

Fabrication of transparent superhydrophobic ZnO thin films by a wet process

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Transparent superhydrophobic ZnO thin films were fabricated on glass substrates by a liquid phase deposition (LPD) method and a surface modification scheme using fluoroalkyltrimethoxysilane (FAS). The hexagonal ZnO rods were perpendicularly grown on glass substrates coated with ZnO seed layers. The diameters of the hexagonal ZnO rods and the thickness of thin films were increased according to the immersion time into an aqueous solution. The structure, surface roughness, transmittance and contact angle of prepared ZnO thin films were measured by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), an atomic force microscope (AFM), a UV-visible spectrophotometer (UV-vis) and contact angle measurements. The XRD pattern of ZnO thin films showed diffraction peaks corresponding to the hexagonal wurtzite-type ZnO structure with an intense XRD peak from the (002) plane. Among the ZnO thin films prepared with different immersion conditions, the ZnO thin film prepared with an immersion time of 10 minutes showed a high transparency above 89% and a superhydrophobic surface property with a water contact angle of approximately 161° after a FAS treatment.

Key words: ZnO thin film, superhydrophobicity, contact angle, transmittance, FAS

Introduction

Superhydrophobic thin films with water contact angles (CA) larger than 150° are used for many applications such as water repellency, prevention of contamination, self-cleaning and antifouling [1-4]. Superhydrophobic thin films are fabricated by creating a rough structure on a substrate and modifying the rough surface by fluorinated or silicon compounds with a low surface free energy [5-7]. Thin films with a rough structure are fabricated using organic or inorganic materials such as polymers, SiO₂ and ZnO [8-11]. To modify a rough surface, fluoroalkyltrimethoxysilane (FAS), CF₃(CF₂)₇CH₂CH₂Si(OCH₃)₃, has been widely used because FAS has a fluoromethyl (-CF₃) group with a very low surface energy (~8 mJ/m²) to modify a solid surface [12-14].

Zinc oxide (ZnO) has been widely investigated as a conductive and nanostructured material because of its typical properties such as a wide band gap (3.2 eV-3.3 eV at room temperature), transparency in the visible range and high-electrochemical stability [15, 16]. Wurtzite zinc oxide (ZnO) thin films have been prepared by various methods such as chemical vapor deposition [17], self-assembly growth [18] and chemical bath deposition [19].

In this study, we fabricated a superhydrophobic ZnO thin films by a wet process and measured the surface morphology, water contact angle, surface roughness and transmittance

of prepared thin films as a function of immersion time into as aqueous solution.

Experimental Details

Zinc acetate dehydrate (Zn(CH₃COO)₂·2H₂O, Wako), monoethanolamine (MEA, Wako) and 2-methoxyethanol (Wako) were mixed to coat the seed layers of ZnO on a glass substrates. This solution was mixed with a molar ratio of zinc acetate dehydrate : monoethanolamine : 2-methoxyethanol = 0.02 : 0.02 : 0.51 at 60 °C for 2 h. Glass substrates were dipped into this solution with a withdrawal speed of 1.0 mm/s and dried at 90 °C for 1 h and then finally heated at 400 °C for 1 h. To fabricate wurtzite-type ZnO thin films, an aqueous solution was synthesized with the molar ratio of zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, Wako) : ammonium chloride (NH₄Cl, Wako) : urea (Co(NH₂)₂, Wako) = 1 : 2 : 1 in 100 ml solution of H₂O and NaOH_(aq) (25%, 5 ml). Glass substrates with ZnO seed layers were immersed into a solution at 90 °C for 1.0 h-2.5 h and rinsed with H₂O. The prepared ZnO thin films with rough surfaces were immersed into 2.0 wt.% of fluoroalkyltrimethoxysilane (FAS) in hexane for 20 minutes to fabricate superhydrophobic ZnO thin films.

The glass substrates were ultrasonically agitated in a KOH solution (1.0 wt.%) mixed with water and ethanol (2 : 3 in volume ratio) for 5 minutes and then, rinsed in pure water.

The structural analysis of ZnO thin films was made by an X-ray diffraction (XRD, KFX-987228-SE, Mac Science) with CuKα radiation (40 kV, 30 mA). The transmittance of thin films was measured using a UV-visible spectrophotometer (UV-vis, V-570, Jasco). The microstructure and

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thickness of thin films were measured by field emission scanning electron microscopy (FE-SEM, JSM6700F, JEOL, Japan). Root mean square (RMS) surface roughness was observed using an atomic force microscope (AFM, JSPM5200, JEOL, Japan). The wettability of thin films was characterized by the measurement of water contact angles on their surfaces (FM 40, KRUS Gmbh Germany). The volume of the distilled water droplet was 10 μ l to measure the contact angle.

