TRANSPARENT SUPERHYDROPHILIC $SiO_2/TiO_2/SiO_2$ TRI-LAYER NANOSTRUCTURED ANTIFOGGING THIN FILM

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$SiO_2/TiO_2/SiO_2$ thin films were deposited on glass substrates using an electron beam physical vapor deposition technique. The structure, morphology, surface composition, surface roughness, optical properties, and hydrophilic properties of the thin film were investigated. The structure measurement shows that only anatase phase was exhibited in the thin film. In the TiO_2 thin film, the crystals nucleated from the thin films was homogeneous and the average crystalline sizes were 35 nm. The transmittance spectra of the films revealed transparency in the visible region of the spectrum. $SiO_2/TiO_2/SiO_2$ thin film showed better hydrophilicity under irradiation and storage in comparison to SiO_2/TiO_2 thin film. $SiO_2/TiO_2/SiO_2$ tri-layer thin film showed superhydrophilicity which greatly encourages the antifogging function of the film.

INTRODUCTION

The self cleaning and antifogging effect of TiO_2 thin film has attracted much attention in recent years especially in the glass industry [1]. The antifogging effect of TiO_2 thin film has been attributed to photoinduced superhydrophilicity [2]. The superhydrophilicity of the surface of TiO_2 thin film allows water spread completely across the surface rather than remaining as droplets, thus making the surface anti-fogging [2-3]. Transparent antifogging TiO_2 thin film on glass substrates has a high potential for practical applications such as mirrors, window panes and automobile windshields [4-5].

However, TiO_2 thin film only exhibits superhydrophilicity under UV light irradiation. In practical applications, UV irradiation light on the TiO_2 surface does not always occur. If TiO_2 thin film is stored in a dark place, the surface of TiO_2 is converted to a hydrophobic state [6]. Therefore, it is preferable that the TiO_2 film retains its super-hydrophilicity for a long time in a dark place. Eshaghi et al [7] indicated that the addition of SiO_2 on TiO_2 and the formation of a TiO_2 -SiO_2 composite film improved the hydrophilicity of TiO_2 especially in a dark place. In this study, $SiO_2/TiO_2/SiO_2$ tri-layer thin films were deposited on glass substrates using electron beam physical vapor deposition. Then, the photoinduced superhydrophilicity and antifogging effect of the thin films were investigated.

EXPERIMENTAL

The SiO_2/TiO_2 and $SiO_2/TiO_2/SiO_2$ thin films were prepared by the use of electron-beam physical vapor deposition via the Balzers Bak 760 technique. The deposition was performed in a vacuum chamber with a base pressure of 10^{-5} mbar. The electron-beam evaporator with a 12 cm crucible pocket was located 70 cm directly beneath the substrate. The targets were a TiO_2 tablet with a purity of 99.99 % for the fabrication of TiO_2 thin film and SiO_2 powder with a purity of 99.99 % for SiO_2 thin film fabrication. The partial pressure of oxygen during the deposition was kept at 1.6×10^{-4} mbar. The substrate temperature was 300°C. The deposition rate and the thickness of the growing films were measured by the use of a quartz-crystal sensor, which was placed near the substrate. Sheets of glass (BK7, 19 mm radius and 3 mm thickness) were used as substrates. The substrate rotation employed was 15 rpm. The thicknesses of the tri-layer $SiO_2/TiO_2/SiO_2$ thin films were kept at approximately 120/240/20 nm as measured by a quartz-crystal sensor, and the deposition rate of the TiO_2 films was kept at 0.3 nm/s and the SiO_2 was kept at 0.5 nm/s. It is necessary to mention, that before coating, the glass substrates were ultrasonically cleaned in deionized (DI) water and then dried in a dichloromethane vapor bath.

