



# Enhancement on photocatalytic activity of an amorphous titanium oxide film with nano-textured surface by selective-fluorination etching process

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## ABSTRACT

A selective-fluorination etching process achieved by an UV light pre-irradiation and the subsequently fluorination etching was developed to enhance the photocatalytic activity of a low-temperature deposited amorphous titanium oxide (a-TiO<sub>x</sub>) film. Textured surface on the a-TiO<sub>x</sub> films formed by this process were investigated using atomic force microscope and field emission scanning electron microscope. Evidence of the fluorine ions introduced into the a-TiO<sub>x</sub> films was examined using Fourier transform infrared spectrometry and X-ray photoelectron spectroscopy. The etching thickness of the a-TiO<sub>x</sub> film was found to be deeply relevant to the film pre-irradiated by the UV light. An a-TiO<sub>x</sub> film with nano-textured surface, which was favorable to enlarge the specific surface area, thus was obtainable from the notable etching selectivity of the film pre-irradiated by UV light through a nano-sized mask. In addition, the surface acidity of the a-TiO<sub>x</sub> film was enhanced by the formation of the Ti–F chemical bonds originating from the fluorination etching process, which also was functional to facilitate the production of surface OH free radicals. Accordingly, the resulting fluorinated a-TiO<sub>x</sub> film with nano-textured surface performed a quality photocatalytic activity comparable to that of the high-temperature achieved TiO<sub>x</sub> film with anatase structures.

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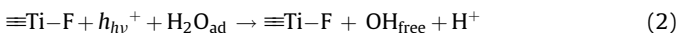
## 1. Introduction

Titanium oxide (TiO<sub>x</sub>) films are comprehensively applied in various industrial fields due to their excellent photocatalytic activity and high refractive index, especially in environmental purification, anti- or high-reflection coating, dye-sensitized solar cell, surface self-cleaning/antifogging functional coating, and biomedical engineering applications [1–5]. The photocatalytic activity of the TiO<sub>x</sub> film is known to be influenced by its crystalline structure, specific surface area, and functional group incorporation [6,7]. Regarding the crystalline structure, most researchers have focused their efforts to prepare TiO<sub>x</sub> films with the anatase structure, which possesses the best photocatalytic activity. However, since the process temperature required to achieve a crystalline TiO<sub>x</sub> film with anatase structures is typically higher than most of the substrates/devices can be withstood, the development of a low-temperature process and/or deposition on the amorphous TiO<sub>x</sub> films with sufficient photocatalytic activity is

very crucial for the application on these low heat-resistant substrates/devices. Recently, plasma-enhanced chemical vapor deposition (PECVD) has become one of the most popular technologies for preparing quality amorphous TiO<sub>x</sub> (a-TiO<sub>x</sub>) film abundant in OH groups at a low temperature. Although the PECVD-deposited a-TiO<sub>x</sub> film performed a better photocatalytic activity than those films prepared by other methods, its photocatalysis was still significantly inferior to that of the TiO<sub>x</sub> film with anatase structure [8,9]. In addition, due to the photocatalytic activity is greatly affected by the adsorption of all reactants as well as the efficiency of the chemical reaction on the film surface, the development on the surface modification process on the TiO<sub>x</sub> film is recommended to strengthen the resulting photocatalytic activity. The surface acidization on the TiO<sub>x</sub> film has been reported to apparently improve the adsorption and reaction of polar molecules and therefore enhances the film's property [10,11]. Among various efforts for the improvement of the photocatalytic activity via acidizing the TiO<sub>x</sub> film surface, fluorination process appeared to be the most interesting method for increasing the surface acidity of the TiO<sub>x</sub> materials due to the strong electronegativity of fluorine [12–14]. When the surface OH groups replaced by the fluorine ions, as given in Eq. (1), it becomes stable against photocorrosion and also

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facilitates the production of surface OH free radicals, as given in Eq. (2), which is beneficial for enhancing the photocatalytic reaction [15]:



In addition to the surface acidization process, recent studies also have sought to prepare a nano-structured  $\text{TiO}_x$  to enrich the specific surface area, which led to the enhancement on the photocatalytic activity [16–18]. Accordingly, an attempt to roughen the surface morphology of the  $\text{TiO}_x$  film to enrich the specific surface area is also crucial to further strengthen the film's photocatalytic activity.

With the aim to prepare a fluorinated a- $\text{TiO}_x$  film with nano-textured surface, which both possessed adequate surface acidity and large specific surface area, we develop a selective-fluorination etching process achieved by pre-irradiating the PECVD-deposited a- $\text{TiO}_x$  film through a nano-sized mask and subsequently fluorinating in the diluted hydrofluoric (HF) etching solution. The origins responsible for the enhancement on the photocatalytic activity of the processed a- $\text{TiO}_x$  films were characterized by their surface morphologies and chemical bond configurations. The results show that the fluorinated a- $\text{TiO}_x$  film with nano-textured surface prepared by the selective-fluorination etching process performed a photocatalytic activity comparable to that of the high-temperature prepared  $\text{TiO}_x$  film with anatase structure.