Results and Discussion

Fig. 1 shows the XRD pattern of a ZnO thin film fabricated by immersing into an aqueous solution for 2.5 h on a glass substrate coated with a seed layer. The XRD pattern showed diffraction peaks corresponding to the hexagonal wurtzite-type ZnO structure with an intense XRD peak from the (002) plane. This fact indicates that the prepared thin film is preferentially oriented along the c-axis to the film plane [11]. Fig. 2 presents the microstructures of hexagonal ZnO rods with a perpendicular growth as a function of immersion time into an aqueous solution. As the immersion time increased, the diameters of ZnO rods increased from approximately 50 nm to approximately 300 nm. Otherwise, hexagonal ZnO rods were randomly oriented over the glass surface in the case without a ZnO seed layer [11]. The cross-sectional images of ZnO thin films as a function of an immersion time are shown in Fig. 3. The thicknesses of ZnO thin films deposited for 1.0, 1.5, 2.0 and 2.5 h were 0.225, 1.434, 2.250 and 3.010 μ m, respectively. As the immersion time increased, the thicknesses of ZnO thin

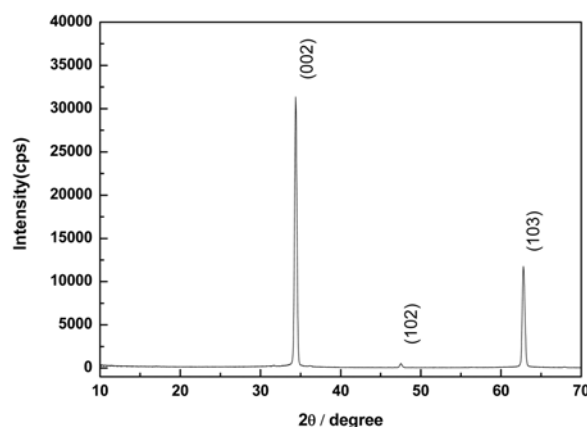


Fig. 1. XRD pattern of ZnO thin film fabricated by immersing a glass substrate with a seed layer into an aqueous solution for 2.5 h.

films were gradually increased. Fig. 4 shows the AFM images of ZnO thin films as a function of an immersion time. The RMS roughnesses of ZnO thin films deposited with immersion times of 1.0, 1.5, 2.0 and 2.5 h were measured to be approximately 151.3, 155.1, 86.8 and 108.6 nm, respectively. ZnO thin films with rod diameters of 50–150 nm showed a relatively high RMS roughness. The transmittance of prepared ZnO thin films is shown in Fig. 5. The ZnO thin film with an immersion time of 10 minutes showed a high transmittance above 89% in the visible light region but UV light was remarkably cut by the ZnO thin films. The surface modification of ZnO thin films with a high roughness was carried out by the hydrophobic treatment using FAS. Fig. 6 shows images