The structure, morphology, surface characteristics and surface roughness of the thin films were determined

using a Bruker X-ray diffractometer (D8ADVANCE, Germany, Ni-filter, Cu Kα radiation λ = 1.5406° A), Field emission scanning electron microscopy (FE-SEM, Hitachi S4160, Cold Field Emission, Voltage 20 kV), Attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR; Bruker Germany, Tensor 27) and Atomic force microscopy (AFM, Veeco CPR USA contact mode), respectively.

The transmittance spectra of the thin films were obtained using a UV-VIS-NIR spectrophotometer (Shimadzu UV-3100). The refractive index of the films was measure using an ellipsometry (Horiba ellipsometry). During a part of the photo induced super-hydrophilic measurements, the samples were stored in a drying oven at 100°C overnight before use. Then, the photo induced super-hydrophilicity of the thin films was evaluated by measuring the contact angle of a water droplet on the film surfaces. A droplet was injected on to the surface using a 1 µl micro-injector. The water contact angle was averaged from five measurements. UV light was irradiated on the surface of the samples by an Xe lamp (Power 30 W, wavelength 365 nm). In addition, the hydrophilic-hydrophobic conversion of the films after storage in a dark place (48 h) was investigated

RESULTS AND DISCUSSION

The XRD pattern of the $SiO_2/TiO_2/SiO_2$ thin film is shown in Figure 1. The XRD measurement shows that only anatase phase is exhibited in the thin film [8].

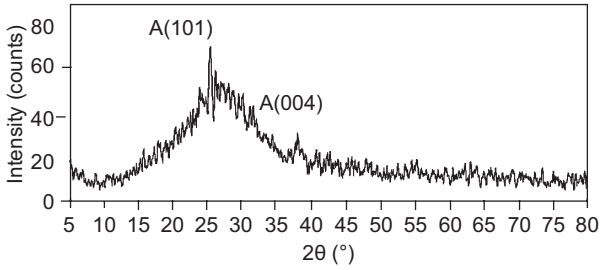
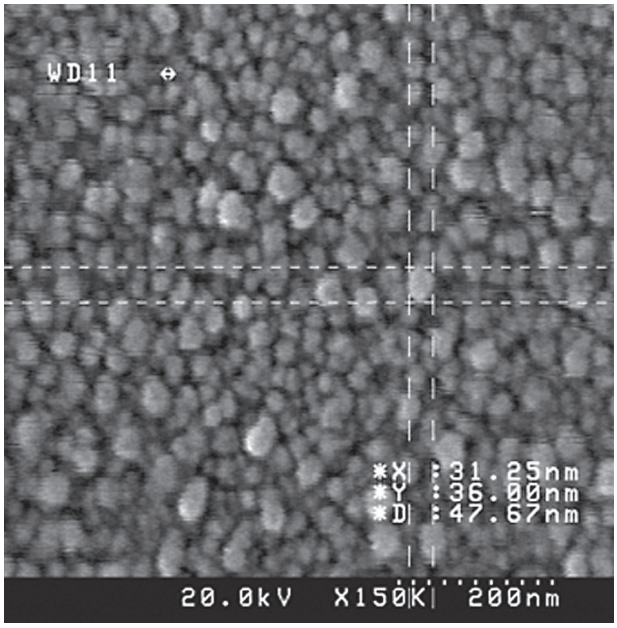


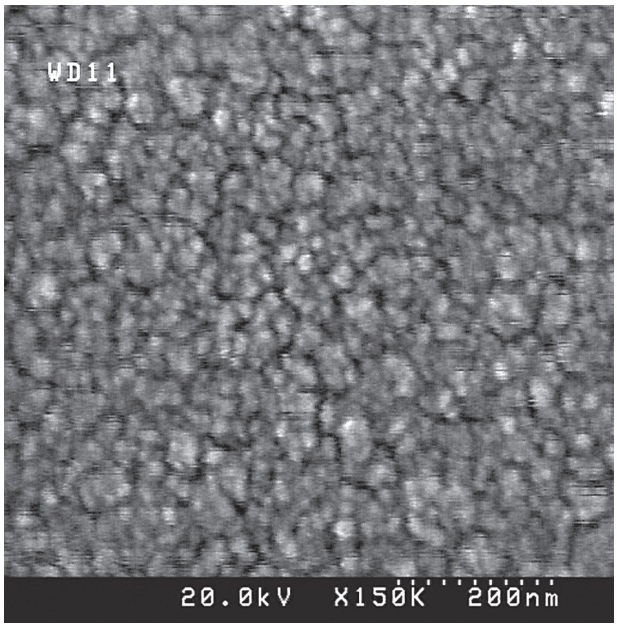
Figure 1. X-ray diffraction pattern of $SiO_2/TiO_2/SiO_2$ thin film.

