

Photoinduced hydroxylation at ZnO surface

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Abstract

We observed UV-stimulated hydroxylation at the surface of ZnO crystals. Reactive defective sites were initially formed in the surface layer via photoreduction induced with energetic photons above the band gap of ZnO. Hydroxyl groups were produced by a chemical reaction of the photoinduced defective sites with water molecules in the atmosphere. Two types of hydroxyl groups were found at the irradiated surface because two kinds of defective sites were induced with the UV illumination.

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Keywords: ZnO; Hydroxylation; Ultraviolet; Photoreduction; Surface

1. Introduction

Photochemistry at the surface of oxide semiconductors such as TiO₂ and ZnO has been studied by many researchers [1–7] because these oxides are practically important materials as a photocatalyst. It is widely known that oxygen ionic species (O⁻, O₂⁻ and O₃⁻) and oxygen atoms are produced from oxygen molecules through photochemical reactions on the surface [1–3]. UV illumination was also found to stimulate desorption of oxygen molecules adsorbed at the surface and grain boundaries of ZnO [4]. These oxygen species are generally associated with the photocatalytic activity. Photoinduced superhydrophilicity is another interesting phenomenon on the metal oxides. Wang et al. [5,6] and Sakai et al. [7] suggested that photoreduction of Ti⁴⁺ to Ti³⁺ at definite sites on the surface of TiO₂ films resulted in the preferential adsorption of hydroxyl groups. Although hydroxylation at the surface of the oxide surface would be essential for the superhydrophilicity, the relationship between photoreduction and hydroxylation and their formation mechanism have not been clarified sufficiently.

We have already reported photoreduction of crystalline and amorphous ZnO films [8,9]. UV illumination with the photon energy above the energy gap resulted

in photodarkening with an increase in the amount of O⁻ ions for amorphous ZnO films. The formation of Zn metal was accompanied with release of oxygen atoms from the Zn–O lattice stimulated by irradiation with energetic photons above 6.7 eV. The photoinduced desorption of oxygen atoms was also observed at the surface of crystalline ZnO films. These changes were basically attributed to cleavage of Zn–O bonds by photoinduced charge transfer from O²⁻ to Zn²⁺ in the distorted states.

In this paper, we directly exhibit photoinduced hydroxylation at the surface of sol–gel-derived ZnO films. The hydroxylation reaction is associated with the formation of highly reactive defective states through photoreduction at the surface of ZnO crystals. We discuss the relationship between the states of the hydroxyl groups and defective sites.

2. Experimental

The preparation procedure of crystalline ZnO films was based on a sol–gel method reported by González et al. [10]. Coating solutions were prepared by hydrolysis of 0.6 M zinc acetate hydrate (Kanto Chemicals) in methanol with addition of the same amount of purified water. Amorphous ZnO gel films were produced by spinning of the precursor solutions on borosilicate glass plates or silicon wafers and subsequent drying in air at 60 °C for 1 h. Crystalline ZnO films were obtained by

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Table 1
Wavelength, photon energy, half width and power of emission light from UV lamps

	Wavelength (nm)	Photon energy (eV)	Half width (nm)	Power (mW cm ⁻²)
Xe ₂ excimer lamp	172	7.21	14	~7 ^a
KrCl excimer lamp	222	5.59	2	~5 ^a

^a The distance between the lamps and a power meter was 50 mm.

heating the dried films at 150 or 400 °C for 1 h in air. The irradiation of UV lights was performed at room temperature using Xe₂ (Ushio UER20H-172) and KrCl (Ushio UER20H-222) excimer lamps in N₂ atmosphere. The distance between the samples and UV sources was 10 mm. The wavelength, photon energy, half width and power of the UV sources are listed in Table 1.

X-ray diffractometry (XRD) was performed with a Rigaku RAD=RC system with Cu K α radiation. Fourier transform infrared (FTIR) absorption was measured in the ambient atmosphere by a BIO RAD FTS-65 spectrometer using ZnO films prepared on a silicon wafer. X-ray photoelectron spectroscopy (XPS) was monitored with a JEOL JPS-9000 spectrometer.

