Influence of the reaction between water and ZnO on the properties of Au Schottky contacts and the photocatalytic activity of ZnO(0001) single crystals

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Abstract
Wet chemical treatment is a conventional surface cleaning method, and metal oxide photocatalysts are commonly used to decompose organic compounds in water. In this study, we have investigated the influence of the reaction between water and ZnO on the properties of Au Schottky contacts and the photocatalytic activity of Zn-face ZnO(0001) single crystals. The ZnO substrate was put in deionized water at temperatures between 40 °C and 90 °C (water treatment). The ZnO substrate was etched with deionized water, and the surface roughness increased with increasing water temperature. Although the water treatment had no significant influence on the surface composition of the ZnO substrate, it changed the properties of the Au contacts. Schottky contacts were formed on the as-received ZnO substrate and the ZnO substrate after the water treatment at 40 °C, whereas ohmic contacts were formed on the ZnO substrate after the water treatment at 90 °C. Photoelectron emission spectra showed that the surface Fermi level in the ZnO substrate after the water treatment at 90 °C was located just below the conduction band. However, the water treatment had no significant influence on the photocatalytic activity of the ZnO substrate. Even when the water treatment was performed at 90 °C, the surface Fermi level of the ZnO substrate in an electrolyte solution, which was estimated from photoelectrochemical measurements, was located about 0.4 eV below the conduction band.

1. Introduction
Zinc oxide (ZnO) is a very versatile oxide semiconductor used in many applications due to its unique properties such as wide bandgap, low resistivity, and non-toxicity [1–3]. ZnO nanorods and nanoflowers have been attracting much attention because they are synthesized using aqueous solutions at low temperatures [4, 5]. Solution-based growth methods have advantages of being simple, low-cost, and relatively easy in operation. ZnO nanostructures with a high surface to volume ratio are known to have good photocatalytic activity. However, the photocatalytic activity of ZnO nanostructures is influenced by its composition, defects, and surface structures [6, 7]. It depends on deposition and post-deposition processes such as impurity doping, surface modification, and annealing [7–9].

It is generally assumed that ZnO is not soluble in water because the complete ionic dissolution of ZnO is hindered by the formation of O²⁻ anions. However, Escorihuela et al showed through computational simulation that small ZnO clusters are dissolved in water [10]. Wet chemical treatment is a conventional surface cleaning method, and metal oxide photocatalysts are commonly used to decompose organic compounds in water. Many types of surface treatments are used for the metal contact formation on ZnO, but good Au and Pt Schottky contacts have been achieved on bulk ZnO substrates with a simple surface cleaning using organic solvents [11, 12]. There are also many studies about ZnO photocatalysts. It has been reported that the photocatalytic activity of oxide semiconductors is enhanced with introducing an appropriate concentration of oxygen vacancies [13, 14]. The properties of metal contacts and photocatalysts are very sensitive to the surface condition.
Thus, it is important to understand the influence of the reaction between water and ZnO on the properties of metal contacts and the photocatalytic activity of ZnO. To the best of our knowledge, however, the influence of the reaction between water and ZnO has not been fully understood.

In this study, we have focused on the properties of Au Schottky contacts and the photocatalytic activity of Zn-face ZnO(0001) single crystals. The influence of the reaction between water and ZnO has been investigated by using current-voltage measurements, photoelectron emission spectroscopy, photocatalytic dye decomposition measurements, and photoelectrochemical measurements.

