Effect of post annealing on properties of N-doped TiO$_2$ films deposited by reactive magnetron sputtering

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Abstract. The paper studies the effect of annealing on the structure and properties of N-doped TiO$_2$ films, deposited by reactive magnetron sputtering. An increase in the annealing temperature results in a reduction of the film thickness and a rise of the refractive index. The post annealing induces the anatase-rutile phase transition and also leads to band gap narrowing and wettability transition.

1. Introduction

Thin films based on titanium dioxide TiO$_2$ are widely investigated and applied in different research fields owing to their unique properties [1–3]. Presently, TiO$_2$ films made for solar cell and self-cleaning coating owing to high photocatalytic activity and tunable wettability have received great attention.

TiO$_2$ films have been reported to exhibit different crystalline structures: amorphous, anatase, and rutile, depending on deposition condition. Amorphous TiO$_2$ films have found potential application as high-refractive and energy-saving coating, whilst anatase and rutile are valued for high photocatalytic activity and thermal stability, respectively. Moreover, polycrystalline TiO$_2$ films with anatase and rutile phases are supposed to present better photocatalytic performance as heterogeneous system. Besides, the self-cleaning function can be promoted by hydrophilic surface, which provides more active sites for photocatalytic reactions in the case of full water contact. Therefore, development of TiO$_2$ film with high photocatalytic activity as well as hydrophilic surface is of great interest.

The photocatalytic activity of TiO$_2$ is the outstanding property, but it is limited by relatively wide band gap (3.2 eV for anatase and 3.0 eV for rutile) and high electron-hole recombination rate. In its turn, the wettability can be easily affected by surface condition and presents low durability.

There are several different approaches to narrow the band gap of TiO$_2$. One of the frequently used methods is doping with third nonmetal and metal elements, especially with nitrogen. N atoms incorporated in TiO$_2$ structure can reduce the band gap by mixing the N2p–O2p states and introducing impurity energy levels. In addition, the photocatalytic performance can be enhanced by post annealing, which can also improve hydrophilicity or cause hydrophobility-hydrophilicity transition.

In this paper we focused on the influence of post annealing on structure and properties of N-doped TiO$_2$ films. The films were produced by sputtering Ti target in mixture of argon, oxygen and nitrogen. Then after subsequent annealing up to different temperatures in air, we investigated the film structure evolution and the change in properties.
2. Materials and methods
N-doped TiO$_2$ films were produced using dual pulsed DC magnetron sputtering system in which two same ring Ti targets were sputtered in Ar+O$_2$+N$_2$ reactive atmosphere. The flow rates of Ar, O$_2$ and N$_2$ were kept at 6.5, 7.5, and 5 sccm, respectively, to maintain the total working pressure at 0.20 Pa. We deposited the films on Si (111) wafers and glass slides and the substrate holder was grounded. The process duration was 90 min, and the discharge power varied as follows: in the first 60 min, the power was 2 kW, whilst in the last 30 min, the deposition was performed with the power of 3 kW. After deposition, N-doped TiO$_2$ films were annealed up to different temperatures from 400 °C to 800 °C for 60 min with a heating rate of 6 °C/min in air.

Spectroscopic ellipsometry (SE) measurement was conducted on spectral ellipsometry complex Ellipse 1891. Grazing incidence x-ray diffraction (GIXRD) was performed on Shimadzu XRD 6000 diffractometer (CuK$\alpha$ radiation with $\lambda = 0.15418$ nm) in the range of 20–80° with incidence angle of 1° and scan speed of 2.0 °/min. Raman spectra were obtained on research complex Centaur using laser with wavelength of 530 nm; the region of spectrum scattering detection was 100–900 cm$^{-1}$. Film surface topography was studied by scanning electron microscope (SEM) on JLU SKLSHM Magellan400, and atomic force microscope (AFM) on Solver HV. Water contact angle (WCa) of the film surface was estimated on Easy Drop DSA20 using water drop of 3 µL. UV-vis spectra of TiO$_2$ and N-doped TiO$_2$ were measured on spectrophotometer SF-256UVI in the range of 200–1000 nm.

3. Results and discussion
Figure 1 shows film thickness $d$, refractive index $n$ at 630 nm and dispersion curves as a function of annealing temperature. It can be noticed that, in general, as the annealing temperature increases, the film thickness decreases and the refractive index increases, with exceptions at 800 °C. The rise of refractive index can be attributed to film densification and anatase–rutile phase transition [4].

![Figure 1](image.png)

**Figure 1.** Dependence of thickness $d$ and refractive index of $n$ films on annealing temperature (left) and dispersion curves of annealed films (right).

Figure 2 presents GIXRD patterns of N-doped TiO$_2$ films as a function of annealing temperature. As-deposited film was found to contain anatase and rutile phases, and the increase of annealing temperature has led to anatase–rutile phase transition. Analysis of the diffraction patterns shows that the peak of anatase at 25.3° weakens with increasing annealing temperature, while the intensity of rutile peak at 27.5° increases. GIXRD results show that with an increase in annealing temperature, the volume fraction of anatase monotonously decreases from 28% in the as-deposited film to 0% in the film heated to 700-800 °C, and the volume fraction of rutile increases from 72% to 100% accordingly.

The thermo-induced phase transition was further studied by Raman spectroscopy. The Raman spectrum of as-deposited N-doped TiO$_2$ film manifests characteristic scattering lines of polycrystalline (anatase+ rutile) film: anatase peaks at 148.93 cm$^{-1}$, 642.65 cm$^{-1}$, and rutile modes at 432.42 cm$^{-1}$,
618.45 cm\(^{-1}\), 816.86 cm\(^{-1}\), etc. [5]. After annealing up to 800 °C, N-doped TiO\(_2\) film presents a typical rutile spectrum and no sign of anatase has been observed.

