

Photoinduced Hydrophilicity of Heteroepitaxially Grown ZnO Thin Films

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Single crystalline ZnO thin films were heteroepitaxially grown on sapphire substrates by rf-magnetron sputtering. The ZnO films on sapphire A and C face were oriented along the (0001) direction, whereas the ZnO film on sapphire R face was oriented along the (11–20) direction. The rate of photoinduced hydrophilic conversion strongly depended on the surface crystal structure. The ZnO film oriented along the (11–20) direction exhibited a higher hydrophilicizing rate than those oriented along the (0001) direction. The high hydrophilicizing rate of the ZnO oriented along the (11–20) direction is due to its surface atomic arrangement. The outermost layer of the ZnO surface of the (11–20) face contains oxygen ions, which are considered to be energetically reactive sites and responsible for the hydrophilic conversion.

Introduction

Wide-gap semiconductors have potential as components in electronic and optical devices because of their transparency and high energies of excited charge carriers. Wide-gap metal oxides are used for efficient photocatalysts, because the decomposition of organic compounds requires a high oxidation power of holes in the valence band and enough reduction power of the electrons in the conduction band. Titanium dioxide (TiO₂) is a well-known, efficient photocatalyst¹ and has various industrial applications such as water or air purification,² antibacterial agents,³ and self-cleaning surface.^{4,5} Recently, intriguing phenomenon of photoinduced hydrophilicity on TiO₂ was reported,⁶ and this reaction has been thoroughly investigated.^{7–12} Although the detailed mechanism of this reaction is still unclear, one of the possible mechanisms is considered to be a result of structural changes in the TiO₂ surface, which proceed in a different fashion than conventional photocatalytic oxidation reactions proceed.^{13–15} The efficiency of the hydrophilicizing reaction strongly depends on the surface crystal structure. Wang et al. investigated the photoinduced hydrophilicity of rutile TiO₂ single crystal on various crystal faces and found that crystal faces with bridge site oxygen molecules exhibited efficient hydrophilicizing under UV irradiation.¹⁶ The controlling surface crystal structure and the thin film fabrication are key factors for a wide application of the photoinduced hydrophilic reaction. In the present study, we focused on zinc oxide (ZnO), since ZnO possesses both features of photocatalytic oxidation and photoinduced hydrophilicity.^{17–19} In addition, thin films of ZnO are heteroepitaxially grown on various substrates.^{20,21} We fabricated single crystalline ZnO thin films with various crystal faces on sapphire substrate by rf-magnetron sputtering and investigated their photoinduced hydrophilicities.

Experimental Section

Thin films of ZnO were fabricated by rf-magnetron sputtering (HSM-752, Shimadzu Co., Tokyo, Japan) using Zn target (Kojundo Chemical Lab. Co. Ltd, 99.999%) on the various sapphire substrates (A-plane: (11–20), C-plane: (0001), and R-plane: (1–102)). Prior to a sputtering process, sapphire

substrates were ultrasonically degreased in ethanol for 30 min. Subsequently, these substrates were immersed in hot sulfuric acid solution (H₂SO₄, 473 K) for 30 min and were then thoroughly rinsed with pure water. Sputtering was carried out under a total gas pressure of 2.66 Pa of Ar/O₂ = 80/20 gas mixture for 60 min. Substrate temperature was 673 K, and rf-sputtering power was 300 W.

Surface morphologies were observed by an atomic force microscope (AFM: Nanoscope 3a, Digital Instruments Co.). Roughness factors *r* were calculated by image processing, where *r* is defined as the ratio of the actual area of a rough surface to the geometric projected area. Cross-sectional images of thin films were observed using a scanning electron microscope (SEM model S-4200, Hitachi Co., Tokyo, Japan). Crystallinity and orientation of ZnO films were investigated by X-ray diffraction patterns of $\theta/2\theta$ and polar angle (Φ) scan with CuK α rays (RINT-2100, Rigaku Co., Tokyo, Japan). XRD patterns of Φ scan were recorded under 2θ of 36.25°, which corresponds to the diffraction from ZnO (10–11) face. UV–vis spectra for thin films were recorded on a spectrophotometer (UV-3150, Shimadzu Co., Kyoto, Japan).

