Fabricating Highly Active Mixed Phase TiO_2 Photocatalysts by Low Angle Reactive DC Magnetron Sputter Deposition

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Titanium dioxide (TiO_2) is one of the most widely studied photocatalysts during the past decades due to its ability to photo-oxidize harmful chemicals in both air and water to CO_2 in the presence of UV light. TiO_2 also shows promise for energy applications such as water splitting [1], as well as in photochemical solar cells [2]. TiO_2 use has also been extended to large scale commercial production such as SunClean® self-cleaning glass by PPG.

Despite the many potential applications of TiO_2, wider practical use requires that its photo-response be extended farther into the visible light region and its photo-efficiency be increased by reducing charge recombination. Anatase, the most commonly used crystal phase of TiO_2, shows good photoactivity only under UV illumination. On the other hand, rutile, the other ubiquitous crystal phase of TiO_2, displays visible light activation, but with low photoactivity due to the very high recombination rate of its photo-generated electrons and holes.

While it has long been observed that mixed phase TiO_2 (anatase and rutile) tends to exhibit higher photoactivity than pure phases alone, a detailed explanation of this phenomenon was lacking. Recent work by Hurum et al., based on EPR (Electron paramagnetic resonance) measurements, however, has revealed surprising insights into the nature of charge separation, trapping and recombination in mixed phase TiO_2 [3-5]. We propose that there is a nanostructured morphology comprised of rutile crystallites interwoven with anatase crystallites creating a solid-solid interface across which photoexcited electrons are transferred from rutile to lower energy anatase lattice trapping sites. Because of its smaller band gap (3.0 ev), rutile acts as an antenna to extend the photoresponse of the mixed phase catalyst into the visible light region. Its association with anatase in a preferred nanostructured arrangement results in spatial separation of the charge carriers and hindered recombination. EPR results documented that recombination reactions are dominated by surface reactions following charge migration via a random flight mechanism [4]. We also identified an interfacial, tetrahedraly coordinated Ti^{4+} site as an electron trapping site that is specific to mixed phase materials such as Degussa P25 and propose that this site may be a catalytic 'hot spot' created at the solid-solid interface between the nano-particles of mixed phase TiO_2 and responsible for its high activity [5].

TiO_2 thin films have been prepared by various deposition methods such as sol-gel [6-8], evaporation [9], ion beam assisted deposition [10] and sputter deposition [11-13]. Compared to the traditional, widely used sol-gel methods, more uniform and mechanically durable films can be prepared over large areas by reactive DC magnetron sputtering without the required

high temperature heat treatment. DC magnetron sputtering also overcomes the low deposition rate problem of RF magnetron sputtering. These advantages make reactive DC magnetron sputtering deposition suitable for the large-scale industrial production [14].

The goal of this research was to probe the relationship between fabrication conditions, TiO_2 structure and photocatalytic performances. Titanium dioxide was deposited by reactive DC magnetron sputtering, with RF bias, at fixed angle, onto cleaned microscope glass slides (borosilicate). Pure titanium (99.95%) was used as the sputtering target. High-purity argon and oxygen were used as sputtering and reactive gas respectively. The base pressure in the coating chamber was maintained below 5.3×10^{-4} Pa. The sputtering system used for this work utilized a dual cathode, closed-field unbalanced magnetron configuration [15].

We show that sputter deposition provides excellent control of the phase and interface formation. We explored the effects of the process parameters of pressure, oxygen partial pressure, target power, substrate bias (RF), deposition incidence angle, and substrates on the structural and functional characteristics of the catalysts. Based on XRD, among all the parameters, oxygen partial pressure didn't affect the formation of anatase or rutile obviously, however low total pressure, high target power and substrate bias favored the formation of rutile. Deposition incidence angle was the key factor of the study. The glass substrates were fixed by steel wires on the sides of a hexagonal-shaped-cylinder, aluminum sample holder. After the sample holder and substrates were placed onto the rotary working table at a distance of about 15 cm from the titanium target, it was rotated to certain designated positions to control the incidence angle for the sputtering processes (Fig.1). The films deposited at low incidence angle were exposed to less bombardment of ions and thus, were usually pure anatase and mixed phase with high proportion of anatase. The film also showed unique surface morphology and catalytic advantages which will be described later. The films deposited on the Si wafers tended to be single phase while the films deposited on the quartz tended to be mixed phase and glass slides showed ability to produce both single phase and mixed phase.

