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Visible-light induced hydrophilicity on nitrogen-substituted titanium dioxide films

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Nitrogen-substituted titanium dioxide thin films were found to undergo hydrophilic conversion under irradiation with visible light. The hydrophilicity was enhanced by increasing the degree of nitrogen substitution at oxygen sites. The water contact angle for the thin film with the greatest hydrophilicity, $TiO_{1.9884}N_{0.0116}$, changed from 20° to 6° following irradiation.

The surface of titanium dioxide (TiO_2) exhibits superhydrophilicity under ultraviolet (UV) light irradiation[1–6] with a water contact angle of 0°. This phenomenon has previously been applied to various industrial items, including self-cleaning tiles and anti-fogging mirrors.[7] These applications, however, have been limited to outdoor use only, as the superhydrophilic conversion requires UV light irradiation of approximately the intensity as natural sunlight.

Recently, nitrogen-doped TiO_2 powders and thin films have been reported to show photocatalytic activity under visible (Vis) light irradiation.[8,9] Sakatani *et al.* reported the photocatalytic decomposition of acetaldehyde to CO_2 under Vis light irradiation in the presence of a powdered photocatalyst, which is presumed to be TiO_2 with nitrogen-substituted at oxygen sites.[8] Asahi *et al.* reported theoretical calculation of the band structure of nitrogen-substituted TiO_2 and its Vis light induced photocatalysis when using powders and thin films.[9] Sakatani *et al.* and Asahi *et al.* showed that nitrogen-doped TiO_2 acts as an oxidizing agent under Vis light irradiation. In regards to the hydrophilic nature of the film, however, Asahi *et al.* only evaluated the hydrophilic maintenance property of the SiO_2-coated nitrogen-substituted TiO_2 thin film under interior lighting after superhydrophilic treatment. Moreover, if the nitrogen-substituted TiO_2 is covered with SiO_2, it is unknown whether the surface of the nitrogen-substituted TiO_2 undergoes a hydrophobic to hydrophilic conversion. As such, there have been no reports regarding hydrophilic conversion of the nitrogen-substituted TiO_2 thin film under Vis light irradiation. Information regarding this conversion is very important both scientifically and practically, as our group has reported that the mechanism of superhydrophilic conversion is different from that of the photocatalytic oxidization process[4,6,11,12] and as this hydrophilic property may be applicable to indoor use. As mentioned above, the nitrogen-doped TiO_2 thin film has been already found out to be Vis light sensitive concerning oxidation reaction,[9] however, has not been yet evaluated the Vis light induced hydrophilic conversion. Under such circumstances, we confirmed that the surface of the nitrogen-substituted TiO_2 film underwent the hydrophilic conversion under Vis light irradiation, with various degrees of nitrogen substitution. Therefore, in this letter, we report the hydrophilic conversion and the nitrogen-concentration dependence on the conversion property of the nitrogen-substituted TiO_2 thin films under Vis light irradiation.

$TiO_{2-x}N_x$ thin films were deposited on SiO_2-coated glass plates by sputtering a Ti metal target under a N_2O (80SCCM)/Ar (20SCCM) gas mixture. An RF magnetron sputtering apparatus (Tokuda, Model CFS-8EP) was used and all substrates were heated to 400 °C. To control the degree of nitrogen substitution, deposited $TiO_{2-x}N_x$ thin films were annealed at 550 °C under O_2, N_2, or NH_3 gas flow. All the resulting $TiO_{2-x}N_x$ thin films were transparent in various shades of yellow. Using an X-ray diffractometer (XRD) the films were identified to have a homogenous anatase phase. TiO_2 thin films were also deposited in a similar way under an O_2(40SCCM)/Ar(60SCCM) gas mixture. The resulting TiO_2 thin film was transparent and whitish, also with a homogenous anatase phase.

Surface morphologies were observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Grain sizes and surface roughness factors (Ra) of all the $TiO_{2-x}N_x$ thin films were identical, 100–200 nm and around 65 nm, respectively. The TiO_2 thin film, however, had grain sizes of 200–400 nm and an Ra of 100 nm.

