Photoinduced Surface Wettability Conversion of ZnO and TiO_2 Thin Films

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The photoinduced surface wettability conversion reactions of ZnO and TiO_2 thin films were investigated by means of water contact angle measurement and X-ray photoelectron spectroscopy. Before ultraviolet (UV) illumination, ZnO and TiO_2 films exhibited water contact angles of ∼109 and ∼54°, respectively. UV illumination turned both surfaces to highly hydrophilic with water contact angles smaller than 10°. Storage in the dark reconverted the highly hydrophilic films to their original states. Reversible surface wettability conversion reactions were achieved by alternate UV illumination and storage in the dark on both the films. The similar behaviors of wettability conversion observed on ZnO and TiO_2 surfaces suggest that they follow a similar conversion mechanism. Preferential adsorption of water molecules on the photogenerated surface defective sites is ascribed to the formation of highly hydrophilic ZnO and TiO_2 surfaces. Achievement of highly hydrophilic ZnO and TiO_2 surfaces by high-temperature annealing and Ar^+ sputtering provided supporting evidence for the explanation that surface defective sites play crucial roles in causing the surface wettability conversion reactions.

Introduction

Controlling and/or modifying the surface wettability of solid substrates is important in many situations.[1−5] For practical applications, both highly hydrophobic (water contact angle > 150°) and highly hydrophilic (water contact angle < 10°) materials are particularly desirable. Although there have been reports concerning the preparation of highly water-repellent surfaces, which were usually achieved by use of low-surface-energy coatings (e.g., fluorine-containing polymer coatings) combined with specially designed surface textures (e.g., fractal surfaces),[2−5] reports on highly hydrophilic materials are far less.

In recent years, we have reported that highly hydrophilic TiO_2 surfaces can be achieved by ultraviolet (UV) illumination.[6] That is, UV illumination turns the originally slightly hydrophilic TiO_2 surface to highly hydrophilic with 0° water contact angle. This wettability conversion phenomenon has been observed on both anatase and rutile TiO_2 surfaces, in the form of polycrystals or a single crystal.[6−10] Several commercial products (e.g., anti-fogging glass and self-cleaning construction materials) have been designed and produced on the basis of this phenomenon.[10] Due to the diversity of the potential applications of this photoinduced surface wettability conversion phenomenon, this discovery has further aroused people's research interest in TiO_2, which will potentially play an important role in environmental purification[10−12] and solar energy conversion.[13]

Since TiO_2 is a well-known photocatalyst, this photoinduced surface wettability conversion phenomenon was initially considered to be directly associated with its photocatalytic activities. That is, the original state of a TiO_2 surface was supposed to be highly hydrophilic. It was thought to become contaminated, turning to hydrophobic (strictly, it should be slightly hydrophilic since the water contact angle is smaller than 90°) due to the adsorption of certain gas components (e.g., organic molecules) contained in the air. Upon UV illumination, these adsorbates are photooxidized and removed from the TiO_2 surface, and thus the surface was thought to reconvert to the original highly hydrophilic state. However, we found that many research results cannot be satisfactorily explained if only using this mechanism. For example:

(1) Although both TiO_2 and strontium titanate ($SrTiO_3$) showed high photocatalytic activities, a decrease of water contact angles on the $SrTiO_3$ surface was not observed even when the illumination time was extended to 48 h.[14]

(2) Ultrasonication of a highly hydrophilic TiO_2 surface in pure water gives rise to great increase of the water contact angle.[9]

(3) As has already been reported, a photogenerated highly hydrophilic TiO_2 surface tends to reconvert to its originally hydrophobic state after the UV illumination is stopped. It was found that the reconversion rate in a cleaner pure oxygen atmosphere is much higher than that in an ambient condition.[8] If carbon contamination is the only reason that gives rise to an increase of the water contact angle, then it might be reasonable to consider that the hydrophilic-to-hydrophobic conversion rate in an ambient condition should be higher than that in pure oxygen due to the relatively high concentration of carbon-containing contaminants in the former condition. However, the result is the reverse.

(4) In our first paper concerning the photoinduced surface wettability conversion reaction on the TiO_2 surface, we have reported that several 10-nm-scale hydrophilic domains are formed on the oleophilic surface, leading to a highly amphiphilic

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surface (both highly hydrophilic and highly oleophilic) after UV illumination.[6] Generation of such a domain structure cannot be explained by the hypothesis that removal and adsorption of carbon contamination is the only reason causing the surface wettability change on the TiO_2 surface.

