

Influence of Ion Beam Assistance on Properties of Nitrogen-doped Titania Films Deposited by Cathodic Vacuum Arc

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Abstract: A nitrogen-doped titania film was prepared by cathodic vacuum arc method with ion beam assistance in a mixed oxygen/nitrogen gas atmosphere. The effect of the ion beam current on the structural, optical properties and photocatalytic activity of nitrogen-doped titania film was studied. The as-deposited films were subjected to annealing with the atmospheric environment, and the change of film properties after annealing was investigated. The structures of all as-deposited films were amorphous. In the annealing process, the ion beam-assisted nitrogen-doped titania films had a phase transition from amorphous to anatase polycrystalline with a strong TiO_2 anatase (101) peak at a temperature of 500°C . When the ion beam assistance was applied, the deposited nitrogen-doped titania films were found to the spectrum response of nitrogen-doped titania film deposited with ion beam assisted extended to the visible region. Photocatalytic activity of nitrogen-doped titania film decreases with ion beam current increase from 80 to 160 mA.

Key words: ion beam assisted deposition; titania film; nitrogen doped; photocatalysis

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1 Introduction

Titania thin film is well known for its outstanding optical, electrical and chemical properties. Photocatalytic TiO_2 film is a very promising material for the removal of organic pollutants in water and air^[1-3]. Anatase TiO_2 has a large band gap of 3.12 eV that requires powerful UV light to initiate the photocatalytic reactions. Therefore, extensive efforts have been made in the development of TiO_2 photocatalysts that can efficiently utilize solar or indoor light^[3-4]. Many modification methods such as metal ion doping, composite semiconductors and metal layer modification have been used to extend the light absorption of the catalyst to the visible light region, but have little effect^[5-8]. In recent years, Asahi^[9] prepared nitrogen-doped TiO_2 and reported that it can work as a photocatalyst under visible light while having a similar photocatalytic activity to pure TiO_2 under UV light. Therefore, many techniques had been used to prepare the visible-light active films, such as sol-gel method^[10], ion implantation^[11], pulsed laser deposition^[12], etc. In this paper, $\text{TiO}_{2-x}\text{N}_x$ films were prepared by cathodic vacuum arc with ion beam

assistance using titanium target under an O_2/N_2 mixture as the reactive gas, the influence of the ion beam current on microstructures, surface morphology, optical properties and photocatalytic behaviors of $\text{TiO}_{2-x}\text{N}_x$ films were investigated.

2 Experimental

$\text{TiO}_{2-x}\text{N}_x$ films were deposited by cathodic vacuum arc with ion beam assistance. A Ti cathode with a purity of 99.99% operated at an arc current of 75 A was used to obtain the plasma, the base pressure was < 560 Pa. A mixture of oxygen and nitrogen with purity of 99.99% was introduced into the plasma stream, and for $\text{TiO}_{2-x}\text{N}_x$ films, ion beam current were controlled. The working ion beam current was increased from 80 to 160 mA. The films were grown on n-Si(100) and glass substrates the working ion beam current was 80 mA, 120 mA and 160 mA. The films are assigned to film 1#, 2# and 3# respectively.

The crystalline structure of $\text{TiO}_{2-x}\text{N}_x$ films was measured using a Y-2000 X-ray diffractometer (XRD) with a $\text{CuK}\alpha$ source. The UV-visible optical transmission spectra of $\text{TiO}_{2-x}\text{N}_x$ films on fused glass substrate

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were measured at room temperature in air using a Shimadzu UV-2550 spectrophotometer in the range from 300 to 800 nm. The surface morphology of TiO_2-xN_x films has been observed by atomic force microscopy (AFM) using auto probe cp research.

In each experiment, a TiO_2-xN_x film was settled on the bottom of a 50 ml beaker, which contained 20 ml aqueous acid fuchsin with a concentration of 10 mg/L. A 150 W Xe lamp was suspended 11 cm above the TiO_2-xN_x films. Acid fuchsin concentration during irradiation was measured using a Shimadzu UV-2550 spectrophotometer. The photocatalytic activity was determined by the degradation rate of aqueous acid fuchsin on TiO_2-xN_x films by visible light irradiation.