3. Results

Fig. 1 shows XRD patterns for sol–gel-derived ZnO films. Crystalline films of the wurtzite-type ZnO phase were obtained by heating at 150 °C, while as-dried films were amorphous. The crystallinity of these ZnO films was not influenced by irradiation of 5.6 and 7.2 eV photons from KrCl and Xe₂ excimer lamps, respectively. Fig. 2 shows the variation of FTIR absorption due to the stretching mode of O–H bonds for ZnO films irradiated with the UV lights. Whereas the amount of

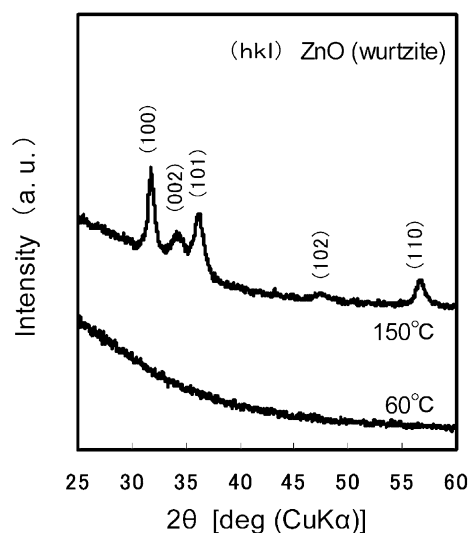


Fig. 1. XRD patterns for sol–gel-derived ZnO films heated at 60 and 150 °C for 1 h.

hydroxyl groups was extremely small on crystalline ZnO films, an absorption band centered at 3450 cm⁻¹ appeared after the 5.6 eV irradiation using a KrF excimer lamp. The irradiation of 7.2 eV photons from a Xe₂ excimer lamp produced a broad absorption, which was decomposed into two Gaussian components centered at 3450 and 3550 cm⁻¹. Interestingly, the intensity of these absorption bands increased upon exposure to the ambient atmosphere in the dark for several days. Since the irradiation experiments were performed in dry N₂ atmosphere, hydroxyl groups giving the infrared absorption bands were produced in the atmosphere after the irradiations.

As shown in Fig. 3, O 1s XPS signals for ZnO films were decomposed into two Gaussian components. A component centered at 529.6 eV (O(II)) was assigned to O²⁻ ions at the hexagonal interstices of Zn²⁺ ion array. Another peak at 531.2 eV (O(I)) was attributable to oxygen in hydroxyl groups or an intermediate state between O²⁻ and dissociated oxygen (O⁻ ions) [11,12]. Fig. 4 illustrates the depth profiles of the intensity of the O(I) and O(II) peaks normalized by the Zn 2s

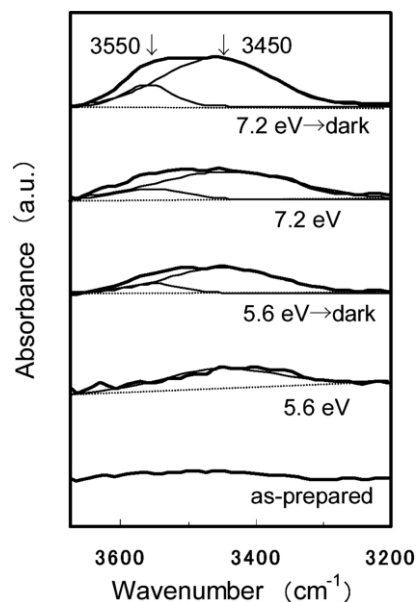


Fig. 2. FTIR absorption spectra of OH-stretching bands of crystalline ZnO films before and after UV irradiation. These films were crystallized at 150 °C. Energy of illuminated photons is indicated in the figure.

