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Fabrication and Photocatalytic Characteristics of TiO_2 Films on Silicon Substrates

☐ YANG Jia-long[1], WANG Fu[1†], ZUO Liang[1], YI Gu-chul[2], CHOI Wong-yong[2]

1. College of Materials and Metallurgy, Northeastern University, Shenyang 110004, Liaoning, China;

2. PoHang University of Science and Technology, PoHang, Korea

Abstract: Silicon (111) and Silicon (100) have been employed for fabrication of TiO_2 films by metal organic chemical vapor deposition (MOCVD). Titanium (Ⅳ) isopropoxide ($Ti[O(C_3H_7)_4]$) was used as a precursor. The as-deposited TiO_2 films have been characterized with Field emission scanning electron microscopy (FE-SEM), X ray diffraction (XRD) and atomic force microscopy (AFM). The photocatalytic properties were investigated by decomposition of aqueous orange Ⅱ. The crystalline and structural properties of TiO_2 film had crucial influences on the photodegradation efficiency. For MOCVD *in-situ* deposited films on Si substrates, the photoactivities varied following a shape of "M": At lower (350 ℃) middle (500 ℃) and higher (800 ℃) temperature of deposition, relative lower photodegradation activities have been observed. At 400 ℃ and 700 ℃ of deposition, relative higher efficiencies of degradation have been obtained, because one predominant crystallite orientation could be obtained as deposition at those two temperatures, especially a single anatase crystalline TiO_2 film could be obtained at 700 ℃ growth.

Key words: MOCVD; photocatalystic degradation; silicon (100)

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Biography: YANG Jia-long (1964), male, Ph. D candidate, research direction: crystal structure. E-mail: jialongyang@163.com

† To whom correspondence should be addressed. E-mail: wangfu_neu@sima.com

0 Introduction

Titanium dioxide is a n-type semiconductor with many interesting properties. It is transparent to visible light, has high refractive index, nontoxic, low absorption, high dielectric constant and chemical stable. Indeed Titanium dioxide has been extensively investigated for many marvelous applications, such as photocatalytic detoxification of polluted water. The Photocatalysis of TiO_2 has been investigated extensively for the advantages of its remarkable activity, low cost, chemical and radiation stability——not prone to photocorrosion[1-3].

Orange Ⅱ is a textile azo-dye, which resistant to light degradation, and not easy to react with O_2, common acids and bases. Further more, Orange Ⅱ does not undergo biological degradation in wastewater treatment plants. For removing this recalcitrant organics, traditional methods like ultra-filtration, extraction, air stripping, carbon adsorption and hydrogen peroxide are non-destructive[4]. TiO_2 photocatalysis may be the best alternative for azo-dye degradation. Bbecause, firstly, this process involves the destruction of organic contaminants rather than transfer them from one phase to another; secondly, utilization of this process has great potential as it operates near ambient temperature and pressure, and solar light can also be used as illuminating source[5].

Up to now, much attention has been paid on the using of fine or ultrafine TiO_2 photocatalytic powders in a slurry state. However, the usage of aqueous suspensions

limits practical applications for problems of separation of fine particles of TiO_2 and the recycling of the photocatalysts[6]. There are many methods for making immobilized TiO_2[7]. Metal-organic Chemical vapor deposition (MOCVD) technique has been widely applied for the preparation of TiO_2 films because of its many advantages[8].

Recently several studies have focused on the influences of different crystallitic structure on photocatalytic activity. The photocatalytic efficiency of TiO_2 is governed by its crystal structure[9]. There exist considerable differences in photocatalytic degradation activity because of different crystallite orientation, even with the same phase of anatase[10,11]. But to our knowledge, there are few systemic studies been done about the relationship between crystal structure and photocatalystic activities especially for that of TiO_2 films produced through MOCVD. Based on the previous investigations on crystallite properties of TiO_2 films, it seemed that there were some controversies about TiO_2 growth behavior, such as phase transforming temperature and the type of predominant orientation etc[12,13]. Thus carrying out researches on the crystal properties and their influence on photocatalytic activities are necessary and essential.

The purpose of this research is systematically investigating the influence of TiO_2 films fabricated at different conditions on crystallization characteristics and photocatalytic activity. In this study, TiO_2 film was deposited on silicon substrates using MOCVD technique. The as-deposited films were used to check crystallite properties, photoactivities of degradation dye solution (orange Ⅱ). Some important conclusions have been obtained and discussed. Reasons that caused some unusual performances have also been analyzed.

