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Effect of substrate roughness and working pressure on photocatalyst of N-doped TiO_x films prepared by reactive sputtering with air

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ABSTRACT

N-doped TiO_x films on the glass substrate were prepared by radio-frequency (RF) magnetron reactive sputtering of Ti target in a mixed gas of argon and dry air. The effect of substrate roughness and working pressure on the physical properties and the photocatalytic properties of the N-doped TiO_x films was investigated. The surface roughness of glass substrate has little influence on the film properties such as produced phases, lattice parameters, introduced nitrogen contents, and atomic bonding configurations, but significant influence on the surface roughness of film resulting in the variation of the photocatalytic ability. The working pressure has little influence on the produced phases and the atomic bonding configurations, but significant influence on the atomic concentration of the N-doped TiO_x film, resulting in the large variation of optical, structural, and photocatalytic properties. It is suggested that the high photocatalysis of N-doped TiO_x film requires a certain range of the N doping concentration which shows the interstitial complex N doping states in TiO_2.

1. Introduction

Anatase TiO_2 (titanium dioxide) has been widely used as a photocatalyst because of its high activity, low cost and environmentally friendly features. However, the photocatalytic activity of anatase TiO_2 is limited to light irradiation wavelengths in the UV (Ultraviolet) region because anatase TiO_2 semiconductor has a wide band-gap of about 3.2 eV and can only absorb UV light with wavelengths below 387 nm. Recently, it is found that N (nitrogen)-doped TiO_2 photocatalyst is activated under visible light irradiation as well as under ultraviolet irradiation [1]. To realize a more efficient utilization of solar irradiation, many studies have been focused on the N-doped TiO_2 powders produced by various routes [2–4]. Various methods for preparing thin films of N-doped TiO_2 by gas condensation techniques have also been reported in recent years [5–7]. Among those techniques, radio-frequency (RF) magnetron reactive sputtering is the most widely used method for thin film preparation and is advantageous to produce uniform and well-crystallized films. The film thickness, crystal structure, composition, microstructure and defect structure are determined by many factors such as sputtering power, substrate temperature, partial pressures of sputtering gas, sputtering time, and distance from the target to the substrate [8–12]. Among them, the working pressure and the partial pressure are very important deposition parameters which control deposition rate, phase composition, crystallite (grain) size, and surface roughness [9].

Meanwhile, many researches have reported the effect of surface roughness of film on the photocatalysis since high photocatalytic efficiency can be achieved by increasing the surface roughness of non-doped TiO_2 film [13–15]. A. P. Xagas et al. [13] reported that the surface of the photocatalyst needs to be as large as possible in order to efficiently absorb the incident light energy. An improvement of the real surface area (to the geometrical surface projection) of the photocatalyst may be achieved by increasing the height and roughness. Based on their results, the surface roughness of film is an important factor in the photocatalytic ability. Many reports have reported the non-doped TiO_2 films prepared by sputtering as photocatalyst on the roughened surface of film, and those reports for realizing high surface roughness of film have focused on the sputtering parameters such as gas pressures [11,14], sputtering power [16], various substrates [17], deposition time [18], and substrate temperatures [10]. However, despite numerous studies on this topic, most researches have investigated the effect of surface roughness for only non-doped TiO_2. To the best of our knowledge, there have been few reports regarding N-doped TiO_x on the effect of surface roughness.

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The purpose of the present work is to investigate the effect of substrate roughness and working pressure for producing the N-doped TiO_x films using RF magnetron reactive sputtering of Ti target in a mixture of Ar gas and dry air with a set N_2/O_2 ratio [19] on the physical properties in conjunction with the photocatalytic properties.

2. Experimental

Depositions were performed using the RF magnetron reactive sputtering apparatus. A titanium disk (99.9% purity) of 75 mm in diameter was used as a target and a glass plate ($28 \times 48 \times 1$ mm) as a substrate. For investigating the effect of surface roughness of the glass substrate on the photocatalytic ability, the glass plate was rubbed by SiC abrasion paper (Fuji Star abrasive paper sheet, Sankyo Rikagaku Co. Ltd., Saitama, Japan). The finest grit was #1500 (S-1 sample) which corresponded to abrasive particles with an average size of 12 μm, and the coarsest grit was #80 (S-8 sample) which corresponded to 150 μm, as shown in Table 1 (average abrasive particle size according to the document of ISO 8486-1:1996). After completing each abrasion step using a particular grit, the samples were cleaned in distilled water by an ultrasonic cleansing for 10 min and then dried in a dry chamber for 1 h at 373 K.

A mixture of Ar gas and dry air (N_2:O_2 = 79:21 (vol.%)), or O_2 gas for comparison (rubbed by No. 80), was used as the sputtering gas [19]. The sputtering conditions such as background pressure, RF power, target to substrate distance, sputtering time, working pressure, Ar and air flow ratio, and substrate temperature were fixed as shown in Table 1. The flow ratios of Ar and dry air were controlled by mass flow controllers. For investigating the effect of working pressure in the sputtering on the photocatalytic ability, the conditions of gas flow ratio and working pressure for each sample (W-1 to W-8) were set as listed in Table 2, and the air flow ratio (f(air)/f(Ar), where f(air) and f(Ar) are the individual flow rates of the gases) was fixed about 0.164 (±0.001). At the beginning of film preparation, a glass substrate was protected by a shutter and then a target was pre-sputtered in Ar atmosphere for about 15 min in order to remove oxide layer and contaminant on the surface of the target, followed by the deposition process under the controlled gas flow. After the deposition, the substrate was slowly cooled in the chamber to room temperature under the flow of the gas mixture.