The contact angle measurement was performed at room temperature (~295 K) using a commercial contact angle meter (CA-X, Kyowa Interface Science, Saitama, Japan), with an experimental error of ± 1 degree. A 10 W black light bulb (Toshiba Co., Tokyo, Japan) was the source of the UV illumination with a light intensity of 1.0 mW/cm² measured by a UV radiometer (UVR-2, Topcon Co., Tokyo, Japan).

The photocatalytic oxidation reaction of thin films was also evaluated by observing the decomposition of adsorbed methylene blue dye in air. Films were dipped in an aqueous solution of 1.0 mM methylene blue at room temperature for 1 h. After dipping, they were stored in the dark for 2 h to allow the adsorbed dye to dry. Dye adsorbed on the opposite side of the coated surface was then wiped off. Ultraviolet radiation with an intensity of 1.0 mW/cm² produced by a 10 W cylindrical black light bulb (BLB: Toshiba Co., Tokyo, Japan) was used to illuminate the films. Light intensity was measured with a UV radiometer (UVR-2, Topcon Co., Tokyo, Japan). The decomposition of the dye on the films was evaluated by the peak absorbance value of methylene blue spanning from 550 to 600 nm. Before each absorbance measurement, thin films

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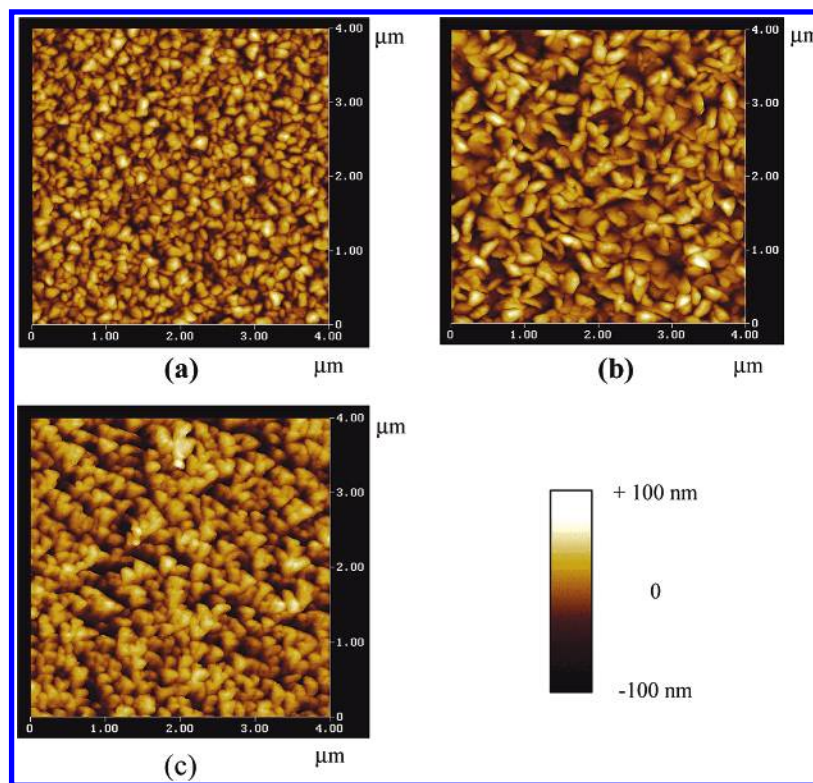


Figure 1. AFM images of ZnO films: (a) on sapphire A face, (b) on sapphire C face, and (c) on sapphire R face, respectively.

were stored in the dark for 2 h, to reconvert the reduced methylene blue of the leuco form (LMB) into its initial state.²² By this procedure, changes in absorbance can be ascribed to the decomposition of the methylene blue by the oxidation reaction. Absorbances were measured with a UV–vis spectrometer (UV-3150, Shimadzu Co., Kyoto, Japan).

