Surface reconstruction, oxygen vacancy distribution and photocatalytic activity of hydrogenated titanium oxide thin film

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ABSTRACT

TiO$_2$ thin film prepared by atomic layer deposition was subjected to annealing in hydrogen at temperatures 350–500 °C. Hydrogenation induced the formation of disordered states and oxygen vacancies that resulted in increased surface roughness. Furthermore, it was discovered that oxygen vacancies were mostly formed on the surface, and their concentration and distribution uniformity increased with increasing temperature. The most uniform distribution of oxygen vacancies with the highest surface density was obtained after annealing at 500 °C, which is consistent with the lowest electron–hole recombination rate and highest photoactivity of the modified TiO$_2$.

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1. Introduction

Titanium dioxide has attracted considerable attention for many environmental applications. Since the discovery of its photoactivity by Fujishima and Honda [1], and owing to its exceptional properties, such as low cost, high stability, high chemical inertness, bio-compatibility, and non-toxicity, TiO$_2$ has been examined widely as an efficient photocatalyst material for purification of water, degradation of dyes and pesticides, etc [2–4]. However, the photocatalytic efficiency of TiO$_2$ is hampered by several obstacles such as wide band gap and easy recombination of photogenerated electron/hole pairs [5–7]. Numerous attempts have been made to overcome these problems including doping by metals or nonmetals [8–12], cocatalyst immobilization [13], and controlled faceting [14].

Recently, a novel approach was suggested to generate disordered TiO$_2$ with extended absorption profile in visible light region and improved photocatalytic efficiency through a hydrogenation process [15]. The enhanced performance was attributed to surface disorder and formation of oxygen vacancies that resulted in decreased electron–hole recombination rate and improved charge transport [16]. Later studies confirmed that higher photoactivity of hydrogenated TiO$_2$ is mainly determined by the high surface

to bulk defect ratio [17–21]. Yet, systematic surface science approach has rarely been applied to study modified TiO$_2$, and most of speculations on the change of surface conditions after hydrogenation were not based on direct surface analysis. For instance, Yu et al. [18] claimed that distribution of surface vacancies was identified by EPR spectroscopy. Yet, the use of probe molecules, which makes this technique surface sensitive [22], was not mentioned. It limits the application of EPR analysis to the examination of the condition of whole sample and only allows to verify the existence of defects without straightforward interpretation of their locations [17,18,21,23]. In another example, visible Raman spectroscopy was used to demonstrate the presence of surface defects in hydrogenated TiO$_2$ [24], and even to determine the consequent reconstruction of surface [25]. However, this type of Raman analysis is more sensitive to the bulk composition and hardly gives any valuable information about the surface conditions [26]. Furthermore, the use of Raman spectroscopy to probe the defect states in modified TiO$_2$ is questionable since the inconsistency of available data in the literature raises doubt about reliability of this technique. In general, hydrogenation of TiO$_2$ leads to positive shift of Raman peaks [20,23,27], but there are several reports where Raman peaks remain almost the same [18,24,28] or even shift to negative side [29]. Therefore, this issue needs to be clarified.

The use of surface-sensitive technique such as XPS has been also reported to probe the change of chemical composition on the surface of hydrogenated TiO$_2$ [17,20,21,23,28,30]. Yet, most of

the discussion from the XPS analysis has been concentrated on the description of chemical bonds between hydrogen and TiO_2 or the role of Ti^{3+}. The detection of oxygen vacancies has been seldom covered in detail. Moreover, this analysis provides information only about specific locations and cannot construct picture of the whole surface area.

Hence, a clear understanding about the exact distribution and concentration of surface oxygen vacancies in hydrogenated TiO_2 and their impact on photocatalytic activity of TiO_2 is necessary for the future controlled synthesis and device application.

In the present work, TiO_2 thin film fabricated by atomic layer deposition (ALD) was subjected to annealing in hydrogen at temperatures 350–500 °C. Concentration of oxygen vacancies and their allocation on the surface of TiO_2 were probed by means of confocal Raman analysis. In addition, reconstruction of surface induced by annealing in hydrogen was examined in detail. Since ALD technique offers several advantages such as atomically smooth surface and precise control of film thickness in the atomic scale [31], it allows to observe even a minor change of the surface.

2. Experimental procedures

N-type silicon wafer (100) was used as a substrate material for deposition of TiO_2 thin film. The substrate was immersed in a solution of H_2SO_4 and H_2O_2 (ratio 3:1) for 90 min to remove the contaminants. TiO_2 thin film was deposited on the surface of silicon by ALD. The temperature of substrate was set at 100 °C. $TiCl_4$ and H_2O were used as precursors for TiO_2. The lengths of pulse time were 0.08 s for $TiCl_4$, 5 s for N_2 purge, and 0.1 s for H_2O. The vacuum inside the chamber was controlled at 10^{-2} torr. The total cycle number of ALD deposition was 400. The ALD system and operation procedure have been presented previously [31,32].

After the deposition was finished, the samples were immediately transferred to a furnace for thermal treatment in hydrogen at 10 bar and 350 °C, 400 °C, 450 °C, or 500 °C for 3 h. The as-deposited TiO_2 was also annealed in air at 500 °C for 3 h as a control sample for comparison.

