Photo-induced hydrophilicity of $TiO_{2-x}N_x$ thin films on PET plates

Hsiu-Yu Chou [a,*], En-Ko Lee [a], Jiang-Wen You [a], Sung-Shih Yu [b]

[a] Department of Chemical and Materials Engineering, Ta-Hwa Institute of Technology, 1, Ta-Hwa Road, Chiunglin, Hsinchu, 30037, Taiwan, ROC
[b] Department of Electronics Engineering, National Chiao Tung University, 1001 Ta-Hsueh Road Hsinchu, 30050, Taiwan, ROC

Abstract

$TiO_{2-x}N_x$ thin films were deposited on PET (polyethylene terephthalate) plates by sputtering a TiN target in a N_2/O_2 plasma and without heating. X-ray photoemission spectroscopy (XPS) was used to investigate the N 1s, Ti 2p core levels and the nitrogen composition in the $TiO_{2-x}N_x$ films. The results indicate that Ti–O–N bonds are formed in the thin films. Two nitrogen states, substitution and interstitial nitrogen atoms, were attributed to peaks at 396 and 399 eV, respectively. It was observed that the nitrogen atoms occupy both the substitutive and interstitial sites in respective of the nitrogen content in the thin films. UV–VIS absorption spectroscopy of PET coated thin films shows a significant shift of the absorption edge to lower energy in the visible-light region. UV and visible-light irradiation are used to activate PET coated thin films for the development of hydrophilicity. The photo-induced surface wettability conversion reaction of the thin films has been investigated by means of water contact angle measurement. PET plates coated with $TiO_{2-x}N_x$ thin films are found to exhibit lower water contact angle than non-coated plates when the surface is illuminated with UV and visible light. The effects of nitrogen doping on photo-generated hydrophilicity of the thin films are investigated in this work.
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Keywords: Hydrophilicity; $TiO_{2-x}N_x$ thin films; Wettability

1. Introduction

The chemically stable and non-toxic material, titanium dioxide, has many applications, such as surface coating, photoelectrodes, high-k dielectrics, paints, and cosmetics, etc. In recent years, its photocatalytic properties, photocatalytic decomposition of organic compounds and photohyrophlilicity have created new applications in surface cleaning. Tremendous utilization of antifogging, antibacterial, antipollution, deodorization, and self-cleaning surface treatments have been attained. The discovery of super-hydrophilicity on TiO_2 thin film surfaces [1] has prompted extensive research on TiO_2, which has been widely adopted as important material for solar cells. It has been proposed that hydrophilicity of TiO_2 can be attributed to the generation of electrons and holes by UV irradiation which are trapped by surface Ti^{+4} and O^{-2} ions to produce Ti and oxygen defects, respectively [1,2]. Then, water molecules are dissolved once they are adsorbed at defect sites on the surface of TiO_2. However, only 4% of the solar energy at the earth's surface can be utilized because of the high intrinsic band gap of rutile TiO_2 (3.2 eV). The main thrust of current development work in TiO_2-based materials is to extend the photoactivity from UV light into the range of visible light which would utilize more of available solar energy. The development of new materials which yield high reactivity under visible-light irradiation will make better use of the main part of solar power spectrum. It is well known that doping with transition metals effectively extends the spectral response of TiO_2 into the visible-light region, but these systems face thermal instability and low conversion efficiency of photo-generated carriers [2–6]. However, doping of transition metals in TiO_2 results in an increase of carrier-recombination centers and the requirement of an expensive ion-implantation facility. One promising approach is to synthesize a stable form of TiO_2 by substituting anions for oxygen into the TiO_2 lattice. This approach produces materials that are not hampered by fast e^-/h^+ recombination to the same extent as TiO_2, while the optical absorption is red-shifted somewhat into the visible-light range. Asahi et al. [6] calculated the density of states (DOSs) of C, N, F, P, or S elements when these are substituted for O in the anatase TiO_2 crystal by the full-potential plane wave in the local density approximation. They concluded that visible-light sensitivity of nitrogen doped into TiO_2 is due to narrowing of the band gap by mixing the N 2p and O 2p states.

* Corresponding author. Tel.: +886 3 5927700x2886; fax: +886 3 5927310.
E-mail address: sophia@thit.edu.tw (H.-Y. Chou).

