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Invited Paper

Optical and Photocatalytic Characteristics of Nitrogen Doped TiO_2 Thin Film Deposited by Magnetron Sputtering

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Abstract. *A nitrogen doped TiO_2 thin film was deposited by a DC reactive magnetron sputtering on glass and SiO_2 substrates, and then annealed at 400° C. Deposition was performed in a Ar + O_2+N_2 gas mixture of 1.0 Pa, and oxygen and nitrogen with constant pressures of 0.2 Pa and 0.1 Pa, respectively. The thicknesses of deposited layers, $TiO_{(2-x)}N_x/TiO_2/ZnO$, were approximately 200 nm, 800 nm and 80 nm, respectively. ZnO was used as a buffer layer. The structure and morphology of the deposited films were evaluated by X-Ray Diffraction (XRD) and scanning electron microscopy (SEM). The average grain sizes of TiO_2 and nitrogen doped annealed thin films were 25 and 18 nm, respectively. The microstructure of the annealed films was anatase. The optical transmittance of the films was measured using ultraviolet-visible light (UV-vis) spectrophotometer. The photocatalytic activity of the samples was evaluated by the degradation of Methylene Blue (MB) dye.*

Keywords: *Nitrogen doped TiO_2 thin films; Sputtering; Structure; Hydrophilicity photocatalytic activity.*

INTRODUCTION

Many investigations have been performed on utilizing solar energy to generate electricity and photocatalytic activity. The huge amount of toxic agents in the atmosphere is one of the main reasons behind diseases that infect humans. One of the most popular photocatalyst materials to degrade the pollutants is TiO_2 , which has been studied widely since 1972 [1]. It shows a relatively high performance on pollutant degradation under UV light [2-6]. The required energy for starting photodegradation exceeds the band gap of 3.2 eV in the anatase crystalline phase to generate electron-hole pairs. By doping TiO_2 with different elements, such as W, Ce, Nb, Fe [7,8] and Au and Ag [9], not only are the electron-hole pairs prevented from recombining, but the visible light could also be useful in generating more electron-hole pairs. The new applicable doping elements that have been more effective in improving the characteristics of TiO_2 thin films are carbon and nitrogen [10-14]. In this study, we doped TiO_2 thin films with nitrogen to increase the absorption of the extended range of visible light wavelengths and to modify the surface morphology. While photocatalytic reactions are performed on TiO_2 thin film surfaces, we doped the film surface with only 200 nm of nitrogen for less change in the optical transmittance percentage.

EXPERIMENTAL PROCEDURE

Deposition Procedure

TiO_2 and *N*-doped TiO_2 thin films were deposited on soda-lime glass and a SiO_2 single crystal with DC reactive magnetron sputtering. The sputtering was carried out for 3 h. The metallic mode of sputtering has been chosen due to high performance. The Ti target was 99.97% pure with dimensions of 98 mm in diameter and 2 mm in thickness. A Zn target with purity of 99.99% was used to fabricate the ZnO barrier layer; its dimensions were 1 mm in thickness and 98 mm in diameter. Both Zn and Ti targets were ultrasonically

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cleaned in pure alcohol and acetone for 10 mins and 30 mins, respectively. The substrates were microscope slides with 26 mm × 76 mm and 2 mm thickness and a SiO_2 single crystal. The prepared substrates were ultrasonically cleaned in alcohol and acetone for 15mins. The mixed gases of argon (99.999%) and oxygen (99.9995%) were used for deposition of the TiO_2 and ZnO barrier layer. To deposit the N-doped TiO_2 film, pure nitrogen gas (99.9995%) was purged into the sputtering chamber. The distances of the target and substrate were fixed at 65 mm in a parallel-horizontal style. The discharge began at a constant current of 100 mA. The pre-sputtering process was performed at 60 W (100 mA × 600 V) for 15 mins to clean the oxide layer from the surface of the titanium and zinc targets. After pre-sputtering of the Zn target, the deposition of the ZnO buffer layer was done at 6 Pa with 67.5 W (450 V × 150 mA) input power and an oxygen pressure of 0.2 Pa, where the deposition rate was 5.3 nm/min. Then, the TiO_2 thin film was deposited on the ZnO buffer layer. The N-doped TiO_2 thin film was deposited following the TiO_2 pure layer deposition. Both TiO_2 and $TiO_2/TiO_{(2-x)}N_x$ films were reactively deposited at a DC input power of 80 W (800 V × 100 mA), where the deposition rate was 5.7 nm/min. A constant oxygen pressure of 0.2 Pa was used as a reactive gas for ZnO, TiO_2, and $TiO_{(2-x)}N_x$ layers. A constant nitrogen pressure of 0.1 Pa was used for doping TiO_2 with nitrogen. The thicknesses of the deposited layers were measured by a piezoelectric thickness measurement (SQM-242 codeposition control and software, Sigma Instrument). The ZnO layer was selected as a barrier layer because of its good transmittance [15,16]. All thin films were annealed at 400°C for 1 h with a rising of temperature of about 6°C/min, and cooled in a furnace for crystallization and less heat stress on the films. The temperature was measured by a type-k thermocouple in touch with the substrate surface.

