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# Synthesis and Characterization of $TiO_2/SiO_2$ Thin Film via Sol-Gel Method

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**Abstract.** $TiO_2/SiO_2$ thin films were prepared by sol-gel spin coating method. Structural, surface morphology and optical properties were investigated for different annealing temperatures at 300°C, 400°C and 500°C. X-ray diffraction pattern show that brookite $TiO_2$ crystalline phase with $SiO_2$ phase presence at 300°C. At higher temperatures of 400-500°C, the only phase presence was brookite. The surface morphology of film was characterized by scanning electron microscopy (SEM). The films annealed at 300°C shows an agglomeration of small flaky with crack free. When the temperature of annealing increase to 400-500°C, the films with large flaky and large cracks film were formed which was due to surface tension between the film and the air during the drying process. The UV-Vis spectroscopy shows that the film exhibits a low transmittance around 30% which was due to the substrate is inhomogeneously covered by the films. In order to improve the coverage of the film on the substrate, it has to repeatable the spin coating to ensure the substrate is fully covered by the films.

## 1. Introduction

$TiO_2$ is a material which have its chemical stability and electronic properties and well known as semiconductor.

It has been used in wide application in semiconductor electrochemistry, solar energy conversion, as gas sensor, in electronic devices, and as antireflective coatings [1]. $TiO_2$ becomes one of the most popular photocatalytic materials.

The $TiO_2$ naturally have existing in several crystalline phase such as rutile, brookite, and anatase. Among of these, anatase and rutile crystalline phase are widely used in application of solar cell. Rutile phase are suitable for protective coating on lense due to stable thermodynamically and high refractive index. At lower temperatures, brookite and anatase phases are more stable however both will change to the rutile phase at certain temperature. Due to the photocatalytic activity, most of the researches tend to use anatase, $TiO_2$. The larger band gap in crystalline phase in anatase because it has better response to ultraviolet photons for photocatalysis.

Photocatalytic is the process in which the solar energy is converted into electrical energy in the solar cell. The photocatalytic performance of these compounds depends on the characteristics of the $TiO_2$ crystallites, such as the size and surface area [2].

Therefore, modification of its physical and chemical property is of interest to researchers [3,4]. One of the possible ways to modify the property of $TiO_2$ crystallites is by adding a second semiconductor into the $TiO_2$ matrix. Silicon dioxide ($SiO_2$) has been incorporated into the $TiO_2$ matrix to enhance the photocatalytic process [5-8].

$SiO_2$ has high thermal stability, excellent mechanical strength and helps to create new catalytic active sites due to interaction between $TiO_2$ and $SiO_2$ [9].

Recently, Zhou et al. [8] demonstrated that mixed metal oxides ($TiO_2$-$SiO_2$) enhance the photocatalytic performance due to improved surface adsorption and increasing surface hydroxyl group in the thin film. Also, at the same time $SiO_2$ acts as the carrier of $TiO_2$ and helps to obtain a large surface area as well as a suitable porous structure [10].

It has been proven by the researchers that by adding $SiO_2$ as a adding material to the $TiO_2$ can improve the photocatalytic activity and hydrophilicity process [11-13].

Based on previous researchers stated, additions of $SiO_2$ to the $TiO_2$ can prevent the formation of rutile phase at high temperature up to 800°C that is the undesired phase for the photocatalytic applications in the solar cell [14].

This research work is focus on synthesized and characterized the structural, morphology and optical properties of $TiO_2/SiO_2$ thin film with three different annealing temperatures in order to improve the properties the self-cleaning property in solar applications.

## 2. Methodology

The sol-gel method was used to synthesize $TiO_2/SiO_2$ thin films. The tetraethyl orthosilicate, TEOS, and tetra-n-butyl orthotitanate, TBOT, were used as the sources of $SiO_2$ and $TiO_2$ respectively to prepare the solutions of $SiO_2$ solutions and $TiO_2$ solutions.

Firstly, TBOT was mixed together with ethanol and deionized water by using molar ratio of mixture (TBOT: ethanol: deionized water) was 1:0.5:3. Next, hydrochloric acid was added drop by drop into the mixing solutions which give the function as a catalyst. Then, this solution was mixing together for 1 hour by using magnetic stirrer.