All these experimental results suggest that the generation of a highly hydrophilic TiO_2 surface is not explained simply by the removal of organic adsorbates from the TiO_2 surface by a photocatalytic decomposition process but also involves other reasons, which have stimulated us to make further efforts on this field. Our studies based on friction force microscopy (FFM), Fourier transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS) have suggested that photoinduced surface structural changes are devoted to the formation of a highly hydrophilic TiO_2 surface,[7−9] which may be caused by the preferential adsorption of water molecules on the photogenerated surface defective sites. However, the details of the mechanism are still not quite clear. To get further insight into this phenomenon, it is necessary to expand the related study from TiO_2 to other oxide semiconductors. In the present study, the wettability conversion of ZnO thin films before and after UV illumination was investigated. The results were compared with those obtained on TiO_2 surfaces. The possible mechanism is discussed on the basis of the results obtained in the present and previous researches.

Experimental Section

Both ZnO and TiO_2 thin films were prepared by the spray pyrolysis method,[15] in which very small uniform droplets of ZnO precursor (zinc acetate/ethanol solution) and TiO_2 precursor emulsion (titanium(IV) oxyacetylacetonate/ethanol) are sprayed onto a heated glass substrate at a constant rate through a glass atomizer. Both zinc acetate and titanium(IV) oxyacetylacetonate were reagent grade from Wako Pure Chemical, Ltd., Tokyo, Japan. Before spraying, the substrate was degreased ultrasonically in ethanol for 30 min and was then rinsed thoroughly with distilled−deionized water. Pure nitrogen was used as the carrier gas. After being sprayed, films were cooled to room temperature and then annealed at 450 °C for ∼2 h. Precursor solutions (300 mL, 0.02 mol/L) were sprayed onto the substrate at a spray rate of 10 mL/min. The substrate temperature was kept at 450 °C during spraying. Obtained ZnO and TiO_2 films were transparent with a thickness of $\sim 0.4\ \mu m$. X-ray diffraction (XRD, RINT 2400, Rigaku Denki Ltd., Tokyo, Japan) measurements showed that the ZnO film is wurtzite structure with (002) preferential orientation. The TiO_2 film is mainly composed of anatase structure.

Surface wettabilities were evaluated by water contact angle measurements, using a commercial contact angle meter (CA-X, Kyowakaimenkagaku Co. Ltd., Saitama, Japan). Lower intensity UV illumination (≤ 2 mW/cm^2) was carried out using fluorescent black-light bulbs, and higher intensity UV light (>2 mW/cm^2) was obtained from a Hg−Xe lamp through a 365 nm filter. Heat treatment was performed in air at each fixed temperature (100, 150, 200, 250, 300, 400, and 500 °C) for 1 h. The sample was then cooled to room temperature under ambient condition, followed by measurement of the water contact angle. X-ray photoelectron spectroscopic measurements were performed on a Perkin-Elmer Model 5600 spectrometer. Aluminum Kα radiation (photon energy, 1486.6 eV) was used, and photoelectrons were collected at a takeoff angle of 45° with respect to the film surface normal. Argon ion sputtering was carried out in the same ultrahigh-vacuum chamber.

Results and Discussion

ZnO and TiO_2 films used in this study showed water contact angles of ∼109 and ∼54°, respectively, after they were stored in the dark for several weeks. Upon UV illumination, the water droplets spread on both ZnO and TiO_2 thin film surfaces, exhibiting water contact angles of ∼5 and 0°, respectively, as shown in Figure 1. The results clearly demonstrated that the photoinduced surface wettability conversion phenomenon takes place not only on TiO_2 but also on ZnO.

Further information was acquired from the measurements of time dependence of water contact angles of ZnO and TiO_2 films under UV illumination with different light intensities (Figure 2). It was shown that, on both ZnO and TiO_2 films, the surface wettability conversion reactions are dependent not only on illumination time but also on the light intensity. At the light intensity greater than 2 mW/cm^2, the conversion reactions proceeded rapidly and were completed within ∼20 min. The reaction slowed at lower light intensity. However, apparent decreases of water contact angles were still observed even at a light intensity as weak as 0.1 mW/cm^2.

Figure 3 presents the O1s spectra of ZnO film (a) before and (b) after UV illumination. The broad shoulder at the higher binding energy side of the main O1s peak of ZnO before UV irradiation (Figure 3a, dashed line) can be fitted with two peaks (solid curves). These two peaks may correspond to the dissociatively adsorbed water (lower binding energy side) and physically adsorbed molecular water (higher binding energy side), respectively,[16] although the possibility due to a small amount of other oxygen-containing adsorbates cannot be completely excluded. According to the results of thermal desorption spectroscopy (TDS) by Zwicker and Jacobi,[17] the adsorption of water molecules on ZnO is quite complicated; i.e., there exist several different adsorption states. Unfortunately, XPS is not sensitive enough to distinguish all those adsorption states. After UV illumination (Figure 3b), the shoulder increased remarkably and both of the fitted peaks' intensities increased, indicating that both the chemisorption and physisorption of water molecules on the ZnO surface are enhanced by UV irradiation. These XPS results are consistent with our previous FT-IR measurements on TiO_2, in which the stretching bands of hydroxyl groups increased after UV illumination.[7] As will be discussed below, this increased water adsorption contributes to the formation of highly hydrophilic ZnO and TiO_2 surfaces.