1 Experimental

Deposition of TiO_2 thin films was carried out in a homemade low-pressure vertical metal organic chemical vapor deposition (MOCVD) system. TIP-titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$) had been used as a single molecular precursor. Argon gas with purity of 99.999% was employed as carrier and diluting gases, oxygen of 99.999% was used to supply oxidative atmosphere for precursor. Pressure of system: 13.33-666.5 Pa the flow rate of diluting gas, TIP carrier gas and O_2 was 10-40, 10-40, 20 mL/min, respectively.

Before mounted onto graphite susceptor, each silicon substrate was cleaned in a sonicator with acetone followed by methanol for about four minutes respectively to degrease, then rinsed in delete ion (DI) water.

The crystal structure of as-deposited specimen were examined by X ray diffraction (XRD), a high quality XG, M18XCE diffractometer (product of MAC Science Co. LTD) using Cu $K\alpha(\lambda = 1.540\ 56\times10^{-3}$ nm) radiation at 40 kV and 200 mA, scanning rate was 8°per min. The surface morphology and cross-sections of films were observed by using a Field emission scanning electron microscopy (FE-SEM). It has resolution of 1.5 nm at 10 kV or higher and 2.5 nm at 1 kV, beam current ranges from 1 pA to 20 nA, magnification ranges (related to image width of 12 cm) from 20 to 800 000, and it was fixed with energy dispersion system (EDS) analysis system.

An autoprobe atomic force microscope (AFM) was introduced to study the surface topography of amorphous and polycrystalline TiO_2 films.

The as-deposited TiO_2 films were immersed into 6.5 mL, 0.01 mmol/L dye solution of orange Ⅱ ($HOC_{10}H_6N{=}{=}C_6H_4SO_3N_a$ dye content 85%, products of Aldrich Chemical Company, Inc). This aqueous solution with pH 6.2 was put into a cylindrical transparent polymeric container with diameter and height of 30 mm and 5 mm respectively. The solution container was located in a homemade chamber equipped with 200 W mercury lamp that can produce UV and visible light that irradiated on TiO_2 films through a Pyrex filter cover. The light intensity on films can be adjusted by changing the distance between UV-lamp and sample supporting plate. The light intensity was measured with a power meter (Newport 1815-c). In this experiment, the intensity of light was controlled to 5.5 mW/cm^2. All of experiments were carried out at ambient temperature (25-40 ℃) and pressure.

After certain period of irradiation, the sample of dyed orange Ⅱ solutions were sent for checking the degradation (decolorization) so as to measure the photocatalytic activity of TiO_2 films. The photocatalytic degradation analytic system was 2401PC UV-Vis recording spectrophotometer (Shimadzu) with scanning wave ranges from 200 nm to 800 nm. The volume of solution container used for scanning in UV-Vis 2401PC spectrophotometer was 0.74 mL. The visible light of 486 nm wavelength was employed for checking the dye declorization. The di-

agram of relationships between absorbance and wavelength would be plotted automatically after finishing the scanning of a sample of dye solution.

2 Results and Discussion

TiO_2 thin films were deposited on Si(100) wafers at a temperature ranges from 360 ℃ to 800 ℃ within 4 h. CSA36, CSA 40, CSA 50, CSA 60, CSA 70, CSA 80, CSA 90, corresponded to the deposition temperature of 360, 400, 500, 600, 700, 800, 900 ℃ respectively. The thickness of films was 2 000-3 000 nm. The as-grown films were immersed in 6.5 mL, 0.01 mmol/L orange Ⅱ solution and irradiated by UV-light (5.5 mW/cm^2) for 2 h.

Figure 1 shows the results of UV-Vis spectra. Fig. 2 shows the relationship between dye concentration variation and thin films synthesized temperatures. These two figures showed that the film fabricating temperature had shown crucial influence on characteristics of photodegradation. As deposition temperature changed from 360 ℃ to 800 ℃, the proportion of dye conversion displayed a "M" shape with somewhat lower on left shoulder. The two shoulders were located on the vicinity of 400 ℃ and 700 ℃. At middle range the lowest position was observed near 500 ℃ deposition. At relative low and high temperatures the values of degrading proportion were also smaller. It seems to be unbelievable and easily confused. So, further discussion is necessary and essential.