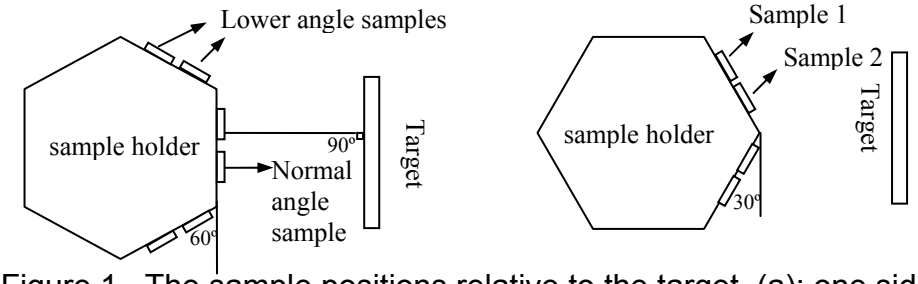
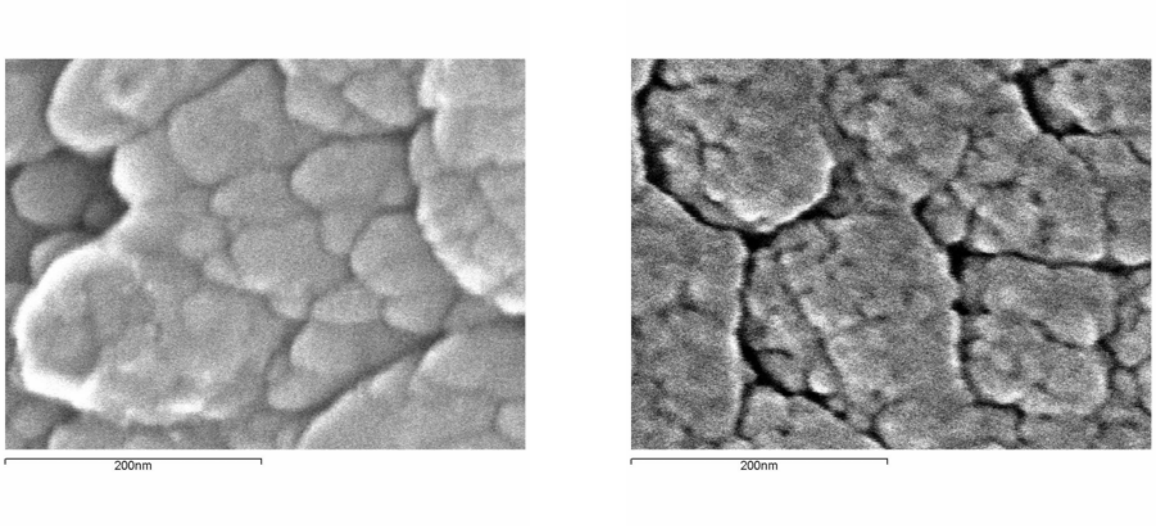


Figure 1. The sample positions relative to the target. (a): one side of the sample holder is parallel to the target to receive the high angle deposition while the samples on the side received deposition at 30°. (b): rotate 30° (relative to (a)) and samples could receive 60º or less angle deposition depending on the positions of the samples on that side. Sample 1 is farther from the target than Sample 2.

