

ВЛИЯНИЕ ТЕМПЕРАТУРЫ ПОДЛОЖКИ НА ОПТИЧЕСКИЕ, ГИДРОФИЛЬНЫЕ И ФОТОКАТАЛИТИЧЕСКИЕ СВОЙСТВА НАНОСТРУКТУРИРОВАННЫХ ТОНКИХ ПЛЕНОК ДИОКСИДА ТИТАНА, НАНЕСЕННЫХ НА СТЕКЛЯННЫЕ ПОДЛОЖКИ

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Наноструктурированные пленки диоксида титана наносились методом электронно-лучевого напыления на стеклянные подложки при различных температурах подложки. Кристаллическая структура, морфология поверхности и оптические свойства тонких пленок изучались методами рентгеновского дифракционного анализа, сканирующей эмиссионной электронной микроскопии и спектроскопии видимого и ультрафиолетового диапазонов соответственно. Гидрофильные и фотокаталитические свойства тонких пленок при их ультрафиолетовом облучении оценивались из измерений контактного угла смачивания и скорости деградации метиленового голубого. Оптические измерения показали, что температура подложки не оказывает заметного влияния на пропускание тонких пленок оксида титана. Измерения контактного угла смачивания и скорости деградации метиленового голубого показали, что тонкие пленки диоксида титана, нанесенные при температуре подложки 300 °C, обладают наилучшими гидрофильными и фотокаталитическими свойствами.

Ключевые слова: диоксид титана, тонкие пленки, оптические свойства, гидрофильность, фотокаталитические свойства.

SUBSTRATE TEMPERATURE EFFECTS ON THE OPTICAL, HYDROPHILIC AND PHOTOCATALYTIC PROPERTIES OF TiO₂ NANOSTRUCTURED THIN FILM DEPOSITED ON GLASS SUBSTRATE

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In this research, TiO₂ nanostructured thin films were deposited on glass substrates at different substrate temperatures by electron beam physical vapor deposition method. Crystalline structure, surface morphology and optical properties of the thin films were investigated by X-ray diffraction, field emission scanning electron microscopy and UV-Vis spectrophotometer, respectively. The hydrophilic and photocatalytic activities of the thin films during UV irradiation were evaluated by a water contact angle measurements and methylene blue degradation. The optical properties showed that substrate temperature did not have significant effect on the transparency of the TiO₂ thin films. In addition, water contact angle measurements and methylene blue degradation indicated that the TiO₂ thin film deposited at 300 °C had the best hydrophilic and photocatalytic properties.

Keywords: titanium dioxide, thin film, optical properties, hydrophilicity, photocatalysis.

OCIS codes: 310.0310, 160.4760, 160.4236

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1. Introduction

In recent years, transparent self-cleaning thin films have attracted deal of attention in many applications such as solar cells, optical lenses, building and automotive industries. Self-cleaning property is a common effect of photocatalytic and hydrophilic properties. Photocatalytic property helps destruction of organic pollutants and prevents from aggregation them on the surface while hydrophilicity causes to spreading water completely on the surface and so the surface clean easier. Titanium dioxide is one of the most important semiconductor metal oxide used in the self-cleaning applications due to simultaneously effects of hydrophilic and photocatalytic properties [1–3]. Transparent TiO₂ thin film with hydrophilic and photocatalytic properties can be used in practical application such as mirrors, windows glass and etc. [4]. There are many methods to immobilize titanium dioxide thin films on glass substrates such as electron beam physical vapor deposition (EBPVD) [5], sputtering [6], pulsed laser deposition, chemical vapor deposition, plasma enhanced chemical vapor deposition [7], sol-gel [8] and etc. Among these methods, EBPVD is one of the best techniques to deposit TiO₂ thin film. In this method there are several parameters which can affect on the TiO₂ thin film properties including substrate temperature, oxygen partial pressure and deposition rate. In the EBPVD method, substrate temperature is one of the major factors which affect on the crystalline structure, optical, hydrophilic and photocatalytic properties of the TiO₂ thin film [9]. In this study, TiO₂ thin films were deposited on glass substrate at different substrate temperatures and then the effect of the substrate temperatures on the hydrophilic, photocatalytic and optical properties of the TiO₂ thin films were investigated.