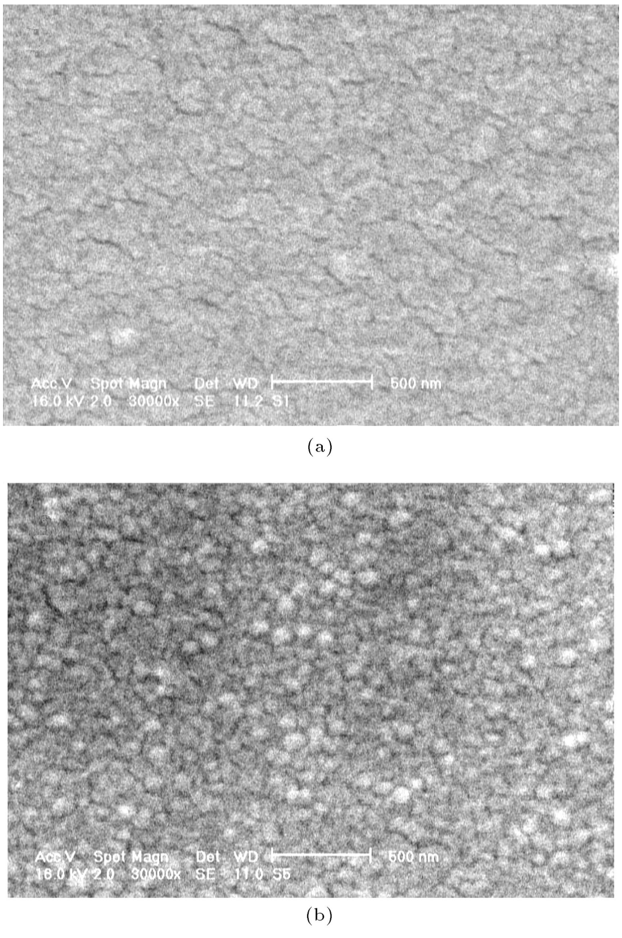
Characterization Techniques

A 30 kV-Philips, XL30 scanning electron microscopy (SEM) was employed to study the microstructure of the deposited films. X-Ray Diffraction (XRD) was used for investigation of phases and grain size calculation. XRD was performed in θ-2θ mode, using Cu-Kα, with a wavelength of 1.5439Å radiation. All XRD experiments were performed at a grazing incident of 3°. The hydrophilicity of the films was measured by angle measurement apparatus (with 1 mW/cm^2 intensity and maximum intensity centered at 369 nm). The transparency percentage and absorption edge were measured by UV-vis spectroscopy apparatus with a wavelength range of 190-1000 nm. The degradation of 2527×10^{-6} gr/lit aqueous Methylen Blue (MB) solution (2.5 ml) was investigated to determine the photocatalytic properties.

RESULTS AND DISCUSSION

Film Surface Characterization

The morphology of surface annealed films is shown in Figure 1. While both TiO_2/ZnO and $TiO_{(2-x)}N_x/TiO_2/ZnO$ films were deposited at the same pressure, the morphology of the surfaces was different. When the nitrogen atoms were doped into TiO_2 thin films, the grain size of the surface decreased due to the accumulation of Ti atoms on the nitrogen. It has been reported that in nitrogen doped TiO_2 thin films, nitrogen atoms can occupy interstitial and/or substitution positions [17]. By doping the nitrogen, the body structure of the TiO_2 thin film will be changed due to the expansion of the structure, because of the bigger volume of nitrogen atoms ($r = 0.7$ Å) compared with oxygen atoms (0.66 Å). Hence by nitrogen doping, the TiO_2 films will be denser and the mechanical strength will be increased [18-21]. It has



