, but it hasn’t been much tried for the preparation of present system of investigation. In our present study, N-doped TiO$_2$ thin films have been prepared on glass substrate by FTS system with different nitrogen partial pressures. Structural, optical and surface morphological properties of the thin
films have been studied and correlated.

2. Experiment

N-doped TiO$_2$ films were deposited on glass slide without substrate temperature by the FTS technique. The detail description of the target arrangement of the sputtering unit are given else where [8]. After the evacuation of the chamber down to $2 \times 10^{-4}$ Pa, N-doped TiO$_2$ films were deposited at a DC input power of 500 W for a fixed total sputtering pressure 0.8 Pa. Nitrogen doping was varied with different nitrogen partial pressures ($P_N$): 0 Pa, 0.03 Pa, 0.05 Pa, 0.07 Pa and 0.08 Pa.

The thicknesses of the films N doped-TiO$_2$ were about 800 nm–950 nm respectively measured by DEKTAK surface profiler. The crystal structures of the TiO$_2$ films were determined by X-ray diffraction analysis with Cu-K$_\alpha$. The optical properties of the films were measured with Jasco V-550 spectrophotometer at room temperature within the wave length range 300 nm–900 nm. The Surface characteristics were analyzed using field emission scanning electron microscope (FE-SEM) (JEOL, FE-SEM 6700) and atomic force microscope (AFM) (SHIMADZU SPM-9500J2).

![Fig 1](image1.png)

**Figure 1.** X-ray diffraction spectrum of N-doped TiO$_2$ thin films. (inset) Variation of peak A(220).

![Fig 2](image2.png)

**Figure 2.** Transmittance spectrum of N-doped TiO$_2$ thin films.

3. Results and discussion

In figure 1 the XRD spectra of as-deposited TiO$_2$ film, prepared without nitrogen gas, shows anatase phase with good crystallinity. The absence of rutile phase is may be due the use of high sputtering pressure of 0.8 Pa when Ti$^+$ and O$_2^+$ are very less in number [8]. For the N-doped TiO$_2$ thin films, initially only anatase phase appears and no specific peaks of TiN or Ti were detected. Interestingly, rutile phase starts to appear with the increase of $P_N$ from 0.05 Pa and the dominance of rutile phase slightly increases with N-doping. Initially introduction of nitrogen doesn’t change the crystallinity of the thin film appreciably but the crystallinity is decreased abruptly due to the use nitrogen partial pressure of 0.07 Pa and almost vanishes for 0.08 Pa. The crystallite sizes derived with Debye–Scherrer’s equation using the anatase peak (220) are 30.7 nm, 30.5 nm, 30.7 nm and 27.3 nm for the N-doped TiO$_2$ thin films, deposited with $P_N$: 0Pa, 0.03 Pa, 0.05 Pa and 0.07 Pa, indicates only appreciable variation is observed in the N-doped TiO$_2$, deposited at $P_N$ of 0.07 Pa. Figure 1 (inset)
Figure 3. \((\alpha h \nu)^{1/2}\) versus energy of N-doped TiO\(_2\) thin films.

Figure 4. Variation of porosity and RMS roughness with different N doping.

shows that diffraction line of TiO\(_2\) anatase (220) shifts from 70.36\(^\circ\) to lower angle 70.18\(^\circ\) as nitrogen is doped in the TiO\(_2\) films. This is may be due to the replacement of O by N, since the atomic radius of nitrogen (\(\approx\) 0.7 Å) is slightly larger than oxygen atom (\(\approx\) 0.66 Å) [9].

In the figure 2, the transmittance spectrum of N-doped TiO\(_2\) reveals definite shift of transmittance edge to the higher wavelength with the increase of N\(_2\) gas flow and in the visible wavelength the average transmittance of N doped TiO\(_2\) is slightly lower than the undoped one. Assuming the N-doped TiO\(_2\) to be an indirect band gap semiconductor, i.e. TiO\(_2\), a plot of \((\alpha h \nu)^{1/2}\) vs photon energy, given in figure 3, reveals the optical band gap of the material, where \(\alpha\) is absorption coefficient. The deduced optical band gap decreases from 3.16 eV to 2.93 eV due to the effect of nitrogen doping.

The refractive index of the thin films \((n_\lambda)\), calculated from the optical transmittance data using the Swanepoel's envelope method [10], are 1.93, 1.94, 1.95, 2.13 and 2.18 respectively for the N-doped TiO\(_2\) films deposited with PN: 0 Pa, 0.03 Pa, 0.05 Pa, 0.07 Pa and 0.08 Pa. The variation of porosity of the thin film, indicated in figure 4, has been determined from the value of refractive index [11]. It reveals that with the increase of N-doping the porosity decreases and the decrease of porosity is much higher for the TiO\(_2\) thin film deposited with nitrogen partial pressure higher than 0.05 Pa. Similar kind of abrupt change is also observed in the variation of rms roughness, revealed from AFM measurement. Initially the rms roughness increases up to PN of 0.05 Pa but it monotonically decreases for higher nitrogen partial pressure.

The surface structure of the undoped TiO\(_2\) thin film, indicated in the FE-SEM image in figure 5(d), shows well grown clusters with distinct grain boundaries. The well formed anatase crystallites make the surface rough and resulted in pores in the surface. As N-doping increases density of the pores decreases. The amorphous N-doped TiO\(_2\) thin film, deposited at PN of 0.08 Pa shows distribution of grain clusters of different sizes with less number of pores. The AFM images show the same trend that is observed in FE-SEM images. The AFM image of the sample, corresponding to PN of 0.08 Pa, shows smaller grains, when vertical scale takes lower value, which indicates smoother surface.

In this investigation it is revealed that the abrupt change observed in the crystallinity, surface roughness, porosity and the similar amount of shift of anatase peak A(220) observed for the N-doped TiO\(_2\) thin film, prepared at PN of 0.05 Pa and 0.07 Pa, indicates that for nitrogen doping with PN of 0.05 Pa initially N replaces O, so crystallinity and other structural properties remain almost same, but
Figure 5. AFM images of N-doped TiO$_2$ thin films prepared at P$_N$ of (a) 0 Pa (b) 0.05 Pa (c) 0.08 Pa and FE-SEM images of N-doped TiO$_2$ thin films prepared at P$_N$ of (d) 0 Pa (e) 0.05 Pa (f) 0.08 Pa.

over P$_N$ of 0.05 Pa, apart from occupying O sites, N starts to occupy interstitials and restrains the growth of N-doped TiO$_2$ crystallite, resulting in amorphous structure.

4. Conclusions

N-doped TiO$_2$ thin films were successfully deposited on glass substrate without substrate heating by facing target reactive sputtering technique. The study of X-ray diffraction confirms nitrogen replacement on the oxygen site of TiO$_2$ crystal. The as-deposited N-doped TiO$_2$ thin films corresponding to the P$_N$ of 0.03 Pa and 0.05 Pa, exhibit good crystallinity. The N-doped TiO$_2$ thin film deposited with P$_N$ of 0.07 Pa shows abrupt change in the structural properties which may have relation with the creation of interstitial defects that restrain the growth of TiO$_2$ crystallite, resulting in amorphous structure with less porosity.

References

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