The corresponding change of the C1s peak before and after UV illumination is shown in Figure 4. To get the information of surface charging, the peak position was not calibrated in this figure (the O 1s peak shown in Figure 3 being calibrated using the C 1s peak of 284.6 eV). It is clear that surface charging leads to the peak position shifting to the higher binding energy side for ∼4.5 eV. Corresponding shifts were also observed in the O 1s and Ti 2p peaks (not shown). UV illumination did not eliminate the surface charging state even after a longer illumination time (curve c, Figure 4). The decrease of peak intensity with increased illumination time was ascribed to the partial removal of carbon contaminants due to the photocatalytic decomposition reaction. It was noticed that, corresponding to the wettability change of the ZnO surface from hydrophobic to highly hydrophilic after UV illumination for 60 min, the C 1s peak intensity decreased only slightly (from curve a to curve b in Figure 4). This indicates that a photogenerated highly hydrophilic surface is far from "clean", which is somewhat deviated from our common knowledge that a clean surface is necessary to get a highly wetting surface.

On the other hand, we found that a short treatment of a ZnO

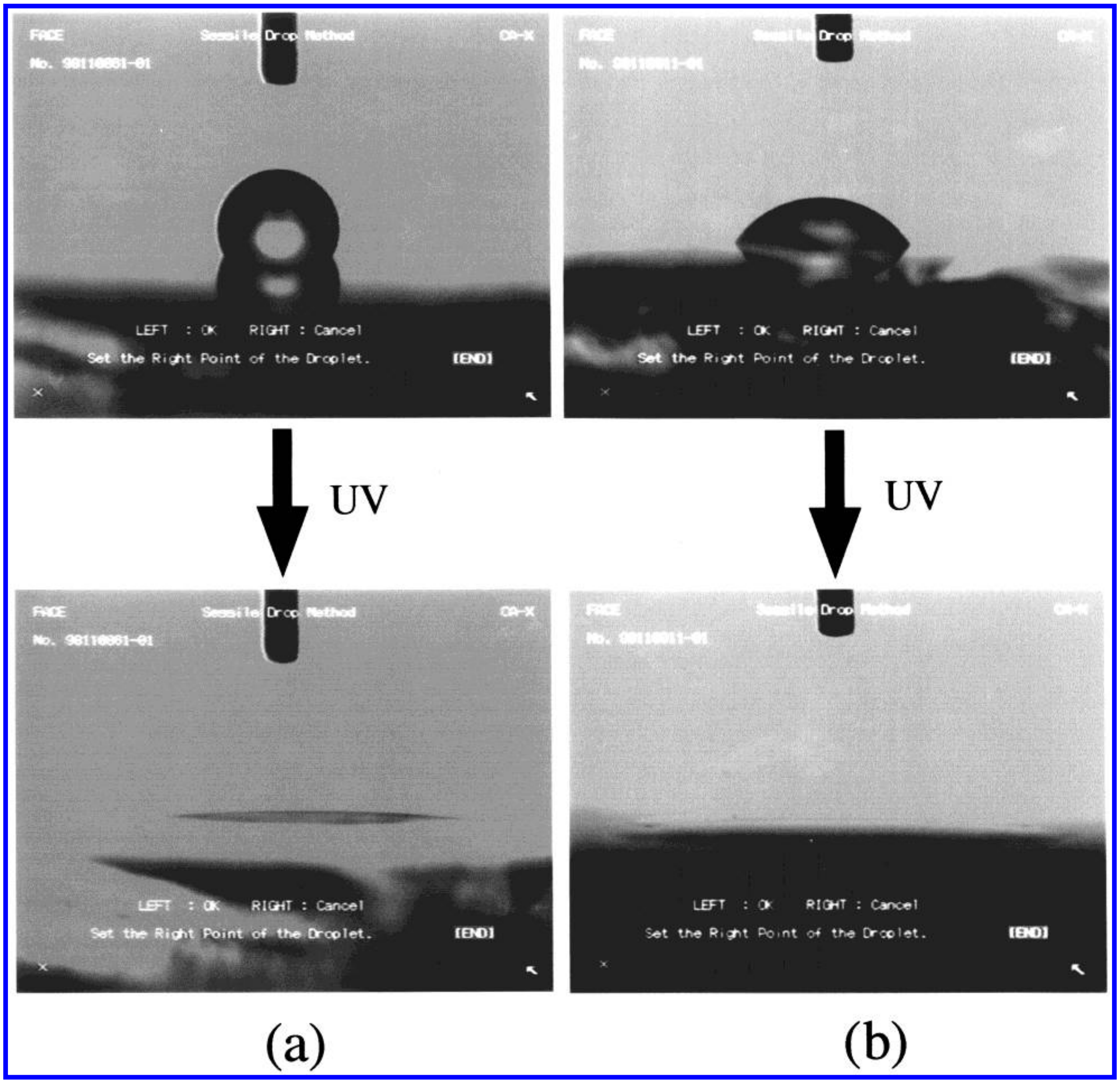

Figure 1. Pictures collected during contact angle measurements, showing changes of water contact angles of (a) ZnO and (b) TiO_2 thin film surfaces before and after UV illumination (20 mW/cm^2) for 1 h under ambient conditions. UV illumination turned the water contact angles of ZnO and TiO_2 thin films from 109 to 5° and from 54 to 0°, respectively.