After 1 hour, a clear solution was obtained then TEOS was added into the solution until the ration of TBOT: TEOS was 1:1. Then, the solution was continued stirred for 30 minutes at 45°C. The final solutions was undergoes aging process for 24 hours. Figure 1 shows the flowchart of the synthesized $TiO_2/SiO_2$ thin film.

Thin films of $TiO_2/SiO_2$ were deposited by the method of spin coating in air at room temperature, on glass substrate with speed at 1000 rpm for 30s. Finally, the films were annealed at 300°C, 400°C and 500°C in air for 3 hours by using muffle furnace.

The crystalline structure was characterized by an X-ray diffractometer (XRD) in 2θ range from 20° to 80°. Scanning electron microscopy (SEM) was used to study the surface morphology and pore distribution of the produced films.

The transmission and absorbance were measure by UV/VIS Perkin-Elmer spectrophotometer.

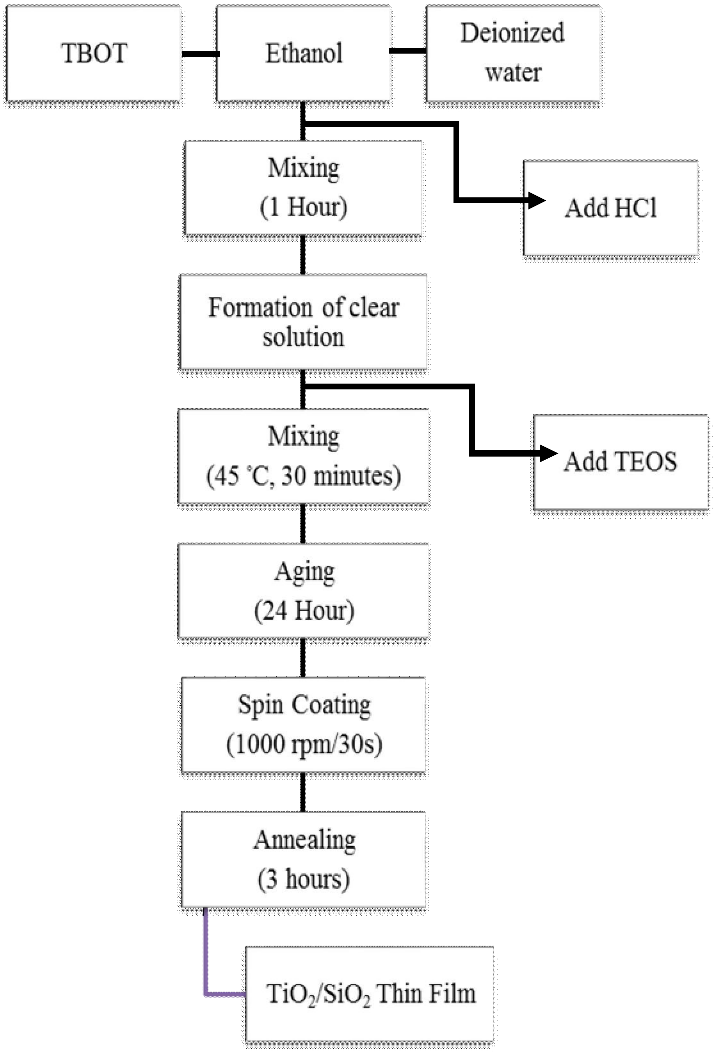



**Figure 1.** The flowchart of the synthesized $TiO_2/SiO_2$ composite thin film.

## 3. Results and discussion

X-ray diffraction pattern has been used to investigate the phase of the prepared $TiO_2/SiO_2$ films. The X-ray diffraction pattern of $TiO_2/SiO_2$ thin films annealed at different temperatures is shown in figure 2. The peaks have been indexed and found to be that of brookite $TiO_2$ and $SiO_2$. The diffraction peak at 2θ = 31.99° was assigned to the characteristic diffraction peak of brookite $TiO_2$ phase and corresponds to (1 2 1) direction. For the $SiO_2$ phase, the diffraction peak at 2θ = 66.54° which is corresponds to (3 0 0) direction. The diffraction pattern shows that an annealing at a