Surface atomic arrangements of ZnO were calculated by CASTEP²³ in Materials Studio of Accelrys Inc., which is the Program Package based on the density functional theory (DFT). The experimentally determined lattice constant of $a = 3.249$ Å, $c = 5.205$ Å was used for the production of ZnO surface models. The slab was repeated periodically with 20 Å of vacuum region between the slabs. In all calculations, we used the generalized gradient approximations (GGA) and the functional of Perdew–Burke–Ernzerh (PBE).²⁴

Results and Discussion

Figure 1 shows AFM images for ZnO films. Calculated roughness factors (r) of ZnO films on sapphire A-plane, C-plane, and R-plane were 1.22, 1.26, and 1.28, respectively. Figure 2 shows cross-sectional SEM images. Grown ZnO films exhibited a dense columnar structure, and the thickness of these films was nearly identical (600 nm).

Figure 3 shows X-ray diffraction patterns of $\theta/2\theta$ scan. As for the ZnO films on sapphire A face and C face substrates, only peaks of (0002) and (0004) planes of ZnO were observed, indicating that these films are highly oriented with the c -axis perpendicular to substrates. In contrast, only the (11–20) diffraction peak was observed in the ZnO film on a sapphire R face substrate. To investigate the two-dimensional crystal orientation in these films, the polar angle (Φ) scan for the (10–11) planes of ZnO was investigated (Figure 4). The sixfold symmetry was clearly observed in the ZnO films on sapphire A and C faces, while the fourfold symmetry was observed in the ZnO film on a sapphire R face. These results indicate that these ZnO films were heteroepitaxially grown on sapphire

substrates. Previous studies reported epitaxial relationships between ZnO and sapphire.²⁵ As for the (0001) oriented ZnO film on sapphire A face, the (–1100) direction of ZnO is parallel to the (01–10) direction of sapphire. As for the (0001) oriented ZnO film on sapphire C face, the (10–10) direction of ZnO is parallel to the (11–20) direction of sapphire. As for the (11–20) oriented ZnO film on sapphire R face, the (–1100) direction of ZnO is parallel to the (11–20) direction of sapphire. The full width at half-maximum (fwhm) is related to the crystallinity of the films, and those of the ZnO films on A-plane, C-plane, and R-plane in the present study were 1.65°, 1.73°, and 1.66°, respectively. These results imply that these films have almost the same crystallinity.

Figure 5 shows UV–vis spectra for ZnO films. These films were optically transparent in the visible light region, while the optical absorption was observed in the UV region, owing to the interband transition of ZnO. It has been reported that the electronic structure of ZnO gives direct transition, and its band-gap energy is 3.0 eV.²⁶ Absorption edges of these films in Figure 5 were found around 400 nm, corresponding to a band-gap energy of ZnO. These films exhibited similar absorption behaviors, since they have almost the same thickness (600 nm). These films can be excited by illumination with light from a black light bulb, whose wavelength ranges from 310 to 400 nm.

Figure 6 shows the changes in the water contact angle under UV illumination. Before the contact angle measurement, these films were stored in clean air (gas mixture of O₂/N₂ = 20/80) in the dark condition to avoid adsorption of contaminants from the air. Initial contact angles of these films are nearly identical (~60°), though morphologies of these films are different. Wenzel proposed a theoretical model describing the contact angle at a rough surface (θ').²⁷ He modified Young's equation by using a roughness factor (r) as follows:

$$\cos \theta' = r(\gamma_{SV} - \gamma_{SL})/\gamma_{LV} = r \cos \theta \quad (1)$$

