

## **The Effect of Nitrogen Partial Pressure and Substrate Temperature on the Characteristics of Photocatalytic N:TiO<sub>2</sub> Thin Films deposited by Filtered Vacuum Arc Deposition**

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### **Abstract**

Nitrogen doped Titanium Oxide (N:TiO<sub>2</sub>) thin films were deposited using filtered vacuum arc deposition, and their structure, composition and morphology were studied as functions of the total pressure, N<sub>2</sub>/O<sub>2</sub> gas ratio and the substrate temperature. The film structure, surface morphology, and composition were determined by XRD, AFM and XPS. The optical characterization of the films was determined with spectrophotometry and ex-situ variable angle spectroscopic ellipsometry (VASE). In addition to the effects of other deposition conditions such as arc current, total deposition pressure, and post-deposition annealing on the film characteristics, photocatalytic activity was also determined as a function of deposition parameters and results were discussed.

**Keywords:** Titanium Oxide, Photocatalytic Coatings, FVAD, Structure, Optical Characterization

### **Introduction**

Most photocatalytic materials respond to only ultra-violet (UV) radiation. A major challenge is to increase the photocatalytic spectral range

to include visible (VIS) light, which composes the largest part of solar radiation, since only a small percent of solar energy (5-7%) is in the UV region [1]. In the recent years, Titanium dioxide (TiO<sub>2</sub>) as a photocatalyst has been practically applied in hospitals and houses [2]. TiO<sub>2</sub> which has a band gap of 3.2 eV (anatase phase) is superior to other semiconductor oxides due to its high chemical stability, low cost and non-toxicity [3,4]. However, un-doped TiO<sub>2</sub> shows photocatalytic activity only under UV light irradiation ( $\lambda < 384$  nm) [2,5].

One of the approaches to activate photocatalysis with VIS- light is to shift the optical band gap of TiO<sub>2</sub> into the VIS spectrum by doping. Because it is non-toxic, N:TiO<sub>2</sub> is very attractive [6-8]. In recent years, TiO<sub>2</sub> and N:TiO<sub>2</sub> thin films have been deposited by un-filtered and filtered vacuum arc deposition (FVAD), utilizing the relatively high deposition rate of this method (up to ~10 nm/s), producing thin films characterized by high adhesion, high density and stability. The published work on FVAD of TiO<sub>2</sub> thin films focused mainly on their structural, compositional and optical properties, and their correlation with deposition parameters (arc current, oxygen pressure and substrate bias and substrate temperature). However, the effects of deposition parameters and nitrogen doping on the composition, structure, morphology, and photocatalytic activity of FVAD N:TiO<sub>2</sub> thin films has not been reported. Upgrading TiO<sub>2</sub> films for VIS-light driven photocatalytic application motivates interest in the growth mechanism and requires more detailed knowledge of the film structure and composition.

The objective of the present work was to determine of the effects of nitrogen partial pressure and substrate temperature on the

structure, composition, morphology, and the optical properties of FVAD N:TiO<sub>2</sub> thin films for its future application as a VIS-light activated photocatalyst.

### Experimental Details

A Ti cathode was used to deposit N:TiO<sub>2</sub> films by FVAD. The deposition system included a vacuum arc plasma source, and a magnetic quarter-torus macro-particle filter. This system was previously described by Ben-Shalom *et al* [9] and Kaplan *et al* [10]. The arc current was 150 or 200 A, and the total pressure in the deposition chamber was 1.06 or 1.33 Pa. The N<sub>2</sub>/N<sub>2</sub>+O<sub>2</sub> gas ratio was varied between experiments from 0 to 69 %. Film deposition times were 150, 180 or 240 s. The films were deposited on 25×76×1 mm glass microscope slide substrates at room temperature (RT), 300 or 500 °C. All of the films were annealed in a nitrogen (N<sub>2</sub>) atmosphere at 400±2 °C for 1 h (preceded by a 20 min heating period and followed by a 40 min cooling period).

The PCA was evaluated by measuring the decomposition of a model pollutant known as Methylene Blue (MB), in an aqueous solution on the basis of the decomposition rate of MB under light irradiation for up to 4 h at the peak absorption of MB at 664 nm. The results were presented as percentage removal (100×(Co-Ct)/Co) where Co and Ct are the concentrations initially and after time t of irradiation respectively. The effect of deposition parameters on photocatalytic activity was evaluated.

## Results

### Film Microstructure, Morphology and Composition

The XRD patterns of the TiO<sub>2</sub> thin films deposited in a pure oxygen environment indicated that films were polycrystalline in the anatase phase, while films deposited in an atmosphere in which the N<sub>2</sub> fraction was greater than 9% were amorphous, for substrate temperatures up to 500°C. Annealing at 400°C in N<sub>2</sub> for one hour generated polycrystalline films with anatase phase independent of %N<sub>2</sub> fraction during deposition. The grain size of the annealed films deposited with some N<sub>2</sub> in the deposition atmosphere decreased from 64 to 44 nm, when the N<sub>2</sub> fraction was increased from 9% to 50%. Increase of the average grain size with the total gas pressure, substrate temperature, and by annealing can be attributed to grain growth and improved crystallinity.