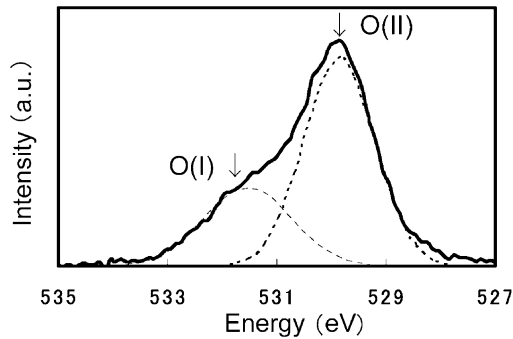


Fig. 3. A typical O 1s XPS spectrum for crystalline ZnO films.

signal for crystalline ZnO films before and after UV irradiation. The variation of the XPS signals was relatively small in the depth profile for unirradiated films. In contrast, a steep increase in the O(I) intensity at the surface was found for ZnO films irradiated with the 5.6 and 7.2 eV photons. It means that a major fraction of hydroxyl groups was formed at the surface of crystalline ZnO films after the irradiations. Although the intensity of O(II) was slightly increased by the 5.6 eV irradiation, the O(II) peak decreased in the shallow region irradiated by the 7.2 eV photons. This result suggests that the release of oxygen atoms from the Zn–O lattice in the surface layer occurred during the high-energy irradiation.

The photoinduced changes in FTIR spectra and XPS signals for ZnO films crystallized at 400 °C were much smaller than those of the films heated at 150 °C. The XRD patterns indicated that the grain size of ZnO crystals in sol–gel films heated at 400 °C was larger than that crystallized at 150 °C. Since the grain growth with increasing heating temperature suppressed the photoinduced changes, it is suggested that the photochemical reactions occurred at the surface of ZnO crystals including the boundary between small grains.

4. Discussion

The results of FTIR absorption and XPS signals indicate that UV irradiation induced hydroxylation at the surface of ZnO crystals although the irradiation experiments were performed in a dry atmosphere. Moreover, the amount of hydroxyl groups at the surface increased upon exposure of the irradiated films to the ambient atmosphere. Thus, it is obvious that the hydroxyl groups were deduced to be formed after the irradiation. We have already observed UV-induced dehydration in ZnO gel films containing a large amount of hydroxyl groups [8]. This observation is apparently reverse to the hydroxylation reported here. On the other hand, we also reported photoreduction of amorphous ZnO induced with energetic photons above the band gap (~ 3.2 eV) [9]. The charge transfer from O^{2-} to Zn^{2+} at distorted sites in amorphous structures caused permanent cleavage of

the Zn–O bonds and formation of oxygen vacancy. Therefore, hydroxylation at the ZnO surface is inferred to be produced by a subsequent reaction of the photoinduced defective sites with atmospheric water molecules. We also observed hydroxylation of the ZnO surface by UV irradiation using a low pressure mercury lamp (4.9 and 6.7 eV) in air. In this case, the formation of hydroxyl groups occurred during the irradiation because the defective sites produced by the irradiation immediately reacted with water molecules surrounding the surface.

The FTIR absorption spectra in Fig. 2 suggested that two types of hydroxyl groups existed at the irradiated surface. The 3550 cm^{-1} band mainly induced by the 7.2 eV irradiation was accompanied with the deficiency of oxygen in the shallow region. We have reported that energetic photons greater than twice the band gap (~ 6.4

