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# Compositional and Structural Properties of $\text{TiO}_{2-x}\text{N}_x$ Thin Films Deposited by Radio-Frequency Magnetron Sputtering \*

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$\text{TiO}_{2-x}\text{N}_x$  thin films are deposited onto Si(100) and quartz substrates by a rf magnetron sputtering method using a titanium metal disc as a target in Ar,  $\text{N}_2$ , and  $\text{O}_2$  atmospheres. The substrate temperature is kept at  $300^\circ\text{C}$ . The  $\text{O}_2$  and Ar gas flow rates are kept to be constants and the N gas flow rate is varied.  $\text{TiO}_{2-x}\text{N}_x$  films with different N contents are characterized by x-ray diffraction and x-ray photoelectron spectroscopy. The results indicate that the  $\text{TiO}_{2-x}\text{N}_x$  thin films can be obtained at 13% N and 15% N contents in the film, and the films with mixed  $\text{TiO}_2$  and TiN crystal can be obtained at 13% N and 15% N contents in the film. In terms of the results of x-ray photoelectron spectroscopy, N 1s of  $\beta\text{-N}$  (396 eV) is the main component in the  $\text{TiO}_{2-x}\text{N}_x$  thin films. Because the energy level of  $\beta\text{-N}$  is positioned above the valence-band maximum of  $\text{TiO}_2$ , an effective optical-energy gap decreases from 2.8 eV (for pure  $\text{TiO}_2$  film deposited by the same rf sputtering system) to 2.3 eV, which is verified by the optical-absorption spectra.

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Titanium dioxide has been applied in optical coatings,<sup>[1]</sup> electronic devices,<sup>[2]</sup> and protective layers.<sup>[3]</sup> As a kind of wide-band-gap semiconductors, electrons in the conduction band and holes in the valence band are produced when  $\text{TiO}_2$  is exposed to light of energy corresponding to the band gap of  $\text{TiO}_2$ . These photo-generated carriers will react with oxygen absorbed onto  $\text{TiO}_2$  surface to cause oxidation and reduction reactions on the  $\text{TiO}_2$  surface. Therefore, titanium dioxide is a very attractive material for applications in photocatalysis.<sup>[4]</sup>

The following three structures occur in  $\text{TiO}_2$  crystal: tetragonal rutile, anatase, and orthorhombic brookite. However, ultraviolet light is needed to excite  $\text{TiO}_2$  with the rutile and the anatase structures. To decrease the band gap and make them useful in visible light, one traditional approach has been to dope transition metals into  $\text{TiO}_2$ <sup>[5,6]</sup> and the other has been to form reduced  $\text{TiO}_x$  photocatalysts.<sup>[7]</sup> Asahi *et al.*<sup>[8]</sup> and Sato<sup>[9]</sup> employed a method to dope N into  $\text{TiO}_2$  to form  $\text{TiO}_{2-x}\text{N}_x$ , the doped N can decrease the band gap to the energy range of visible light by producing states just above the valence-band maximum (VBM) of  $\text{TiO}_2$ . Thus a high photocatalytic activity under visible light is expected for  $\text{TiO}_{2-x}\text{N}_x$ . At present,  $\text{TiO}_2$  thin films for the photocatalytic applications are mainly produced by sol-gel processes.<sup>[4]</sup> However, an

increasingly-used deposition technique is magnetron sputtering.<sup>[10–14]</sup> This method is the most interesting technique because the stoichiometry of the deposited film can be controlled, a metal target can be used, and a high deposition rate can be obtained. The deposition process can fabricate large-scale uniform coatings with high density at a relatively-low deposition temperature. In this study,  $\text{TiO}_{2-x}\text{N}_x$  thin films were prepared by the rf magnetron sputtering method using a metallic titanium target and a gas mixture of Ar,  $\text{N}_2$ , and  $\text{O}_2$ . To form  $\text{TiO}_{2-x}\text{N}_x$  films, the lower oxygen and higher nitrogen gas-flow rates were maintained in the experiment. The formation of these films occurred because the activity of oxygen was higher than that of nitrogen. If the oxygen content in the vacuum system was high, the Ti atoms would react easily with O atoms. Low  $\text{O}_2$  gas flow rate was maintained in the experiments to make it easy to form  $\text{TiO}_{2-x}\text{N}_x$  thin films. The compositional and structural properties are characterized.