In contrast to GIXRD results, Raman spectra reveal that with increasing annealing temperature to 600 °C, the content of both anatase and rutile increases. Particularly after annealing up to 600 °C, typical anatase peaks at 399 cm\(^{-1}\), 639 cm\(^{-1}\) and intense peak at 144 cm\(^{-1}\) have been observed in Raman spectrum. However, in annealed film at 700 °C the intensity of anatase peaks have apparently decreased and further increase of annealing temperature to 800 °C leads to higher intensity of rutile peaks with no anatase peaks being recognized.

This phenomenon can be related to the possible bi-layer structure of the film, as GIXRD gives the information about the top layer of the film, corresponding to the discharge power of 3 kW, and Raman spectroscopy collects the signal from the entire volume of the film. Moreover, in bottom layer corresponding to the power of 2 kW, the annealing at temperature from 400 °C to 600 °C results in the phase transition from amorphous to anatase, and the higher temperatures lead to a full transition to rutile.

![Figure 2. GIXRD patterns (left) and Raman spectra (right) of as-deposited and annealed N-doped TiO\(_2\) films.](image)

The thickness of the N-TiO\(_2\) film decreases and the refractive index increases with the rise of annealing temperature, and this can be explained based on phase composition studies. As is known, the refractive index at 550 nm for anatase and rutile is 2.55 and 2.70, respectively. Therefore, the effective refractive index of a polycrystalline film with a predominant anatase content should be less compared to the film with higher volume ratio of rutile. Figure 1 shows that the effective refractive index of the film increases from \(n = 2.25\) to \(n = 2.6\) after annealing up to 800 °C as a result of the increase in the fraction of rutile in the film. Moreover, the unit cell volume of anatase (136.27 Å\(^3\)) is larger than that of rutile (62.43 Å\(^3\)), therefore the film thickness will decrease with increasing content of the rutile phase in the film composition. In addition, the refractive index can be affected by film density, and, to some extent, thermo-induced film densification and phase transition can be considered as two competing processes during heat treatment. Thus, the decrease of refractive index in the film annealed at 800 °C can be assigned to the phase transition, which in this case is more pronounced than film densification.

The morphology of the film was studied using SEM and AFM. Figure 3(a), (b) and (c) present SEM images of films without annealing and heated to 400°C and 500°C, respectively. The roughness and surface area ratio (ratio of film surface area and projected area) were obtained from AFM measurement and are shown in figure 3(d) as a function of the annealing temperature.

Figure 3(a), (b) and (c) show the trend of change in grain shape without visible increase of grain size. Moreover, the film roughness and the surface area ratio decrease and then slightly increase with rising annealing temperature, with an exception at annealing temperature of 600 °C.
The initial increase of RMS and $r$ values can be related to the phase transition, while the subsequent increase appears as a result of monocrystalline grain growth. The unusual behavior of RMS and $r$ of N-doped TiO$_2$ film annealed at 600 °C we attribute to the difference of phase transition processes in the bottom and top layers.

**Figure 3.** SEM images of the films without annealing (a) and heated to 400 °C (b) and 500 °C (c); graphs of RMS roughness and surface area ratio $r$ (d).

Figure 4 shows the UV-vis transmission spectra of N-TiO$_2$ films without annealing and after heating to 400 °C and 500 °C.

**Figure 4.** UV-vis transmission spectra of N-doped TiO$_2$ films without annealing and heated to 400 °C and 500 °C (left) and Tauc curves (right) to determine the band gap energy.
The width of the band gap of the corresponding films was determined using Tauc law [6]:
\[ a h v = A (h v - E_g)^m \]
where \( E_g \) is the band gap energy, \( A \) is the constant, \( h v \) is the phonon energy, \( \alpha \) is the absorption coefficient, and \( m=2 \) accounts for indirect allowed electron transition.

Our findings show that each film is characterized with two values of \( E_g \), whilst the higher one with increasing annealing temperature decreases from 3.24 to 3.11 eV, and the lower \( E_g \), accounting for formation of impurity states due to N-doping, decreases from 3.02 to 2.68 eV. The narrowing of band gap caused by post annealing can be attributed to phase transition and grain growth [7].

Figure 5 illustrates the annealing induced wettability transition of N-doped TiO\(_2\) films. The as-deposited film, formed on the glass slide, is found to possess a hydrophobic surface with water contact angle of 92°, which after annealing at 400 °C and 500 °C shows a remarkable decrease down to about 30°. This may be related to the enhancement of crystalline structure and formation of oxygen vacancies on film surface [8]. However, there is a difference in wettability transition between films deposited onto Si wafer and glass slide, and it still needs to be investigated in further.

4. Conclusions
The paper addresses the effect of post annealing on the structure and properties of N-doped TiO\(_2\) films, fabricated using reactive magnetron sputtering method. Based on the obtained results several conclusions have been drawn. First, annealing leads to a decrease in the film thickness and an increase in the refractive index due to anatase-rutile phase transition and film densification. Second, with an increase in annealing temperature, the anatase turns into rutile and at the same time the degree of crystallization increases. Third, annealing significantly affects band gap energy, which is associated with the enlargement of the grains and the phase transition. We assume that the N-doped TiO\(_2\) film annealed at 500 °C with the lowest \( E_g \) and WC\(_{Ca}\) may find potential applications in the fields of photocatalysis and self-cleaning coatings.

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