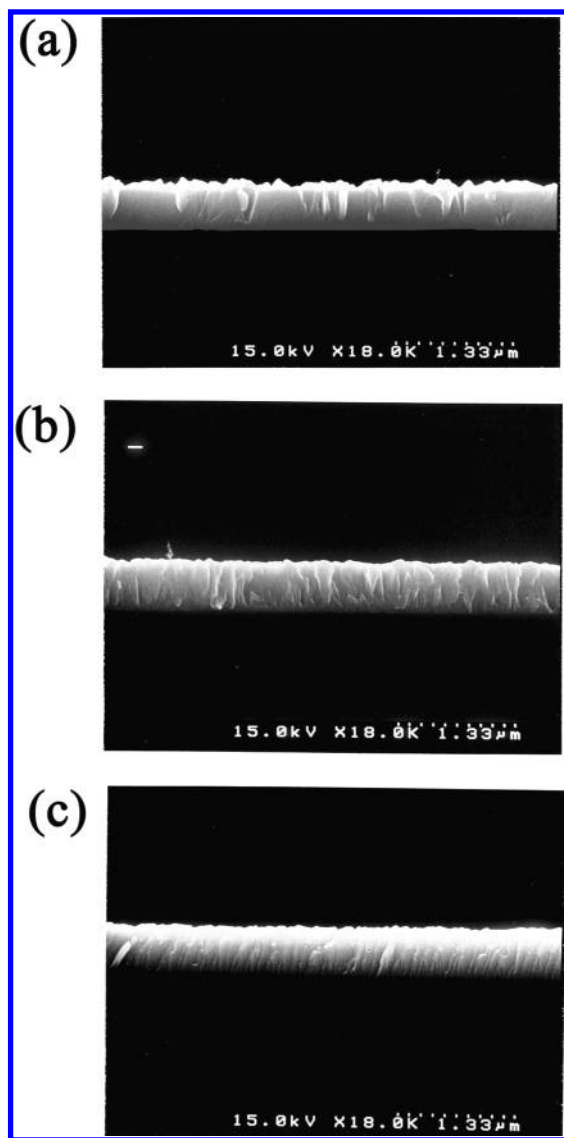


Figure 2. Cross-sectional SEM images of ZnO films: (a) on sapphire A face, (b) on sapphire C face, and (c) on sapphire R face.

where r is defined as the ratio of the actual area of rough surface to the geometric projected area, and γ_{SL} , γ_{SV} , and γ_{LV} are the interfacial free energy per unit area of the solid–liquid, solid–gas, and liquid–gas interfaces, respectively. Wenzel's eq 1 contains an r factor which depends on the local slope of the roughness. On the basis of our AFM analysis, r factors of these films were almost the same value (1.22–1.28); thus, it is reasonable that the initial contact angles of these films are nearly identical. These films became hydrophilic under UV illumination. The hydrophilicizing rate of ZnO on R-plane sapphire was higher than those on A-plane or C-plane sapphire substrates, although their crystallinities were nearly identical. As is mentioned above, the ZnO film on R-plane sapphire was heteroepitaxially grown and oriented to the (11–20) direction, while the ZnO films on A-plane and C-plane sapphire were oriented to the (0001) direction. These results imply that the photoinduced hydrophilicity of ZnO depends on the surface crystal structure. We also investigated the photocatalytic oxidation activities of these ZnO films by the decomposition of methylene blue adsorbed on the film surface. However, these films exhibited almost the same activities. These results imply that the photoinduced hydrophilic reaction proceeds in a different fashion than the photocatalytic oxidation reaction proceeds.