(a)

(b)

Figure 1. Surface morphology of a) TiO_2/ZnO and b) $TiO_{(2-x)}N_x/TiO_2/ZnO$ films annealed at 400°C.

been reported that the highest percentage of nitrogen occupies substitution positions [22]. Figure 1a shows the pure TiO_2 thin film which was deposited on the glass substrate by using the ZnO thin film as a barrier. As shown in Figure 1b, by doping the nitrogen, the nucleation centre of grains is increased. Hence surface roughness and grain size are decreased and the surface gets more uniformity.

X-Ray Diffraction

Figure 2 shows the X-ray diffraction pattern of deposited TiO_2/ZnO and $TiO_{(2-x)}N_x/TiO_2$/ZnO thin films annealed at 400°C. The whole phases of TiO_2 are anatase and the diffraction planes are (101), (004), (112), (200), (105) and (204). Mohamed et al. [23] and Hukari et al. [24] have reported that the nitrogen atoms in TiO_2 thin films act as a crystallization inhibitor for amorphous $TiO_{(2-x)}N_x$ films. They claimed that by adding nitrogen atoms, the mobility of titanium and oxygen atoms was decreased and the nucleation of crystalline phases was reduced. This is due to the large atomic radius of nitrogen as compared with oxygen. As shown in Figure 2, by doping the nitrogen atoms in TiO_2 thin films, the crystallinity of N-doped TiO_2 thin films is decreased [25]. The average grain size of anatase for TiO_2 and nitrogen doped TiO_2 is calculated by Deby-Scherrer's equation [26], about 25 nm and 18 nm, respectively. The smaller crystal size of doped thin films can be attributed to the increasing of produced nucleation centers due to higher concentration of Ti atoms on the surface.

Optical Properties

Figure 3 shows the optical transmittance spectra of the deposited ZnO barrier layer, N-doped TiO_2 and undoped TiO_2 thin films grown on unheated glass substrates and annealed at 400°C. The average band gap of anatase TiO_2 crystal is 3.2 eV, so it absorbs the light below a threshold wavelength of $\lambda g = 387$ nm [27]. The optical band gap of ZnO (3.24 eV) is very close to the optical band gap of TiO_2 (3.2 eV), thus the absorption edge of ZnO could not affect the absorption edge of TiO_2 [28]. As shown in Figure 3, by doping the nitrogen atoms into TiO_2 thin films, the absorption edge of the N-doped TiO_2 thin film is shifted to a visible region or less energy photons. This means that the doped nitrogen atoms will enhance the absorption of a higher range of light wavelengths than the undoped TiO_2 thin films. By doping the nitrogen atoms in TiO_2 thin films, the transparency of the layer is decreased due to the structure distortion of TiO_2 thin films. As shown in Table 1, the absorption edge of doped TiO_2/ZnO has some shift to higher wavelengths, as compared with the TiO_2 absorption edge.

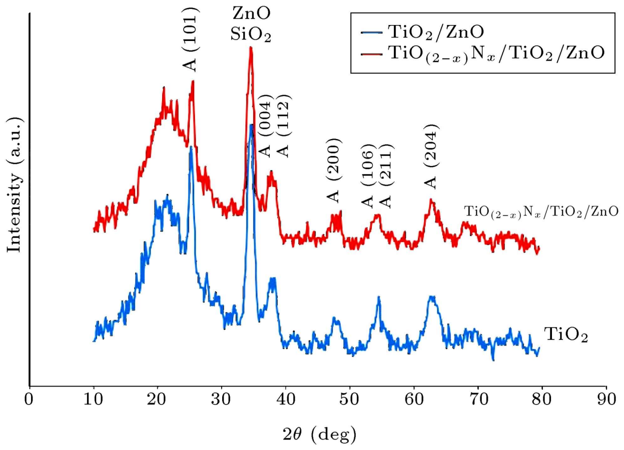


Figure 2. XRD patterns of TiO_2/ZnO and $TiO_{(2-x)}N_x/TiO_2$/ZnO thin films annealed at 400°C. The grazing incidence angle was 3°.