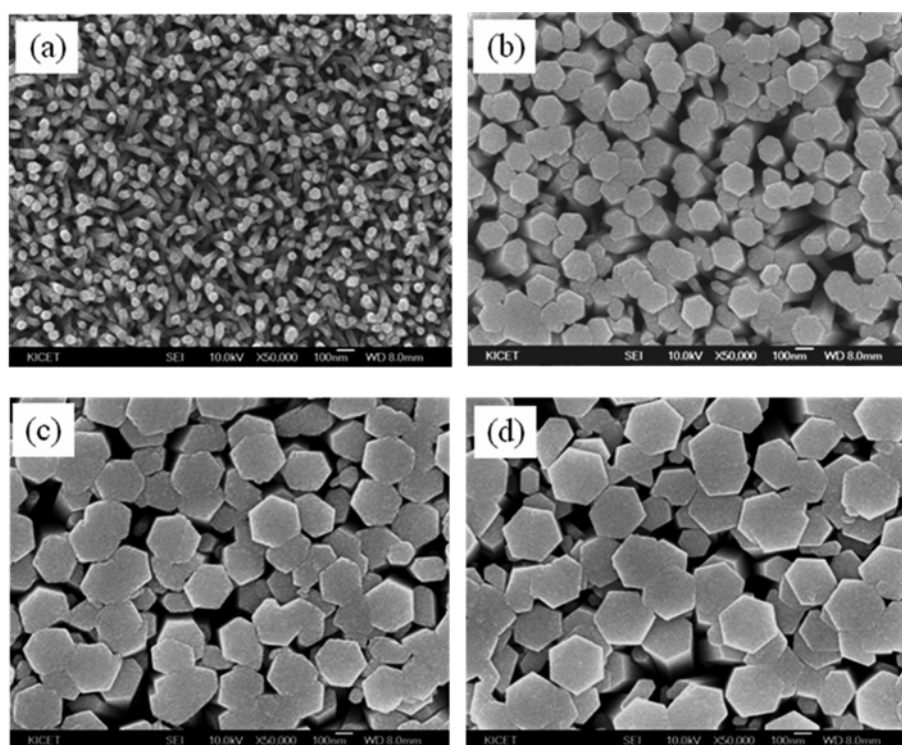


Fig. 2. FE-SEM images of ZnO thin films as a function of immersion time into an aqueous solution: (a) 1.0 h, (b) 1.5 h, (c) 2.0 h, (d) 2.5 h.

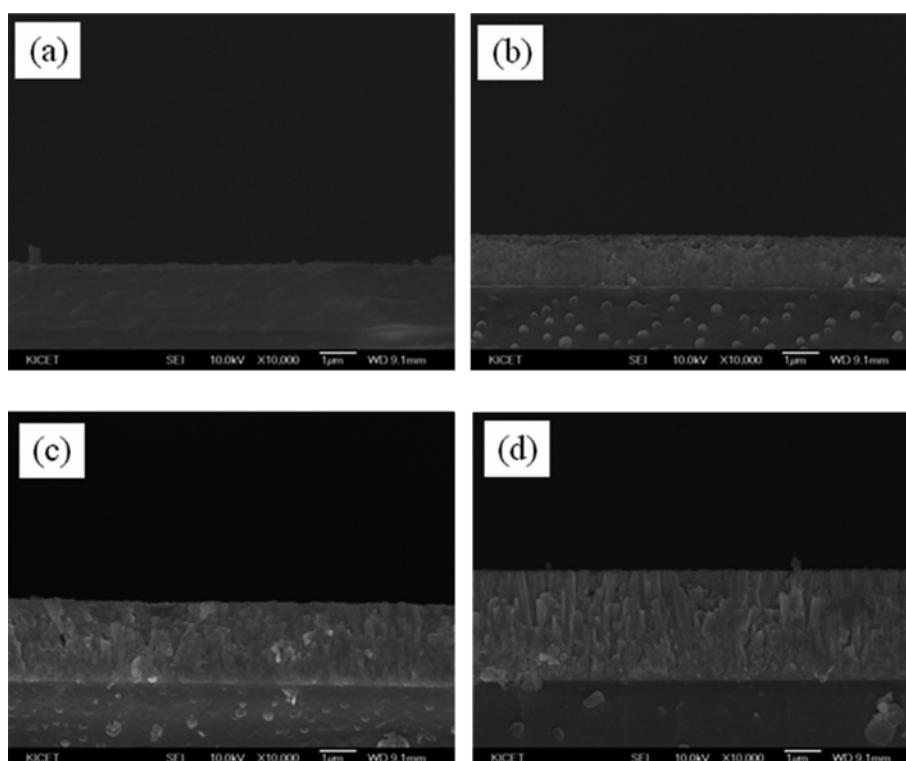


Fig. 3. Cross-sectional images of ZnO thin films as a function of immersion time into an aqueous solution: (a) 1.0 h, (b) 1.5 h, (c) 2.0 h, (d) 2.5 h.

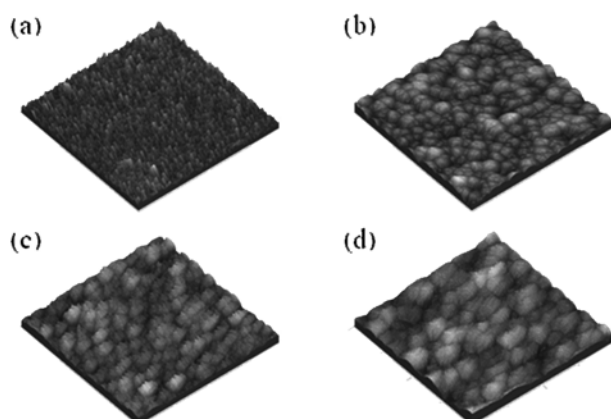


Fig. 4. AFM images of ZnO thin films as a function of immersion time into an aqueous solution: (a) 1.0 h, (b) 1.5 h, (c) 2.0 h, (d) 2.5 h.