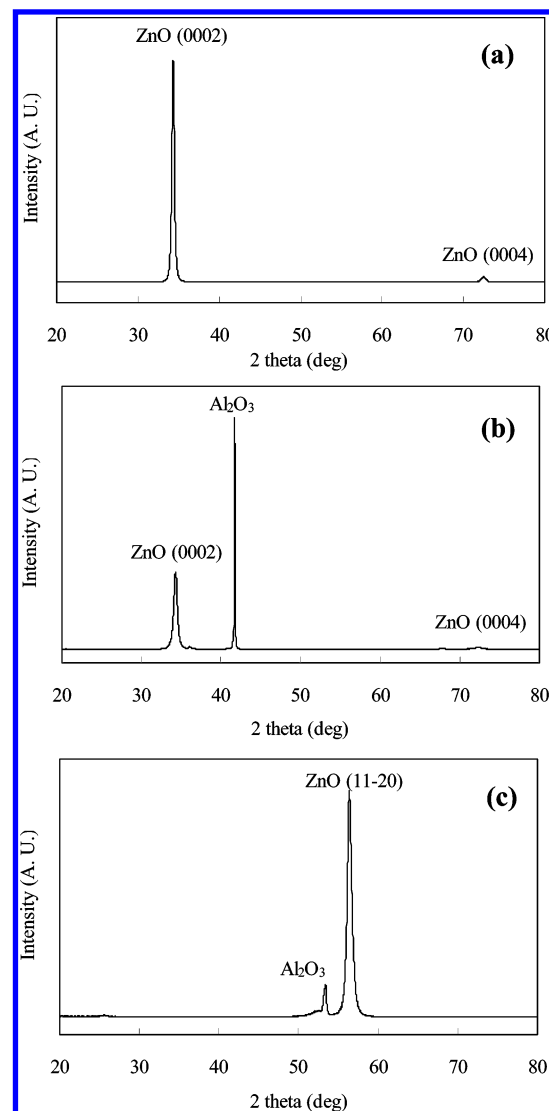


Figure 3. XRD patterns of ZnO films by $\theta/2\theta$ scan: (a) on sapphire A face, (b) on sapphire C face, (c) on sapphire R face.

Several groups reported that the UV illumination on photocatalysts led to changes in adsorbed water molecules. Nakamura et al. reported that surface-enhanced IR absorption spectroscopy (SEIRAS) indicated the photoadsorption of water molecules, and photoadsorbed water was removed easily by O_2 .¹⁰ Nosaka et al. reported that the water molecules adsorbed on the TiO_2 surface were categorized into three types by H NMR analysis: (I) mobile and weakly adsorbed water in the outermost layer, (II) less mobile water in the inner layer, and (III) rigid water near the solid surface. Their H NMR results exhibited substantial increases in type I and II water and a slight increase in type III water.¹¹ In addition, Uosaki et al. recently investigated the interfacial water structure at the TiO_2 surface by sum frequency generation (SFG) and quartz crystal microbalance (QCM)¹² and found that UV illumination led to an increase in the amount not only of all adsorbed water but also of the ordered adsorbed water on the TiO_2 surface. Sakai et al. proposed a mechanism of the photoinduced hydrophilicity of TiO_2 , which originates from an increase in the hydroxyl groups on the TiO_2 surface.¹³ Photogenerated holes diffuse to the surface of photocatalysts and react with surface lattice oxygen atoms, which is followed by the dissociative adsorption of a water molecule. Furthermore, Shibata et al. reported that residual stress in a TiO_2 film affected photoinduced hydrophilicity, though it did not affect photo-

