Photoelectrochemical Etching on Zinc Oxide Single Crystals: Crystallographic Surface Dependence and Wettability Control

Hiroshi Irie, a, * Ken Obata, a Tatsuo Shibata, a,c and Kazuhiro Hashimoto, a,b, *

Department of Applied Chemistry (The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan)

Research Center for Advanced Science and Technology (RCAST) (The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan)

Present Address: National Institute for Materials Science (Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan)

Received September 14, 2007 ; Accepted November 16, 2007

Photoelectrochemical etching was applied to (0001), (000-1), and (10-10) surfaces of ZnO single crystals to produce unique surface structures, which depend on the crystallographic face. These surfaces turned hydrophilic with a water contact angle of 5°-10° under ultraviolet light irradiation, but the hydrophilicity gradually became small in the dark. Among them, we successfully generated a hydrophobic surface (contact angle > 120°) stored in a dark under ambient conditions on the etched (000-1) face with hexagonal holes that had a diameter of approximately 100 nm along the c-axis. In addition, storing at 75°C in a dry oven greatly shortened the period of the hydrophobic conversion.

Key Words: ZnO Single Crystal, Photoetching, Hydrophobicity, Wettability Control

1 Introduction

Photoelectrochemical etching is generally used to treat semiconductor surfaces. Fine etching patterns, which depend on the crystallographic faces, have been observed after photoetching procedures. 1,6 For example, Sugiuira et al. have reported that the etching patterns on the (0002) and (002-2) faces of a CdSe single crystal are quite different even though both faces are perpendicular to the c-axis and the etching proceeds along the c-axis. 3, 4 They have also applied etching to polycrystalline ZnO pellets, and observed unique morphologies on their surfaces, which depend on the crystallographic orientations. 5 In contrast, it has been reported that single crystals of reduced rutile TiO₂ selectively produce rectangular holes along the c-axis direction. 2,6 We applied photoetching to rutile TiO₂ pellets to produce random directions of ditches and hydrophobic TiO₂ with a water contact angle (CA) of approximately 120°. Such a surface turns into a highly hydrophilic state with a CA of 0° when ultraviolet (UV) light irradiates it, but returns to the initial hydrophobic state with the CA of 120° when stored in the dark. However, to reach 120° from 0°, dark storage for 15 days was required. 7

Feng et al. have reported a highly hydrophobic conversion on a ZnO nanorod film kept in the dark for seven days. 8 Moreover, they reported a good reversibility between high hydrophobicity and high hydrophilicity by alternating between UV light irradiation and dark storage. Therefore, it is expected that ZnO surfaces with unique morphologies introduced by a photoetching process will become a hydrophobic state.

In the present study, we applied photoetching to the (0001), (000-1), and (10-10) surfaces of ZnO single crystals, and tried to realize hydrophobic surfaces as well as an accelerated hydrophobic conversion rate in the dark.

2 Experimental

ZnO (0001), (000-1), and (10-10) single crystals (Orbe Pioneer Co., Japan) were used in the present study. These single crystals were washed ultrasonically in acetone and subsequently rinsed in pure water. The washed crystals were heated at 1200°C for 2 h under atmospheric conditions to obtain n-type conductivity. The sintered crystals with ohmic contacts by an In-Ga alloy served as the working electrodes. Photoelectrochemical etching using the procedure of Sugiuira et al. 6 was conducted by illuminating the electrode with UV light, which was generated by a Hg-Xe lamp (Luminer Ace LA-210UV, Hayashi Watch-works Co., Ltd) with a glass filter (UV-D35, Asahi Technoglass Corp.) in a 1 M H₂SO₄ aqueous solution at +0.5 V vs. Ag/AgCl/3M-NaCl reference electrode. A platinum wire was used as the counter electrode. The etching quantity was controlled by monitoring the charge passed in the photocurrent (20-40 C/cm²) using a potentiostat (HSV-100, Hokuto Denko Corp.) Currents were negligibly small before illuminating the ZnO electrodes, so it can be assumed that the etching scarcely proceeds in the dark. The surfaces of the crystals after etching were inspected using a scanning electron microscope (SEM, S-4200, Hitachi Ltd.). The surface wettabilities were evaluated by measuring CAs using a commercial contact angle meter (CA-X, Kyowa Interface Science Co., Ltd). Each CA was measured at least three times, and the average value was used. UV light irradiation was performed using a 10-W black light bulb (FL10LB, Toshiba Co., Ltd.). The UV light intensities (1 mW/cm²) were measured by a spectrophotometer (USR-30, Ushio Inc.). Dark storage was performed in a vessel
at room temperature (R.T.) in an ambient atmosphere and at 75 °C in a dry oven.