temperature equal or lower than 300°C would be largely sufficient to form $TiO_2/SiO_2$ completely. It is well agreed with Maeda & Yamasaki [15] which found that when the films was annealed at 250°C for 180 min, the phase of titania–silica ($TiO_2$-$SiO_2$) mixed films exist. They also reported on addition of $SiO_2$ into the $TiO_2$ films can prevents the recrystallization of the $TiO_2$ composites. When the temperature of annealing was increase to 400°C and 500°C, the only peak reveal was brookite $TiO_2$ films. Mechiakh et al. [16] was reported, at higher temperatures (400°C and 450°C), in addition to anatase $TiO_2$ the formation of brookite $TiO_2$ which crystallizes with the (1 2 1) plane parallel to the surface. No peak corresponding to the $SiO_2$ phase is seen in the diffraction pattern of films annealed at 400°C and 500°C.

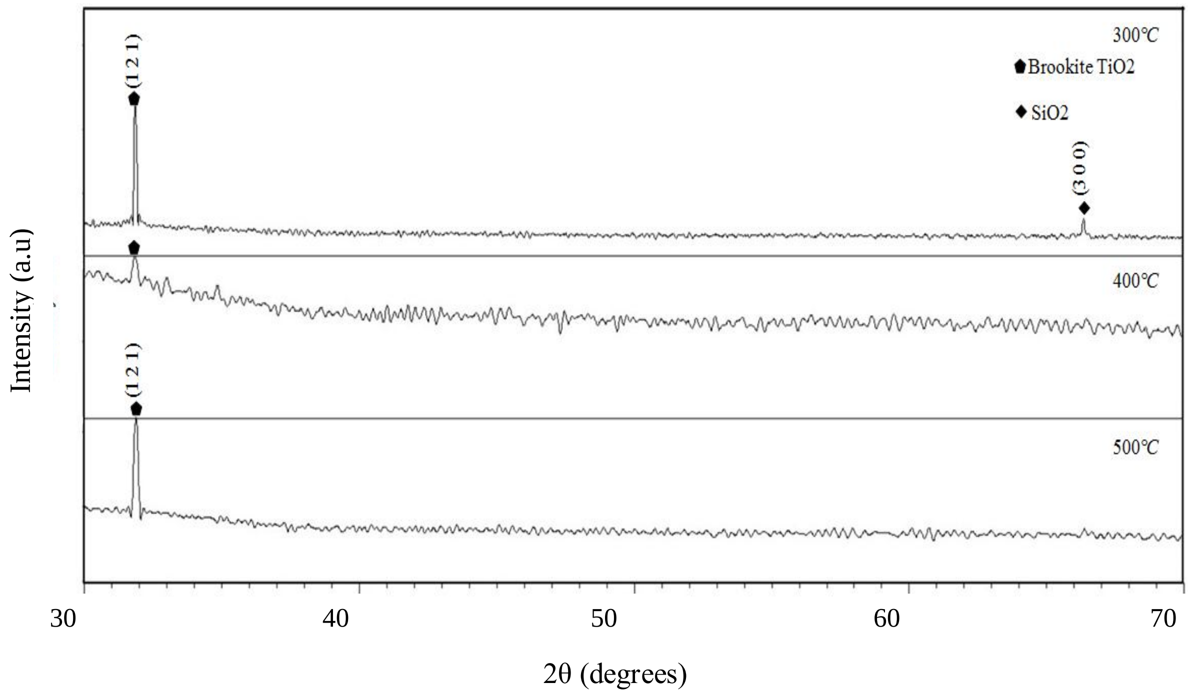



**Figure 2.** X-ray diffraction pattern of $TiO_2/SiO_2$ films annealed at different temperatures.

Many efforts have been made to modify the $TiO_2$ by impurities for improving the photocatalytic activity under visible light [17-19]. Modification of $TiO_2$ with $SiO_2$ has been attracted in the past decades and widely used due to photocatalysis and hydrophilicity properties [20]. The characteristic of $SiO_2$ itself, such as its water-trapping effect, is suggested to play an important role for surface hydrophilicity of the $TiO_2/SiO_2$ films. In the $TiO_2/SiO_2$ films, therefore, the synergistic effects of anatase polycrystalline structure of the $TiO_2$ and water-trapping effect of the $SiO_2$ are important for their strong photo-induced hydrophilicity [15].

