Influence of nitrogen ratios on rutile to anatase phase transition of titanium oxynitride thin films deposited via reactive magnetron sputtering

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Abstract. Thin films of titanium oxynitride deposited via reactive direct current (DC) magnetron sputtering method followed by annealing treatment at 500 °C for crystallization improvement. The thin films were grown under the Ar/O₂/N₂ gases mixture by various nitrogen ratios. The crystalline structure, surface morphology, and optical properties of the obtained thin films were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), and ultraviolet-visible spectrophotometer, respectively. The rutile to anatase phase transition could be detected that increased with increasing the nitrogen ratio and also affected the crystallite size and the thickness of the thin films. The optical bandgap evaluated by the Tauc plot is in the range of 2.78–3.17 eV.

1. Introduction

Titanium dioxide (TiO₂) is well-known as the most effective photocatalyst widely used in many applications such as air purification [1,2], water treatment [3], water splitting [4], bacterial inactivation [5], self-cleaning glass [4,6], organics dye degradation, and so on, because it is not toxic to the user and the environment. TiO₂ naturally exists in three crystallographic forms including rutile, anatase, and brookite phases. The rutile is thermodynamically stable while anatase and brookite are metastable phases. It is known that the anatase and brookite phase transform irreversibly to rutile when increasing the temperatures [7]. The anatase to rutile phase transition temperature is not exactly defined, however, high purity TiO₂ compound exhibits irreversibly phase transition from anatase to rutile at the temperature range of about 600–700 °C [7,8].

Thin film is one of the most widely studied patterns of reversible rutile to anatase phase transition of TiO₂. Recently, Breeson et al. [9] reported that the anatase/rutile mixed-phase thin films exhibit a higher photocatalytic activity owing to charge separation across between the phases. So, the preparation of the compositied phase of TiO₂ is essential for improving the photocatalytic properties of the TiO₂ compound. The anatase phase transforms irreversibly to the rutile phase at high temperature, fortunately, the rutile to the anatase phase transition of the TiO₂ thin film can be achieved by doping with the nitrogen atoms because the incorporated nitrogen can be increasing the anatase to rutile phase transition temperature [9,10], which the TiO₂ thin films that contain an amount of nitrogen atoms can be called a nitrogen-doped titanium dioxide or titanium oxynitride thin films. Doping by nitrogen into the TiO₂ lattice not only elevated the transition temperatures but also narrowed an optical bandgap of
the thin films. This makes it possible to activate the photocatalytic properties by a longer wavelength of light or visible light.

In this work, the titanium oxynitride thin films deposited via reactive direct current (DC) magnetron sputtering method with various N$_2$ ratios. The crystal structure, surface morphology, optical bandgap, and rutile to anatase phase transition of the obtain films were studied as a function of the N$_2$ ratios.

2. Experimental details

2.1. Thin film preparation

The titanium oxynitride thin films were deposited via the reactive DC magnetron sputtering method on Si-wafer substrates size of 1×1 cm$^2$ for crystalline structure and morphology investigation and microscope slide substrates size of 2.54×7.62 cm$^2$ for optical properties measurement. Prior to deposition, all substrates were ultrasonically cleaned with acetone and ethanol for 10 min, then loads them to the substrate holder located apart from the sputtering target of 10 cm. The coating chamber was evacuated to the base pressure of ≤3.0×10$^{-3}$ mbar by an oil diffusion pump backed with the rotary pump. The Ti disc (99.97% purity) with a diameter and thickness of 2" and 0.125", respectively, was used as a sputtered target. An argon gas with a high purity of 99.999% was used as a sputtered gas, while nitrogen and oxygen with a purity of 99.8% and 99.999%, respectively, were used as reactive gases. Before coating, pre-sputtering of 5 min was done to remove the surface contamination. All thin films were deposited under a constant argon flow rate of 8.0 sccm. The O$_2$ flow rate was set at 1.0 sccm for the TiO$_2$ thin film deposition. In the case of the titanium oxynitride thin film deposition, the nitrogen flow rate varied at the ratios (N$_2$/O$_2$+N$_2$) of 0.56, 0.63, 0.83, and 0.91. The sputtering current, the working pressure, and the deposition time were kept constant at 800 mA, 1.2×10$^{-3}$ mbar, and 20 min, respectively, for all conditions. All samples were post-annealed at the temperature of 500 °C in the air ambient to improve the crystallization.