or TiO_2 thin film in a warm concentrated NaOH solution (4.0 M, 50 °C) leads to removal of the carbon contaminants from the surface, as confirmed by the XPS measurements. In Figure 5 were representatively shown the C 1s spectra of ZnO before and after rinsing in the above NaOH solution for 1 min. No obvious carbon peaks were detected on the treated ZnO surface within the experimental error (curve b, Figure 5). However, we found that such a “clean” surface showed a water contact angle of $\sim$15°, which is much higher than that of $\sim$5° induced by UV illumination. A similar phenomenon was observed on the TiO_2 surface. Treatment of a TiO_2 surface in the above NaOH solution did not produce a highly hydrophilic surface with a contact angle of 0° but produced a surface with a water contact angle $\sim$20°. At this point, a C 1s peak was not detected in the XPS measurements either. It should be noted that partial dissolution of the ZnO film was visually observed after rinsing in the NaOH solution. Slight dissolution of the TiO_2 film may also occur though it was not observed visually in this experiment. These experiments inferred that photogeneration of a highly hydrophilic TiO_2 or ZnO surface cannot be explained only by the photocatalytic removal of surface carbon contaminants but may involve another mechanism.

Previous studies on TiO_2 surfaces have disclosed that the photogenerated highly hydrophilic state tends to reconvert gradually to its originally slightly hydrophilic state in the dark.[7−9] A similar result was also observed on the ZnO thin film surface. In Figure 6 are shown the typical reconversion processes of ZnO and TiO_2 surfaces with dark storage time. During the first several storage days, water contact angles on both films increased remarkably, followed by a slow increment in the next several days. Further increases were not observed after the water contact angles reached the values close to those at their original states. The recovered hydrophobic states of ZnO can be converted to the highly hydrophilic states again by exposing the films to UV light (Figure 2), which implies that the surface wettability conversion can be reversibly produced on both ZnO and TiO_2 film surfaces.

Similar to the case of TiO_2,[8] storage atmospheres influenced

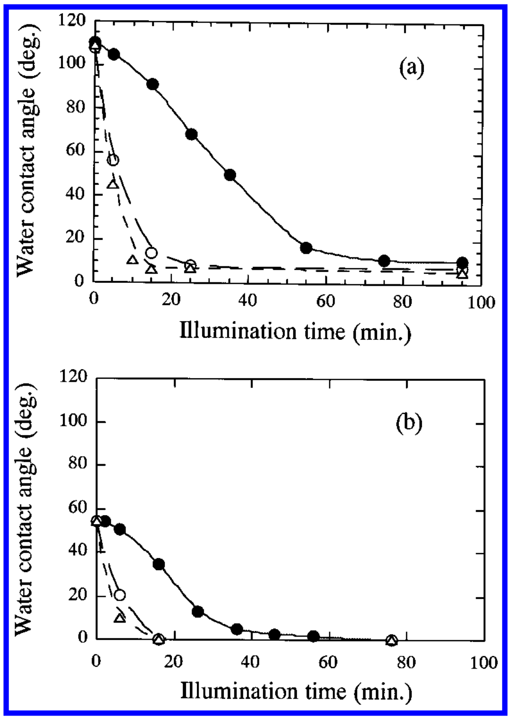

Figure 2. Time dependence of water contact angles of (a) ZnO and (b) TiO_2 films under UV illumination with different light intensities: (●) 0.1, (○) 2.0, and (△) 50 mW/cm^2.

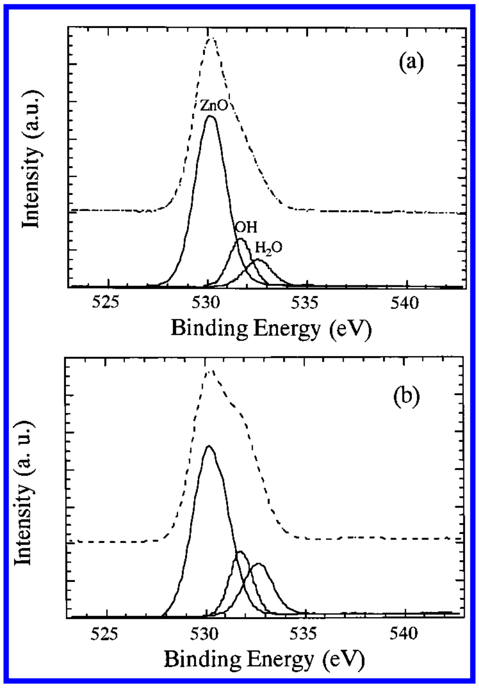

Figure 3. Changes of XPS spectra of ZnO in the O 1s peak region (a) before and (b) after UV illumination for 12 h at a light intensity of 2.0 mW/cm^2: (--) experimental data; (—) fitted curves.