Figure 3 shows the SEM micrographs of $TiO_2/SiO_2$ annealed at 300°C, 400°C and 500°C. The SEM micrographs revealed that the surface morphology of the $TiO_2/SiO_2$ films depend strongly upon annealing temperature. It was observed that the average grain size of the films increases significantly when annealing temperature increases. In the presence of $SiO_2$ for the films annealed at 300°C (figure 3(a)), it can be seen many nucleation centers are present on the substrate and agglomeration of small flaky are produced. Then, the films with small flaky size are not able to grow into bigger ones and prevent crack. Whereas for higher annealing temperatures as seen in figure 3(b) and (c) it revealed large flaky size and large cracks throughout the coatings. Temperature increasing may lead to non-uniform and cracked coating and reduce coating lucidity and transparency [21].

It also clearly seen that the substrate is inhomogeneously covered by large flaky size and it may formed during drying process due to surface tension between the film and the air [22]. In the case of sol-gel coated films, during drying process, the capillary forces might have generated which provides cracks on the surface [23].

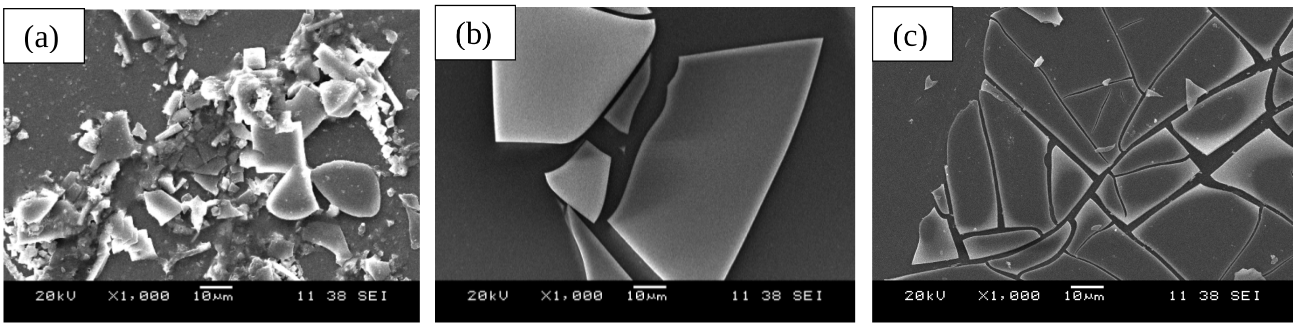
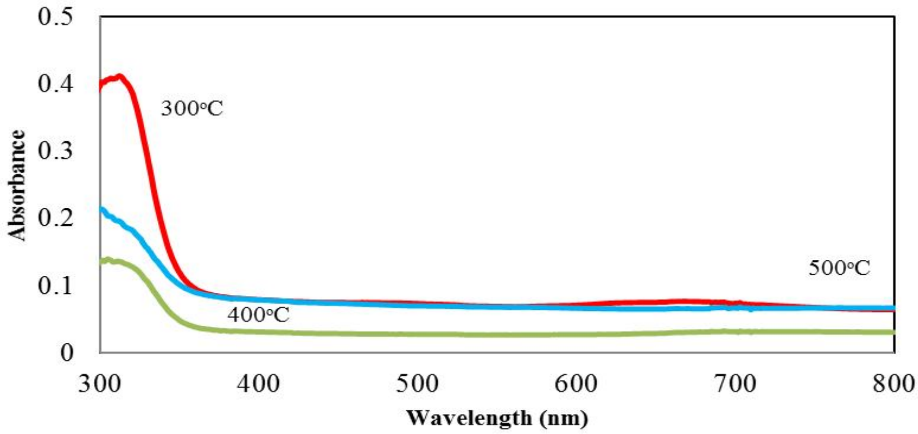
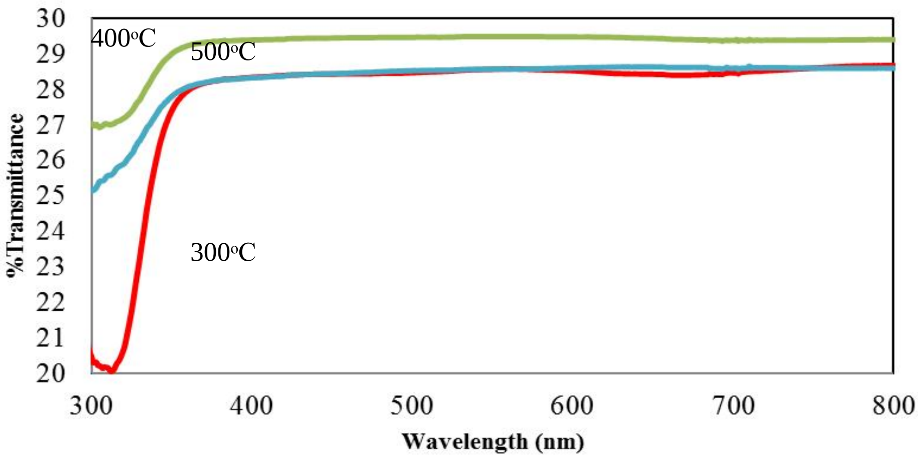