2. Experimental

TiO₂ thin films were deposited by electron beam physical vapor deposition via the Balzers-Bak 760 technique on sheets of BK7 glass substrates with 19 mm radius and 3 mm thickness. The target was a TiO₂ tablet with a purity of 99.99%. Before coating, the glass substrates were ultrasonically cleaned in deionized water and isopropyl alcohol and then dried in a dichloromethane vapor bath. The deposition was carried out in a vacuum chamber with a base pressure

of 10⁻⁵ mbar. Oxygen partial pressure during the deposition was kept at 1.6×10⁻⁴ mbar. The thicknesses of the TiO₂ thin films was maintained at approximately 240 nm as measured by a quartz-crystal sensor and the deposition rate of the TiO₂ thin films was kept at 0.3 nm s⁻¹. The thin films was prepared at different substrate temperatures (150, 200, 250 and 300 °C).

The crystalline structure, surface morphology and optical properties of the thin films were characterized by the use of Bruker X-ray diffractometer (XRD, D8ADVANCE, Germany, Ni-filter, Cu-Radiation K = 1.5406 Å), field emission scanning electron microscopy (FE-SEM, Hitachi S4 160, cold field emission, voltage 20 kV) and UV-VIS-NIR spectrophotometer (Shimadzu UV-3100), respectively. In order to investigation of hydrophilic activities, the thin films were irradiated by a Xe lamp (power 30 W, maximum intensity at wavelength λ_{max} = 365 nm) and then water contact angle was measured at the 30 min intervals.

The photocatalytic activities of the thin films were evaluated by the degradation of methylene blue (MB). For the photocatalytic experiment, the glass coated samples were horizontally immersed in an aqueous solution of MB (15 ml, 3×10⁻⁴ M) and irradiated with UV light. After the irradiation, degradation of the MB was determined by measuring absorbance of the MB of each decanted solution using UV-VIS spectrophotometer at λ_{max} = 664 nm which is the maximum absorption of MB.

3. Results and discussion

Figure 1 displays XRD patterns of the TiO₂ thin films. Figure 1 shows that TiO₂ thin film deposited at 150 °C substrate temperature contain both rutile and anatase phases. During substrate temperature increasing, rutile intensity decreases as TiO₂ thin film deposited at 300 °C substrate temperature contains only anatase phase [6].

Figure 2 shows FE-SEM images of the TiO₂ thin films. The FE-SEM images of the thin films show homogeneous surface, quasi-spherical grains and crack free. Also, FE-SEM images indicate that there is some porosity in the thin films. By increasing substrate temperature, films become dense and porosity decreases.

Figure 3 and Fig. 4 show transmittance and reflectance spectra of the thin films, respectively. According to Fig. 3, it can be seen that trans-

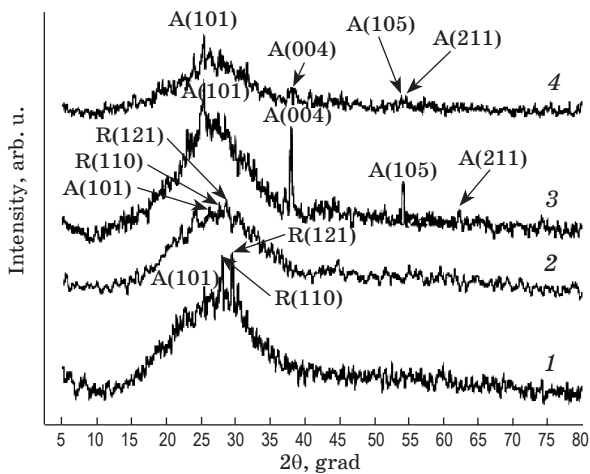


Fig. 1. XRD patterns of the TiO₂ thin films at different substrate temperatures (1 – 150, 2 – 200, 3 – 250, 4 – 300 °C).