3 Results and discussion

3.1 X-ray diffraction measurements

XRD measurements were carried out to study the crystalline properties of the prepared TiO_2-xN_x films at the annealing temperature of 500°C for 1 h in an atmospheric environment. Fig 1 shows XRD patterns of the films as difference ion beam current in nitrogen oxygen mixture gas. The as-deposited films are amorphous. TiO_2-xN_x thin films at the annealing temperature of 500°C , the crystalline structure appears some peaks corresponding to the anatase structure show a strong peak of anatase A(101), and the deposits exhibit a preferential orientation along the (101) planes.

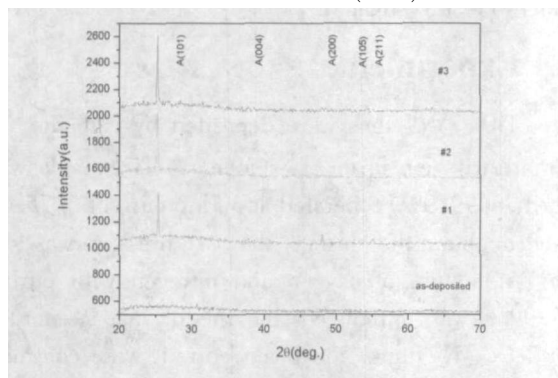


Fig 1 XRD patterns of TiO_2-xN_x films at different ion beam current

3.2 Surface morphology observed by AFM

The surface morphology of TiO_2-xN_x films deposited on silicon wafers were observed by AFM. The surface morphology picture of TiO_2-xN_x film at ion beam current 80 mA is shown in Fig 2. The films show small gross voids. Sample is composed of grains 25 ~ 80 nm size. The values of the surface roughness R (root mean square) was 2.114 nm within $0.5\mu\text{m} \times 0.5\mu\text{m}$ scan.

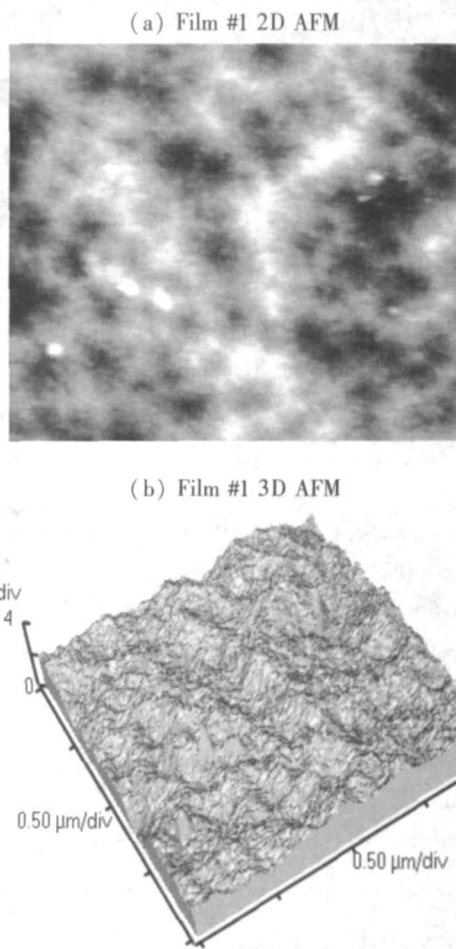


Fig 2 Surface morphologies by AFM of the TiO_2-xN_x films

3.3 Optical properties

Fig 3 shows the UV-Vis absorption spectra of the TiO_2-xN_x thin films prepared by ion beam assisted. In visible region, the average transmittance of TiO_2-xN_x film by ion beam assisted is higher than 70%. Which demonstrates that there is little energy loss caused by film absorption in this range, the result reveals that the spectrum response of TiO_2-xN_x film deposited with ion beam assisted shifted to the visible region.

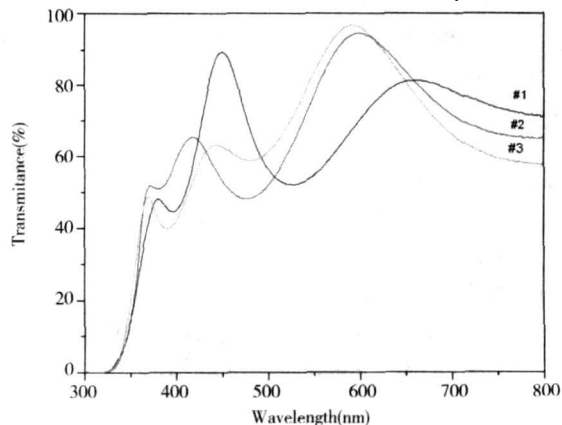


Fig 3 Transmittance spectra of the TiO_2-xN_x film deposited by ion beam assisted