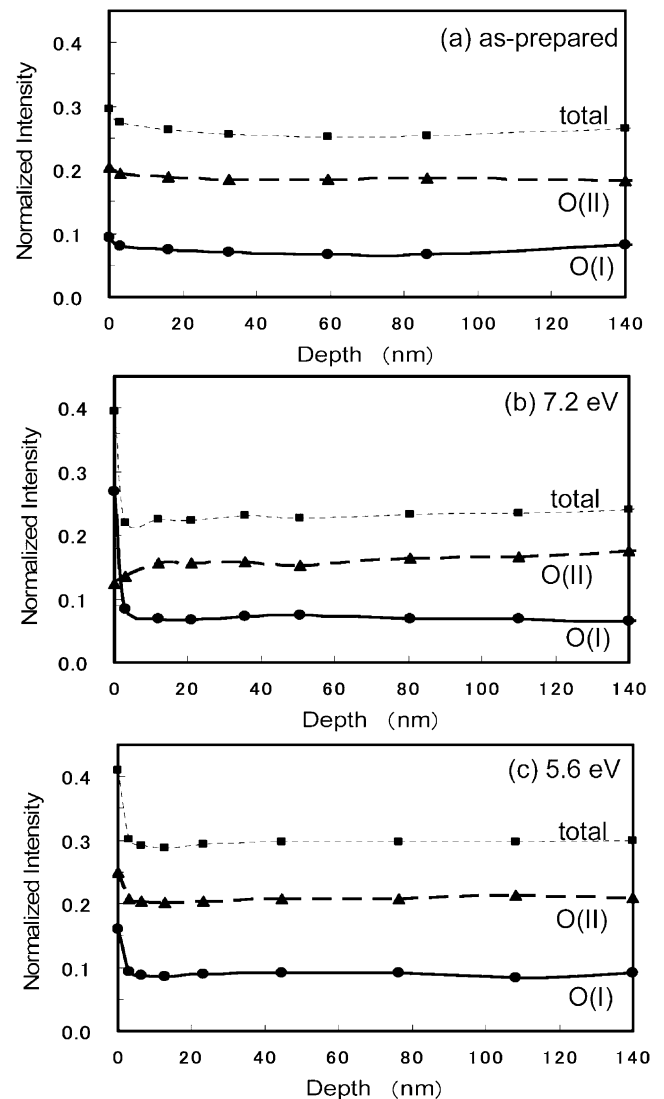


Fig. 4. Depth profiles of the intensity of O(I) and O(II) peaks in O 1s XPS signals for crystalline ZnO films before and after UV irradiation. The intensity was normalized by the Zn 2s peak.

eV) induced release of oxygen atoms and formation of Zn metal in amorphous ZnO via two-electron excitation on a disordered Zn–O network [9]. Although the drastic changes due to photoreduction were not observed in crystalline ZnO, a decrease of the O(II) peak in O 1s XPS signals means that desorption of oxygen also occurred at the surface of the crystals. The formation of hydroxyl groups causing the 3550 cm⁻¹ band is presumed to be ascribed to replacement of the oxygen-deficient site with an hydroxyl group from a water molecule.

Since the 3450 cm⁻¹ band was induced by both 5.6 and 7.2 eV photons, hydroxyl groups causing the absorption band are deduced to be commonly produced by UV irradiation. Photodarkening and an increase of the O(I) intensity in O 1s XPS signals were observed on sol-gel-derived amorphous ZnO films. In this case, defective sites originating from bond cleavage were proposed to be formed through charge transfer from O²⁻ to Zn²⁺ at distorted Zn–O bonds with irradiation of energetic photons above the band gap. The defective sites are highly reactive and easily transformed into hydroxyl groups by hydroxylation with water molecules in air. This reaction would produce a pair of hydroxyl groups as shown by



The FTIR absorption due to a pair of hydroxyl groups shifted into a lower wavenumber because of hydrogen bonding between the hydroxyl groups. These type of defective sites were not always accompanied with the oxygen vacancy. It is supported by the fact that the O(II) intensity at the surface was not decreased by the 5.6 eV irradiation.

5. Summary

Hydroxylation at the surface of ZnO crystals was observed on sol-gel-derived crystalline films by irradiation of UV photons with energy above the band gap.

The formation of hydroxyl groups was attributed to a reaction of atmospheric water molecules with defective sites induced via photoreduction. Two types of hydroxyl groups were produced from two kinds of defective sites associated with oxygen vacancy and bond cleavage.

Acknowledgments

This work was supported by Grant-in-Aid for the 21st Century COE program ‘KEIO Life Conjugate Chemistry’ from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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