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ARTICLE

Structural and Hydrophilic Characteristics of N-doped TiO_x Films Deposited by RF-Magnetron Sputtering

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Abstract: Nitrogen doped titanium oxides (N-doped TiO_x) films were deposited by sputtering the TiO_2 target in N_2/Ar gas mixture to control the doping amount of nitrogen accurately. In order to modify the resultant films, the samples were annealed in air in a temperature range of 300 ~ 600 °C, and then they were irradiated under visible-light (VIS) after being placed in dark. X-ray photoelectron spectroscopy (XPS) spectra show that N-Ti-O (β-N) and hydroxyl form in the films due to nitrogen doped into TiO_x lattice. And the content of hydroxyl increases with annealing temperatures increasing, which leads to the better hydrophilicity. X-ray diffraction (XRD) was used to investigate the crystallinity of the films annealed at different temperatures and the results indicate that the amorphous films transform into crystalline phase as a consequence of annealing. Scanning electron microscopy (SEM) results reveal that the particle size becomes bigger at the higher temperature. Hydrophilicity was tested by contact angle meter. The results show that the water contact angle decreases with raising heat treatment temperature due to the change of particle size and the content of –OH. Hydrophilicity is also influenced by the storing process, and the water contact angles increase with time. Furthermore, the hydrophilicity of N-doped TiO_x films increases under visible light (VIS) irradiation.

Key words: N-doped TiO_x films; RF-magnetron sputtering; anneal; hydrophilicity

Titanium oxide (TiO_x) films have attracted the interest of many researchers due to their exceptional properties, such as high biocompatibility. And their applications on clinic are becoming popular increasingly. For biological systems, the nature of hydrophilicity plays a key role on the mediation of solute (e.g. protein) adsorption and cell adhesion [1-3]. Therefore alteration of wetting behavior is of great importance for its biomedical application. To improve the hydrophilicity, researchers doped titanium with different material. After reporting DOS calculation results that suggested the potential benefits of certain nonmetal dopants, many papers demonstrated the advantages of using C, N and S for this purpose [4-6]. As one of the most promising dopant candidates for TiO_x films, nitrogen was used more widely than others in spite of disputed mechanisms leading to the behavior. Some authors suggested a model in which incorporation of nitrogen via oxygen substitution results in band gap narrowing, due to the mixing of the N 2p and O 2p states [4,5]. According to a second model, the red shift is rather related to the occurrence of new N 2p states, close to the upper limit of the valence band [7]. High temperature treatment could modify the films, which has the effect on changing the films structure as well as nitrogen doping [8].

Different techniques have been used to prepare N-doped TiO_x films, such as magnetron sputtering, thermal evaporation, or various chemical vapor deposition methods. Among them, RF magnetron sputtering method can control the doping amount of nitrogen accurately and allow for the preparation of dense, homogenous and smooth-surface films [8,9].

Nowadays, the possibility to modify and control the surface hydrophilicity of N-doped TiO_x films has attracted significant scientific and technological interest. N-doped TiO_x films were widely used as biocompatible films and photocatalytic films. Ultraviolet (UV) light and visible (VIS) light have already been reported to control the surface hydrophilicity of N-doped TiO_x films [8].

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It is expected that the morphology and chemical composition of N-doped TiO_x films influence the hydrophilicity as well as the subsequent adhesion properties of proteins. The aim of the present study is to investigate the effect of the surface properties (chemical composition, surface topography as well as microstructure) on hydrophilicity of N-doped TiO_x films.

1 Experiment

A TiO_2 target (99.7%) was used to deposit N-doped TiO_x films onto Si and Co-Cr disks as substrates by RF-magnetron sputtering method. The distance between the target and the substrate was 60 mm. High-purity argon (99.999%) and nitrogen (99.999%) were used as the sputtering and reactive gas, respectively.

After being polished and sonicated in alcohol and then in deionized water, the samples were dried before deposition process. The vacuum chamber was pumped with both a mechanical pump and a turbo molecular pump. When the chamber was pumped down to a base pressure of 7.8×10^{-4} Pa, argon was introduced into the chamber with a flow rate ~10 cm^3/min to clean the TiO_2 target surface for pre-sputtering for about 20 min, and the target-substrate distance was 60 mm. During the sputtering progress, the working pressure and the RF power was kept at 1.5 Pa and 250 W, respectively. 5 types of N-doped TiO_x films were processed with different annealing temperatures (ranging from 0 ^{o}C to 600 ^{o}C). For each type, five samples were synthesized at the same time to meet the need of characteristics. Gaseous mixture (Ar flow was 5 cm^3/min and N_2 flow was 2 cm^3/min) was fed into the reactor through mass flow controllers during the deposition runs.