3 Results and Discussion

3.1 Photoelectrochemical etched surface

Figures 1 (a), (b), and (c) show the surface SEM images for the (0001), (000-1), and (10-10) faces after phototetching with passed charges of 40, 30, and 20 C/cm², respectively. Figure 1 (d) shows the cross sectional SEM image for the phototetched (000-1), i.e., Fig. 1(b). It is known that the (0001) and (000-1) faces are Zn-terminated and O-terminated, respectively, and that Zn and O are exposed on the (10-10) face. On the (0001) surface, shallow hexagons with steps were formed as shown in Fig. 1 (a). In contrast, on the (000-1) surface, deep hexagonal holes approximately 100 nm in diameter and 11 μm long were selectively produced along the c-axis direction, as shown in Fig. 1 (b) and (d). From the etching experiments, it was found that the (000-1) face etched more easily in the oxidizing etchant (H₂SO₄) used than the (0001) face. The difference in the etching behaviors between the Zn (0001) and O (000-1) faces was explained as follows. A surface bonding model was proposed for ZnO. The Zn atoms have no electron dangling bonds at the surface whereas the O atoms have a dangling bond with two electrons at the surface. As a result, the Zn atom bonds are more severely strained than the O atom bonds and thus the Zn surface is more resistant to etching. In addition, the chemical reactivity of the Zn and O surfaces was argued that the O atoms are more reactive than the Zn atoms in reactions where oxidizing (electrophilic) agents are involved because they have an unshared pair of electrons available for oxidation.

We assumed that the area ratio of hexagonal holes to the entire surface was 30% in Fig. 1(b). ZnO is corroded according to the equation, ZnO + hν → Zn²⁺ + (1/2)O₂ + 2e⁻, the density of ZnO is 5.67 g/cm³, and the etching depth was found to be 11 μm in Fig. 1 (d). Then, we could estimate the efficiency of the passed charges to the etching and obtained 17%. The efficiency was high compared to that for the rutile TiO₂ (3%). This can be assumed that the photogenerated holes on ZnO surface are consumed for the photoetching, in contrast, those on rutile TiO₂ cause the photoetching to some extent, competitively with the water oxidation. It is reasonable that straight ditches parallel to c-axis appeared on the (10-10) surface, as shown in Fig. 1(c), because photoetching proceeds along the c-axis in ZnO. The width of the ditches varied and was ca. 100 nm at the maximum, similar to the diameter of hexagonal holes on the (0001) surface. So, it might be considered that the cross sections of a number of hexagonal prisms along the c-axis were observed as the straight ditches.

3.2 Hydrophobic conversion property

The hydrophobic conversion behaviors in dark storage at R.T. after UV light irradiation were investigated on the etched (000-1) and non-etched flat (000-1) faces, as shown in Fig. 2. It should be noted that the CA on the non-etched surface reached a minimum near 30° under UV light. In contrast, the CA on the etched surface under UV light decreased to near 5°; that is, a high hydrophilicity was achieved. The enhanced hydrophilicity after UV irradiation on the etched surface (CA ~ 5°) compared to the non-etched surface (CA ~ 30°) is plausi-

---

Fig. 1 SEM images of photoetched surfaces on (a) Zn-terminated (0001), (b) O-terminated (000-1), and (c) Zn, O-terminated (10-10). SEM image of photoetched cross section of (d) O-terminated (000-1).
ble considering Wenzel’s equation which is related to the wettability on a rough surface.

The CAs on both the etched and non-etched surfaces in the dark storage increased, but the behaviors of the increasing CAs were quite different and depended on the surface. That is, the CAs on the non-etched surface increased and reached near 70° in the early period of the dark storage. Then the CAs stopped increasing near 80° after one month, and remained constant even after storing the surface for an additional three months. In contrast, the CAs on the etched surface increased with an S-shaped behavior. In early dark storage, the CAs increased gradually, especially around 5-30 days. In that period, the CAs on the etched surface were lower than those on the non-etched surface. Then the CAs increased suddenly and reached about 120°, i.e., the hydrophobic region. Upon further dark storage, the CAs remained constant. These hydrophobic conversion behaviors will be discussed later. Although hydrophobicity on the (000-1) face after the etching treatment could be realized, hydrophobic conversion took a lot of time. The generation of hydrophobicity on the etched surface is explained by Cassie’s equation, and the hydrophobicity is caused by the intrusion of air into roughness structure.

Now, let us discuss the S-shaped behavior in the hydrophobic conversion process. The Wenzel mode dominates the early stage, for 30 days, of dark storage, and the CAs on the etched surface were lower than those on the non-etched surface. The sharp increase in the CAs up to 120° suggests that the air intruded suddenly, and converted the mode into the Cassie, which coincides with the previous report. Once the air intruded, the air did not intrude further, resulting in constant CAs near 120° even upon further dark storage.