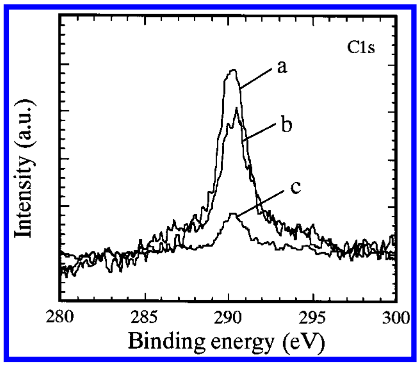

Figure 4. Changes of XPS spectra of ZnO in the C 1s peak region: (a) before illumination, (b) after UV illumination for 60 min, and (c) after UV illumination for 12 h at a light intensity of 2.0 mW/cm^2.

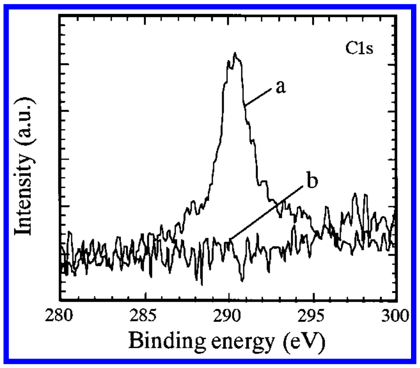

Figure 5. Changes of XPS spectra of ZnO in the C 1s peak region (a) before and (b) after being rinsed in a 4.0 M NaOH solution (50 °C) for 1 min.

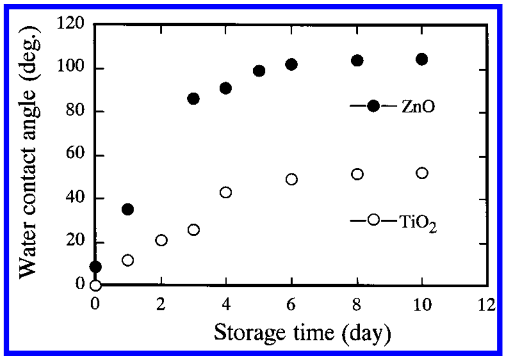

Figure 6. Changes of the water contact angles of the photogenerated highly hydrophilic ZnO and TiO_2 thin films when subjected to alternate storage in the dark and UV illumination in ambient conditions: (●) ZnO; (○) TiO_2.

the reconversion process of ZnO. Comparative studies of water contact angle changes in the atmospheres of pure oxygen (relative humidity, RH < 10%), synthetic air (RH < 10%), ambient air (RH > 60%), and argon (RH < 10%) showed that the storage in pure oxygen leads to the highest reconversion rate (Figure 7). The time necessary to reach the maximum water contact angles increased in the order of pure oxygen < synthetic air < ambient air < argon. A water contact angle greater than 100° was not achieved in an argon atmosphere even at an extended storage time. These results showed that oxygen plays an important role in the reconversion process of ZnO, similar to the case of TiO_2.

The comparison of the present results on ZnO and TiO_2 thin film surfaces suggests that they follow a similar photoinduced wettability conversion mechanism. Both ZnO and TiO_2 are well-known photosensitive oxide semiconductors with band gap energies of ~3.2 [18,19] and ~3.0 eV,[20,21] respectively, despite their different crystal structures (hexagonal wurtzite structure for ZnO and tetragonal structure for both anatase and rutile TiO_2). It is also well-known that band gap illumination generates electron−hole pairs in both ZnO and TiO_2. These electrons and holes can either recombine or move to the surface to react with species adsorbed on the surface, which is known to be the basis of photocatalysis.[10−12] Conversely, some of the holes can also react with lattice oxygen, leading to the formation of surface oxygen vacancies; while some of the electrons react with lattice metal ions (Zn^{2+} or Ti^{4+}) to form Zn^+ or Ti^{3+} defective sites (surface

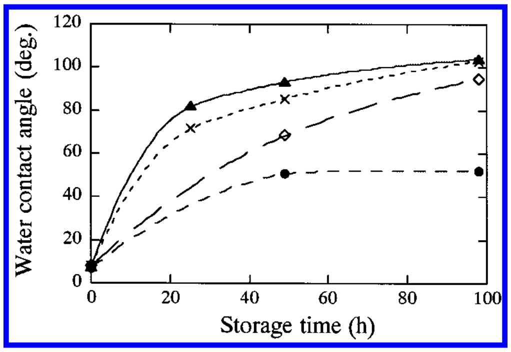

Figure 7. Change of water contact angle of the photogenerated highly hydrophilic ZnO thin film with storage time in various atmospheres: (▲) pure oxygen (relative humidity, RH < 10%); (×) synthetic air (RH < 10%); (◇) ambient air (RH > 60%); (●) pure argon (RH < 10%).