The main objective of the present work is to determine the effect of post-deposition annealing on the structure of N-doped TiO_x films. The samples were annealed at 300, 500 and 600 ℃ for 1 h. After being annealed, the samples were placed at room temperature in dark. After 2 d, the samples were taken out and their contact angles were measured to observe their performance. Then visible-light (VIS) irradiation was carried out by a 150 W xenon lamp (64478 IM, Osram Halolux Ceran, Germany). The wavelength of VIS irradiation was above 430 nm. Which was performed in ambient air, i.e. the temperature was 298 K, and relative humidity (RH) 60 at%.

The structure and surface morphology of the films were evaluated by XRD and FESEM. The contact angle was measured with distilled water as a test liquid. The volume of water was 1.5 μL every drop. Experimental data was the mean value of 5 times. The sessile drop method was used for measuring contact angle with a commercial contact angle meter (SL200B, Kino, America). Its resolution was 0.01 ° and measurement accuracy was ±1 °.

2 Results and Discussion

2.1 Surface morphology, structure and composition

Fig.1 shows surface morphologies of N doped TiO_x films at different annealing temperatures. For the unannealed sample the surface topography is relatively smooth and dense. Some small size grains can be seen (Fig.1a). After annealed at 300 ℃ (Fig.1b), the grains grow. The average particle size is about 30 nm. After annealed at 500 ℃ (Fig.1c), the grains grow further. And particle size is more uniform. The average particle size is about 50 nm. After annealed at 600 ℃ (Fig.1d), the nanocrystals are precipitated, which indicates that the amorphous films are crystallized fully. The average particle size is about 80 nm.

Fig.2a shows the XRD patterns of the unannealed sample. The film is polycrystalline mainly in the anatase phase [A (110), A (200), and A (211)] with crystalline direction. Except A (110), other peaks aren't obvious and the background noise is clutter, which implies that the film is still amorphous. There are few TiN diffraction peaks, which are likely to originate from the less N_2. The nitrogen atoms diffuse into the films uniformly and replace oxygen atoms of TiO_x lattice. After the sample is annealed at 600 ℃, more characteristic peaks appear (Fig.2). They are assigned to a mixed structure of the anatase and rutile crystalline phases, as determined by XRD, implying that the film transforms into anatase and rutile phase.

Chemical composition of N-doped TiO_x films was investigated by XPS (Fig.3). The films have typical high resolution from contributions of Ti 2p (~458.8 eV), O 1s (~531.0 eV) and N 1s (398.1 eV). N 1s peak (398.1 eV) indicates that N element has been incorporated into the N-doped TiO_x films.

XPS peak software was used to fit the Ti 2p, O 1s and N 1s peaks of the unannealed samples and the ones annealed at 600 ℃. Then we get the states of Ti, O and N at different valent Ti ions and hydroxyl shown in Fig.3 and Fig.4, and t h e i r

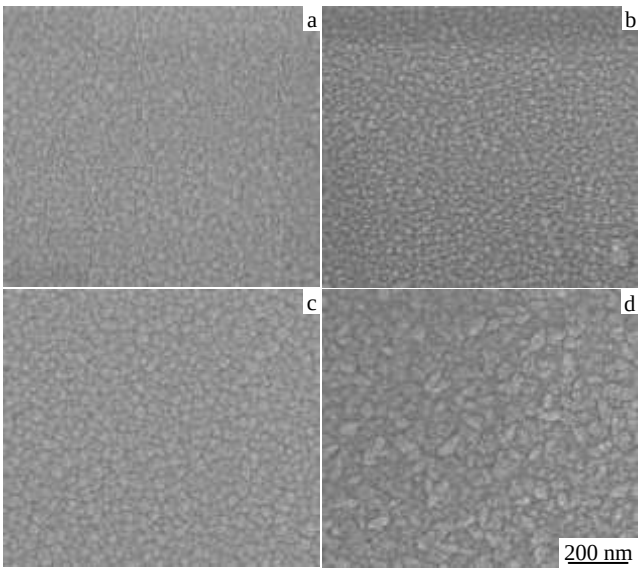

Fig.1 SEM surface morphologies of N doped TiO_x films annealed at different temperatures: (a) unannealed, (b) 300 ^{o}C, (c) 500 ^{o}C,