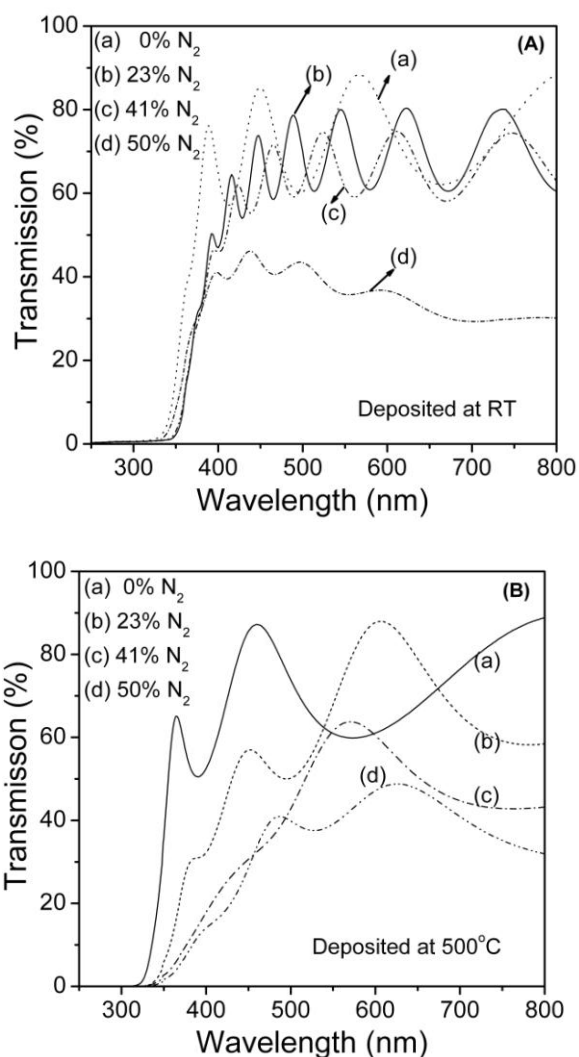
AFM analysis of films deposited in a 41% N<sub>2</sub> atmosphere indicated that the surface roughness increased from 0.5 up to 3.2 nm when the substrate temperature was increased from RT to 500°C, and it was higher for films deposited at 23% N<sub>2</sub> partial pressure (~5.7 nm) compared to films deposited on RT substrates at 23% N<sub>2</sub>. In addition, the average grain size of the films increased with substrate temperature and with annealing, up to 54.2 nm and 36.3 nm, respectively. Furthermore, the surface roughness decreased with the increased N<sub>2</sub>%, except for films deposited at 200 A arc current and which were also crystalline. This decrease might be explained by the amorphous phase formation with increased N<sub>2</sub>% and also the increase in ion flux and plasma density which plays a key role also in surface modification of TiO<sub>2</sub> films deposited by FVAD.

XPS analysis indicated that all films deposited in 0% N<sub>2</sub> were stoichiometric TiO<sub>2</sub>. N content in the films increased with %N<sub>2</sub> in the deposition atmosphere, however the N-content in the film, 1.3 at.% N, was much less than that in the gas mixture (9-69%N<sub>2</sub>). Annealing decreased the N-content in these films to <1 at.%. In addition, the XPS revealed that all N:TiO<sub>2</sub> films had two main N 1s components, at 396-397 eV and at 399-400 eV, associated with substitutional and interstitial nitrogen, respectively. The N 1s peaks around 396 and 397 eV might indicate that there are multiple nitrogen states connected to these peaks, and the binding energy of N 1s at ~397 eV is associated with Ti-N bonding and indicates a substitution of O atoms by N atoms.

### Film Optical Properties

Optical transmission spectroscopy and ellipsometry indicated that the average film transmission (T%) was approximately 80% in the visible spectrum for films deposited at lower N<sub>2</sub> partial pressures (<41%), and it decreased to ~50% for higher %N<sub>2</sub> (see Fig.1).

The deposition rate varied between 0.8 and 4 nm/s. The refractive indices of the films were in the range 2.48 - 2.78, and the extinction coefficients were  $\sim 10^{-3}$  - 0.5. The absorption edge of the films shifted to longer wavelengths with increased substrate temperature and %N<sub>2</sub>, from ~380 nm up to ~485 nm for films deposited with 41% N<sub>2</sub> and a substrate temperature of 500°C.

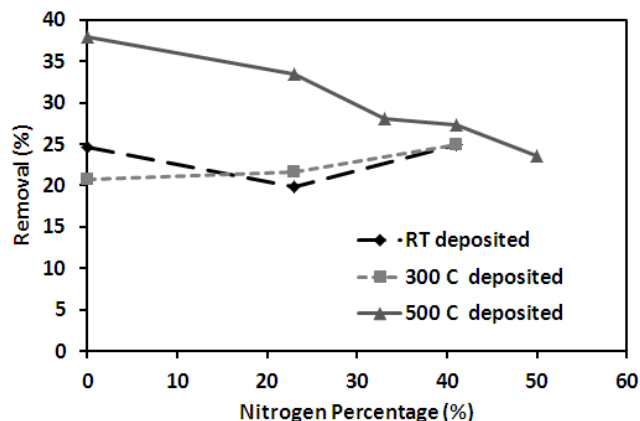


**Figure 1.** Typical transmission spectra for N:TiO<sub>2</sub> samples deposited at: a) RT and b) 500°C substrate temperatures for different nitrogen partial pressures.