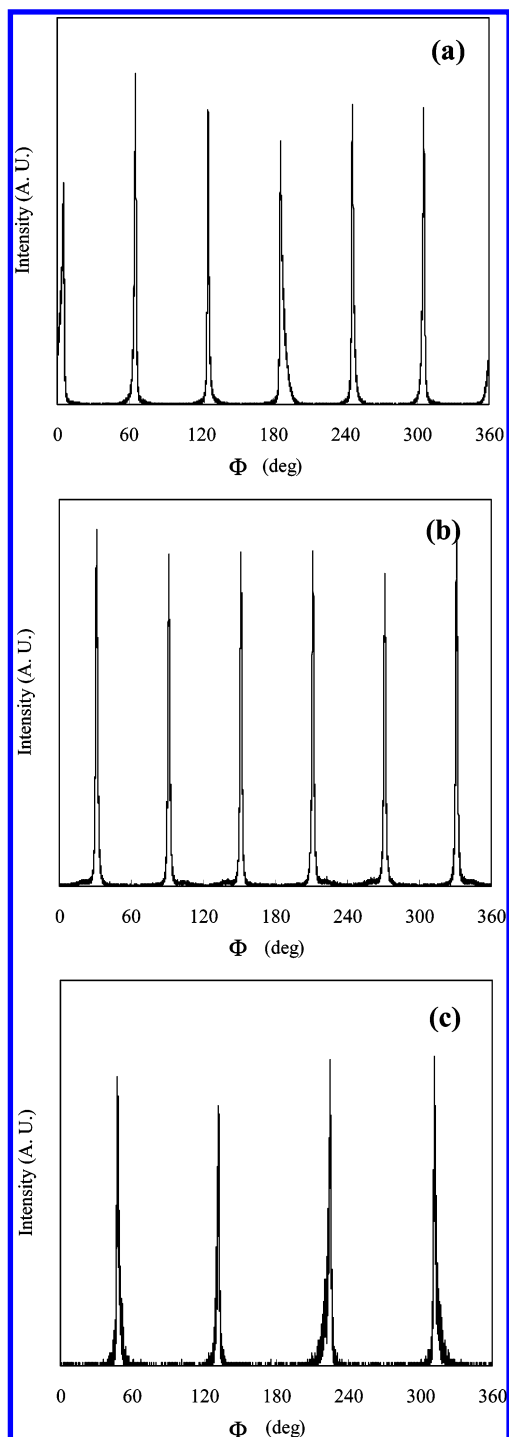


Figure 4. XRD patterns of ZnO films by polar angle (Φ) scan: (a) on sapphire A face, (b) on sapphire C face, (c) on sapphire R face. The 2θ angle was set to 36.25° , which corresponds to the diffraction from ZnO (10–11) face.

catalytic oxidation activity.¹⁵ The photoinduced hydrophilic conversion rate of a TiO_2 film with tensile stress was higher than that without residual stress. These results indicate that the photoinduced hydrophilic reaction proceeds with volume changes at the surface of the crystal. Recently, lattice expansion of a rutile single crystal under UV illumination has been confirmed by a totally reflected X-ray in-plane diffraction method and a Kelvin force microscopy.²⁸ It has also been reported that the photoinduced hydrophilicity depends on the surface crystal structure, that is, rutile single crystals with bridge site oxygen {(110) and (100) plane} exhibited a higher hydrophilicizing rate

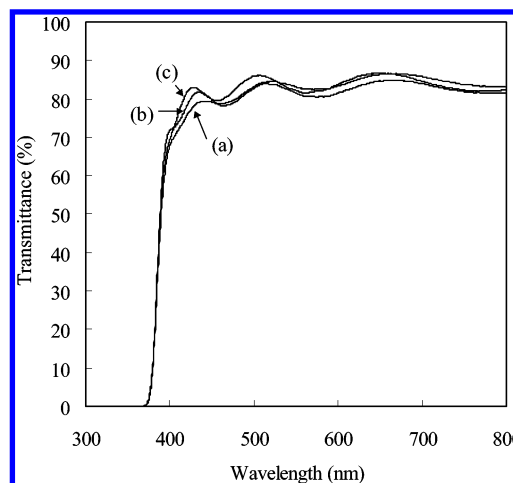


Figure 5. UV-vis spectra of the thin films: (a) on sapphire A face, (b) on sapphire C face, (c) on sapphire R face.