trapped electrons). The formation processes of defective sites on ZnO and TiO_2 surfaces are represented in eqs 1−4.[14,18,19,22]

$$\mathrm{ZnO\ (TiO_2)} + 2h\nu \rightarrow 2\mathrm{h}^+ + 2\mathrm{e}^- \tag{1}$$

$$\mathrm{O}^{2-} + \mathrm{h}^+ \rightarrow \mathrm{O_l}^- \quad \text{(surface trapped hole)} \tag{2}$$

$$\mathrm{O_l}^- + \mathrm{h}^+ \rightarrow {}^1/{}_2\mathrm{O}_2 + \square \quad \text{(oxygen vacancy)} \tag{3}$$

$$\mathrm{Zn}^{2+}\ (\mathrm{Ti}^{4+}) + \mathrm{e}^- \rightarrow \mathrm{Zn_s}^+\ (\mathrm{Ti_s}^{3+}) \quad \text{(surface trapped electron)} \tag{4}$$

In ambient conditions, upon generation by UV illumination, the surface trapped electrons ($\mathrm{Zn_s}^+$ or $\mathrm{Ti_s}^{3+}$) tend to react immediately with oxygen molecules adsorbed on the surface (eq 5).

$$\mathrm{Zn_s}^+\ (\mathrm{Ti_s}^{3+}) + \mathrm{O}_2 \rightarrow \mathrm{Zn_s}^{2+}\ (\mathrm{Ti_s}^{4+}) + \mathrm{O_2}^- \tag{5}$$

Meanwhile, water molecules may coordinate into the oxygen vacancy sites (□), which leads to dissociative adsorption of the water molecules on the surface. This process gives rise to increased water adsorption on the illuminated ZnO and TiO_2 surfaces, which has been confirmed by XPS measurements on ZnO in the present work (Figure 3) and by FT-IR combined with XPS measurements on TiO_2 in our previous work.[7,8] As a consequenece, the hydrophilicities of both the ZnO and TiO_2 surfaces are improved greatly.

Adsorption behavior of water molecules on defective and defect-free TiO_2 single-crystal surfaces has been studied extensively,[23−26] and it was reported that water molecules are favorable to adsorb dissociatively on the defective sites on the surface. Our previously mechanistic studies on the photoinduced hydrophobic-to-hydrophilic conversion reactions on both polycrystalline and single crystalline TiO_2 surfaces have disclosed that generation of a highly hydrophilic TiO_2 surface is closely related to the preferential adsorption of water on the photogenerated surface defective sites.[7,8] Corresponding reports concerning the preferential adsorption of water molecules on ZnO were not available in the literature; however, XPS measurements in the present work also revealed increased adsorption of water on the ZnO surface after UV illumination (Figure 3). Since UV illumination is also able to produce defects on ZnO surfaces as described above, it is reasonable to consider that the increased water adsorption on a UV illuminated ZnO surface is due to the adsorption of water on the photogenerated surface defective sites.

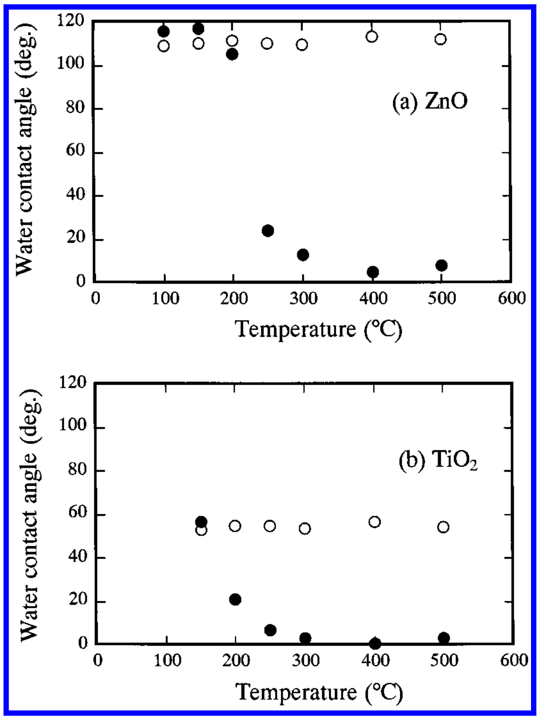

Figure 8. Changes of water contact angles of (a) ZnO and (b) TiO_2 thin films upon heating treatment for 1 h at various temperatures: (○) water contact angle value before heating treatment; (●) water contact angle value after heating treatment.