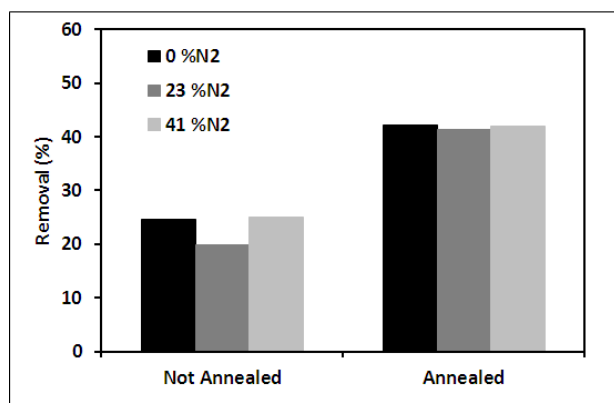
### Photocatalytic Properties

MB could be successfully degraded by N:TiO<sub>2</sub> films at RT. The arc current, total gas pressure, deposition time and %N<sub>2</sub> had a minor effect on the PCA, but increasing the substrate temperature from RT to 500 °C increased the MB removal from 20% to 35% removal and the post-deposition annealing significantly increased the MB removal from 20% to 50% removal (see Figs. 2 and 3). The increased MB removal in annealed films is attributed to crystallization of the thin films in the anatase phase. PCA was found to be correlated with the

396-397 eV to 399-400 eV peak intensity ratio. The choice of substrate significantly affected both MB adsorption and PCA.



**Figure 2.** Removal percentage as a function of %N<sub>2</sub> for films deposited at 1.06 Pa, 150 A, at various substrate temperatures



**Figure 3.** Removal percentage for films deposited at RT, 1.06 Pa, 150 A, at various %N<sub>2</sub> with and without annealing in a nitrogen environment for one hour at 400°C

## Conclusions

As-deposited TiO<sub>2</sub> thin films were crystalline, the addition of nitrogen with various percentages of the total gas pressure during the deposition produced amorphous N:TiO<sub>2</sub> thin films. Annealing them at 400°C for 1 h in N<sub>2</sub> transformed them to polycrystalline. The crystallinity and the grain size of these films increased with annealing. As-deposited N:TiO<sub>2</sub> films had 1-3 at.%N<sub>2</sub> while annealing

decreased the %N<sub>2</sub> to <1 at.%N<sub>2</sub>. The O:Ti ratio in the films varied between 2.2 to 2.7. Two main N 1s XPS peaks were observed at ~396-397 eV and ~399-400 eV for all N:TiO<sub>2</sub> samples. The intensity ratio of the N 1s peak at 396-397 eV to N 1s peak at 399-400 eV increased with the total pressure, %N<sub>2</sub> and by the annealing. The absorption edge of the deposited films shifted to longer wavelengths in the VIS spectrum with %N<sub>2</sub> >23%, and the strongest shift up to 490 nm was observed for films deposited on 500°C substrates.

In order to achieve high PCA, the photocatalytic N:TiO<sub>2</sub> thin film should be crystalline with large grain size and surface roughness and high 396-397 eV to 399-400 eV XPS nitrogen peak intensity ratio.

## References

- [1] D. Reyes-Coronado, G. Rodriguez-Gattorno, M. E. Espinosa-Pesqueira, C. Cab, R. de Coss, G. Oskam, *Nanotechnology* 19(14) (2008) 145605.
- [2] A. Fujishima, X. Zhang, C. R. Chimie 9 (2006) 750-760
- [3] S. Rehman, R. Ullah, A. M. Butt, N. D. Gohar, *J. Hazard. Mater.* 170 (2009) 560.
- [4] M. A. Fox and M. Dulay, *Chem. Rev.* 83 (1995) 341357.
- [5] K. Hashimoto, H. Irie, A. Fujishima, *Jpn. J. Appl. Phys.*, 44(12) (2005) 8269
- [6] J. Zhang, Y. Wu, M. Xing, S. A. K. Leghari, S. Sajjad, *Energy Environ. Sci.* 3 (2010) 715
- [7] N. Serpone, *J. Phys. Chem. B* 110 (2006) 24287-24293
- [8] K. Balasubramanian, X. F. Han, K. H. Guenther, *Appl. Opt.* 32(28) (1993) 5594.
- [9] A. Ben-Shalom, L. Kaplan, R. L. Boxman, S. Goldsmith, M. Nathan, *Thin Solid Films* 236 (1993) 20.
- [10] L. Kaplan, I. Rusman, R. L. Boxman, S. Goldsmith, M. Nathan, E. Ben-Jacob, *Thin Solid Films* 290-291 (1996) 355.