The morphologies and the microstructures of the samples were characterized by field emission scanning electron microscopy (FESEM, Hitachi SU-8010) and atomic force microscopy (Bruker, Dimension ICON, scan rate 1 Hz, resonant frequency 1.3 MHz). The phases and crystal structures were analyzed by X-ray diffraction (XRD, Shimadzu XRD 6000) with Cu K_α radiation. The band gaps were estimated by a UV–vis spectrometer (Hitachi UV-3010) with an integrating sphere attachment. Raman spectra were obtained using a microzone confocal Raman spectroscopy (Horiba Jobin Yvon, Labram HR 800). The excitation wavelength was 325 nm (He–Cd laser, Kimon IK3301R-G) with a laser power of 30 mW. The instrument was equipped with an LMU-NUV 40× objective lens resulting in a spot size of 0.79 μm^2. The visible Raman spectra were measured in a backscattering geometry using 514.5 nm Ar laser line (Stellar-Pro 514/50) with a power of 50 mW as the light source. The MPL 100× objective lens with a spot of 0.70 μm^2 was adopted for this analysis. The photoluminescence (PL) was measured by a fluorescence spectrophotometer (Perkin Elmer LS55).

For photocatalysis test, the samples were cut to a size of 1.2 cm × 1.5 cm, immersed in a Petri dish containing 4 ml of methylene blue (MB, initial concentration 5 × 10^{-5} M) and covered with a quartz plate. Before the measurement started, the sample was held in dark for 1 h to establish the absorption and desorption equilibrium. A 1.5 AM solar simulator (XES-40S, DIS C8912) with an intensity of incident light of 100 mW/cm^2 was used as the light source to irradiate the dye solution. The absorbance of the testing solution was measured every 30 min using a UV–vis spectrometer (Hitachi, UV-3010).

3. Results and discussion

3.1. Structural characterization

SEM micrography (Fig. 1(a)) confirms the uniform and smooth surface of the as-deposited TiO_2 film. The thickness of thin film is estimated to be 22–24 nm (Fig. 1(a), inset). After annealing in air at 500 °C, the morphology of the thin film did not change much (Fig. 1(b)), except that some microcracks were present. For the samples annealed in hydrogen at 350–500 °C, the surface morphologies were very different from those of original and annealed in air. The cracks on the film surface became longer and larger, and they were spread over the entire surface, as shown in Fig. 1(c)–(f).

XRD analysis (Fig. 2) shows the amorphous nature of the as-deposited TiO_2, which is converted to anatase phase after thermal treatment in hydrogen or air. Moreover, the peak intensities of hydrogenated TiO_2 thin films are reduced with respect to the sample annealed in air. The annealing in a reducing environment appears to have created defects in the TiO_2 lattices [20,27]. The shift of a main anatase peak (1 0 1) to higher angles for samples annealed in hydrogen increases with the annealing temperature (Fig. 2, inset) [30,33]. The shift to higher angle is usually attributed to formation of oxygen vacancies, which are major defects for TiO_2 annealed in hydrogen at such low temperature [34].

In order to have a full picture of variation of surface morphology, AFM analysis was made, as shown in Fig. 3. The as-deposited TiO_2 film has a very uniform and smooth surface with low roughness. Annealing in air induces higher roughness of the surface, and annealing in hydrogen results in even more drastic change. The degree of surface roughness can be described by the value of R_a (arithmetic average of the roughness profile) and R_q (root mean square roughness), as listed in Table 1. It is seen that the roughness of the hydrogenated TiO_2 thin films increases with increasing temperature of thermal treatment. The surface of TiO_2 annealed at 500 °C in hydrogen has the values of R_a and R_q several times higher than those annealed in air at the same temperature.

The explanation of dramatic change of TiO_2 surface after interaction with hydrogen was recently proposed in the literature [34,35]. First, when the annealing temperature exceeds 300 °C, electrons are transferred from hydrogen atoms to oxygen atoms in the lattice of TiO_2. Oxygen vacancies are formed when the oxygen atoms bond with hydrogen atoms and leave the surface of TiO_2 in the form of H_2O. When the temperature is raised to 450 °C, the interaction between H_2 and TiO_2 becomes more vigorous, which results in electron transfer from oxygen vacancies to Ti^{4+} ions, and Ti^{3+} ions are formed. It is generally assumed that the point defects, such as oxygen vacancies, are the low-energy bulk defects [36–39]. Since the free energy of surface becomes different from that of the bulk due to the presence of these defects, the search for new local thermodynamic equilibrium can only be proceeded by reconstruction of surface. It was proposed that in an isothermal process the surface density of TiO_2 is changed by redistribution of mass [39–41], i.e., mass flow between surface and bulk [42,43] or mass perturbations beneath the surface [39]. The preferred reconstruction is established when the lowest surface energy is reached [42]. The higher annealing temperature leads to generation of more point defects on the surface of TiO_2 thin film [44], which results in a higher mass flow of surface species toward locations of lower energy. Therefore, the increased surface roughness of TiO_2 thin film after annealing in hydrogen can be attributed to the minimization of surface free energy due to the presence of oxygen vacancies.

3.2. Raman spectroscopic analysis

UV Raman spectroscopy was employed to evaluate oxygen vacancies with a higher accuracy. It has been reported that UV