2. Experimental

Commercial Zn-face ZnO(0001) single crystals (Tokyo Denpa, Japan) were used as samples. The ZnO substrate was cleaned with an ultrasonic bath of acetone. Then, it was put in deionized water at temperatures between 40 °C and 90 °C for 5 min (water treatment). The surface of the ZnO substrate after the water treatment was observed by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). The mass reduction of the ZnO substrate as a function of time in deionized water at 90 °C was measured using an analytical balance (Mettler Toledo UMX2). Au Schottky contacts (diameter: 0.6 mm) were deposited on ZnO(0001) surface by thermal evaporation at a base pressure of ~10⁻⁴ Pa. Indium with a relatively low work function was used for ohmic contact formation, and the backside ohmic contacts were formed by thermal evaporation. Current-voltage (I-V) measurements of the Schottky diodes were performed at room temperature. Photoelectron emission spectroscopy (PES) measurements were carried out in vacuum. The wavelength of the incident UV light was varied with a monochromator (Jobin Yvon H-UV20). The photoelectrons emitted from the ZnO substrate surface were detected by a simple electronic counting method [15].

The photocatalytic activity of the as-received ZnO substrate and the ZnO substrate after the water treatment at 90 °C was estimated from the decomposition of methylene blue (MB). The ZnO photocatalyst (1 × 0.5 cm²) was put into 20 ml of the MB aqueous solution, and the MB aqueous solution was continuously stirred under the polychromatic irradiation of a high-pressure mercury lamp. The incident radiation power was 37 mW cm⁻². The initial MB aqueous solution contained C₀ = 2.1 mg l⁻¹ of methylene blue trihydrate. The MB concentration during the UV light irradiation (C) was determined by the absorption at 664 nm. The flat band voltage of the ZnO substrate in an electrolyte solution was estimated from photoelectrochemical (PEC) measurements. PEC measurements were performed in a three-electrode cell with the 0.1 M Na₂SO₄ electrolyte solution under xenon lamp irradiation. The PEC measurement system was composed of a potentiostat (Mettler Toledo UMX2), working electrode (sample), counter electrode (Pt plate), reference electrode (Ag/AgCl), and 150 W xenon lamp.

3. Results and discussion

Figure 1 shows AFM images of the ZnO substrate after the water treatment at various temperatures. The water treatment was repeated for one ZnO substrate, and the water treatment temperature was increased from 40 °C to 80 °C. A step and terrace structure with straight step edges was observed on the as-received substrate surface. The root mean square (RMS) roughness of the as-received ZnO was 0.19 nm. The RMS roughness of the ZnO substrate after the water treatment at 40 °C and 50 °C is 0.19 and 0.16 nm, respectively. The surface roughness increased with increasing water treatment temperature above 60 °C. The RMS roughness after the water treatment at 60 °C, 70 °C, and 80 °C was 0.24, 0.37, and 0.32, respectively. Macro steps were observed on the surface after the water treatment at temperatures above 60 °C. Figure 2 shows the mass reduction of the ZnO substrate (0.5 × 0.25 × 0.05 cm³) as a function of time in deionized water at 90 °C. The mass of the ZnO substrate linearly decreased with increasing time. It was found that ZnO is etched by deionized water. When the ZnO substrate is immersed in deionized water at 90 °C, both (0001) Zn-face and (000–1) O-face of the ZnO substrate can be etched by deionized water. It is known that etching rate of ZnO is strongly dependent on the crystalline orientation [16]. Therefore, we could not estimate the etching rate from the mass reduction. Figure 3 shows the O 1 s XPS spectra of the ZnO substrates. The asymmetric peaks were deconvoluted into three components. The main component at ~530.1 eV (O1) is attributed to O–Zn bonds. The smaller components at ~531.3 eV and ~532.3 eV (O₂ and O₃) can be attributed to O²⁻ ions in oxygen- deficient ZnO and adsorbed OH group, respectively. The O2/O1 ratio for the as-received ZnO substrate was 0.39 and that for the ZnO substrate after the water treatment at 90 °C was 0.42. The O3/O1 ratio was also not varied by the water treatment. The water treatment had no significant influence on the oxygen vacancy (V₀) concentration and OH group adsorption.