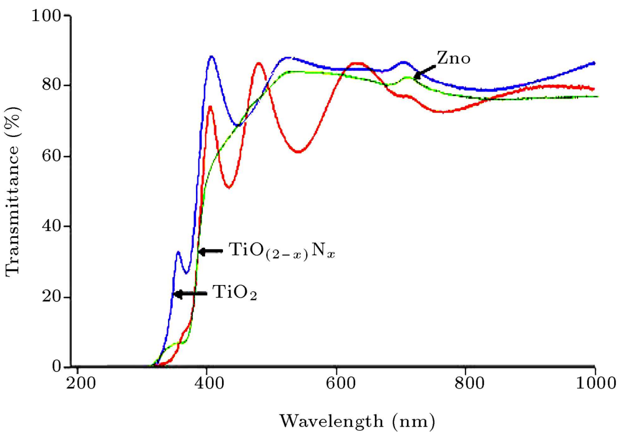


Figure 3. The effect of the nitrogen doped atoms on the optical transmittance spectra and absorption edge of TiO_2 thin films.

Hydrophilic Properties

The photo-induced hydrophilicity of thin films was evaluated by measuring the contact angle of water droplets during irradiation with UV-visible light, as shown in Figure 4. Since the $TiO_{(2-x)}N_x$ thin film has the lowest optical band gap, it exhibits the lowest water contact angle. By irradiation with UV light for 50 mins, the water contact angles of TiO_2/ZnO and $TiO_{(2-x)}N_x$/ZnO were 8 and 5 degrees, respectively. The reason for the small contact angle of the doped TiO_2/ZnO thin film can be attributed to the production of more electron-hole pairs, whereas more hydroxyl agents are formed on the film surface.

Chemical Photoactivity

The chemical photoactivity of doped and undoped TiO_2/ZnO thin films has been investigated by degra-

Table 1. The optical properties of TiO_2/ZnO and $TiO_{(2-x)}N_x/TiO_2/ZnO$ thin films.

Layer	Deposition Pressure (Pa)	Oxygen Pressure (Pa)	Nitrogen Pressure (Pa)	Thickness (nm)	Transmittance (%) (400-1000 nm)	Absorption Edge (nm)
ZnO	6 Pa	0.2	0	80	73.4	523
ZnO/TiO_2	1 Pa	0.2	0	1000/80	87	401
$TiO_{(2-x)}N_x/TiO_2/ZnO$	1 Pa	0.2	0.1	200/800/80	82	405

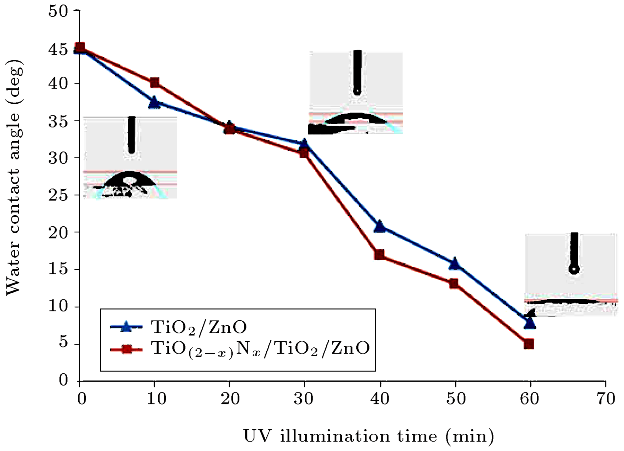


Figure 4. Dependence of water contact angle of as-deposited film annealed at 400°C on the UV light illumination time.

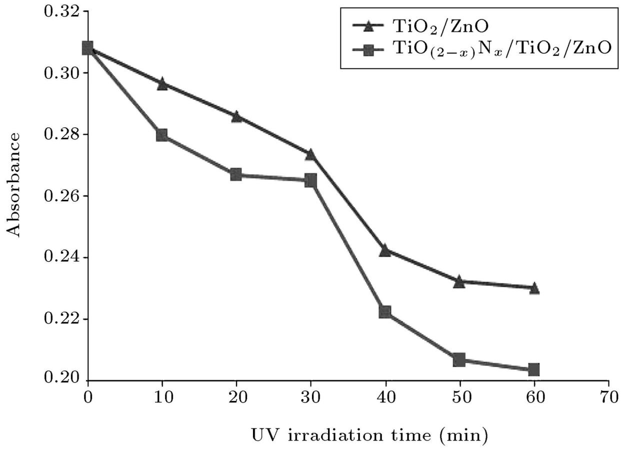


Figure 5. Photocatalytic degradation of MB using TiO_2/ZnO and $TiO_{(2-x)}N_x/TiO_2/ZnO$ thin films annealed at 400°C.