Figure 2 shows the FE-SEM images of TiO_2 and $SiO_2/TiO_2/SiO_2$ thin film. The FE-SEM image of $SiO_2/TiO_2/SiO_2$ film indicates a homogeneous surface and crack free. Due to coverage of amorphous SiO_2 in the tri-layer surface, this figure is not clear and do not show crystalline sizes of under layer TiO_2 thin film. In the TiO_2 thin film, the crystals nucleated from the thin films are homogeneous and the average crystalline sizes are 35 nm.

Energy dispersive x-ray (EDX) analysis of the $SiO_2/TiO_2/SiO_2$ thin film was carried out to identify the elements present on the coated surface. The EDX spectrum of the surface of the $SiO_2/TiO_2/SiO_2$ thin film is illustrated



a) TiO_2



b) TiO_2/SiO_2 thin film

Figure 2. FE-SEM images of TiO_2 (a) and TiO_2/SiO_2 thin film (b).

in Figure 3. Figure 3 shows the presence of titanium and silicon along with oxygen in the $SiO_2/TiO_2/SiO_2$ thin film.

In order to understand the photoinduced super-hydrophilicity on the surface, the characterization of the functional groups on the film surface is important. The transmission spectra of the films were measured in the range of 4000 - 600 cm^{-1} with a resolution of 4 cm^{-1}. Figure 4 shows the ATR-FTIR spectrum of the $SiO_2/TiO_2/SiO_2$ thin film. The adsorption band at about 3600 - 2800 cm^{-1} is assigned to the stretching modes of the O–H bonds and is related to surface adsorbed water. The adsorption

band at 1640 cm^{-1} is attributed to the bending vibration of H–O–H bonds, which are assigned to the chemisorbed water [9]. The adsorption band at about 850 and 1070 cm^{-1} is assigned to the stretching vibration of the Si–O–Si band which indicated on amorphous silica [10-14].

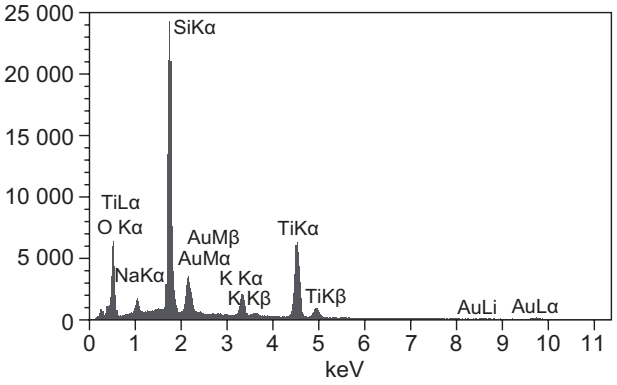


Figure 3. EDX spectrum of $SiO_2/TiO_2/SiO_2$ thin film.

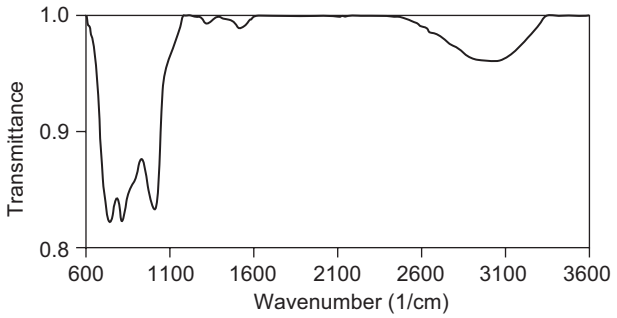


Figure 4. ATR- FTIR spectrum of $SiO_2/TiO_2/SiO_2$ thin film.