After dark storages on the etched (0001) and (10-10) surfaces, the CAs remained in the hydrophilic region (not shown here), indicating that the surfaces did not convert into the Cassie mode, but remained in the Wenzel mode because the roughness on the surfaces were too shallow for air to intrude.

Next, we tried to shorten the period of the hydrophobic conversion. To date, the hydrophobic conversion requires seven days on a ZnO nano-rod surface and 15 days on rutile TiO2. In the present study, it took 60 days to achieve hydrophobicity on an etched (000-1) ZnO surface. We have previously observed that the rate of the back reaction (i.e., highly hydrophilic-to-less hydrophilic reaction) is enhanced on a TiO2 surface by increasing the ambient temperature and decreasing the ambient humidity. Moreover, we consider that the mechanisms for the hydrophilic conversion and the back reaction are the same between TiO2 and ZnO surfaces. Therefore, in order to shorten the period of the hydrophobic conversion, the etched (000-1) surface was stored in the dark at 75°C in a dry oven, as shown in Fig. 2. The period of the highly hydrophilic to hydrophobic conversion was greatly shortened, and only 24 hours were required to reach the hydrophobic region, as shown in the inset of Fig. 2. In this case, the S-shaped behavior in the hydrophobic conversion was not observed because the conversion from the Wenzel mode to the Cassie one proceeded quickly. Thus, we conclude that either increasing the ambient temperature or decreasing the ambient humidity is a candidate to shorten the period of the hydrophobic conversion.

Finally, we evaluated the reversibility of the high hydrophilicity and hydrophobicity. Figure 3 shows the switching of the wettability on the etched surface when alternating between UV light irradiation for 10 minutes and dark storage for 24 hours at 75°C in a dry oven. The process between high hydrophilicity and hydrophobicity could be repeated at least five times, indicating good reversibility of the surface wettability.

4 Conclusion

Photoelectrochemical etching produced unique surface structures, which depended on the crystallographic face of ZnO (0001), (000-1), and (10-10) surfaces. Among them, we successfully created a hydrophobic state on the etched (000-1) surface stored in the dark. In addition, storing at a higher temperature (at 75°C) and lower humidity (in a dry oven) greatly shortened the period of
the hydrophobic conversion and produced the hydrophobic state in 24 hours. Consequently, we could reversibly control the wettability between high hydrophilicity and hydrophobicity in a rather short time. However, the hydrophobicity must be further enhanced (more than 150°, high hydrophobicity). We are currently investigating this improvement.

Acknowledgement
This work was supported by CREST, Japan Science and Technology Agency (JST).

References
11) According to Wenzel’s equation (cosθ' = r cosθ), surface roughness enhances the hydrophilicity of hydrophilic surfaces (CA(θ)<90°) as well as the hydrophobicity of hydrophobic surfaces (CA(θ)>90°) because r is always larger than 1. The ZnO (000-1), (0001), and (10-10) faces are hydrophilic. In fact, the CAs on a flat (000-1) surface stopped increasing near 80°, as shown in Fig. 2. Thus, θ' is smaller than θ. When applying the CA of 30° on the non-etched surface and that of 5° on the etched surface after UV irradiation to the Wenzel’s equation, we can obtain cos5° = r cos30°. Then, r is calculated to be 1.2. In contrast, considering from the observations in Figs. 1 (b) and (d) that one side of a hexagon and a depth of a hexagonal hole are 60 nm and 11 μm, respectively, and the assumption that the area ratio of hexagonal holes to the entire surface was 30% in Fig. 1 (b), r is calculated to be ca. 130, which is much larger than the value obtained by Wenzel’s equation. This can be explained that a water droplet cannot intrude into hexagonal holes because air in them cannot come out.
12) Ra was obtained by atomic force microscopy (AFM; SPI 3700, Seiko Instruments, Inc.). The (000-1) surface before etching had the Ra of 4.7 nm. The Ra of the etched (000-1) surface could not be obtained because its roughness was too deep to measure.
14) Cassie proposed an equation for a surface composed of solid and air. When a unit area of the surface has an area fraction, f, where a water-droplet contacts the solid surface with a CA. of θ, then θ' on the surface can be expressed as Cassie’s equation, which assumes the CA for air is 180°: cosθ' = f cosθ + (1-f) cos180° = f cosθ + f-1. In the present data, θ and θ’ are 80° and 120°, respectively, and the calculated f value is 0.42. The hydrophobicity on the etched surface is caused by the intrusion of air among roughness structures.