High-temperature annealing and Ar^+ sputtering in a vacuum are two methods that are often employed to produce defects on some oxide surfaces for certain research purposes.[27−32] For example, it was reported that annealing of TiO_2 in vacuo at temperatures higher than 500 K leads to the formation of surface oxygen vacancies.[27] Two Ti^{3+} sites are present for one oxygen vacancy. Formation of surface defects by annealing on ZnO was also reported.[18,31,32] Different from the case of annealing, in which a slightly defective surface is formed, Ar^+ sputtering usually produces a heavily defective surface.[30] On the basis of those facts, the effects of annealing and Ar^+ sputtering on the wettabilities of ZnO and TiO_2 thin films were investigated. Figure 8 shows the changes of water contact angles of (a) ZnO and (b) TiO_2 surfaces before and after being treated at various temperatures in air for 1 h. No substantial changes of water contact angles were observable after relatively low temperatures' treatment (e.g., 100, 150 °C). However, after higher temperature's treatments, apparent decreases of water contact angles were observed on both ZnO and TiO_2. Particularly, after these films were heated at temperatures higher than 300 °C, the water contact angles decreased so remarkably that the ZnO and TiO_2 films turned highly hydrophilic. This demonstrated that high-temperature annealing can induce wettability changes on ZnO and TiO_2 film surfaces.

The lowest temperature for initializing the decrease of the water contact angle on TiO_2 (∼200 °C) is consistent with the corresponding temperature for producing surface defects (∼500 K) as reported by Lu et al.[27] Correspondingly, Bhattacharyya et al.[33] reported that, at temperatures higher than 230 °C, adsorption of water molecules on ZnO was accompanied with the evolution of hydrogen, which might be the product of the dissociative adsorption of water on defective sites. This temperature is also in accordance with that (200−250 °C) for initializing the decrease of water contact angle on the ZnO surface (Figure 8). Taking into account the possible relation between the surface defective sites and the wettability conversion

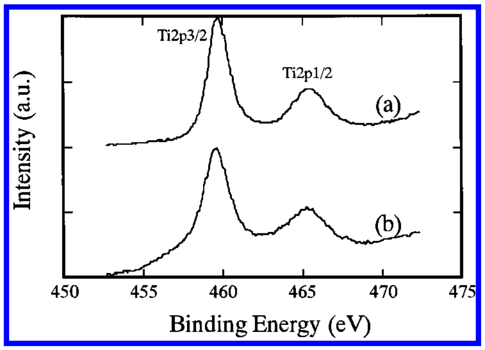

Figure 9. XPS spectra of TiO_2 thin film in the Ti 2p region: (a) before and (b) after heating treatment at 400 °C in a vacuum for 1 h.

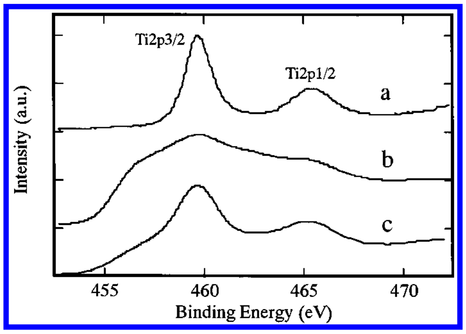

Figure 10. XPS spectra of TiO_2 thin film in the Ti 2p region: (a) before Ar^+ sputtering, (b) after sputtering for 5 min, and (c) after exposure of b to air for 30 s.

phenomenon, we believe that these agreements are not accidental. Figure 9 shows the XPS spectra of TiO_2 in the Ti 2p region (a) before and (b) after being annealed at 400 °C for 60 min in a vacuum. Compared to spectrum a, the shoulder at the lower binding energy side of the Ti $2p_{3/2}$ peak in spectrum b became slightly broader. This broader shoulder is ascribed to the formation of lower valent titanium species (e.g., Ti^{3+}),[30] which confirms that high-temperature annealing produces surface defective sites.

Surface wettability conversion induced by Ar^+ sputtering was also observed on ZnO and TiO_2 thin films. It was found that Ar^+ sputtering of ZnO and TiO_2 thin films for 5 min turned both surfaces to highly hydrophilic (from 109 to 9° for ZnO and 54 to 4° for TiO_2), similar to the cases of UV illumination and high-temperature annealing. Figure 10 presents the changes of the XPS spectra of the TiO_2 surface in the Ti 2p region before and after sputtering. It is obvious that Ar^+ sputtering produces a heavily defective surface (spectrum b). The defects involve not only Ti^{3+} but also Ti^{2+} and even lower valent species.[30] Thus formed surface defects are unstable, and they can be healed rapidly by oxygen or water contained in the air (spectrum c, Figure 10). It was reported that[30] the thermally induced, slightly oxygen-deficient TiO_2 surface can be fully healed after exposure in O_2 at room temperature. However, the highly oxygen-deficient TiO_2 surface generated by Ar^+ sputtering cannot be completely healed by oxygen exposure, perhaps due to the defects formed in the subsurface region or the formation of localized reduced subsurface oxide structures such as Ti_2O_3 and TiO.[30,34] We observed that the XPS spectrum scarcely changed even though the exposure time of the sputtered TiO_2 surface to air was extended from 30 s (spectrum c, Figure 10) to 120 min (data not shown), which agrees with the literature's reports.