dation of an aqueous methylene blue solution. The generated electrons and holes move on the surface and react with pollutants, directly or indirectly, which degrades the pollutants. From Figure 5, it is shown that the breaking down of the aqueous MB dye *N*-doped TiO_2/ZnO film is greater than the TiO_2/ZnO film during the degradation process. By more investigation, it was found that during the degradation of MB for 60 mins, the TiO_2/ZnO thin film was degraded by approximately 25% of MB, whereas, for the $TiO_{(2-x)}N_x/TiO_2/ZnO$ film, it was 34%. As mentioned before, all TiO_2 phases are anatase, which has a stronger photochemical activity than rutile. The phothocatalytic activity of mixed phases increases by increasing the anatase ratio [29]. The small grain size and roughness of the nitrogen doped TiO_2 surface are another reason for the further degradation ability compared with undoped TiO_2 thin films.

CONCLUSION

N-doped TiO_2/ZnO and TiO_2 thin films were deposited by a DC reactive magnetron sputtering technique on soda lime glass and SiO_2 single crystal substrates. By doping the TiO_2 film, the structure and crystallinity of TiO_2 were changed. The average grain sizes of undoped and doped TiO_2 nanocrystals were 25 and 18 nm, respectively. The *N*-doped TiO_2/ZnO thin film absorption edge is shifted to higher wavelengths to absorb visible light wavelengths. The difference in the aqueous MB degradation ability of doped and undoped TiO_2/ZnO was measured at about 9%. The doped TiO_2/ZnO thin film showed more hydrophilicity in comparison with the undoped TiO_2/ZnO thin film.

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REFERENCES

1. Fujishima, A. and Honda, K. "Electrochemical photolysis of water at a semiconductor electrode", *Nature*, **238**, pp. 37-38 (1972).
2. Hadjiivanov, K.I. and Klissurski, D.K. "Surface chemistry of titania (anatase) and titania-supported catalysts", *Chem. Soc. Rev.*, **25**(1), pp. 61-69 (1996).
3. Heller, A. "Chemistry and applications of photocatalytic oxidation of thin organic films", *Acc. Chem. Res.*, **28**(12), pp. 503-508 (1995).
4. Ohko, Y., Tryk, D.A., Hashimoto, K. and Fujishima, A. "Autoxidation of acetaldehyde initiated by TiO_2 photocatalysis under weak UV illumination", *J. Phys. Chem. B*, **102**(15), pp. 2699-2704 (1998).