AFM was used to characterize the surface roughness of the thin films. Figure 5 shows AFM images of the TiO_2 and $SiO_2/TiO_2/SiO_2$. The root mean square roughness values (Rrms) of the TiO_2 and $SiO_2/TiO_2/SiO_2$ thin films are 5.523 and 2.296 nm, respectively. According to the AFM results, the surface roughness was decreased by the formation of $SiO_2/TiO_2/SiO_2$ thin film.

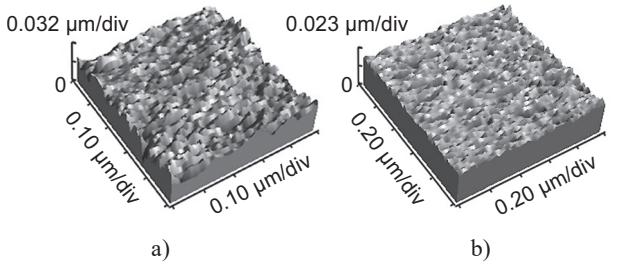


Figure 5. AFM images of SiO_2/TiO_2 (a) and $SiO_2/TiO_2/SiO_2$ thin film (b).

Figure 6 displays the transmission spectra of the SiO_2/TiO_2 (TiO_2 top layer), and $SiO_2/TiO_2/SiO_2$ tri-layer thin films. The transmittance spectra of the thin films reveal transparency in the visible region of the spectrum (380 - 760 nm). The average transmittance of the thin films was measured as 80.45 and 76.8 for STS and ST thin films, respectively.

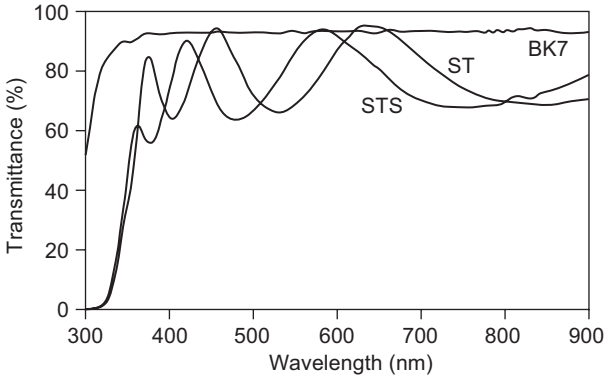


Figure 6. Transmittance spectra of SiO_2/TiO_2 (ST) and $SiO_2/TiO_2/SiO_2$ (STS) thin film

According to Figure 6, a decrease in the transmittance of the TiO_2 film in comparison to $SiO_2/TiO_2/SiO_2$ can be attributed to the formation of larger crystals and an increase in the surface roughness of the TiO_2 thin films (as shown in the Figure 5), which causes light to scatter [3].

The refrative index of the thin films measured by ellipsometer is shown in Figure 7. It can be seen that the refractive index was decreased by the formation of $SiO_2/TiO_2/SiO_2$ thin film. This can be used to explain the higher transmittance of $SiO_2/TiO_2/SiO_2$ in comparison to the TiO_2 thin film (Figure 6). A decrease in the transmittance of the TiO_2 with in comparison to the $SiO_2/TiO_2/SiO_2$ film can be attributed to a higher refractive index which causes light to be reflected [3].