To investigate nitrogen states and to determine the degrees of x in the $TiO_{2-x}N_x$ thin films, N 1s and O 1s core levels were measured by X-ray photoemission spectroscopy (XPS), as shown in Figs. 1(a) and (b), respectively. According to Saha *et al.*,[10] the peak at 396 eV arises from Ti–N bonds. Considering the XRD and XPS results described above, we conclude that O–Ti–N bonds were formed in the $TiO_{2-x}N_x$ thin films. The x values were determined by the ratio of the peak areas at 396 eV and at 531 eV, which corresponds to O 1s, Ti–O bonds. The peak ratios were found to be 0.0046, 0.0072 and 0.0116 for the thin films annealed under O_2, N_2 and NH_3, respectively. In contrast, the peak at 396 eV was not observed for the TiO_2 thin film. The peak at 400 eV, which was assigned to molecularly chemisorbed N_2,[10] was observed for the TiO_2 thin film, but not for $TiO_{2-x}N_x$ thin films. This is a result of differences in surface etching. Before XPS measurements, the film surfaces were etched several nanometers in depth, therefore, the molecularly chemisorbed N_2 may not have been detected or may have been detected as a lower value, compared with XPS measurements without etching. Therefore, it is assumed that the difference in grain sizes between $TiO_{2-x}N_x$ thin films and the TiO_2 thin film

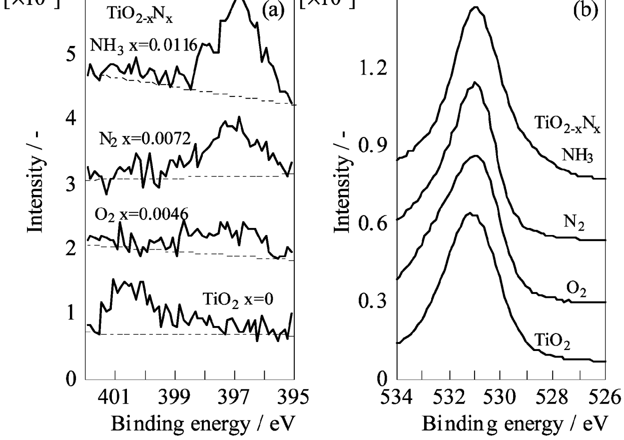

Fig. 1 N 1s (a) and O 1s (b) XPS spectra of $TiO_{2-x}N_x$ and TiO_2 thin films.

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leads to variance in the states of chemisorbed N_2, which affect the existence of the 400 eV peak.

Fig. 2 shows the optical spectra of $TiO_{2-x}N_x$ and TiO_2 thin films. Noticeable shifts of the absorbance shoulder to the visible-light region were observed for the $TiO_{2-x}N_x$ thin films, but not for the TiO_2 thin film. The absorbance shoulders were higher with increasing x values for $TiO_{2-x}N_x$.

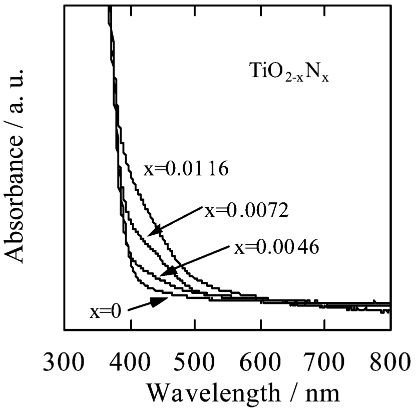

Fig. 2 Optical properties of $TiO_{2-x}N_x$ and TiO_2 thin films.

The photo-induced hydrophilicity was evaluated by analysis of the change in water contact angles under Vis light irradiation, as shown in Fig. 3. The Vis light, with an intensity of 0.2 mW cm^{-2} and a wavelength of 400–500 nm, was generated by a Xe lamp (Hayashi Tokei, Luminar Ace 210) with glass filters (Toshiba Glass, B-47, L-42 and C-40C). Prior to Vis light irradiation, all the $TiO_{2-x}N_x$ thin films showed water contact angles of around 20°, which were taken as the initial water contact angles. After irradiation, the critical water contact angles decreased to 13°, 9° and 6°, on thin films annealed under O_2, N_2 and NH_3, respectively.