5. Fujishima, A. and Rao, T.N. and Tryk, D.A. "Titanium dioxide photocatalysis", *J. Photochem Photobiol C Photochem Rev.*, **1**, pp. 1-21 (2000).
6. Anpo, M. and Chiba, K. "Photocatalytic reduction of CO_2 on anchored titanium-oxide catalysts", *J. Mol. Catal.*, **74**(1-3), pp. 207-212 (1992).
7. Mardare, D., Tasca, M., Delibas, M. and Rusu, G.I. "On the structural properties and optical transmittance of TiO_2 r.f. sputtered thin films", *Appl. Sci.*, **156**, pp. 200-206 (2000).
8. Zheng, S.K., Wang, T.M., Wang, C. and Xiang, G. "Photocatalytic activity study of TiO_2 thin films with and without Fe ion implantation", *Nucl. Instr. Meth. B*, **187**(6), pp. 479-484 (2002).
9. Zakrzewska, K., Radecka, M., Kruk, A. and Osuch, W. "Noble metal/titanium dioxide nanocermets for photoelectrochemical applications", *Thin Solid Films*, **157**(1-4), pp. 349-356 (2003).
10. Asahi, A., Morikawa, T., Ohwaki, T., Aoki, K. and Taga, Y. "Visible-light photocatalysis in nitrogen-doped titanium oxides", *Science*, **293**(7), pp. 269-271 (2001).
11. Burda, C., Lou, Y., Chen, X., Samia, A.C.S., Stout J. and Gole, J.L. "Enhanced nitrogen doping in TiO_2 nanoparticles", *Nano. Lett.*, **8**(3), p. 1049 (2003).
12. Martyanov, I.N., Uma, S., Rodrigues, S. and Klabunde, K.J. "Structural defects cause TiO_2-based photocatalysts to be active in visible light", *Chem. Commun.*, **21**, pp. 2476-2477 (2004).
13. Sakthivel, S. and Kisch, H. "Photocatalytic and photoelectrochemical properties of nitrogen-doped titanium dioxide", *Chem. Ent. Ed.*, **42**, p. 4908 (2003).
14. Vos, D.E., Dams, M., Sels, B.F. and Jacobs, P.A. "Ordered mesoporous and microporous molecular sieves functionalized with transition metal complexes as catalysts for selective organic transformations", *Chem. Rev.*, **102**(10), pp. 3615-3640 (2002).
15. Subramanyam, T.K., Srinivasulu, B. and Uthanna, S. "Physical properties of zinc oxide films prepared by dc reactive magnetron sputtering at different sputtering pressures", *Cryst. Res. Technol.*, **35**(10), pp. 1193-1202 (2000).
16. Kao, M.C., Chen, H.Z. and Young, S.L. "Preparation and characterization of nanostructured ZnO/TiO_2 bilayer thin films for dye-sensitized solar cells", *Appl. Physics A*, **97**(2), pp. 469-474 (2009).
17. Valentin, C.D., Finazzi, E., Pacchioni, G., Selloni, A., Livraghi, S., Paganini, M.C. and Giamello, E. "N-doped TiO_2: Theory and experiment", *Chem. Phys.*, **339**, p. 44 (2007).
18. Prabakar, K., Takahashi, T., Nezuka, T., Takahashi, K., Nakashima, T., Kubota, Y. and Fujishima, A. "Visible light-active nitrogen-doped TiO_2 thin films prepared by DC magnetron sputtering used as a photocatalyst", *Renewable Energy*, **33**(2), pp. 277-281 (2008).
19. Li, Z.G., Miyake, S., Makino, M. and Wu, Y.X. "Metallic sputtering growth of crystalline titanium oxide films on unheated glass substrate using inductively coupled plasma assisted direct current magnetron sputtering", *Thin Solid Films*, **517**(2), p. 699 (2008).
20. Baroch, P., Musil, J., Vlcek, J., Nam, K.H. and Han, J.G. "Reactive magnetron sputtering of TiO_x films", *Surf. Coat. Technol.*, **193**(1-3), pp. 107-111 (2005).
21. Muscat, J., Swamy, V. and Harrison, N.M. "First-principles calculations of the phase stability of TiO_2", *Phys. Rev. B*, **65**, pp. 224112-224126 (2002).
22. Li, Z.G. and Miyake, S. "Characteristics of N-doped TiO_2 thin films grown on unheated glass substrate by inductively coupled plasma assisted dc reactive magnetron sputtering", *Applied Surface Science*, **255**(22), pp. 9149-9153 (2009).
23. Mohamed, S.H., Kappertz, O., Niemeier, T., Drese, R., Wakkad, M.M. and Wuttig, M. "Effect of heat treatment on structural, optical and mechanical properties of sputtered TiO_xN_y films", *Thin Solid Films*, **468**(1-2), pp. 48-56 (2004).
24. Hukari, K., Dannenberg, R. and Stach, E.A. "Nitrogen effects on crystallization kinetics of amorphous TiO_xN_y thin films", *J. Mater. Res.*, **17**(3), pp. 550-555 (2002).
25. Shannon, R.D. "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides", *Acta Crystal. A*, **32**(5), pp. 751-767 (1976).
26. Cullity, B.D., *Elements of X-ray Diffraction*, Addison-Wesley, Reading, p. 293, MA, USA (1978).
27. Linsebigler, A.L., Lu, G.Q. and Yates, J.T. "Photocatalysis on TiO_2 surfaces: Principles, mechanisms, and selected results", *Chem. Rev.*, **95**(3), p. 735 (1995).
28. Zhang, W., Zhu, Sh., Li, Y. and Wang, F. "Photocatalytic Zn-doped TiO_2 films prepared by dc reactive magnetron sputtering", *Vacuum*, **82**, pp. 328-335 (2008).
29. Kaneko, M. and Okura, I., *Photocatalysis Science and Technology*, 3th Edn., Tokyo and New York (1994).

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