3.4 Photocatalytic activity

The photocatalytic activity of the nitrogen-doped titania films prepared at different ion beam has been tested by the photo degradation of Acid fuchsin. For comparison the relative amount of AF solution degraded by $\text{TiO}_{2-x}\text{N}_x$ films after an illumination period of 30 min are illustrated in Fig.4. From these figures, the film #1 exhibits the best photocatalytic activity with the rate constant(k) about 0.0128 min^{-1} at 80 mA, assuming first order reaction kinetics. Film #3 displays the least photocatalytic activity with the rate constant(k) about 0.0103 min^{-1} at 160 mA under visible light illumination. It is revealed that the photocatalytic activity of $\text{TiO}_{2-x}\text{N}_x$ film decreases with ion beam current increase from 80 to 160 mA.

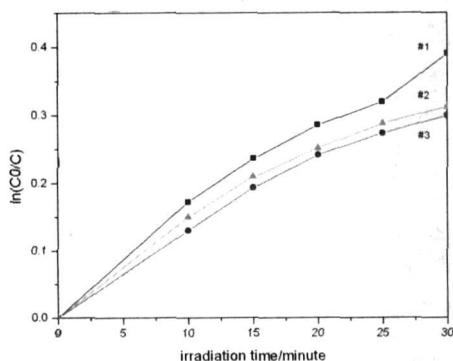


Fig.4 Photocatalytic degradation rates for the $\text{TiO}_{2-x}\text{N}_x$ film Prepared at different ion beam current

It might be explained by assisted ion beam source during deposition. It seems that some of the N ions and electrons from the Hall ion source might play a role in increasing the deposition rate, the momentum transfer of N ion beam bombardment on the growing thin films may result in absorbing more light irradiation, more electron-hole pairs can be generated in $\text{TiO}_{2-x}\text{N}_x$ films. $\text{TiO}_{2-x}\text{N}_x$ film deposited with ion beam assisted shifted to the visible region, and consequently gives rise to the enhancement of the photocatalytic activity.

4 Conclusions

In this paper, the influence of different ion beam parameters was investigated on property of $\text{TiO}_{2-x}\text{N}_x$ thin films prepared by cathodic vacuum arc. The crystalline structure of the as-deposited $\text{TiO}_{2-x}\text{N}_x$ film at the annealing temperature of 500°C was examined to be of anatase structure with a (101) preferential orientation. The values of the surface roughness R (root mean square) was 2.114 nm within $0.5\text{ }\mu\text{m} \times 0.5\text{ }\mu\text{m}$ scan.

When the ion beam assistance was applied, the deposi-

tioned nitrogen-doped titania films were found to the spectrum response of nitrogen-doped titania film deposited with ion beam assisted extended to the visible region. Photocatalytic activity of nitrogen-doped titania film decreases with ion beam current increase from 80 to 160 mA.

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椭圆偏振法研究四方氧化锆对 ZrSnNb合金氧化膜耐腐蚀性能的影响

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摘 要: 将经过不同热处理的 ZrSnNb合金样品放在 350℃、16.8mol/L Pa 0.01mol/L LOH溶液的高压釜中进行腐蚀。用椭圆偏振法研究氧化膜中的四方氧化锆,发现经过 580℃/冷轧/500℃处理的样品在腐蚀 42天和 190天后氧化膜中的四方氧化锆比其它样品的多。四方氧化锆是影响合金耐腐蚀性能的一个主要因素,四方氧化锆的形成有利于提高合金的耐腐蚀性能。

关键词: 锆合金; 氧化膜; 耐腐蚀性; 椭圆偏振法

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离子束辅助对真空电弧沉积掺氮二氧化钛薄膜特性的影响

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摘 要: 在氮氧混合气体中,通过离子束辅助,采用真空电弧沉积了氮掺杂的 TiO₂薄膜样品,研究了离子束流对掺氮二氧化钛薄膜的结构、光学性质和光催化性能的影响。实验结果表明:离子束辅助沉积的薄膜为非晶态结构,薄膜经 500℃热处理后向锐钛矿转变,且锐钛矿的 (101) 面的峰最强。通过 UV分析发现离子束辅助沉积的掺氮二氧化钛薄膜的吸收峰发生红移,其光催化活性随着离子束流的增大而减小。

关键词: 离子束辅助沉积; 二氧化钛薄膜; 氮掺杂; 光催化

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