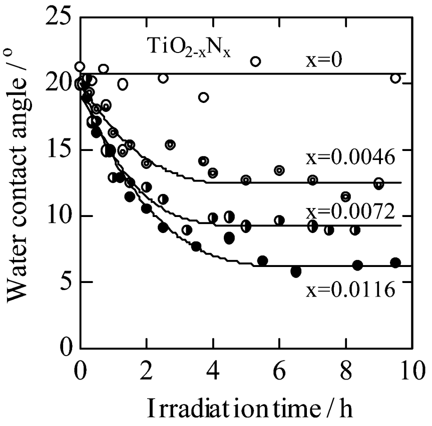

Fig. 3 Changes in water contact angles of $TiO_{2-x}N_x$ and TiO_2 thin films under Vis light irradiation.

Water contact angles on the TiO_2 thin film, however, were unchanged. Fig. 4 shows plots of the reciprocal of water contact angles *vs*. the Vis light irradiation time. When the reciprocal of water contact angles is plotted against the irradiation time, a linear relationship is obtained as shown in Fig. 4. We have previously proposed that the slope of this straight line can be defined as the rate constant for the hydrophilic conversion process.[13] The critical water contact angles decreased and the rate constant for the hydrophilic conversion increased with increasing the degree of nitrogen concentrations, as shown in Figs. 3 and 4. For 450 nm light, an incident Vis light intensity of 0.2 mW cm^{-2} corresponds to a photon flux of 4.5×10^{14} quanta·cm^{-1}·s^{-1}. The $TiO_{2-x}N_x$ thin films can absorb 2.6×10^{13}, 6.0×10^{13} and 8.2×10^{13} quanta·cm^{-1}·s^{-1}, annealed under O_2, N_2 and NH_3, respectively. Asahi *et al.* have reported that Vis light sensitivity in $TiO_{2-x}N_x$ is caused by narrowing of the band gap from mixing N 2p and O 2p states,[9] where the O 2p state forms the valence band of TiO_2. It can also be considered that N 2p levels are separated (not mixed) from the valence band, which then consists of an O 2p state. The localized N 2p level, thus is the origin of Vis light sensitivity in $TiO_{2-x}N_x$. The mechanism for Vis light sensitivity remains unclear, however, the observation that hydrophilic properties were enhanced by increasing the degree of nitrogen substitution, which was suggested to be dominated by the increases in the absorbed photon number, rather than changes in the band structure.

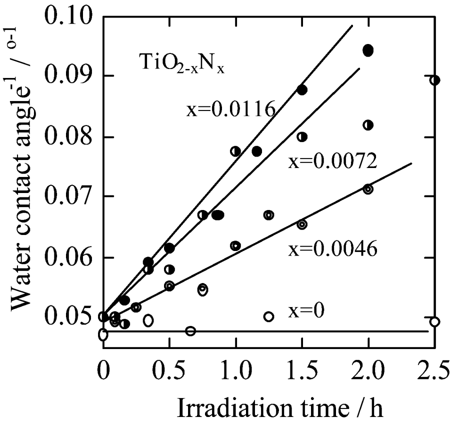

Fig. 4 The reciprocal of water contact angles of $TiO_{2-x}N_x$ and TiO_2 thin films under Vis light irradiation.

In summary, we have fabricated $TiO_{2-x}N_x$ thin films, which undergo hydrophilic conversion under Vis light irradiation. The hydrophilicity was enhanced by increasing the degree of nitrogen substitution at oxygen sites, leading to an increase in the absorbed photon numbers.

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12 We have proposed that the hydrophilic conversion mechanism was caused by the increase in the amount of hydroxyl groups on the TiO_2 surface, which are formed by the photogenerated holes. The oxidation reaction is also led by the photogenerated holes, reacting directly or generating highly reactive hydroxyl radicals (·OH) as an oxidant. Therefore, the hydrophilic conversion and the oxidation reaction proceed competitively on the TiO_2 surface.
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