The crystal structure of the films was evaluated by X-ray diffraction (XRD) with Cu K_α radiation at 40 kV and 30 mA working in the θ–2θ mode (Rint 2100, Rigaku). Scanning electron microscope (SEM) was used for micro-structural analysis (JSM-5800, JEOL). The surface topography and surface roughness of the samples was examined by atomic force microscopy (AFM, SII Nanotechnology SPA-300HV + SPI-3800N) in tapping mode at a scan rate of 0.5 Hz using a silicon cantilever probe (Seiko Instruments Inc., SIDF20, force constant of 15 N m^{-1}). A UV–Vis spectrophotometer (Lambda 900, Perkin Elmer) was used to determine the UV–Vis transmission spectra from 340 nm to 700 nm. Chemical bonding states and concentration of each element at the film surface were analyzed by X-ray photoelectron spectroscopy (XPS) using monochromatic Mg K_α radiation (10 mA, 10 kV). The spectra were calibrated with C 1s, which exhibits the binding energy of 284.0 eV. The background pressure of the XPS system was less than 10^{-6} Pa. Before the XPS measurement the film surface was cleaned in distilled water by an ultrasonic cleansing for 30 min and then dried in a dry chamber for 6 h at 373 K. The CASA XPS program with a Gaussian-Lorentzian mix function (70:30 ratios) and Shirley background subtraction was used to deconvolute the spectra (before deconvolute, each peak was smoothed using Savitzky-Golay algorithm). The surface atomic concentration of Ti, O and N was calculated from the corresponding spectra.

The evaluation on photocatalytic activity of the film was performed by photocatalytic oxidation of NO gas using a chemiluminescence detector (HORIBA APNA-360) [19]. The film on glass substrate was put in the center of acrylic container ($200 \times 120 \times 10$ mm) with the inner volume of 79 ml. The air and NO gas (197.4 ppm, N_2 balance) were mixed to obtain the desired concentration (NO: 1.0 ppm) in a gas blender. After attaining the steady state of NO concentration through the by-pass line, the film in the main line was irradiated with a Xenon lamp (USHIO, UXL-500D-O, 500 W) from a distance of 700 mm through the quartz window for 5 min (300 s) at the beginning of the measurement, and then the NO gas was flown into a longitudinal direction of the container (main line) for 1200 s with light irradiation at a flow rate of 1.1 l/min. The UV light intensity at the film surface was 30 W/m^2 measured by a UV Monitor (EKO, CEK-MS211-I). For the visible light irradiation, the UV-filtered light (Koshin Kogaku Co., Ltd, >400 nm) was used.

3. Results

3.1. Effect of substrate roughness

Fig. 1(a)–(d) shows the SEM images of the abraded glass substrate surface for the samples S-1, -3, -5, and -8. The S-1 sample substrate shows a smooth surface without any scratches. As increasing the abrasive particle size, the partially scratches of substrate surface increase (Fig. 1(b)), and then show deep scratches with holes (Fig. 1(c)), even show obviously high roughness (Fig. 1(d)). The surface morphology of the films sputtered on various abrasive particle sizes is shown in Fig. 1(e)–(h). As increasing the abrasive particle size, the partially scratched traces of the film surface increase (Fig. 1(f)), and then show deep scratches with holes (Fig. 1(g)), even show obviously high roughness (Fig. 1(h)). Compared with the morphology of before and after film deposition the surface morphology of both is similar to each other.

The cross-sectional morphology of the glass substrates and the films is shown in Fig. 2 ((a, c) S-1, (b, d) S-8). The substrate cross-sectional morphology for the S-1 sample exhibits a smooth cross-section, while the S-8 sample exhibits a quite roughness, as shown in Fig. 2(a and b). The film for S-1 sample exhibits a columnar structure with smooth cross-section without any crack, while the S-8 sample exhibits a quite rough surface with columnar structure caused by the roughened substrate, and those thicknesses are approximately 1.8–1.9 μm as shown in Fig. 2(c and d).

The AFM surface topography, cross-sectional height analysis, and average roughness (Ra) of the films are shown in Fig. 3. The surface topography was resolved on a micrometer scale with a scan range of 10 μm × 10 μm, where white and black areas correspond to higher and lower parts (hill and valley) in the AFM topographic images. For the cross-sectional height analysis (horizontal line in the surface topography images) the vertical scale is varied from 33 nm to 680 nm per figure, while the horizontal scales are varied from 9.53 μm to 8.3 μm per figure. The degree of hill-to-valley (vertical scale) for the film surface is gradually increased with increasing the abrasive particle size (from S-1 to S-8). The Ra (film) is largely decreased from S-8 to S-5 (53 nm–12 nm) and gradually decreased from S-5 to S-1 samples (12 nm–3 nm) (The Ra data is comparable to the root-mean-square (RMS) data [20]).

The X-ray diffraction patterns for the films are shown in Fig. 4. The polycrystalline anatase structure was observed for the samples from S-1 to S-8 and O-1, with small trace of rutile (1 1 0) peak. The XRD patterns of the as-deposited films showed similar halo patterns at around 2θ = 15–35° for all samples, implying that these films were composed of the crystalline and the amorphous. The (estimated) full-width at half-maximum (FWHM) and