2.2. Thin films characterization

The crystalline structure of the obtained thin films was investigated by an X-ray diffractometer (XRD, BRUKER AXS-D8 DISCOVER) with 0–2θ geometry using a grazing incidence angle of 2°. The 2θ scan was performed in the range of 20°–50°. The surface morphology and thickness of thin films were measured by scanning electron microscope (SEM, Hitachi S-4700). The transmittance of the obtained thin films was examined by an UV-visible spectrophotometer (Shimadzu UV-2600). The optical bandgap of the thin films was estimated by applying the Tauc plot.

3. Results and discussions

3.1. Crystalline structure

The XRD patterns of the titanium oxynitride thin films demonstrated that the thin films deposited at the N$_2$ ratios of 0–0.63 exhibited a diffraction peak only at 2θ = 27.5° which corresponding to (110) plane of rutile phase (JCPDS card No. 21–1276). As the N$_2$ ratios increased to 0.83 and 0.91, strong and weak diffraction peak at 2θ = 25.3° and 48.1° which corresponding to (101) and (200) plane of anatase phase (JCPDS card No. 21–1272), respectively, were detected. Also, it was found that the rutile peak was less prominent while the anatase peaks were more prominent with increasing the N$_2$ ratio. This is due to the incorporation of nitrogen atoms in the TiO$_2$ lattice at the substitutional or interstitial of oxygen sites resulting in the anatase to rutile transition temperature increased [9,10]. In addition, the involvement of the nitrogen atoms can also distort the crystal structure, inhibiting the rutile formation as explained by Bu et al. [11]. The crystallite size was calculated by Scherrer’s equation, as shown in Table 1. It was found that the crystallite size of the rutile phase slightly increased from 7.5 nm to 12.0 nm with increasing the N$_2$ ratios from 0 to 0.63, respectively, this may be due to the incorporation of N atoms in the TiO$_2$ lattice. Then the crystallite size of the rutile
decreased with increasing the N\textsubscript{2} ratios equal to 0.83 and higher. The crystallite size of anatase became larger compared with that of rutile, which indicated the better crystallinity of the titanium oxynitride thin film.

![XRD patterns of the titanium oxynitride thin films deposited with different N\textsubscript{2} ratios.](image)

**Figure 1.** XRD patterns of the titanium oxynitride thin films deposited with different N\textsubscript{2} ratios.

**Table 1.** The crystallite size and thickness of the TiO\textsubscript{2} and titanium oxynitride thin films.

| N\textsubscript{2} ratios | Crystallite size (nm) | Thin film thickness (nm) |
|---------------------------|-----------------------|-------------------------|
| 0 (TiO\textsubscript{2} thin film) | 7.5 (R) | 140 |
| 0.56 | 10.0 (R) | 90 |
| 0.63 | 12.0 (R) | 150 |
| 0.83 | 26.5 (A), 8.9 (R) | 170 |
| 0.91 | 22.3 (A), 5.1 (R) | 210 |