In our experiment, the  $\text{TiO}_{2-x}\text{N}_x$  films were deposited onto Si (100) and quartz substrates by rf magnetron sputtering. A titanium disc (purity 99.99%, 9 cm in diameter) was used as the target. The system was evacuated to an ultimate vacuum of  $1 \times 10^{-5}$  Pa with a molecular pump. High-purity argon, nitrogen, and oxygen gases were introduced into the sys-

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tem through a set of mass flow controllers. The pressure was maintained at 1 Pa. Before deposition, the titanium target was dipped into a 5% hydrogen fluoride (HF) solution to remove the surface-oxide layer. Si substrates were cleaned by the normal Radio Corporation of America (RCA) method. The substrate temperature was kept at 300°C and the rf power was

100 W. The target-substrate distance was 60 mm. In general, the gas-flow-rate ratio (GFRR) had an obvious influence on the film quality. In order to obtain the optimized experimental parameters, a set of samples (about 900 nm in thickness) with different GFRRs of Ar:N<sub>2</sub>:O<sub>2</sub> were prepared. The detailed growth conditions are listed in Table 1.

Table 1. The deposition conditions of TiO<sub>2-x</sub>N<sub>x</sub> thin films.

Sample	Ar (sccm)	N <sub>2</sub> (sccm)	O <sub>2</sub> (sccm)	Substrate temperature (°C)	rf power (W)	Deposition time (min)
<i>a</i>	200	20	1	300	100	100
<i>b</i>	200	30	1	300	100	100
<i>c</i>	200	40	1	300	100	100
<i>d</i>	200	50	1	300	100	100

To characterize the crystal structure of TiO<sub>2-x</sub>N<sub>x</sub> films, x-ray diffraction (XRD) was measured using a D/max-RA x-ray spectrometer (Rigaku) with Cu K<sub>α</sub> line of 0.154 nm, x-ray photoelectron spectroscopy (XPS) measurements was carried out using a VG ESCALAB MK II x-ray photoemission spectrometer to identify the chemical components. To obtain binding energies of the constituent elements, the binding energy of 284.6 eV for the C 1s line from the residual carbon on the surface was used as a reference. For the optical characterization, a Shimadga UV-350 double beam spectrophotometer was used to measure absorption spectra for the film grown on the quartz substrate.

Figure 1 shows the x-ray diffraction spectra of the TiO<sub>2-x</sub>N<sub>x</sub> thin films prepared by rf magnetron sputtering with different GFRRs of Ar:N<sub>2</sub>:O<sub>2</sub>. For all samples, there are two peaks, one at 2θ = 25.5° (*d* = 3.520 Å), and the other at 2θ = 37.6° (*d* = 2.379 Å), which are from the refraction peaks of anatase TiO<sub>2</sub> (101) and (004), respectively. For samples *c* and *d* with 16% N and 19% N contents in the film, there appears to be peaks at 2θ = 40.8° (*d* = 2.209 Å) and 2θ = 43.3° (*d* = 2.069 Å) which are attributed to the refraction peaks of TiN (210) and (200), respectively. The XRD results show that O<sub>2</sub> in the system is still the main reactant material with Ti under the condition of low N<sub>2</sub> content. This is because the reaction activity of oxygen is higher than that of N. From Fig. 2 for samples *a* and *b* with 13% N and 15% N contents in the film, respectively, TiO<sub>2</sub> phase dominates the x-ray refraction peaks, only little TiN phase could be observed in the samples. With the increase of N content in the system, N atoms may have more chance to react with Ti atoms to form TiN. As a result, the samples *c* and *d* are mainly the mixture of TiO<sub>2</sub> and TiN crystal as shown in Fig. 1. The mean grain size of the thin films is evaluated by using the Scherrer formula. The sizes of TiO<sub>2</sub> and TiN grains are 7 and 9 nm in sample *c*, 10 and 18 nm in sample *d*, respectively. The TiO<sub>2-x</sub>N<sub>x</sub> contents of samples *a* and *b*

are more than those in samples *c* and *d*. The above discussion is confirmed by the following XPS results.