## 2. Experiment

A 300-nm-thick hydro-generated a- $\text{TiO}_x$  film was deposited onto silicon and glass substrates (10 mm × 10 mm) by a capacitively coupled radio-frequency (13.56 MHz) discharge PECVD system. A titanium tetraisopropoxide [ $\text{Ti}(\text{OC}_3\text{H}_7)_4$ , TTIP] liquid source was utilized as the primary titanium precursor through a heated bubbling cylinder at 70 °C with nitrogen carrier gas. Pure oxygen gas was employed as a reactant gas and intermixed with TTIP vapor in a mixbox. All the gas line also was heated to 100 °C to prevent condensation. The TTIP-oxygen gas mixture was dispersed through a showerhead array at the upper electrode. The substrates were placed on the lower electrode, 50 mm from the upper electrode. The deposition pressure, rf power, and gas flow rate of TTIP/ $\text{O}_2$  were controlled at 40 Pa, 100 W, and 120/20 sccm, respectively. Prior to the film fluorination etching by the diluted HF solution (1.0% vol.%), the a- $\text{TiO}_x$  film was pre-irradiated by an UV

light (TLD 10 W/08, Philips; centered at 365 nm with a constant intensity of 5 mW/cm<sup>2</sup>) through an anodic alumina membranes (AAM) (the diameter of the pores was approximately 20 nm) mask. Fig. 1 illustrates a schematic flowchart for preparing the a- $\text{TiO}_x$  film with nano-textured surface by using the selective-fluorination etching process. The  $\text{TiO}_x$  film with anatase structures also was prepared from the untreated a- $\text{TiO}_x$  film post-annealed at 500 °C for 30 min under oxygen ambient (hereafter denoted as annealed  $\text{TiO}_x$ ) for comparison.

The film thickness of these a- $\text{TiO}_x$  films with and without the surface modification process was measured using a surface profile system (Dektak 6 M, Veeco). Root-mean-square surface roughness ( $R_q$ ) and structural morphologies were respectively observed using an atomic force microscopy (AFM, DI-3100, Veeco) by tapping mode and a field emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL) operated at 3 kV. Optical transmittance was measured by a UV-vis spectrophotometer (UVD 3500, Labomed, Inc.). A Fourier transform infrared (FTIR) spectrometry (FT/IR-4100, JASCO) and an X-ray photoelectron spectroscope (XPS; PHI Quantera SXM, ULVAC-PHI) with monochromatic Al K $\alpha$  radiation were employed to examine the chemical bonding states and surface bond nature of these films. The pass energy for the XPS narrow scans was 20 eV with a step size of 0.1 eV. The energy scale of the spectrometer was calibrated using the core level of C 1s at 284.6 eV. The crystalline structures of these films were conducted using a grazing incident X-ray diffractometer (GIXRD) at 30 kV and 30 mA using Cu K $\alpha_1$  radiation (D-500, Siemens). The associated photocatalytic activity illuminated by the UV light with a constant intensity of 1 mW/cm<sup>2</sup> was determined by the decolorization of a 20 ppm concentrated methylene blue (MB) solution using the UV-vis spectrophotometer from the absorbance at 665 nm under atmosphere ambient.

## 3. Results and discussions

Fig. 2 shows the etching thickness of the a- $\text{TiO}_x$  films immersed in the diluted HF solution for 15 s as a function of the UV light pre-irradiation time. In agreement with the previous reports [19–21], the a- $\text{TiO}_x$  films pre-irradiated by the UV light and subsequently etched in the dilute HF solution led to an etching thickness much smaller than that of the a- $\text{TiO}_x$  film directly immersed in the solution (~50 nm), revealing that the etching process on the film surface was alleviated by an UV light pre-irradiation. It is related to the generated electrons under UV light irradiation tend to reduce Ti(IV) cation to Ti(III) state and therefore caused the film surface is

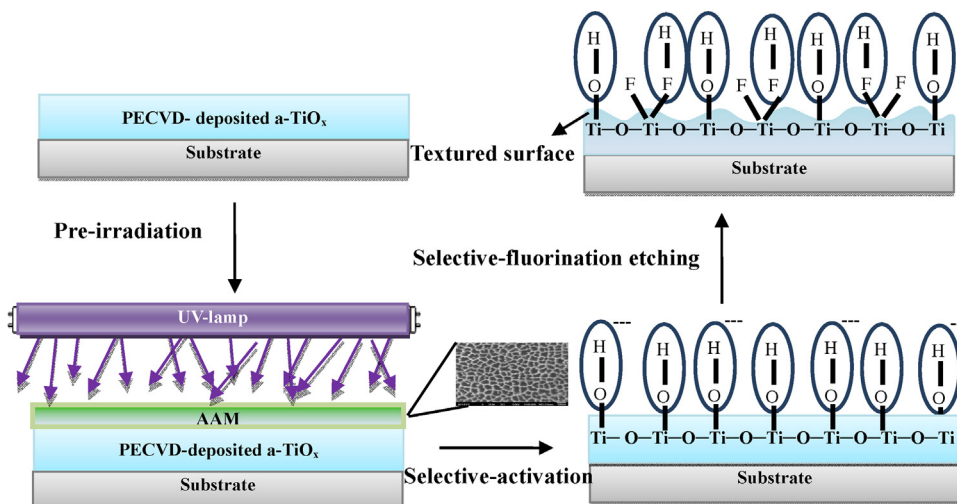


Fig. 1. A schematic flowchart for preparing the a- $\text{TiO}_x$  film with nano-textured surface by using the selective-fluorination etching process.

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