and (d) 600 °C

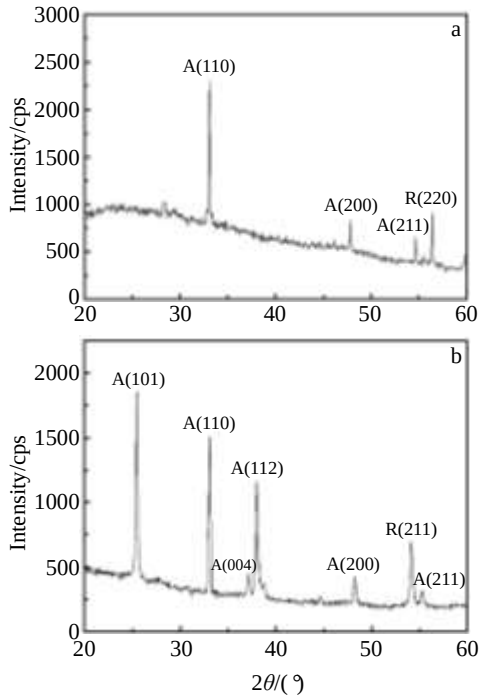

Fig.2 XRD patterns of the samples unannealed (a) and annealed at 600 ℃ (b)

content is shown at Table 1. All measured samples reveal similar Ti 2p, O 1s and N 1s spectra independent of the deposition conditions. In Ref.[10], the oxidation states of Ti at binding energies of 455.1, 456.7 and 458.7 eV correspond to Ti^{2+}, Ti^{3+} and Ti^{4+}, respectively. Compared with the unannealed ones, the content of Ti^{3+} of the samples annealed at 600 ℃ is elevated. This is because that Ti is oxidized in the air.

Nitrogen is doped into TiO_x lattice forming N-Ti-O, which are proved by β-N 1s (~396 eV) by XPS. While the second one is associated with terminally bonded well screened nitrogen in the so-called γ-N state with a binding energy around 400~402 eV, which is derived from the chemical state of the adsorbed molecules N_2 or embedded in TiO_x lattice gap in the form of N_2 molecules [11].

Usually oxygen in pure TiO_2 crystal is single Ti-O octahedral lattice oxygen, and the XPS peak of it is a normal distribution [12-14]. N, as the foreign substance, changes surrounding chemical environment of O element in a way, which changes the peak position and peak shape of O 1s in the XPS spectra (Fig.3b). A distinct peak appears at 531.1 eV in O 1s spectrum, which could be attributed to the Ti-O bond of N-doped TiO_x films [15]. Another apparent peak with a higher binding energy around 532.2 eV is also observed, which could be assigned to -OH bonds.

2.2 Hydrophilicity

The relationship of hydrophilicity and annealing temperature is shown in Fig.5. It is found that after high temperature treatment, water contact angles decrease apparently. This may