Figure 4(a) shows typical I-V curves of the Au contacts formed on the as-received ZnO substrate and the ZnO substrate after the water treatment at 40 °C. The Au contacts formed on the as-received ZnO substrate and
ZnO substrate after the water treatment at 40 °C showed Schottky behavior, whereas the Au contacts formed on the ZnO substrate after the water treatment at 90 °C showed ohmic behavior (inset). The forward bias region of the Au contacts was analyzed using the thermionic emission theory. The current density $J$ through a Schottky contact can be described by using

$$
J = A^* T^2 \exp \left\{ - \frac{\Phi_B}{k_B T} \right\} \left\{ \exp \left( \frac{q(V - IR_S)}{nk_B T} \right) - 1 \right\},
$$

where $A^*$ is the effective Richardson constant, $V$ is the applied voltage, $I$ is the current, $R_S$ is the series resistance, $\Phi_B$ is the Schottky barrier height, and $n$ is the ideality factor. The value of $A^*$ for ZnO is 32 A cm$^{-2}$ K$^{-2}$.

Equation (1) was used to determine $\Phi_B$ and $n$ for each Au Schottky contact. The $\Phi_B$ and $n$ values are shown in figure 4(b). The barrier height obtained from I-V curves is known to depend on the ideality factor because of.

Figure 1. AFM images of the ZnO substrate after the water treatment at various temperatures; (a) as-received substrate, (b) 40 °C, (c) 50 °C, (d) 60 °C, (e) 70 °C, and (f) 80 °C.
inhomogeneity of Schottky contacts [17, 18]. To estimate the real Schottky barrier height of laterally homogeneous contacts, the plots was extrapolated to the image force-controlled ideality factor \((n = 1.01)\). The real Schottky barrier height for the Au contacts on the as-received ZnO substrate and the ZnO substrate after the water treatment at 40 °C was 0.85 eV and 0.74 eV, respectively. The real Schottky barrier height was decreased by the water treatment at a low temperature of 40 °C. Schottky barrier height for metal contacts has been reported to be affected by \(V_O\) concentration in ZnO [12, 19]. However, the XPS spectra in figure 3 reveals that the \(V_O\) concentration is not changed by the water treatment. These results indicate that defects which decrease the Schottky barrier height of the Au contacts are formed by the water treatment. We believe that the ohmic behavior is due to high defect concentration after the water treatment at 90 °C.

The ionization potential \(\Phi\) can be estimated by fitting the near threshold region in PES spectra using

\[
\text{Yield} \propto (h\nu - \varphi)^m,
\]

where \(h\nu\) is the photon energy, and \(m\) is the exponent \((m = 3)\) [20, 21]. Figure 5 shows PES spectra obtained from the as-received ZnO substrate and the ZnO substrate after the water treatment at 90 °C. The vertical axis represents the cube root of the photoelectron yield. The photoelectron yield for the as-received ZnO substrate

![Figure 2](image-url) Figure 2. Mass reduction of the ZnO substrate as a function of time in deionized water at 90 °C.

