



Effect of N₂ ion flux on the photocatalysis of nitrogen-doped titanium oxide films by electron-beam evaporation

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Received 30 November 2004; received in revised form 9 May 2005; accepted 30 May 2005

Available online 14 July 2005

Abstract

Nitrogen-doped titanium oxide (TiO_xN_y) films were prepared with ion-assisted electron-beam evaporation. The nitrogen (N) incorporated in the film is influenced by the N₂ flux modulated by the N₂ flow rate through an ion gun. The TiO_xN_y films have the absorption edge of TiO₂ red-shifted to 500 nm and exhibit visible light-induced photocatalytic properties in the surface hydrophilicity and the degradation of methylene blue. The structures and states of nitrogen in the films are investigated by X-ray diffraction patterns (XRD), and X-ray photoelectron spectroscopy (XPS) and related to their visible light-induced photocatalytic properties. The results indicate that the substitutional N in anatase TiO₂ can induce visible light photocatalysis. The substitutional N is readily doped by the energetic nitrogen ions from the ion gun. The best photocatalytic activity is obtained at the largest N loading about 5.6 at.%, corresponding to the most substitutional N in anatase TiO₂. The film exhibits the degradation of methylene blue with a rate-constant (k) about 0.065 h⁻¹ and retaining 7° water contact angle on the surface under visible light illumination.

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Keywords: Titanium oxide; Nitrogen-doped titanium oxide; Photocatalysis; Visible light photocatalyst; Electron-beam evaporation; Nanostructure

1. Introduction

Titanium dioxide (TiO₂) has a wide range of applications because of its outstanding and beneficial physical as well as chemical properties, and anatase

TiO₂ has been identified as the most effective and useful photocatalyst [1–4]. However, the widespread application of TiO₂ as a photocatalyst has been retarded by its wide band gap with 3.2 eV for the anatase phase, hence, the requirement of ultraviolet (UV) radiation with wavelength (λ) < 387 nm, which accounts for part (<5%) of the solar irradiation used in the photocatalytic activation. To improve its photocatalytic efficiency, it is charming to extend the high

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reactivity towards the absorption of visible light (λ) > 380 nm, thereby allowing the use of the primary part of solar light, and even poor radiation of interior lighting.

Several current attempts have been reported to convert the absorption edge of TiO₂ from UV to visible region by organic-dyes attachment [5], transition-metal doping [6–8] or hydrogen-plasma reduction [9–11]. Although the organic-dyes attachment has been successful in solar-cell application, the stability and adhesion of organic-dyes on TiO₂ employed in aqueous solution are questioned [5]. Doping transition-metal suffered from a thermal instability, an increase of carrier-recombination centers and the usage of an expensive ion-implantation facility [6–8]. Reduction of TiO₂ introduced localized oxygen vacancy states located with 0.75–1.18 eV below the conduction band minimum (CBM) of TiO₂, which inhibited the photocatalytic activity for the reduction reaction with the redox potential higher than the CBM, and then, the photo-generated electrons would be readily refined the oxygen vacancies [9,10].

Asahi et al. [12] has reported that the band gap narrowing by nitrogen doping into TiO₂ is efficient to yield high photocatalytic activities under illumination of visible light. They prepared N-doped TiO₂ films by means of reactive magnetron sputtering in N₂ (40%)/Ar gas mixture and then annealed at 550 °C in N₂ for 4 h, and N-doped TiO₂ powders were synthesized by treating anatase TiO₂ powders (ST01) in the NH₃ (67%)/Ar atmosphere at 600 °C for 3 h. Many reports have followed the procedures with some modification to prepare films by magnetron sputtering [13–15] or powders by amination [16–18]. Most of the TiO_xN_y films or powders reported in the literature possessed visible-induced photocatalytic activity. Asahi et al. [12] declared that the active sites of photocatalysis under visible light were the substitutional nitrogen, which can be identified with the atomic β -N states peaking at 396 eV in the XPS spectra. Gole et al. [18] were surprised to find little evidence for the 396 eV XPS peak for the TiO_xN_y nanopowders with some photocatalytic activity. As we know, no one has demonstrated unambiguously the states of nitrogen relative to their photocatalytic activity.

Electron-beam evaporation deposition is a powerful technique to prepare well-crystallized ceramic films with controlled stoichiometry, and can heat

promptly a pot of ceramic source up to 2000 °C without heating the surrounding component. Metal oxide molecules thermally evaporated in high vacuum are condensed onto a substrate and react with a reactive gas [19]. Stoichiometry of the deposited films can be controlled precisely, by modifying the evaporation conditions such as gas pressure, substrate temperature, and evaporation rate. The TiO_xN_y film as a photocatalyst deposited by the electron-beam evaporation technique has not been found in literature. Therefore, we try to use ion-assisted electron-beam evaporation to deposit the TiO_xN_y films. Prior to our successful preparation of the TiO_xN_y films with visible light-induced photocatalytic activity, we have carried out experiments to deposit the films without the assistance of ion gun. Without the bombardment of the nitrogen ions, scarce nitrogen atoms are incorporated in the resulting films which exhibit no noticeable red-shift of the absorption edges and photocatalytic activity under illumination of visible light [20]. From the XPS analyses, we have demonstrated clearly the key state of nitrogen in the TiO_xN_y films to promote the visible light-induced photocatalytic activity.

2. Experimental

2.1. Preparation of TiO_xN_y films

The TiO_xN_y films were prepared using the ion-assisted electron-beam evaporation system assembled by Branchy Vacuum Technology Co. Ltd. (Toayuan, Taiwan). The details of the preparation were described elsewhere [19]. The distance between the rotating substrate holder and the e-beam evaporation source was ~550 mm. The chamber was evacuated by a mechanical pump (ALCATEL-2033SD) and a cryo-pump (CTI-Cryo-Torr8[®]). The base pressure is 5.3×10^{-5} Pa. The films were deposited using rutile TiO₂ (99.99%) as a source material in oxygen atmosphere of 1.3×10^{-2} Pa supplied with 12 sccm O₂ at a constant pumping speed. The total working pressure was increased to $1.6\text{--}5.2 \times 10^{-2}$ Pa when the nitrogen ions and molecules flux entered the chamber through the ion gun. The series of the TiO_xN_y films were assigned to TiON-0, -2, -4, -15, and -25 corresponding to various nitrogen fluxes through ion gun, modulated by the nitrogen flow rate at 0 (without

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