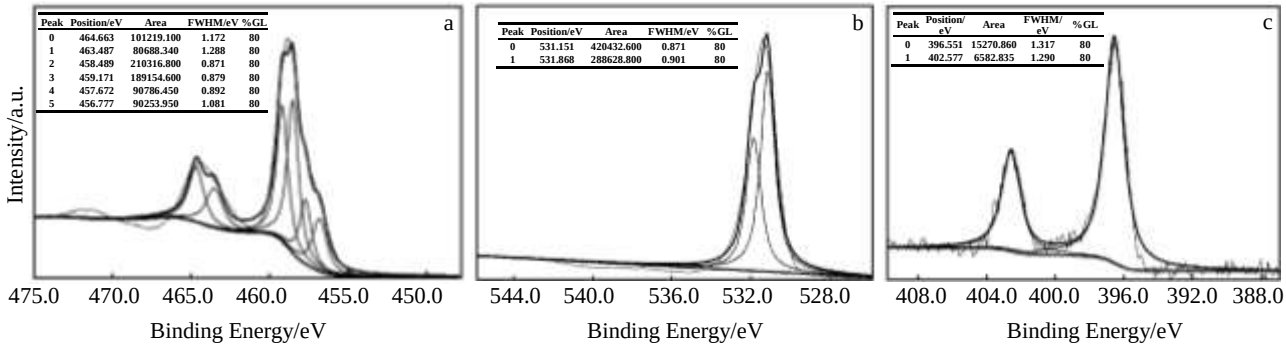

Fig.3 XPS spectra of the samples unannealed: (a) Ti 2p, (b) O 1s, and (c) N 1s

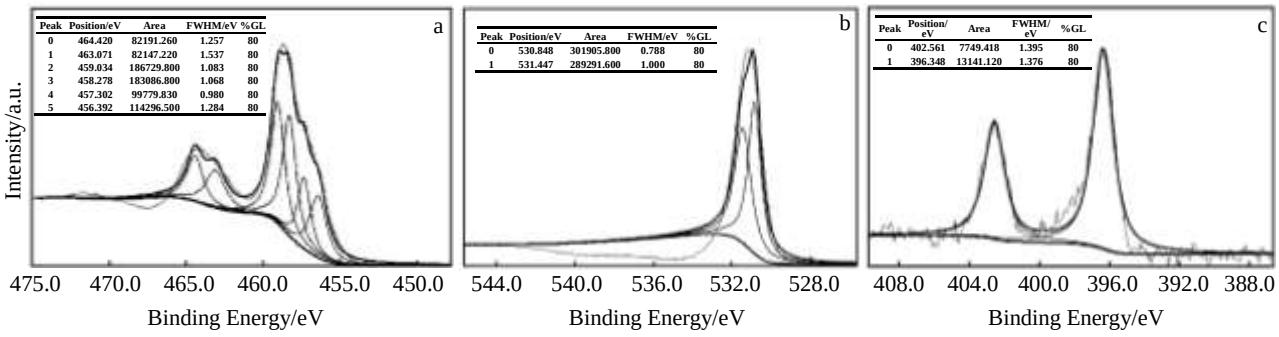

Fig.4 XPS spectra of the samples annealed at 600 ℃: (a) Ti 2p, (b) O 1s, and (c) N 1s

Table 1 O 1s analyzing parameter of samples at 0 and 600 ℃

Temperature/ ℃	Peak		Content/%
0	O 1s	O^{2-}	59.3
		-OH	40.7
600	O 1s	O^{2-}	51.1
		-OH	48.9

be because of defective sites on surface exposed in the air, where water and oxygen may compete to adsorb dissociatively. Since high-temperature annealing leads to highly hydrophilic surface, the defective sites are considered to be kinetically more favorable for hydroxyl adsorption than oxygen adsorption. However, the adsorption of -OH groups distorts the surface in both electronic structure and geometric structure, and thus the surface is unstable energetically[16]. Aside from microstructure and chemical composition, particle size also influences hydrophilicity of N-doped TiO_x films. Comparing the particle size (Fig.1), it can be known that the bigger size is the more conducive for improving the hydrophilicity. Water adsorbing on oxygen vacancies results in a highly hydrophilic surface[17]. According to the XPS results of Nobuyuki Sakai[18], the hydrophilicity conversion of TiO_x films is attributed to the structural change. With annealing temperature rising, the amorphous TiO_x transforms into anatase and rutile phase, causing the evident hydrophilicity change. The unannealed films are not crystallographic completely, which leads to the poor hydrophilicity. After being annealing at 600 ℃, the films show mostly anatase phase and part of rutile phase are crystallographic completely. From Table 1, it can be seen that after heat treatment, the content of hydroxyl groups increases. The high concentration of reactive hydroxyl groups causes good hydrophilicity.

After being annealed at 600 ℃, the samples were placed at room temperature in dark. Their water contact angles were tested, as shown in Fig.6. From the figure, it can be seen that the contact angles grow slowly. In the 20th day, the contact angle of the samples is 15.78°. The hydrophilicity of the surface becomes worse. This may be because that surface defects are healed by the adsorption of the hydroxyls