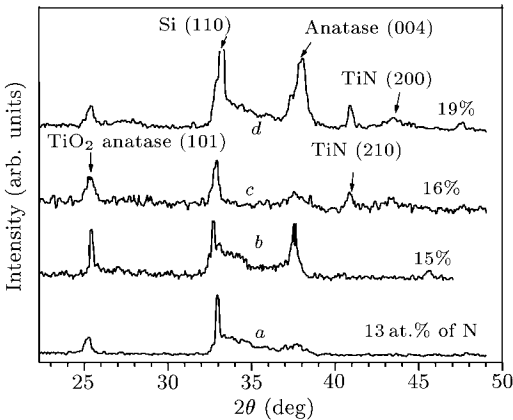
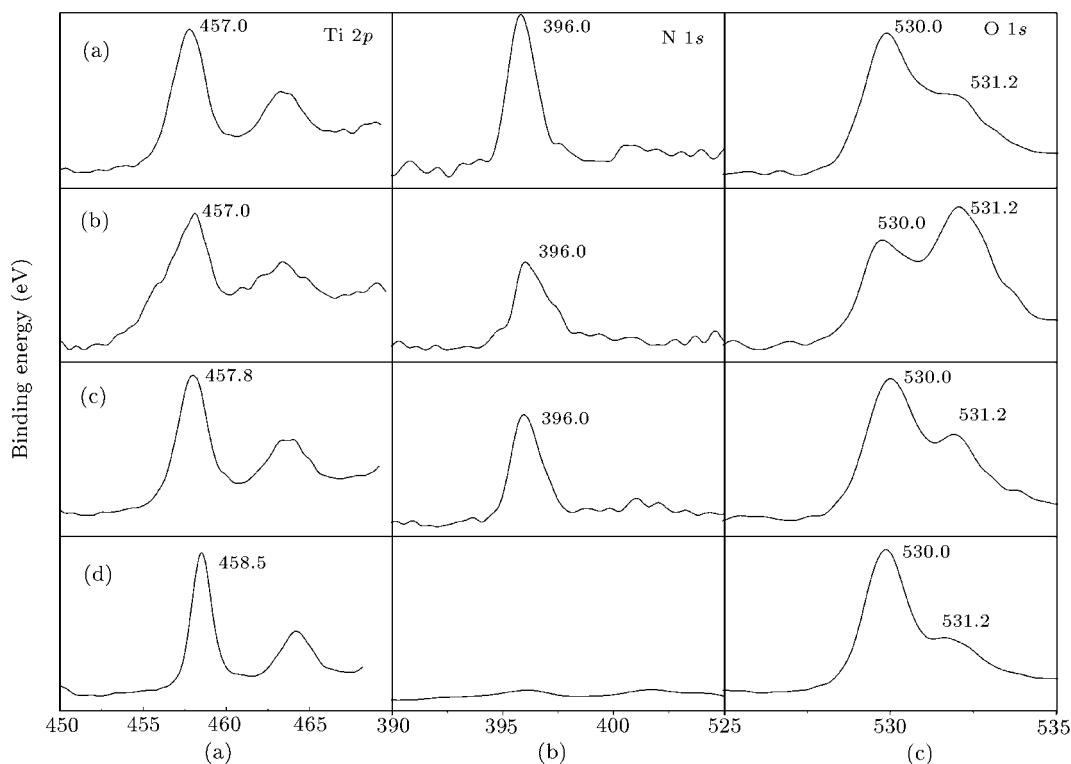


Fig. 1. X-ray diffraction patterns of the TiO<sub>2-x</sub>N<sub>x</sub> thin films grown on Si (100) substrates by rf magnetron sputtering with different N contents in the film: (a) 13%, (b) 15%, (c) 16%, (d) 19%.