Contrary to the results after the thermal treatments and Ar^+ sputtering both in vacuo, no corresponding changes of the XPS spectra in the Ti 2p region were detectable on the samples that were illuminated by UV light in ambient conditions. This is because the Ti^{3+} easily gives electrons to adsorbed oxygen, recovering the Ti^{3+} to Ti^{4+} on the surface (eq 5). For ZnO, however, no changes of the XPS spectra in the Zn 2p and 3p regions were detected even on the samples treated in a vacuum in the present work, perhaps due to the nonlocalization of electrons because of the easiness of Zn^+ ion to give out an electron to the conduction band. It was reported that the energy level of Zn^+ donor sites lies just 0.02−0.05 eV below the conduction band,[18] which is much shallower than that of Ti^{3+} sites (∼0.7 eV below the conduction band).[23] To our knowledge, evidence for detection of surface defects on the ZnO surface from XPS, Auger electron spectroscopy (AES), and UV photoelectron spectroscopy (UPS) are not available so far, even on surfaces treated with ion bombardment or high-temperature annealing in high vacuum. However, the formation of surface oxygen vacancies on ZnO has been confirmed by several other methods. For example, Göpel studied the interactions of oxygen with the stoichiometric and nonstoichiometric ZnO prismatic surfaces.[31] He failed to detect any changes of AES spectra on the ZnO treated at high temperature in high vacuum; however, increased O_2 partial pressure was detected at higher temperatures by thermal desorption spectroscopy (TDS), which implies the generation of increased oxygen vacancies on the ZnO surface. Formation of oxygen vacancies was also confirmed by EPR measurements on thermally treated ZnO powder[35] and electron irradiated crystals.[36]

As we discussed previously,[7,8] when a surface defective site is generated in the air, water and oxygen may compete to dissociatively adsorb on it. Since light illumination (or high-temperature annealing or Ar^+ sputtering) leads to a highly hydrophilic TiO_2 (or ZnO) surface, the defective sites are considered to be kinetically more favorable for hydroxyl adsorption than oxygen adsorption. However, the adsorption of OH^- groups distorts the surface in both electronic structure and geometric structure, and thus the surface is energetically unstable compared to the native hydrophobic surface.[8] Exposure of the surface to an atmosphere containing a higher oxygen partial pressure (e.g., in ambient condition or pure oxygen) tends to break the adsorption equilibrium and improve the thermodynamically preferred oxygen adsorption, and thus the hydroxyl groups adsorbed on the defective sites can be replaced gradually by oxygen atoms, which returns the surface geometric and electronic structures to their original states. Correspondingly, the surface wettability reconverted from hydrophilic to hydrophobic. According to the above analysis, it is reasonable to consider that a higher oxygen partial pressure leads to a higher reconversion rate. This explained the different reconversion rates in various atmospheres in Figure 7. The lower reconversion rate in ambient air than that in synthetic air may be due to the effect of humidity. It was proved that higher humidity tends to inhibit the reconversion process in air, and reversely promote the achievement of a highly hydrophilic state under UV illumination.[8]

It is noteworthy that, although the photoinduced surface wettability conversion phenomena on ZnO and TiO_2 showed many similarities, differences were also observed, e.g., their maximum and minimum water contact angles before and after UV illumination, their hydrophilic-to-hydrophobic reconversion rates. These differences are considered to be related not only to their inherent different chemical natures but also to their surface structures (e.g., surface texture, surface roughness). These two factors are known to affect the wettability of a solid surface greatly. The details remain unclear, and related investigation is under way.

Conclusion

Highly hydrophilic surfaces with water contact angles smaller than 10° were achieved by UV illumination on both the ZnO and TiO_2 thin film surfaces that were originally hydrophobic and slightly hydrophilic, respectively. It was concluded from the comparative studies that the photoinduced surface wettability conversion reactions on the ZnO and TiO_2 surfaces follow a similar conversion mechanism. Preferential adsorption of water molecules with dissociation on the photogenerated surface defective sites contributes to the formation of highly hydrophilic ZnO and TiO_2 surfaces. Strong supporting evidence for this explanation provided by the present work is the achievement of highly hydrophilic ZnO and TiO_2 surfaces by high-temperature annealing and Ar^+ sputtering. This discovery also provided two alternative methods for creating highly hydrophilic ZnO and TiO_2 surfaces.

The reversible change of surface wettability is a completely new concept for ZnO, and the present work provides an effective approach for controlling the surface wettability of ZnO thin films. The importance of the present work also lies in the fact that it reveals the possibility of expanding the related work from TiO_2 to other oxide semiconductors, which is certainly significant for further understanding this wettability conversion phenomenon.

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