The low angle deposited pure and mixed phase TiO_2 films we successfully prepared, were characterized with AFM, SEM, TEM, and XRD to determine surface morphology, phase distribution and phase content. The films deposited at low angle (about 30 degrees) displayed columnar microstructure with comparable surface roughness (r.m.s. 13.5 nm) and columnar aggregates around 200 nm in diameter and the columns were grown into scale-like surface due to the influence of low angles (Fig. 2) From TEM observation (fig 3), diffraction patterns

were obtained from random locations on the sample, and all of them had the reflections of both anatase crystals and rutile crystals. These data provided evidence that all anatase crystals and rutile crystals were completely mixed together, and indicated that a high density of rutile-anatase interfaces were created.



Mixed Phase Pure Anatase

Figure 2. SEM images of the mixed phase and pure anatase films prepared by magnetron sputtering.

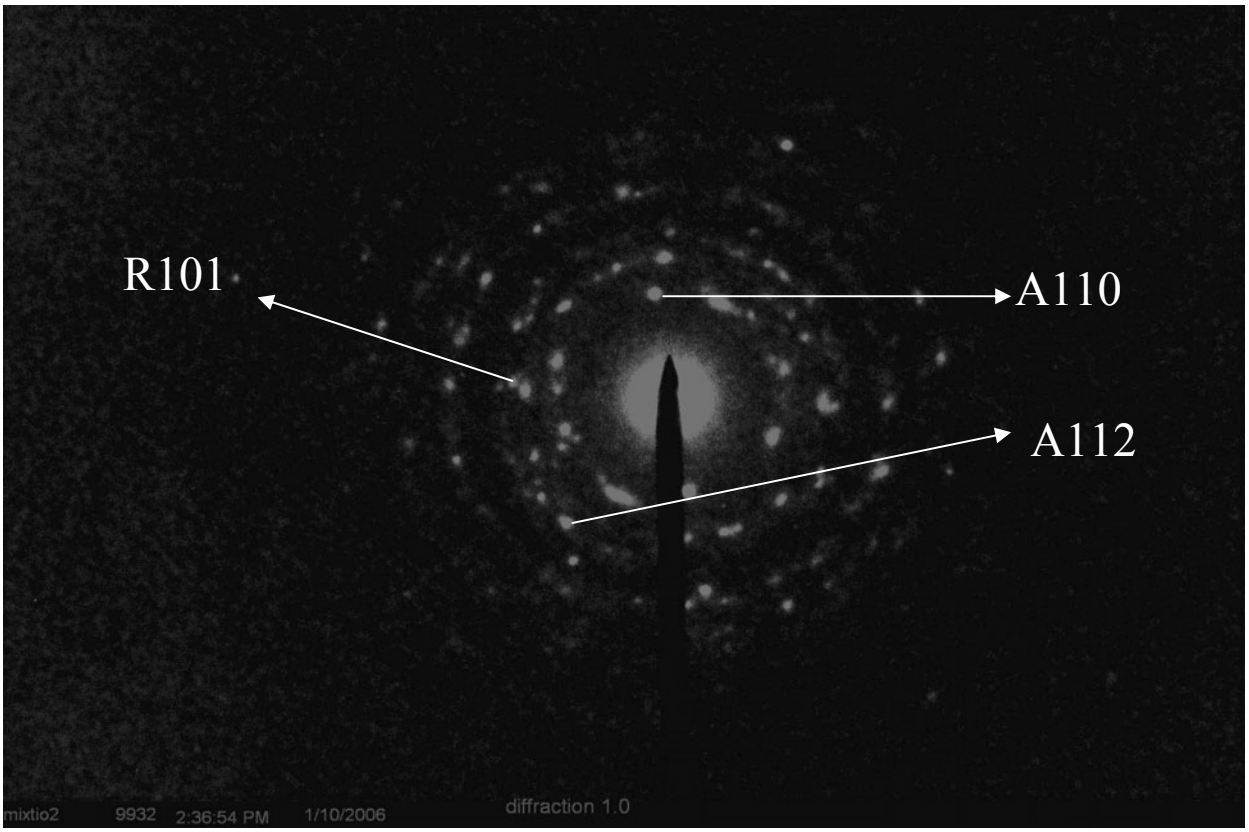


Figure 3. TEM plan-view selected area diffraction pattern of the sputtered mixed phase film.