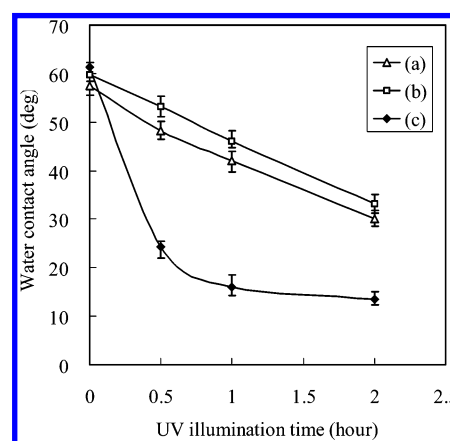


Figure 6. Changes in water contact angle under a UV intensity of 1.0 mW/cm^2 illuminated by a 10 W black light bulb: (a) on sapphire A face, (b) on sapphire C face, (c) on sapphire R face.

than that without bridge site oxygen {(001) plane}.¹⁶ Rammamoorthy et al. reported that the (001) surface of rutile TiO_2 , which does not have bridge site oxygens, has a lower surface energy than (110) or (100) surface.²⁹ Bridge site oxygens are in a higher position and are energetically more reactive than their surrounding atoms; thus, these sites are considered to be a reactive site for the surface structural change. Figure 7 shows the surface atomic arrangements on ideal (0001) and (11–20) faces of ZnO. Zinc oxide has wurtzite-type symmetry and thus belongs to the space group C_{6v}^4 . On the (11–20) surface, both oxygen and zinc ions are terminated in the same plane. On the other hand, there are two possibilities of surface-terminated ions on the (0001) face, that is, oxygen ions or zinc ions. We calculated the total energy of these two surface models by DFT, and the total energy of the oxygen-terminated surface was 430 eV/atom higher than that of the zinc-terminated surface. These results imply that the zinc ions terminated structure is more energetically stable than the oxygen ions termination. Under this stable structure, oxygen ions are not exposed at the surface. Similar to the TiO_2 case, surface oxygen ions are considered to act as reactive sites for increasing OH species on the surface. Therefore, it is reasonable that the hydrophilicizing rate of (11–20) oriented ZnO film is faster than those of (0001) oriented ZnO films. Although detailed investigations on surface atomic arrangement of ZnO, such as coaxial impact collision ion scattering spectroscopy (CAICISS), will be required for further understanding the surface wettability conversion, the present

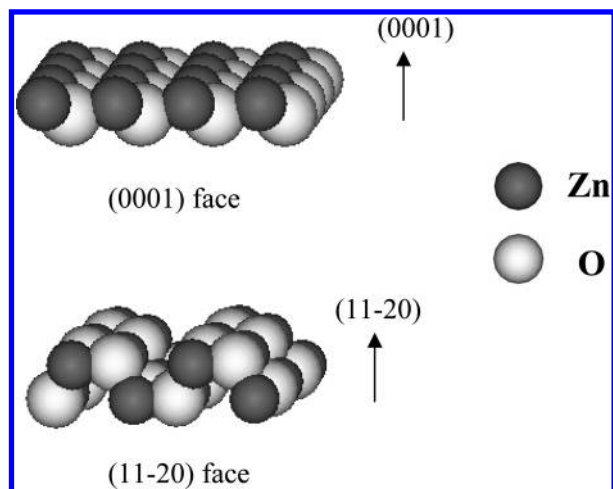


Figure 7. Schematic illustration of the atomic alignments on ideal ZnO (0001) and (11-20) crystal faces.

study offers some insights into the photoinduced hydrophilic conversion. It shows that the crystal orientation is very important for the rate of the photoinduced hydrophilic reaction. This result would contribute to developing highly hydrophilic thin films.

Conclusions

The rate for photoinduced hydrophilic conversion on single crystalline ZnO films depended on the crystal face of the surface. The hydrophilicizing rate on the (11-20) face of ZnO was much higher than that on the (0001) face. According to DFT calculations, both oxygen and zinc ions are exposed on the (11-20) face, whereas zinc ions are terminated on the (0001) face. The highly hydrophilic property of (11-20) face is due to its terminated oxygen ions, which are reactive sites for hydrophilicizing. This study demonstrates that the photoinduced hydrophilicity can be controlled by the surface crystal faces. The present study is quite valuable because this technique can potentially be applied to various industrial items, which have antifogging and self-cleaning properties.

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