Glass is widely used for exterior walls, windows and windshields [7–9]. A self-cleaning surface treatment on glass is necessary to prevent organic contamination. Coating TiO_2 films on glass substrates has proved to be a practical solution. Even though, a large body of research has been concerned with coating TiO_2 films on glass substrates, not much attention has been paid to coating plastic substrates such as PET. In this work, we have proposed a room temperature process which promotes the formation of nitrogen-doped and stable thin films on PET substrates. The structure and optical properties of $TiO_{2-x}N_x$ thin films on PET substrates are investigated.

2. Experiment

$TiO_{2-x}N_x$ thin films were deposited on PET substrates by sputtering a TiN target in an O_2/N_2 plasma. The thin films were deposited with the plasma of oxygen and nitrogen and various nitrogen levels without heating. Various ratios of N_2/O_2 gas flow were tested to control the degree of nitrogen substitution on $TiO_{2-x}N_x$ thin films. Film thickness and morphology were determined using cross section and surface scanning electron microscopy (SEM) images, respectively. Surface roughness of the thin films was analyzed by using atomic force microscopy. UV–visible absorption spectra were recorded by a UV–VIS spectrophotometer. The band gap energy was calculated from the absorption coefficient (α) using the measured values of absorbance at each wavelength of interest. A plot of the square root of the absorbance coefficient versus the energy of light defines the optical band gap energy. The hydrophilicity of thin films was measured by observing the water contact angle under UV light irradiation with an intensity of 77 $\mu W/cm^2$ (approximately 300–400 nm) from a cylindrical black-light lamp. To investigate nitrogen states and the degrees of x in the $TiO_{2-x}N_x$ thin films, N 1s, Ti 2p and O 1s core levels were measured by X-ray photoemission spectroscopy (XPS).

3. Results and discussion

The surface morphologies of the thin films from AFM and SEM images are very similar (SEM image in Fig 1). $TiO_{2-x}N_x$
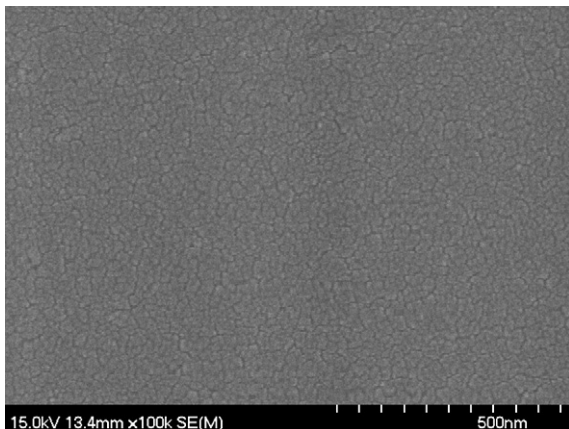

Fig. 1. SEM micrograph of the $TiO_{2-x}N_x$ thin films deposited on PET plates with 60 min sputtered time.
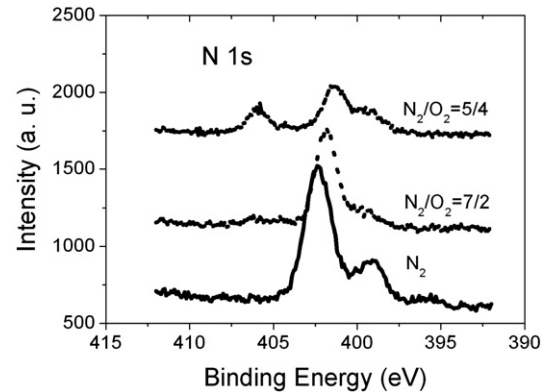

Fig. 2. N 1s XPS spectra of $TiO_{2-x}N_x$ thin films with various N_2/O_2 gas flow.

thin films exhibited uniform and smooth surfaces in this work. The surface roughness was Ra=2.94 nm measured by AFM. The thickness of thin films obtained after 60 min of sputtering is around 45 nm.

The surface electronic states of nitrogen in these films was examined by XPS. Fig. 2 shows the spectrum for the N 1s core levels. In this structure, three binding energy peaks of 402, 399 and 396 eV are observed for the $TiO_{2-x}N_x$ thin films. The peaks over 402 eV are attributed to chemisorbed N_2 molecules [10–12]. Electron binding energies of 396, 399 eV are assigned to the nitrogen atoms substituting for the oxygen atoms (N_{sub}) and inserted into interstitial sites in the TiO_2 matrices (N_{int}), respectively [6,10]. The peak at 402 eV is attributed to the N–O bonds by referring to the XPS database of the National Institute of Standards and Technology (NIST). According to Saha and Tompkins [10] the peak at 396 eV arises from Ti–N bonds. It can be concluded that Ti–O–N bonds are formed in the $TiO_{2-x}N_x$ thin films.