![Figure 3](image-url) Figure 3. XPS spectra of the as-received ZnO substrate and the ZnO substrate after the water treatment at 90 °C.
increased with increasing photon energy above 5 eV. The ionization potential of a semiconductor is defined as the energy between the vacuum level and valence band maximum. Since the bandgap and electron affinity of ZnO are 3.37 eV and ∼4.3 eV, respectively, the threshold energy of about 5 eV is much smaller than the ionization potential of ZnO. Nakano et al. have reported that the photoelectron threshold energy of TiO₂ is attributed to the nitrogen-induced defect levels [22]. The VO level in ZnO is located at 0.5–0.7 eV below the conduction band [23, 24], and the VO level measured from the vacuum level is 4.8–5.0 eV. The threshold energy for the as-received ZnO substrate is consistent with the VO level measured from the vacuum level. It was found that the surface Fermi level in the as-received ZnO substrate is located near the VO level. A similar increase in the photoelectron yield was also observed in the PES spectrum for the ZnO substrate after the water treatment at 90 °C. However, when the water treatment at 90 °C was performed, a higher photoelectron yield was obtained at photon energies ranging from 4.2 to 5 eV. This increase in the photoelectron yield indicates that the surface Fermi level in the ZnO substrate after the water treatment at 90 °C is located just below the conduction band. The ohmic behavior obtained from the Au contacts on the ZnO substrate after the water treatment at 90 °C is attributed to the Fermi level pinning near the conduction band minimum.
The influence of the reaction between water and ZnO on the photocatalytic activity of ZnO was evaluated from MB decomposition in the aqueous solution. The MB decomposition \(\frac{C}{C_0}\) versus UV irradiation time for the as-received ZnO substrates and the ZnO substrates after the water treatment at 90 °C is shown in figure 6. The MB decomposition measurements were performed for six samples including three ZnO substrates after the water treatment. The photocatalytic activity of the samples was almost same. The separation and transfer of photogenerated carriers, which depend on the surface band bending in semiconductors, play an important role in photocatalysis. However, the defects induced by the reaction between water and ZnO had little influence on the photocatalytic activity. Figure 7 shows the PEC measurement result for the ZnO substrate after the water treatment at 90 °C. The current density increased with increasing potential, and it was dropped when the light was off. The photocurrent observed in the PEC measurement is mainly due to minority carriers. As the conduction type of the ZnO substrate was n-type, large photocurrent was observed in the anodic potential region. On the other hand, the current density in the cathodic potential below −0.3 V was negligible small. The current density versus potential in semi-log scale is shown in figure 7(b). We defined the flat band potential as the potential at which the current density reversed the direction. The flat band potential determined from the PEC measurement was 0.27 V. The electron concentration of the ZnO substrate used for the PEC measurement,
which was measured by Hall effect measurements using van der Pauw configuration, was \(8.2 \times 10^{15} \text{ cm}^{-2}\), and the bulk Fermi level was located 0.15 eV below the conduction band. Therefore, the surface Fermi level is estimated to lie about 0.4 eV below the conduction band. The surface Fermi level obtained from the PEC measurement was different from the result of the PES measurement performed in vacuum. We believe that the surface Fermi level of the ZnO substrate is affected by the electrolyte solution. The surface Fermi level pinning at about 0.4 eV below the conduction band could be a reason that the photocatalytic activity is not changed by the water treatment at 90 °C.

4. Conclusion

Influence of the reaction between water and ZnO on the properties of Au Schottky contacts and the photocatalytic activity of ZnO(0001) single crystals has been investigated. The ZnO substrate was etched with deionized water, and its surface roughness increased with increasing water temperature. Although the water treatment had no significant influence on the surface composition of the ZnO substrate, it changed the properties of the Au contacts. The Au contacts on the as-received ZnO substrate and the ZnO substrate after the water treatment at 40 °C had Schottky behavior. However, the Schottky barrier height was decreased from 0.85 eV to 0.74 eV by the water treatment at 40 °C. Moreover, the Au contacts on the ZnO substrate after the water treatment at 90 °C had ohmic behavior. The PES spectra showed that the surface Fermi level in the as-received ZnO substrate was located near the Vo level. On the other hand, the surface Fermi level in the ZnO substrate after the water treatment at 90 °C was located just below the conduction band. However, the photocatalytic activity of the ZnO substrate after the water treatment at 90 °C was almost same as that of the as-received ZnO substrate. The reaction between water and ZnO had no significant influence on the photocatalytic activity of ZnO. The PEC measurement, which was performed in the electrolyte solution, showed that the surface Fermi level of the ZnO substrate after the water treatment at 90 °C was located about 0.4 eV below the conduction band. The surface Fermi level was affected by the electrolyte solution around the ZnO substrate. The surface Fermi level pinning at about 0.4 eV below the conduction band could be a reason that the photocatalytic activity is not changed by the water treatment at 90 °C.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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