High-resolution XPS spectra of TiO<sub>2-x</sub>N<sub>x</sub> thin films prepared with different GFRRs of Ar:N<sub>2</sub>:O<sub>2</sub> are shown in Fig. 2. According to the literature,<sup>[15]</sup> the binding energies of Ti 2p<sub>3/2</sub> for different oxidation states of titanium are positioned on the graph as follows: Ti<sup>0</sup> at 454.1 eV; Ti<sup>2+</sup> at 455.3 eV; Ti<sup>3+</sup> at 457.2 eV; and Ti<sup>4+</sup> at 459.2 eV, characteristics of rutile and anatase titanium dioxide. Saha and Tompkins<sup>[16]</sup> also show that the typical XPS data of Ti 2p<sub>3/2</sub> of pure TiO<sub>2</sub> is 459.1 eV. The electronegativity of O is stronger than that of N, and the electron screen effect of Ti atoms in TiO<sub>2</sub> is weaker than that of Ti atoms in TiO<sub>2-x</sub>N<sub>x</sub> or TiN, so Ti 2p<sub>3/2</sub> has relatively higher binding energy in TiO<sub>2</sub>, as compared with TiO<sub>2-x</sub>N<sub>x</sub> or TiN. In our study, the TiO<sub>2-x</sub>N<sub>x</sub> thin film has already formed in sample *a* as shown in Fig. 2(a), because the core lines of Ti 2p<sub>3/2</sub> shift to 458.5 eV. It is lower than the Ti 2p core level of the pure TiO<sub>2</sub>. Saha and Tompkins<sup>[16]</sup> suggested that TiO<sub>2</sub> for 458.5 eV may be amorphous. However, we consider that N

atoms emerge into the  $\text{TiO}_2$  crystal and displace O atoms partially to form  $\text{TiO}_{2-x}\text{N}_x$ . For sample *a*, the influence of N may be small because the N content at 13% in the film is relatively low. With the increase of  $\text{N}_2$  in the system, the Ti  $2p$  binding energy shifts towards the low-energy direction (457.8 eV for sample *b* and 457.0 eV for samples *c* and *d*, respectively, as shown in Fig. 2(a)), which illustrates more transformation appearing from  $\text{TiO}_2$  to  $\text{TiO}_{2-x}\text{N}_x$  or TiN in films. The N  $1s$  peak appears at about 396 eV for all the samples, as shown in Fig. 2(b). The peak does not come from the N  $1s$  (397.0 eV)<sup>[15]</sup> of the pure TiN sample, but from atomic  $\beta$ -N. The states of  $\beta$ -N are positioned above the VBM of  $\text{TiO}_2$  thus leading to a decrease of the energy gap discussed later. Asahi *et al.*<sup>[7]</sup> proved experimentally an increase of photocatalysis activity with an increase of the component of N with the XPS peak at 396 eV and the active sites of N for photocatalyst under visible light. Figure 2(c)

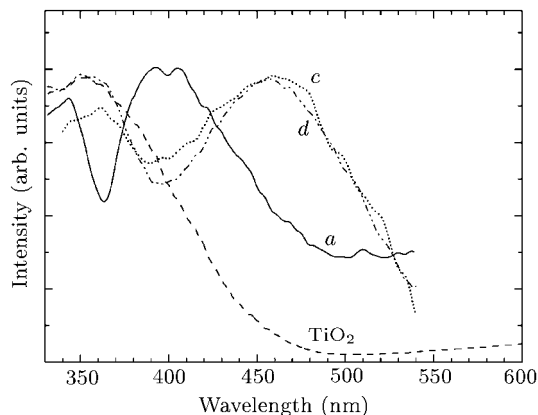
shows the XPS spectra of the O  $1s$  core level. Because of their asymmetrical line shape, the O  $1s$  peaks of these films could be described as the superposition of two component peaks and be consistently fitted by two Gaussian peaks centred at 530.0 eV and 531.2 eV, respectively. The high binding-energy component centred at 531.2 eV is associated with a substoichiometric oxide or an oxynitride. In this case, the number of extra electrons attracted by the O atom is less than that in the case of  $\text{TiO}_2$ , which results in a weaker screen effect. Because the O  $1s$  core level for the pure  $\text{TiO}_2$  sample is 530.0 eV, the peak positioned at 530.0 eV in Fig. 2(c) is associated with O in  $\text{TiO}_2$ .<sup>[17]</sup> The atomic composition of O and N is calculated by using the integrated intensity and sensitivity factors. The atomic ratio of N to O is approximately 0.152, 0.181, 0.191, and 0.232 for samples *a-d*, respectively. It can be concluded that Ti-N bonds in the films increase with the increasing N gas flow rate.