From XRD patterns and FE-SEM top-graphs and cross-sectional images, we can explain the results appeared in Fig. 1, 2. Fig. 3(a) showed that the particulate

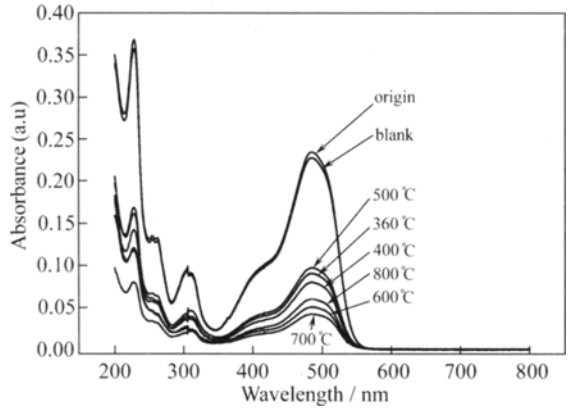

Fig. 1 UV-VIS scanning spectra of dye solution photo-degraded by TiO_2 thin films with thickness of 2 000-3 000 nm deposited at different temperature ranges from 360 ℃ to 800 ℃

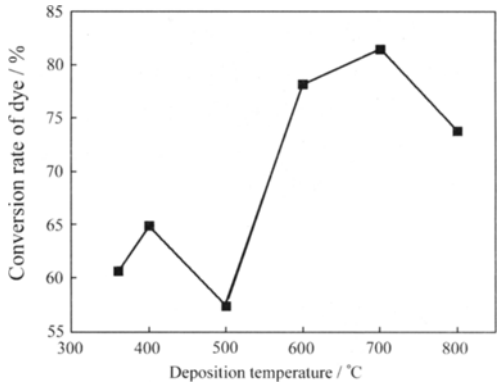

Fig. 2 The influence of TiO_2 thin film depositing temperature on the activity of photo catalytic degradation of dye solution

and crystallite size at 360 ℃ were larger than that of deposited at 400 ℃ (referring Fig. 4), so the films' activity at 360 ℃ deposition should be higher than that of at 400 ℃. But on the other hand the crystallization at 400 ℃ was better than that of at 360 ℃ (Fig. 5), thus the photoactivity increased with temperature increasing. At 500 ℃, the crystallite structure and microstructure changed, for example anatane (101), (200) almost disappeared and (220) became predominant orientation, corresponding with the rapid decrement of crystallite size (Fig. 3(c) and Fig. 4), that would lead to quickly decreasing of the photoinduced oxidation ability. So 500 ℃ deposited TiO_2 films showed the lowest position of "M" shape. At 600 ℃, A(112) appeared and became a dominant orientation, loosely scattered arrays formed, crystallite size enlarged (Fig. 3 (d) and (d1)), therefore result in the enhancement of photoactivity of TiO_2 films. As film growth temperature changed to 700 ℃, there was almost only one peak of anatase (112) left, that means the crystalline of anatase growing in one direction (shows in Fig. 3 (e) and (e1)), thus well standing columnar structure was formed and vacancies enlarged between columns, as a result lead to the increment of micro-scale porosities. For anatase (112) crystalline, well standing loosely scattered columnar microstructure, high percentage of micro-scale porosities etc., induced a great improvement of TiO_2 films photoactivity as illustrated in Fig. 2. At 800 ℃, though a few large particles distributed on the film, meantime many small sized particulates appeared which could not been seen in the sample of 700 ℃ (see Fig. 3 (f)), the calculated crystallite size decreased from 58.96 nm at 700 ℃ to 55.94 nm at 800 ℃. On the other hand, a weak peak of anatase (204) ap-

