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Photocatalytic performance of TiO_2 films produced with combination of oxygen-plasma and rapid thermal annealing

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ABSTRACT

In this work, a combination of oxygen plasma and rapid thermal annealing was suggested in order to oxidize the surface of titanium into TiO_2. A plasma was formed by employing pure oxygen at 150 W, 300 W, and 400 W under a pressure of 7.5 to 8.5 Pa for 5 to 10 min. The TiO_2 was then subjected to rapid thermal annealing (RTA) at a temperature of 400 to 500 °C for 1 min. From the attained results, an RF power of 300 W for 5 min was observed to be sufficient to produce an optimal photocatalytic TiO_2 film. Optimal conditions were confirmed by additional experiments involving humic acid (HA) degradation of the TiO_2 films. When compared to a traditional TiO_2 film, a TiO_2 film prepared with an oxygen-plasma treatment and RTA system exhibited improved photocatalytic capability for HA photodegradation in an aqueous solution. Therefore, this process proposed in this work can be an excellent alternative to the traditional method for fabricating photocatalytic TiO_2 films.

1. Introduction

Semiconductor photocatalyst can be used to mineralize many organic contaminants, such as aromatics, halohydrocarbons, insecticides, and pesticides, and so on [1–4]. Titanium dioxide (TiO_2) has been researched extensively due to its biological and chemical inertness, high photoactivity, abundance, and low cost. It has been mostly used in powder form [2,4–6]. Since it can be bound to an inert substrate, such as glass [7–10] or glass fiber [11], it has become increasingly clear that the more practical form of a semiconductor photocatalyst is a film, strongly bound to an inert glass or ceramic substrate[7,8,12–23].

Immobilization of TiO_2 can be carried out by a variety of conventional methods. Of these methods, the sol–gel process is the most widely used. In this technique, an organotitanium compound or a titanium sol material is applied to a support material and then subjected to heat treatment [12,13,15,16,24–26]. Metal oxidation is a method to oxidize a surface of a target object with TiO_2 by heating metallic titanium in air or subjecting it to anodization [15,21,27]. Other developed methods are mainly based on the aerosol pyrolysis and alkyloxide hydrolysis, using different kinds of alkyloxide or other titanium-containing compounds [28–30].

Plasma oxidation is employed in many industrial fields to deposit thin films or as a surface treatment technique. The oxidation process in oxygen plasma can produce highly pure and uniform thin films, even if the surface of a substrate has a complex shape. In spite of these advantages, there has been little effort to apply this technique to TiO_2 photocatalyst that is ever increasingly used in environmental decontamination [31–33].

The aforementioned fabrication methods involve heating TiO_2 in the range of 400 to 500 °C for 1 to 3 h. However, such a long heat treatment leads to continuous growth of the TiO_2 crystal structure and causes both a decrease in surface area and poor economic efficiency. TiO_2 also exhibits low photocatalytic properties in its amorphous state. Therefore, photocatalytic properties should be enhanced by converting TiO_2 into crystalline anatase through thermal annealing [24–26]. Rapid thermal annealing (RTA) involves rapid increase of temperature in short time, heat treatment duration of approximately one minute, and cooling down. This can lead to excellent photocatalytic properties. The RTA methods are based on heating by localized high-energy light irradiation, either from a laser, xenon tube, or tungsten-halogen lamps [14]. Recently, RTA was used in a semiconductor process to fabricate crystal nanofilms without diffusion and diffraction [34,35].

The objective of this research was to develop a process to fabricate a TiO_2 film by incorporating an oxygen plasma treatment (OPT) and RTA. The TiO_2 films by this process are expected to exhibit excellent photocatalytic properties. It is the report in which both an oxygen plasma and RTA were used to produce a TiO_2 film on titanium. As

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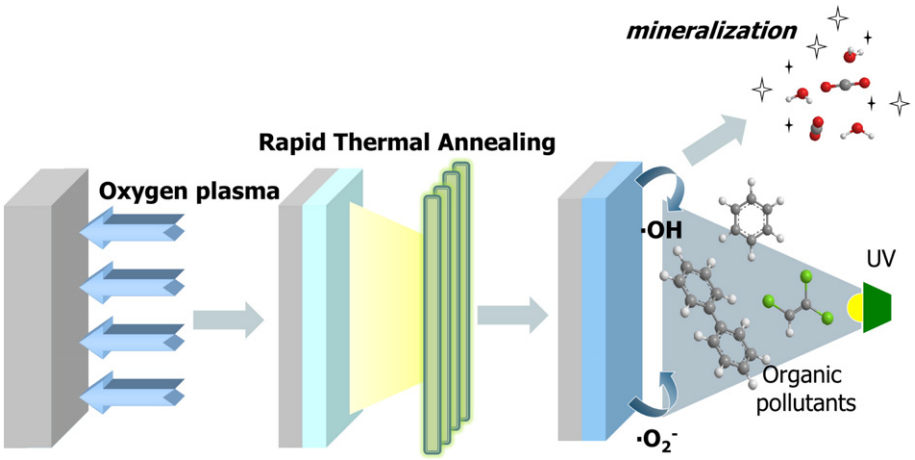

Fig. 1. TiO_2 film formation through an oxygen plasma treatment and rapid thermal annealing.