Another spectrum for the Ti 2p core levels may also be used to check the formation of $TiO_{2-x}N_x$ compound. Wan defined a Ti–N–O ternary phase diagram which was constructed from the thermodynamic data of Ti–N, Ti–O and N–O system.[13] The phase diagram shows that the TiN_xO_y solid solution is located in the bottom half of the phase diagram with lower oxygen content. It also shows the TiN_xO_y/TiO and TiN_xO_y/Ti_2O_3 two-phase regions and $TiN_xO_y/TiO/Ti_2O$ and $TiN_xO_y/Ti_2O_3/TiO_2$ three-phase regions above the TiN_xO_y solid solution region area. The binding energy of the Ti $2p_{3/2}$ peaks for TiO, Ti_2O_3, TiO_2, TiN are 454.6±0.2, 455±0.2 and 459.1±0.2, 455.3±0.2 eV, respectively [10,11,13–16]. The binding energy of the Ti $2p_{3/2}$ peaks in our thin films is at 458 eV, which does not correlate to the binding energy of ether TiN or TiO_2. This peak does match with that predicted for the intermediate TiN_xO_y type compounds in the Wan's study. It can be concluded that only $TiO_{2-x}N_x$ compounds formed in our thin films. The $TiO_{2-x}N_x$ thin films with Ti–O–N bonding are synthesized by sputtering method without heat treatment.

The N, Ti, O compositions of $TiO_{2-x}N_x$ thin films are calculated from the ratios of the peak areas at 402, 458, 531 eV, respectively, which are listed on Table 1. The nitrogen concentrations in the films are function of N_2/O_2 flow ratios. The nitrogen content in these films increased from 5.0 to 12.3 atom % when the N_2/O_2 flow ratio increased from 0.15 to 1.

Table 1
The composition of $TiO_{2-x}N_x$ thin films

N_2/O_2 flowing ratios	N (at.%)	O (at.%)	Ti (at.%)
N_2	12.3	59.2	28.5
7/2	8.2	62.6	29.6
5/4	5.0	65.7	29.3

In Table 1, high oxygen content was found in the film deposited in a pure nitrogen environment. The reaction $TiN + O_2 \rightarrow TiO_2 + 1/2\ N_2$ is thermodynamically favorable and has a $\Delta G°$ value of -139 kcal/mole [10]. Although TiN is thermodynamically stable, it is easily oxidized when exposed to oxygen or air. A thin oxidized over layer on the TiN films has been demonstrated in many past studies [16,17]. Since the results of Table 1 come from analysis of only the surface of these thin films, it may simply be due to oxidation in air.