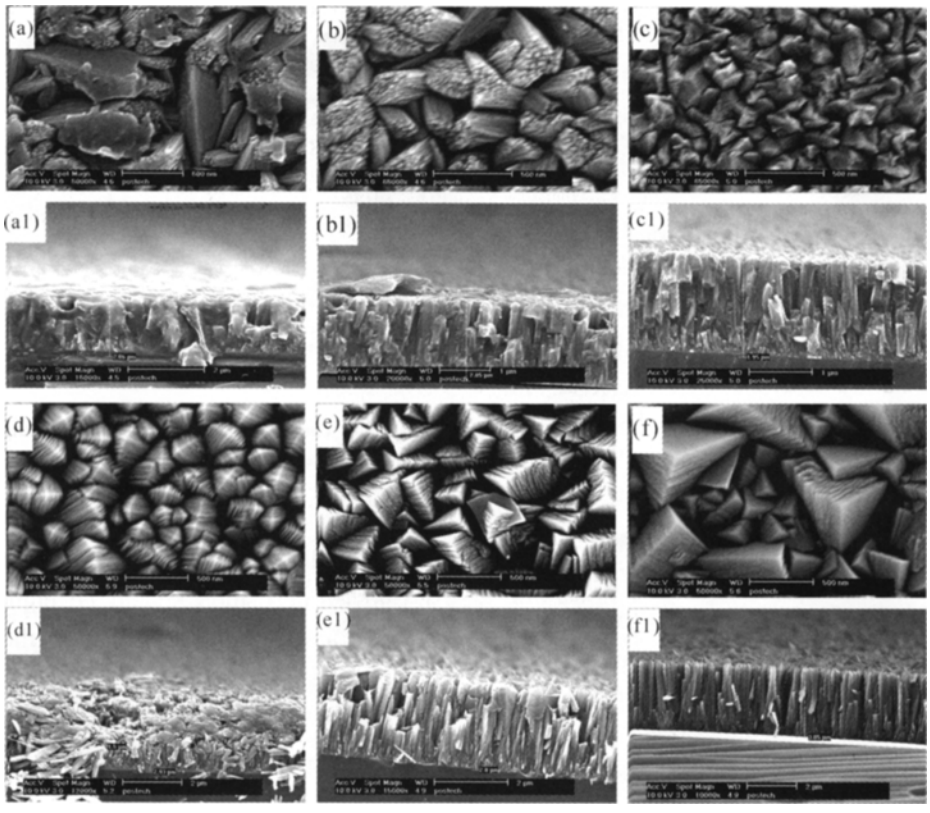

Fig. 3 The FE-SEM images of TiO_2 thin films deposited at different temperatures

(a-f) show the top-graph images of TiO_2 films deposited at 360, 400, 500, 600, 700, 800 ℃ respectively; (a1-f1) show the cross-sectional images of TiO_2 films deposited at 360, 400, 500, 600, 700, 800 ℃ respectively

peared and coexisted with A(112). As a result, though FE-SEM showed a loosely scattered well standing column images, the activity of photodegradation still was not as good as that of 700 ℃ deposited TiO_2 films. Moreover, the results of AFM checking showed that the roughness of films deposited at 500 ℃ and 700 ℃ was 9.5 nm and 13.9 nm respectively. This also coincided with the conclusion that films synthesizes at 500 ℃ and 700 ℃ dis-

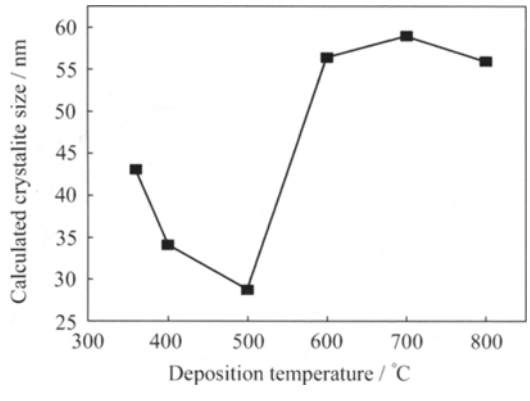

Fig. 4 The crystallite size (calculated with Sherrer formula) varied with depositing temperatures as fixed deposition time of 4 h

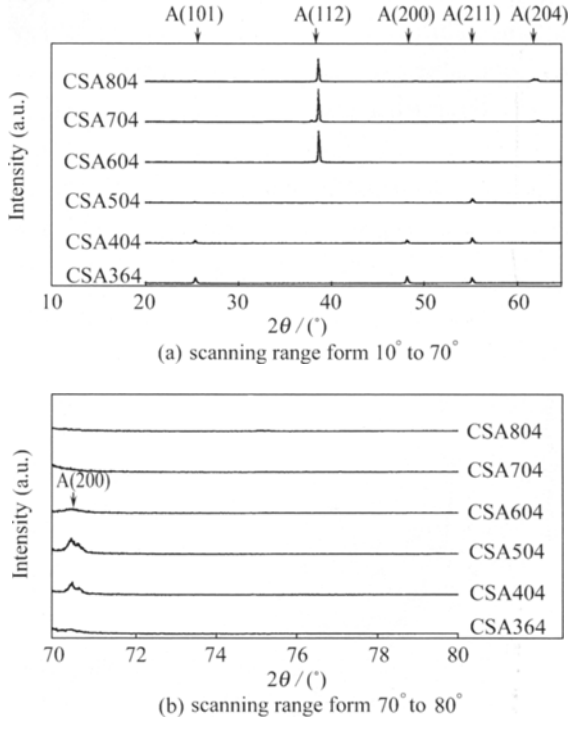

Fig. 5 The XRD patterns of TiO_2 films deposited at different temperature on Si substrates

played lowest and highest photoactivity respectively.