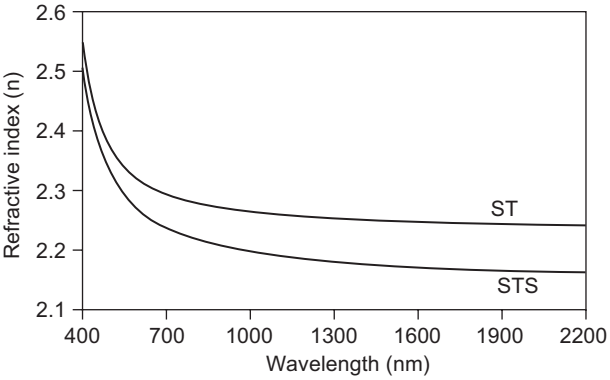
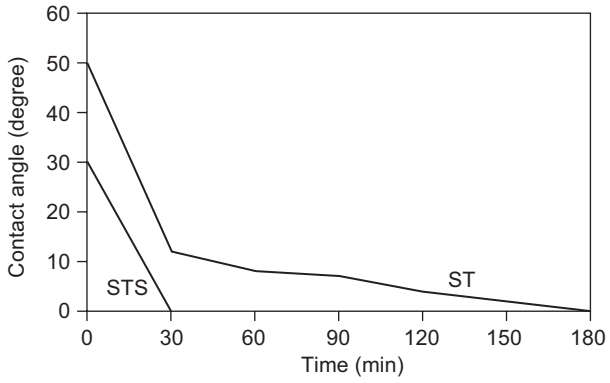


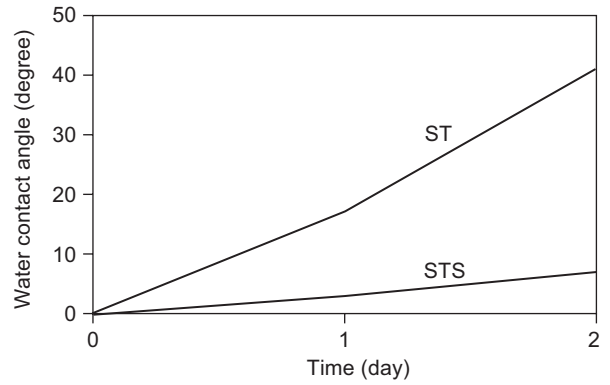
Figure 7. Refractive index of SiO_2/TiO_2 (ST) and $SiO_2/TiO_2/SiO_2$ (STS) thin film.

Figure 8 represents the results of the water contact angle measurements on the film surfaces under UV irradiation. In the $SiO_2/TiO_2/SiO_2$ thin film, the water contact angle decreased significantly due to the surface properties. After 30 min of UV exposure, the STS thin film shows a water contact angle of nearly 0°. That is, the

water has completely spread over the film surface and the film shows superhydrophilicity. If films are stored in a dark place, the water contact angle increases (Figure 8b) and the surface of the films converts to a hydrophobic state. The hydrophilic- hydrophobic conversion rate is slower for $SiO_2/TiO_2/SiO_2$ thin film than for SiO_2/TiO_2 thin film. After storage in dark place for 24 h, the water contact angle is almost unchanged. From the second day (48 h), it rises. It is clear that $SiO_2/TiO_2/SiO_2$ thin film, after storage in a dark place retains a hydrophilic state better in comparison to SiO_2/TiO_2 thin film.



a)



b)

Figure 8. Water contact angle on surfacess during irradiation (a) and storage in dark place (b).

The antifogging performance of the superhydrophilic $SiO_2/TiO_2/SiO_2$ thin film was demonstrated by irradiation with UV light for 2 h and exposure to a vapor maker (KANGFUER CE SPS 828A 220V/50Hz 38W) after storage at -19°C in a refrigerator for 30 min. As shown in Figure 9, the bare glass slide (left side) fogged immediately and the words written under it are blurred by strong light scattering. In contrast, the slide coated with the $SiO_2/TiO_2/SiO_2$ thin film (right side) significantly prevents fogging formation by almost instantaneously spreading the condensed water droplets to form a thin water layer. Therefore, the slide with the $SiO_2/TiO_2/SiO_2$ coated glass remains highly transparent and the words written under it are clearly seen.