Fig. 3(a) shows the absorption spectra of $TiO_{2-x}N_x$ thin films at various ratios of N_2/O_2 gas flow. UV–visible absorption spectra for $TiO_{2-x}N_x$ thin films are red-shifted into the visible range with increasing N_2/O_2 flow ratios, as shown in Fig. 3(a). The absorption edge appears more red-shifted into the visible region for the $TiO_{2-x}N_x$ thin film under pure N_2 gas flow. The optical band gaps of the $TiO_{2-x}N_x$ thin films can be estimated from the tangent lines in the plots of the square root of the
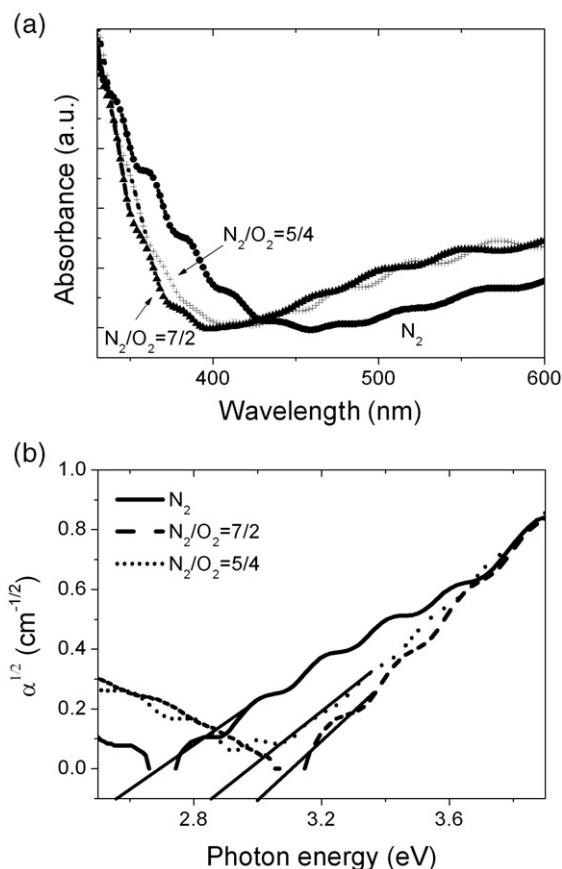
Kubelka–MunK functions [18] against the photon energy, as shown in Fig. 3(b). The tangent lines extrapolated to zero indicate the optical band gaps of $TiO_{2-x}N_x$ thin films near 3.0, 2.85, 2.78 eV. Those results indicate that band gap narrowing has been successfully achieved by doping N into the TiO_2 lattice. The absorption bands extend into the visible range was dependent on the N content of substitute and interstitial site in the $TiO_{2-x}N_x$ thin films. The film with pure nitrogen flow has lowest optical band gap than the other thin films. The film with 1.25 flow ratios has lower optical band gap than that with 3.5 flow ratios. Those are predominantly attributed to the total peak areas of the substitute and the interstitial site N content in the $TiO_{2-x}N_x$ thin films. The film with 1.25 flow ratios appears higher total peak areas of 396 and 399 eV for substitute and interstitial site N content than that with 3.5 flow ratios, as shown in Fig. 2. Since the film with pure nitrogen flow shows the highest total peak areas of 396 and 399 eV for substitute and interstitial site N content, there is a lowest optical band gap.

The photo-induced hydrophilicity of these thin films was evaluated by measuring the contact angle of water droplet during irradiation with UV and visible light, and shown in Fig. 4(a) and (b) respectively. The $TiO_{2-x}N_x$ thin films irradiated by UV light resulted in higher wettability than those exposed to visible light. This trend is plausible because UV light excites electrons in both
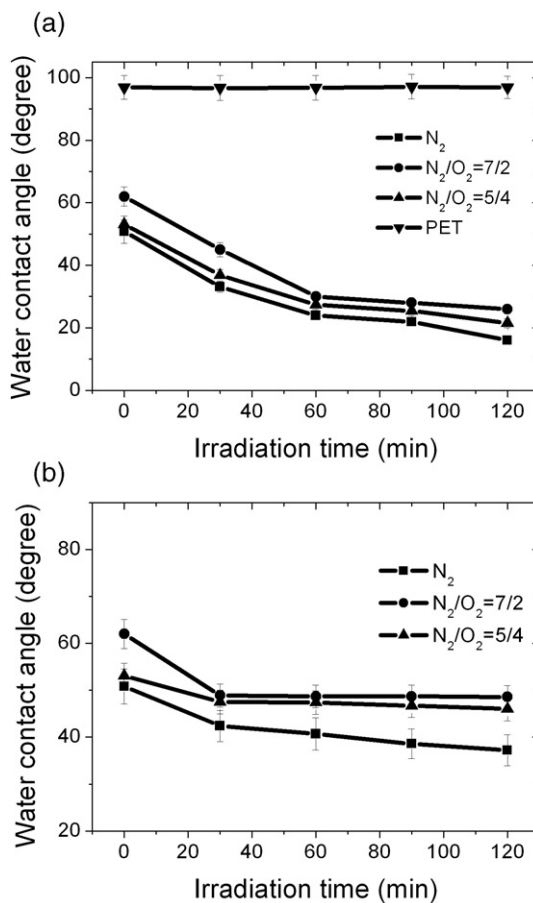

Fig. 3. (a) UV–VIS absorption spectra of $TiO_{2-x}N_x$ thin films with various N_2/O_2 gas flow. (b) Plots of the square root of absorption against the photon energy of $TiO_{2-x}N_x$ thin films.