The performance as photocatalytic surfaces was measured by degrading acetaldehyde in a closed batch reactor and compared (normalized for surface area) to mixed phase TiO_2 on glass slides fabricated by other methods, including flame hydrolysis powders, and sol-gel deposited TiO_2 films. (Fig. 4) The low angle sputtered mixed phase materials were far superior to the commercial standard (Degussa P25) and sol-gel TiO_2 as measured by the gas phase degradation of the air pollutant acetaldehyde under UV illumination. The low angle sputtered mixed phase films also displayed visible light response based on the measurement of UV-Vis. (Fig.5) These results demonstrate that reactive DC magnetron sputtering is a powerful tool for investigating the role of the solid-solid interface in influencing photocatalytic activity. The further study on electron transfer at the interface is being studied by EPR right now. In addition, our work illustrates the feasibility of reactive DC magnetron sputtering as a practical commercial technique for manufacturing highly active nanostructured TiO_2 photocatalysts.

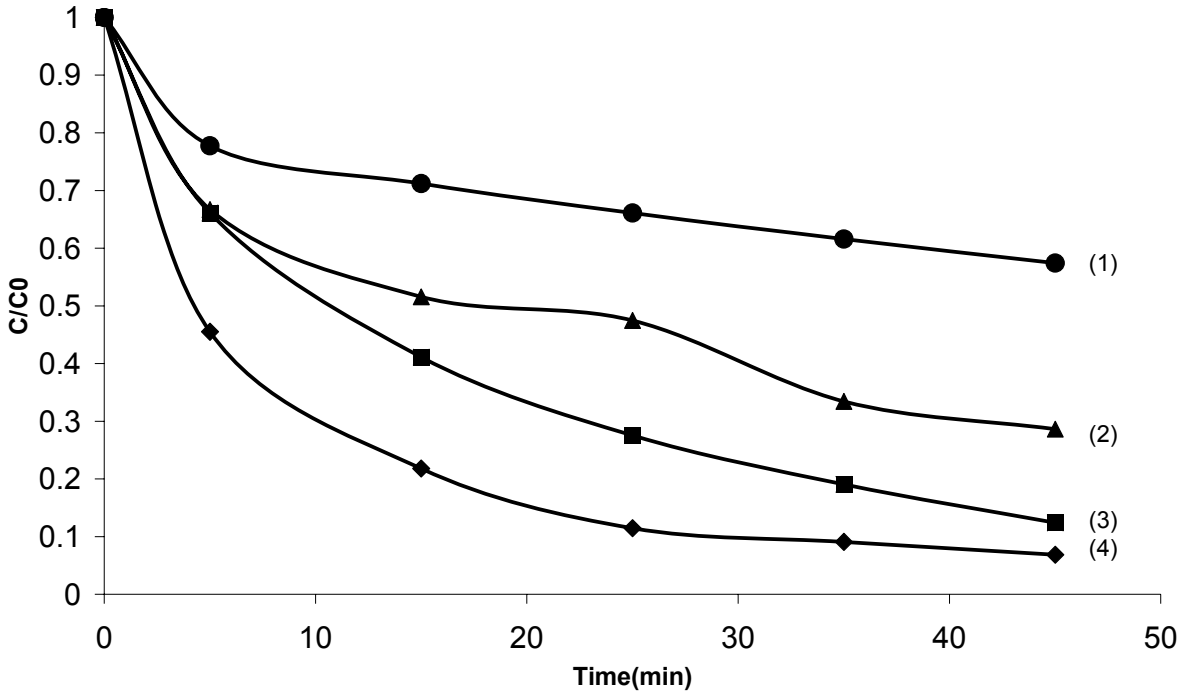


Figure 4. Degradation of acetaldehyde by various samples normalized by the surface areas of the films. The surface area here is expressed as the ratio of the measured surface area to the nominal or projected area. (1) P25, dip-coated film (2.18um^2/um^2); (2) anatase, magnetron sputtered film (1.10$um^2/um^{2)}$; (3) mixed phase, sol-gel film (70% Anatase) (1.09 um^2/um^2); (4) mixed phase magnetron sputtered film (70%Anatase) (1.12um^2/um^2)

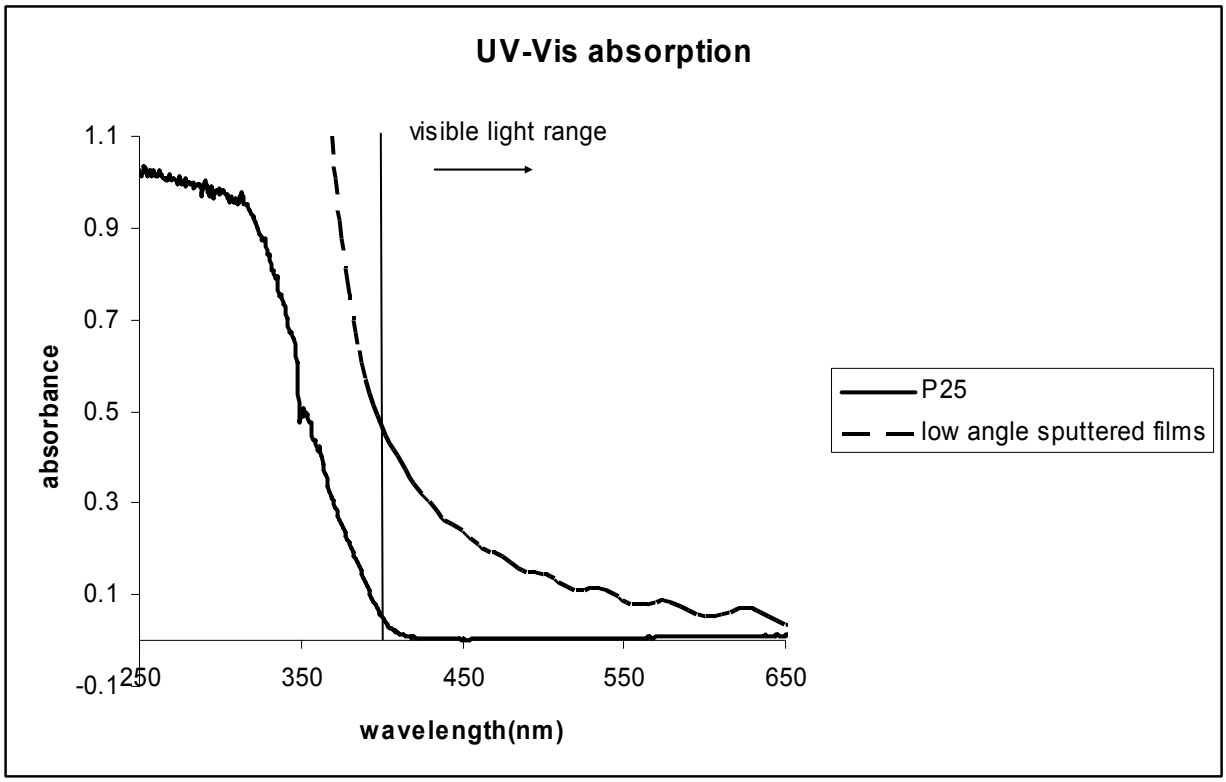


Figure 5. UV-Vis absorbance of P25 coated film and low angle magnetron sputtered film respectively.

Acknowledgements

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