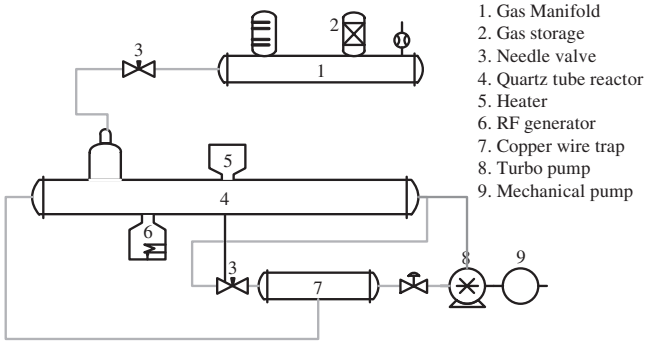

Fig. 2. The plasma treatment system in this research.

shown in Fig. 1, the semiconductor photocatalyst was fabricated in the form of a film using oxygen plasma. The TiO_2 film was then subjected to RTA at a temperature of 400 to 500 °C for 1 min.

2. Experimental details

2.1. Materials and characterization

Titanium (Ti) film (99.5% pure and 200 μm thick) was purchased from Alfa Aesar. Prior to experimentation, the samples were chemically etched by immersion in a hydrofluoric acid, nitric acid, and distilled water mixture (1:4:5 v/v/v) so as to remove the native oxide layer. The samples were then stored under vacuum, rinsed in an ultrasonic bath containing cold deionized water for 30 min, and kept in vacuum desiccators. TiO_2 powder (P-25, 80% anatase and 20% rutile) was obtained from Degussa based in Germany for comparison with the film samples. The powders were filtered (0.22 μm Millipore durapore membrane) to remove precipitates and analyzed for total organic carbon content (Analytic Jena, Multi N/C 3100). The resultant powders had a Brunauer Emmett Teller (BET) surface area of 55 m^2/g and an average particle diameter of 30 nm. Lastly, aerosol pyrolysis was performed for comparison. The aerosol-pyrolysis TiO_2 films were produced using a torch flame for 10 min, and then heating the thermally oxidized films at 500 °C for 1 h. Humic acid (HA) was purchased from Sigma Aldrich. A 1000 mg/L stock solution of HA was prepared by dissolving 1 g of HA in 20 mL of a 1 M NaOH solution. The solution was then diluted to 1 L. All chemicals used in this process were of analytical grade.

Phase detection and analysis were performed with X-ray diffractometry (XRD) (RIGAKU, D/MAX-2500/PC) with CuKR radiation (λ) 1.5406 Å from 20° to 80° at a scanning speed of 5° min^{-1}. X-ray tube voltage and current were set at 40 kV and 100 mA, respectively. X-ray photoelectron spectroscopy (XPS) (OMICRON-UHV, VG) using MgKα X-ray source (1253.6 eV) was used to determine the surface composition of the oxygen plasma-treated films. The binding energies were measured in reference to the C 1s peak at 284.6 eV. In some samples, an argon-ion sputtering procedure was performed during 30 min with an energy beam of 2 keV (1 cm^2, flux = 0.5 mA). The BET surface area was measured at 77.35 K (MICROMETRICS, ASAP 2010). The surface morphologies of the samples were observed using scanning electron microscopy (SEM) (JEOL, JJSM-6340F) with an acceleration voltage of 15.0 kV.

Table 1
Experimental conditions for titanium film with oxygen-plasma treatment.

Treatments (PTS)	Gasses	Time (min)
Pre-treatment	Ar	10 min
Cleaning	O_2	10 min
Oxygen plasma generation	O_2	5, 10 min
Parameter	**Value**	
Cleaning gas flow rate	80 cm^3/min	
Plasma generation gas flow rate	20 cm^3/min	
Pre-treatment pressure (p)	1.0–2.0 Pa	
Working reactor pressure (p)	7.0–8.5 Pa	
Radio frequency (RF) power (P)	150 W, 300 W, 400 W	

Underlined data signify pretreatment for reactor cleaning was formed by employing pure oxygen under a working pressure of 1.0 to 2.0 Pa. A plasma was formed by employing pure oxygen under a working pressure of 7.0 to 8.5 Pa.

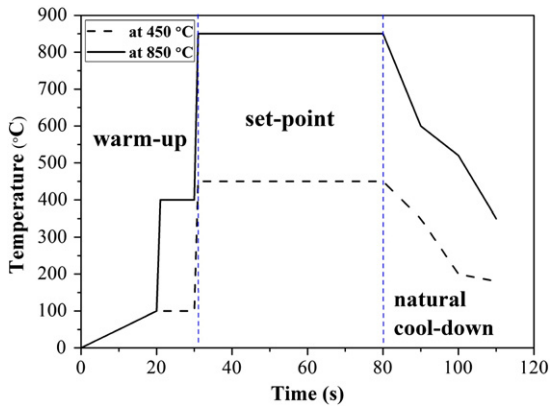

Fig. 3. Rapid thermal annealing temperature change for TiO_2 crystal formation.