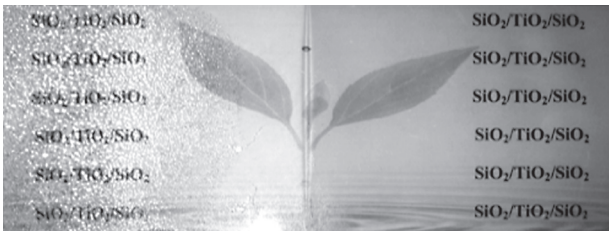


Figure 9. The photo illustrated of, antifogging glass (right) versus conventional glass (left).

Many researchers have investigated the photoinduced superhydrophilic mechanism of TiO_2 thin film. When TiO_2 is exposed under UV light irradiation, the electrons and holes are produced in the conduction and valence bands, respectively. In the following, on the TiO_2 crystal surface is reduced by surface trapped electrons and the holes oxidize the anions. In the process, the oxygen atoms are ejected and oxygen vacancies are created. Then, water molecules can occupy these oxygen vacancies, producing adsorbed OH groups, which tend to make the surface hydrophilic. Hydroxyl groups existing in the films are attributed to the chemically adsorbed water molecules and also some water molecules are physically adsorbed on the surface of TiO_2. It can be explained that some adsorbed water molecules react with the TiO_2 and form Ti–OH groups. Generally, with the increase of chemically absorbed –OH on the surface of TiO_2 films, van der Waals forces and hydrogen bonds interactions between the H_2O and –OH will be increased. Consequently, water can easily spread across the surface and the super-hydrophilic property will be enhanced [2-3].

The enhanced superhydrophilicity of TiO_2 thin film in the presence of a SiO_2 top layer under UV light irradiation and storage in dark place can be explained as follows:

In the $SiO_2/TiO_2/SiO_2$ thin film, the photogenerated holes in the TiO_2 mid-layer can migrate to the uppermost $SiO_2/TiO_2/SiO_2$ surface through the SiO_2 layer. SiO_2 layer has an amorphous structure which makes it easier for the holes to move through it to the uppermost surface. This process can separate a photoelectron hole pair away, and then decrease the recombination rate of the photogenerated pair and retain the hole longer. The photogenerated electrons in the interface between the TiO_2 and SiO_2 tend to reduce the Ti^{+4} to the Ti^{+3} state, whereas the photogenerated holes transmitted to uppermost surface can dissociate adsorbed water on the surface and produce stable hydroxyl groups, which tend to make the surface hydrophilic [15-16]. So, we can understand the reason for the increased hydrophilicity in the $SiO_2/TiO_2/SiO_2$ thin film.

According to bonding dissociation energy SiOH (975 kJ/mol) and TiOH (668 kJ/mol), it is clear that SiOH is more stable than TiOH [9, 15-16]. This means that stable hydroxyl groups (Si–OH) on the $SiO_2/TiO_2/SiO_2$ thin film

surface can result in increased superhydrophilicity and in the capability of maintaining absorbed water molecules. This indicates that the hydrophilic state of $SiO_2/TiO_2/SiO_2$ film can be maintained for a long time, especially in a dark place.

CONCLUSION

In this research, $SiO_2/TiO_2/SiO_2$ thin film was deposited on glass substrates using an electron beam physical vapor deposition technique. XRD measurements indicated the presence of anatase phase in the films. The $SiO_2/TiO_2/SiO_2$ thin film showed excellent super-hydrophilicity under UV radiation and storage in a dark place in comparison to SiO_2/TiO_2 thin film. In addition, the $SiO_2/TiO_2/SiO_2$ film showed higher transmittance and a lower refractive index in comparison to SiO_2/TiO_2 thin film. It was demonstrated that by covering TiO_2 thin film with a SiO_2 overlayer the hydrophilicity was significantly improved and an antifogging effect was obtained. Therefore, we suggest that $SiO_2/TiO_2/SiO_2$ thin film would be very useful where super-hydrophilicity and an antifogging effect are desired for automobile and optical lens applications.

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