The results of proportion conversion of dye achieved by 200-400 nm (series of OSA), 400-600 nm (series of MSA), 2 000-3 000 nm (series of CSA) thickness of TiO_2 films fabricated at various temperatures and irradiated 2 h in 6.5 mL 0.01 mmol/L orange Ⅱ solution under UV light were shown in Fig. 6. Checking this Figure, it could be concluded that with TiO_2 film's thickness increasing the activities of photodegradation increased at deposition temperature range from 500 ℃ to 900 ℃. It was obvious that almost all of TiO_2 films In-situ fabricated (not post-annealing) by MOCVD method displayed a "500 ℃ affect" phenomenon shown a seriously negative influence on dye degradation activity of TiO_2 film photocatalyst. So it is necessary for future practical operations to avoid manufacturing TiO_2 films around 500 ℃. Meanwhile for the *in-situ* deposited TiO_2 film on Si(100) substrate also showed a marvelous crystallization phenomenon of "700 ℃ effect", which would be very useful for improving the degradation abilities of TiO_2 films photocatalyst. The "700 ℃ effect" implied that at 700 ℃ deposition, almost one growing orientation of (112) anatase could be gained. This kind of crystallite structure displayed a well standing loosely and regularly scattered nanorod-like parallel columnar microstructure. This kind of microstructure can greatly improve the kinetic reaction condition of degradation at the interfacial area of solid and solution. Therefore it is reasonable to expect for obtaining an improved photo-activity of TiO_2 films synthesized by MOCVD system. Here, many experiments with different thickness of TiO_2 film have proved that this expectation is approachable. Some other researchers such as Kim Bum-joon *et al*[14] also try to get anatase (112) orientation dominated crystal structure, and further more to obtain columnar microstructure of TiO_2 films for improving the photoactivity of degradation. But they needed to control the deposition temperature exactly at 360 ℃, because even 2 ℃ of deviation would cause abruptly decreasing of peak (112) intensity. However In our experiments, a single anatase (112) has been obtained around 700 ℃.

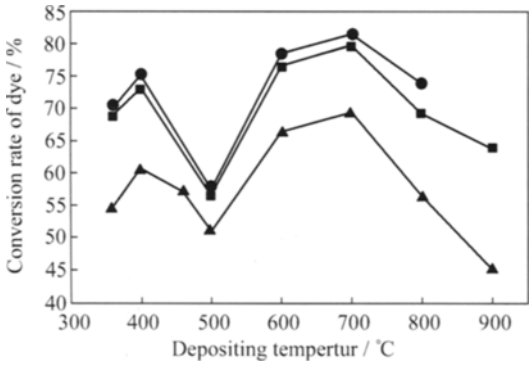

Fig. 6 The relationship between photoactivities and TiO_2 film growth temperatures under three different depositing times
—●—: CSA; —■—: MSA; —▲—: OSA

For the films deposited at relative lower temperature ranges from 360 ℃ to 460 ℃, when thickness was less than 600 nm, with TiO_2 film thickness increasing the activity would increase correspondingly, but when increase film thickness from 600 nm to 2 000 nm the photoactivity showed a smaller value of increment. This is because UV light can only penetrated into TiO_2 films to a limited distance. So when film thickness exceeds a certain value, photocatalytic reaction would not take place anymore. Choi Won-yong *et al* [15] found that thicker TiO_2 film has higher catalytic activity but the activity saturated at the thickness round 800 nm. As shown in Fig. 3, the thickness of all employed samples was larger than 2 000 nm, it was much thicker than 800 nm. Therefore, the photoactivities of samples with different thickness could be comparable one another. Meantime we can conclude that a strategy for preparing very thick TiO_2 film is not necessary and essential for the purpose of improving the activities of immobilized TiO_2 photocalysts.

3 Conclusions

The in-situ depositing temperatures of TiO_2 films on silicon (100) substrates have showed crucial influences on the photodegradation efficiency. The photoactivities varied following a shape of "M", at lower (360 ℃), middle (500 ℃) and higher(800 ℃) temperatures showed a relative lower photodegradation activites, while films deposited at 400℃ and 700℃, demonstrated a relative higher efficiencies of photodegradation, especially for 700 ℃ deposition. There appeared "500 ℃ affect" and "700 ℃ effect" tendencies. All of these phenomena should be ascribed to the variation of microstructures at different films synthesized temperatures. Crystallization and single anatase structures (single orientation or poly-orientations) have displayed significant influences on photocatalytic properties. Films grown at 700 ℃, one single anatase crystalline orientation of (112), and well-standing loosely scattered columnar structures had been obtained, which resulted in obviously promotion of photodegradation

activity.

Increasing thickness of TiO_2 films from 200 nm to 600 nm would significantly enhance the films' photoactivity, but a further thickening TiO_2 film to about 3 000 nm showed only relative smaller increment of photodegradation efficiency, that means photoactivity was saturated at a little more than 600 nm of TiO_2 films.

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