Fig. 4. (a) Water contact angles of the $TiO_{2-x}N_x$ thin films under UV light irradiation. (b) Water contact angles of the $TiO_{2-x}N_x$ thin films under VIS light irradiation.

the valence band and the conduction band, but visible light only excites electrons in the conduction band. The photo-induced hydrophilicity of thin films with a lower energy optical band gap is superior to that induced on a thin film with a higher energy optical band gap under UV and visible-light irradiation. The reason is that the thin film with lower energy optical band gap has more excited electrons contributed from the valence band and the conduction band. The more electrons that are excited, the more reactive the surface is to water on the thin film. The wettability of a thin film with 1.25 flow ratio is higher than a film with a 3.5 flow ratio. The film with 1.25 flow ratio has a lower optical band gap, produces more excited electrons, and exhibits more wettability. Since the $TiO_{2-x}N_x$ thin film with N_2 gas flow has the lowest optical band gap, it exhibits the lowest water contact angle near 10° and 35° for illumination with UV and visible light, respectively. Prior to UV and Visible-light irradiation, the water contact angles of PET plate surfaces are all near 98° in Fig. 4(a). After PET plates are coated with $TiO_{2-x}N_x$ thin film, the water contact angles of the surfaces decreases to about 30°–40°. Under UV and visible-light irradiation, the water contact angles of PET plate surfaces coated with thin films decrease monotonically with increased irradiation time. The results clearly demonstrate that the photo-induced surface wettability conversion phenomenon take place on PET plates coated with $TiO_{2-x}N_x$ thin films.

4. Conclusions

$TiO_{2-x}N_x$ thin films have been fabricated by RF magnetron sputtering of a TiN target, depositing films on PET plate substrates without heating. The $TiO_{2-x}N_x$ thin films examined by XPS formed O–Ti–N bonds. The PET plates coated with $TiO_{2-x}N_x$ thin films show an obvious improvement in hydrophilicity under UV and visible-light irradiation. The PET surfaces deposited with polycrystalline $TiO_{2-x}N_x$ thin films are found to exhibit lower water contact angle when the surfaces are illuminated with UV and visible light in the air. The $TiO_{2-x}N_x$ thin film sputtered with only N_2 plasma exhibits the lowest water contact angle near 10° and 35° upon illumination with UV and Visible light, respectively. The amount of nitrogen doping of $TiO_{2-x}N_x$ thin films appears to strongly influence the photo-generated hydrophilicity of the thin films.

References

[1] A. Fujishima, K. Honda, Nature 238 (1972) 37.
[2] A.K. Ghosh, H.P. Muruska, J. Electrochem. Soc. 124 (1977) 1516.
[3] E. Borgarello, J. Kiwi, M. Graetzel, E. Pelizzetti, M. Visca, J. Am. Chem. Soc. 104 (1982) 2996.
[4] Y. Matsumoto, J. Kurimoto, Y. Amagasaki, E. Sato, J. Electrochem. Soc. 127 (1980) 2148.
[5] W. Choi, A. Termin, M.R. Hoffman, Phys. Chem. 98 (1994) 13669.
[6] R. Asahi, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269.
[7] S. Sokolov, A. Stein, Mater. Lett. 57 (2003) 3593.
[8] J.C. Lytle, H. Yan, N.S. Ergang, W.H. Smyrl, A. Stein, J. Mater. Chem. 14 (2004) 1614.
[9] L. Kavan, J. Rathousky, M. Gratzel, V. Shklover, A. Zukal, Microporous Mesoporous Mater. 44–45 (2001) 653.
[10] N.C. Saha, H.G. Tompkins, J. Appl. Phys. 72 (1992) 3072.
[11] H.Z. Wu, T.C. Chou, A. Mishra, D.R. Anderson, J.K. Lamper, S.C. Gujrathi, Thin Solid Films 191 (1990) 55.
[12] N.D. Shinn, K.L. Tsang, J. Vac. Sci. Technol., A, Vac. Surf. Films 9 (1991) 1558.
[13] C.F. Wan, F.C. Sulzbach, J.D. Luttmer, J. Vac. Sci. Technol., B 10 (1992) 1658.
[14] N. Kaufherr, D. Lichtman, J. Vac. Sci. Technol., A, Vac. Surf. Films 3 (1985) 1969.
[15] http://www.lasurface.com/database/liaisonxps.php.
[16] I. Montero, C. Jimenez, J. Perriere, Surf. Sci. 251 (1991) 1038.
[17] C. Ernsberger, J. Nickerson, T. Smith, A.E. Miller, D. Banlks, J. Vac. Sci. Technol., A, Vac. Surf. Films 4 (1986) 2784.
[18] Y.I. Kim, S.J. Atherton, E.S. Brigham, T.E. Mallouk, J. Phys. Chem. 97 (1993) 11802.