**Figure 3.** SEM micrographs of $TiO_2/SiO_2$ annealed at (a) 300°C, (b) 400°C and (c) 500°C.




**(a)**




**(b)**

**Figure 4**. UV-Vis spectra of absorbance and transmittance for $TiO_2/SiO_2$ films annealed at different temperatures.

The optical absorbance and transmittance spectra of $TiO_2/SiO_2$ films deposited on glass substrates with different annealing temperatures were shown in figure 4(a) and (b). The films show sharp absorption edge in ultraviolet region at a wavelength of about 320 nm as seen in figure 4(a). The absorbance is much higher for the films which annealed at 300°C with the formation of $TiO_2/SiO_2$ and the films are crack free. The transmittance within the visible and near infrared region is lower than 30% including the glass substrates, which reveals the poor optical properties of $TiO_2/SiO_2$ produced in this study. It is well agreement with the SEM micrograph which the substrate was not fully covered with the films and the films have large cracks. When the films are having large cracks, the UV light will be scattered in all direction.

Optical transparency is prerequisite for the application of self-cleaning coating on transparent glass or plastic surface. The films annealed at 400°C and 500°C shows the same trends of spectra for absorbance and transmittance with the only brookite phase exist. The transmittance of film annealed at 400°C is much higher compared to the film annealed at 500°C is due to pure $TiO_2$ film at 400°C is having less crack and bigger crystal size. The increased of cracking crystal size is responsible for the slight loss in optical transmission in the visible range. The process of spin coating needs to repeat a few times, in order to ensure the substrate is fully covered by the films and it also can enhance the transmittance and the absorbance of the films [24].

## 4. Conclusions

This work deals with the preparation and characterization of $TiO_2/SiO_2$ thin films using a simple and cost effective method: sol-gel spin coating. The deposition was performed on glass substrate at room temperature and annealed at three different annealing temperatures; 300°C, 400°C and 500°C. This work presents the annealing temperature effect on the properties of $TiO_2/SiO_2$. X-ray diffraction pattern shows that the thin films obtained at annealing temperature 300°C, having a phase of $TiO_2/SiO_2$. At higher annealing temperature (400-500°C), the formation of brookite phase presence. The SEM micrograph of the film annealed at 300°C show that the film consist of agglomeration of small flaky size without any crack. The analysis of UV-Vis transmission spectra shows that $TiO_2/SiO_2$ thin films are transparent in the visible range with a poor transmittance due to large crack and non-uniform film. This research proved that annealing temperature is an important parameter which affects the structure; surface morphology, and optical properties of the films.

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