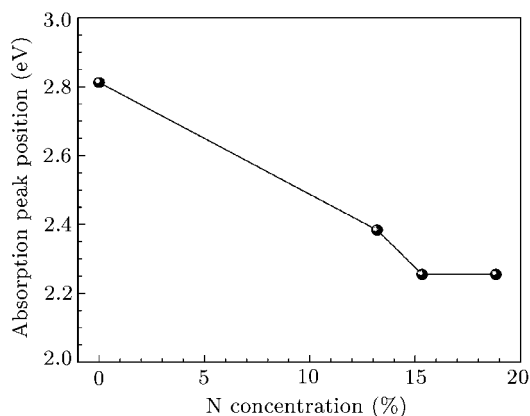
**Fig. 2.** XPS spectra (Ti  $2p$ , O  $1s$ , N  $1s$ ) of  $\text{TiO}_{2-x}\text{N}_x$  with different N content in the film: (a) 13%, (b) 15%, (c) 16%, (d) 19%.

The absorption spectra of  $\text{TiO}_{2-x}\text{N}_x$  thin films compared with  $\text{TiO}_2$  are shown in Fig. 3. For the pure  $\text{TiO}_2$  sample, there is only a UV absorption at 450 nm. However, for  $\text{TiO}_{2-x}\text{N}_x$  thin films (samples *a*, *c*, and *d*), a noticeable absorption of visible light can be seen in Fig. 3. For sample *a*, the absorption edge shifts to 520 nm, while for samples *c* and *d* the absorption edge shifts obviously to 550 nm. Values of the optical energy gap of the samples are shown in Fig. 4. For the

$\text{TiO}_2$  sample deposited in the same rf magnetron sputtering system the optical energy gap is 2.8 eV and it changes to 2.4 eV at 13% of N content in the film and to 2.3 eV at 16% and 19% of N content in the film. The large shift of the absorption edge indicates that the optical energy gap of  $\text{TiO}_{2-x}\text{N}_x$  films decreases by doping N into the film but it does not decrease monotonously with the increasing N content in the films and has an ultimate value.



**Fig. 3.** Absorption spectra of pure  $\text{TiO}_2$  and  $\text{TiO}_{2-x}\text{N}_x$  with different N content in the film: (a) 13%, (c) 16%, (d) 19%.



**Fig. 4.** Optical energy gap of  $\text{TiO}_2$  and  $\text{TiO}_{2-x}\text{N}_x$  as a function of N content in the film.

In summary, we have investigated the influence of the gas-flow-rate ratio of  $\text{Ar}:\text{N}_2:\text{O}_2$  on the film composition and the structure of  $\text{TiO}_{2-x}\text{N}_x$  thin films. In these results, XRD indicates that  $\text{TiO}_{2-x}\text{N}_x$  thin films

could be prepared successfully by the rf magnetron-sputtering method and XPS indicates that the N  $1s$   $\beta$ -N (396 eV) is the main component in the  $\text{TiO}_{2-x}\text{N}_x$  thin films. Since  $\beta$ -N is positioned above the VBM of  $\text{TiO}_2$  and decreases the energy gap, which is proven by the absorption spectra. For photocatalysis applications, this kind of  $\text{TiO}_{2-x}\text{N}_x$  thin films with  $\beta$ -N is more useful because the  $\text{TiO}_{2-x}\text{N}_x$  photocatalyst can be utilized under visible light. The improvement of catalysis activity of the  $\text{TiO}_{2-x}\text{N}_x$  thin films compared with  $\text{TiO}_2$  will be discussed in another paper soon.

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