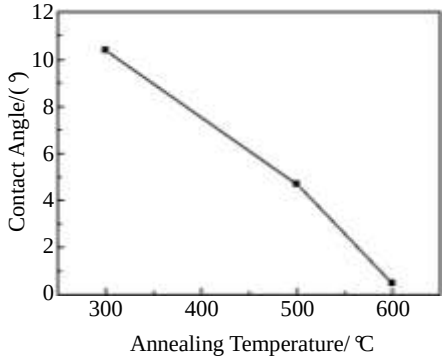

Fig.5 Water contact angles on the films annealed at different temperatures

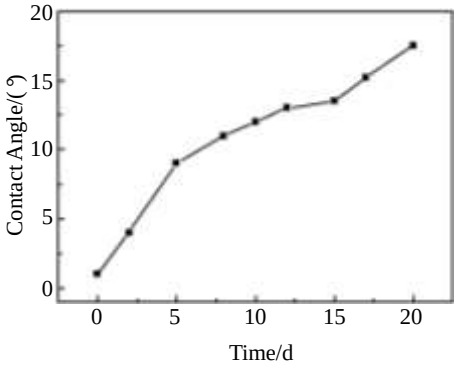

Fig.6 Maintenance of hydrophilicity of the films

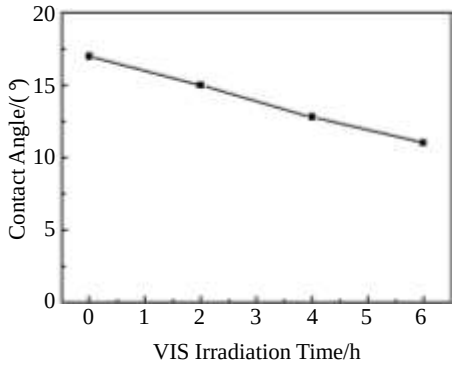

Fig.7 Hydrophilicity increase of thin films after VIS irradiation

(dissociated water) which coexist with the additionally adsorbed molecular water. The significant increase in water contact angle after storage in dark is consistent with this surface conversion. The surface conversion is ascribed to the replacement of the chemisorbed hydroxyl groups with the oxygens in the air[19]. After VIS irradiation, however, the contact angles of the films decrease, shown in Fig.7. And the hydrophilicity improves with VIS irradiation time[20]. After VIS irradiation for 2 h, the contact angles are down to about 14°. With the irradiation time increasing, the contact angles gradually decrease to less than 10°. There are disputed mechanisms leading to this behavior. A model is that β-N atomic state formed by N replacing the oxygen of TiO_x lattice leads to good hydrophilicity after VIS irradiation. N doping can improve the VIS absorption of TiO_x films and the red shift increases with the N content increasing, due to the effect of the localized N 2p states within the band gap, when dopant concentration is below 2.1 at%[5,7]. Manole [4] reported that the N-doped TiO_x films becomes highly hydrophilic when irradiated with photons of energy higher than the band gap of the films. They processed the transmittance data to derive the optical band gap of the materials and found that the oxygen content in

their films remains little affected by the increasing amount of O_2 in the discharge.

3 Conclusions

1) N is doped into TiO_x lattice to form β-N which is intrinsic factors to influence the hydrophilicity of N-doped TiO_x films. There are –OH bonds related to the hydrophilicity in the films due to that N changes the surrounding chemical environment of O element in a way.

2) Annealing influences the crystallinity of the films as well as hydrophilicity. After the samples are annealed, the amorphous films transform into anatase and rutile phase and the crystallinity increases with the temperatures rising, which increases the particle size.

3) The water contact angles decrease apparently due to microstructure, chemical composition and particle size of the films change, after high temperature treatment.

4) After the films are placed in dark, surface defects are healed or replaced by oxygen atoms in the air, which increases the water contact angles while VIS irradiation decreases the contact angles.

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射频磁控溅射方法制备掺氮 TiO_x 薄膜及其结构和亲水性研究

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摘　要：采用磁控溅射方法制备掺氮TiO_x薄膜。将TiO_x作为靶材，通以N_2/Ar混合气体来精确控制N的掺杂量。为改善掺氮TiO_x薄膜的性能，首先将试样放于退火炉中退火，退火温度范围为300~600 ℃；再将试样放于黑暗处一段时间；最后用可见光（VIS）照射。采用扫描电子显微镜（SEM）观察薄膜的表面形貌，结果表明，颗粒尺寸随退火温度升高而增大。采用X射线光电子能谱（XPS）研究薄膜的化学成分，结果表明，薄膜中生成了N-Ti-O (β-N)和羟基，这可能是因为N掺杂入TiO_x晶格引起的；且羟基含量随退火温度升高而增加，使得基片有更好的亲水性。采用X射线衍射（XRD）研究薄膜的晶体结构，结果表明，退火后非晶薄膜转变为晶态。采用接触角仪测试薄膜的亲水性，结果表明，水接触角随退火温度升高而减小，这可能是由于颗粒尺寸和羟基含量的改变造成的。亲水性也受避光储存时间的影响，实验结果表明，随着储存时间的增加，水接触角增加。可见光照射实验表明，可见光照射后薄膜的亲水性增加。

关键词：掺氮 TiO_2 薄膜；磁控溅射；退火；亲水性

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