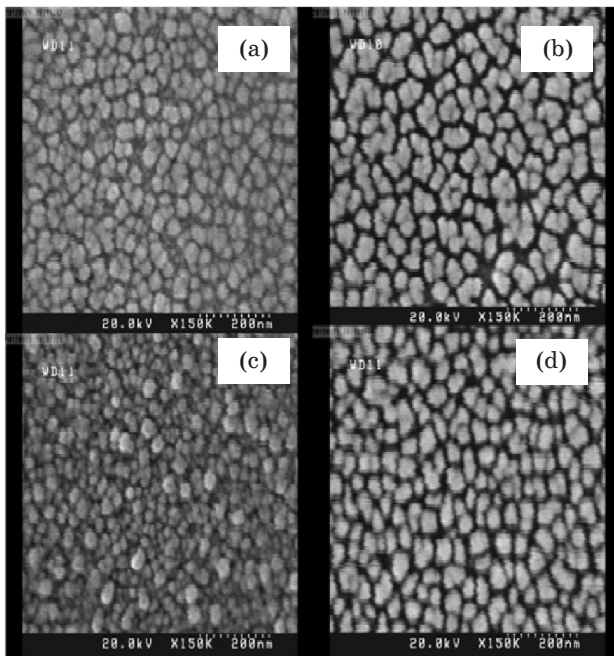


Fig. 2. FE-SEM images of the TiO₂ thin films at different substrate temperatures (a – 150, b – 200, c – 250, d – 300 °C).

mittance of the thin films decreases by substrate temperature increasing. This can be related to thin film morphology and particle size as indicated in the FE-SEM images. One may observe that the particle size of the TiO₂ increases with substrate temperature increasing. Therefore, a decrease in the transmittance of the TiO₂ thin film with increasing substrate temperature can be assigned to the formation of larger particle size and an increase in the surface roughness in the TiO₂ thin films, which causes scattering of light. Then, the higher transmittance of the TiO₂ films

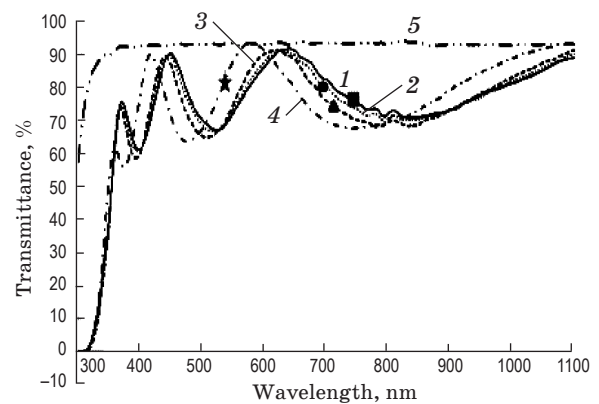


Fig. 3. Transmittance spectra of the TiO₂ thin films at different substrate temperatures (1 – 150, 2 – 200, 3 – 250, 4 – 300 °C, 5 – BK7).

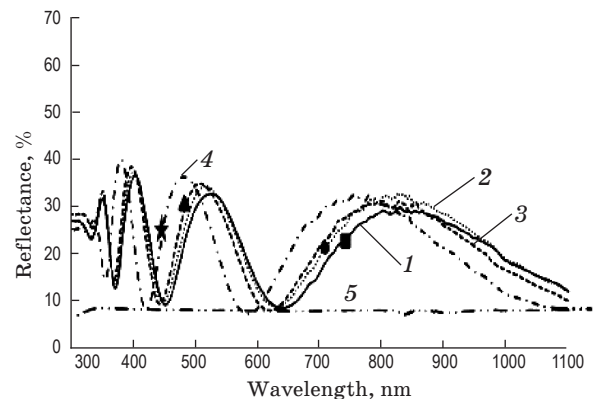


Fig. 4. Reflectance spectra of the TiO₂ thin films at different substrate temperatures (1 – 150, 2 – 200, 3 – 250, 4 – 300 °C, 5 – BK7).