(A) is anatase  
(R) is rutile

3.2. **Surface morphology**

The surface morphology of the thin films measured by SEM demonstrates that the spherical grains of the rutile phase of the TiO\textsubscript{2} thin film and the titanium oxynitride thin films deposited at the N\textsubscript{2} ratios of 0.56 and 0.63 as shown in Figure 2(a–c). The grain size measured by SEM displays the values of about 25, 30, and 40 nm for N\textsubscript{2} ratios of 0, 0.56, and 0.63, respectively. In the case of the N\textsubscript{2} ratio of 0.56, the SEM image shows the small grains of rutile indicating poor crystallinity of this film, which is consistent with the XRD results. When the N\textsubscript{2} ratios increased equal to 0.83 and higher, shown in Figure 2(d–e), it becomes clear that the decrease of grain density and spherical shape of grains disappeared, resulting in a void between the grain boundary caused by the phase transition from rutile to anatase. The SEM images show grain sizes of about 80 and 60 nm for the titanium oxynitride thin
films deposited at N₂ ratios of 0.83 and 0.91, respectively. The average thickness of the thin films evaluated from cross-sectional SEM image (Figure 2(f)), as shown in Table 1., displays the value of about 140 nm for the TiO₂ thin film and found that the sample of 0.56 N₂ ratio shows the lowest thickness of thin film due to the highest relative amount of O₂ in the reactive gases used in this experiment gave rise to a poisoning target which resulted in a lower coated rate.

Figure 2. The SEM images of the thin films deposited at N₂ ratios of (a) 0, (b) 0.56, (c) 0.63, (d) 0.83, (e) 0.91, and (f) cross-section of all samples

3.3. Optical properties

The transmission spectra of the thin films measured by UV-VIS spectrophotometer in the wavelength range of 300–900 nm shown in Figure 3. The result showed that all the thin films exhibited oscillatory characteristic owing to interference effects of light reflected from the top of the thin film surface and the thin film-substrate interface, excepted the thin film prepared at the N₂ ratio of 0.56, this may be due to this thin film is not uniform. The average transmittance of the thin films in the visible region (λ=380–780 nm) is about 74, 73, 80, 74, and 77 % for the titanium oxynitride thin films deposited at the N₂ ratios of 0, 0.56, 0.63, 0.83, and 0.91, respectively.

Absorption coefficient (α) was calculated by the following equation [12]:

\[ \alpha = \frac{1}{d} \ln \left( \frac{1}{T} \right) \]  

where \( d \) denotes the thin film thickness and \( T \) represents the light transmittance of the thin films. In the case of an indirect allowed transition, the absorption coefficient and optical bandgap (\( E_g \)) of the TiO₂ and titanium oxynitride thin films were related as [12]:

\[ (\alpha h\nu)^{1/2} = A(h\nu - E_g) \]  

where, \( A \) is the constant, and \( h\nu \) is the incident light energy. The optical band gap can be evaluated by extrapolating the straight line to zero absorption in the Tauc plot, as shown in Figure 4. The optical band gap value of the TiO₂ thin film is about 2.90 eV and decreased to 2.78 eV when introducing the N₂ into the sputtering chamber at the ratio of 0.56. Then the optical band gap values increased to about 2.90, 3.13, and 3.16 eV with increasing the N₂ ratios of 0.63, 0.83, and 0.91, respectively. This
increased in optical bandgap values due to the phase changed from rutile to anatase, which is in good agreement with the bandgap of anatase higher than that of rutile [13,14].

![Image of transmission spectra](image1)

**Figure 3.** Transmission spectra of the TiO$_2$ and titanium oxynitride thin films with different N$_2$ ratios.

![Image of Tauc plot](image2)

**Figure 4.** Tauc plot of the TiO$_2$ and titanium oxynitride thin films.

4. Conclusions
The TiO$_2$ and titanium oxynitride thin films were deposited by reactive DC magnetron sputtering method with different N$_2$ ratios. The XRD results indicated that the crystalline phase of thin films has been a reversible transition from rutile to anatase phase as a function of the N$_2$ ratios. The surface morphology has been changed clearly from the spherical grain of the rutile phase to larger flattened...
grains of the anatase phase. The optical bandgap of the titanium oxynitride thin films increased when the crystalline phase changed from rutile to anatase phase.

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