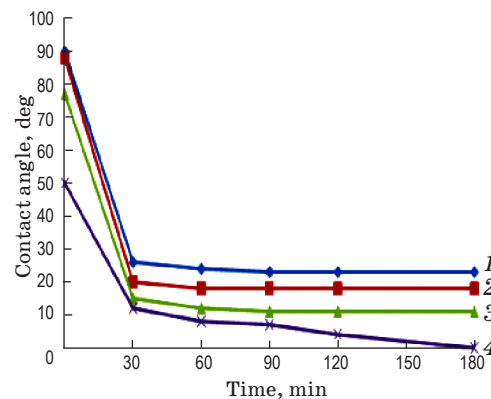


Fig. 5. Water contact angle on thin film surfaces during UV light irradiation (1 – 150, 2 – 200, 3 – 250, 4 – 300 °C).

deposited at lower substrate temperatures can be related to a decrease in light scattering from smaller particles [10].

Figure 5 represents the results of the water contact angle measurements on the thin film surfaces under UV light irradiation. Figure 5 shows

that reduction rate of water contact angle increases with substrate temperature increasing. According to Fig. 5, it can be seen that the water contact angle on the TiO₂ thin film deposited at 300 °C substrate temperature during irradiation decreased faster than other thin films. Water contact angle in TiO₂ thin film deposited at 300 °C substrate temperature become zero after 180 min UV light irradiation.

The higher superhydrophilicity of the TiO₂ thin film deposited at 300 °C substrate temperature can be explained in the following:

During the increasing substrate temperature, surface roughness increases as shown by FE-SEM images. Surface roughness has an intense effect on the superhydrophilicity. The roughness of a given surface is usually related to its apparent contact angle (θ^*), i.e., the measured contact angle, through the Wenzel equation [11]

$$\cos\theta^* = r\cos\theta,$$

where r is the roughness parameter and θ is the Young contact angle induced only by chemical surface interactions, i.e., which would be measured on an ideally flat surface. From this equation, it appears that the roughness enhances the surface wetting behavior, i.e., $\theta^* < \theta$, of a naturally hydrophilic surface ($\theta > 90$). These results showed that TiO₂ thin film deposited at 300 °C substrate temperature possess hydrophilicity and as a consequence a high content of hydroxyl groups are present on the titania surface which are absolutely necessary for the successful adsorption of water to the TiO₂ surface. This can be explained by the rough surface of the films with the combined effect of various pore channels and cracks or small ditches, which may provide enough capillary force to suck water into the film [12].

Figure 6 shows photocatalytic properties of the thin films. It is found that the photocatalytic

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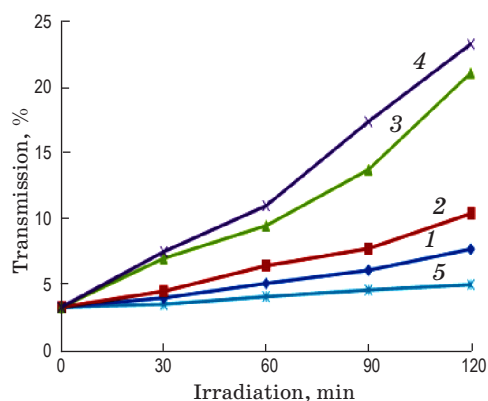


Fig. 6. Photodegradation of the methylen blue (1 – TiO₂-150, 2 – TiO₂-200, 3 – TiO₂-250, 4 – TiO₂-300 °C, 5 – solution methylene blue).

activity of the thin films increase with increasing substrate temperatures.

It is well known that anatase has higher photocatalytic activity than rutile phase. TiO₂ thin film deposited at 300 °C substrate temperature contain anatase phase. So, we can deduce the reason the higher photocatalytic degradation of methylen blue in the presence of TiO₂ thin film deposited at 300 °C substrate temperature than other thin films.

4. Conclusion

In this research, TiO₂ thin films were deposited on glass substrates using an electron beam physical vapor deposition technique at different substrate temperatures. TiO₂ thin films deposited at 300 °C showed excellent super-hydrophilicity and photocatalytic activity under UV irradiation. In addition, TiO₂ thin films deposited at 150 °C showed slightly higher transmittance and a lower reflectance in comparison to other thin films. Therefore, we suggest that TiO₂ thin films deposited at 300 °C would be very useful where self cleaning effect is desired for optical instruments.

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