of water droplets on the surface of ZnO thin films with high water contact angles. Among the prepared ZnO thin films, the ZnO thin films fabricated with immersion times of 1.0 or 1.5 h showed a superhydrophobic surface. The RMS roughness, contact angle and transmittance properties of ZnO thin films with different immersion times are summarized in Table 1. From these results, it was found that the ZnO thin films prepared with rough surfaces showed hydrophobic or superhydrophobic properties and in particular, the ZnO thin film prepared with an immersion time of 10 minutes showed a transparent superhydrophobic thin film with a water contact angle of approximately 161° after a FAS treatment. As the immersion time increased, the transmittance of prepared ZnO thin films decreased with

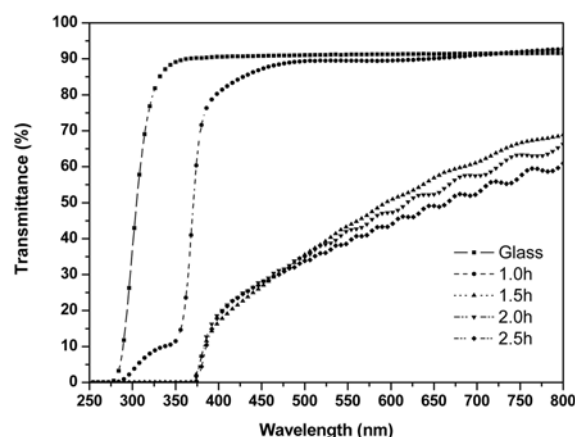


Fig. 5. Transmittance spectra of ZnO thin films as a function of immersion time into an aqueous solution.

the increase of film thickness.

Conclusions

Hydrophobic or superhydrophobic ZnO thin films were fabricated by a wet process using an aqueous solution at 90°C . Hexagonal ZnO rods were grown perpendicularly on the glass surfaces with ZnO seed layers as a function of the immersion time. Wurtzite-type ZnO thin films showed an intense XRD diffraction peak from the (002) plane. As the immersion time increased from 1.0 h to 2.5 h, the diameters of ZnO rods increased from approximately 50 nm to 300 nm. ZnO thin films with a high RMS roughness above approximately 150 nm were fabricated by immersing glass

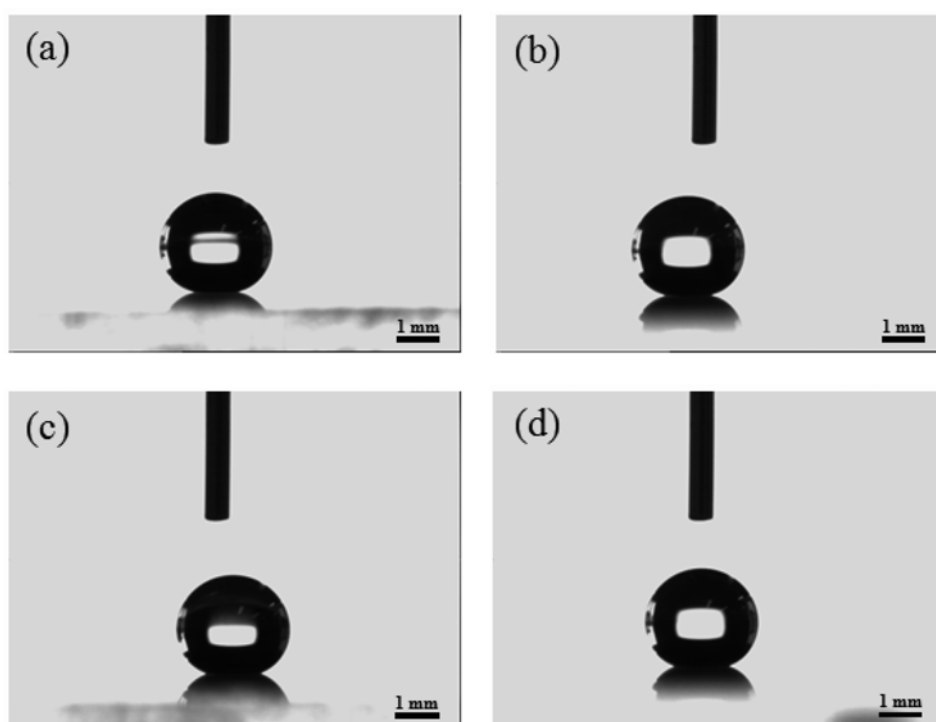


Fig. 6. Photographs of water droplets on the surface of ZnO thin films as a function of immersion time into an aqueous solution: (a) 1.0 h, (b) 1.5 h, (c) 2.0 h, (d) 2.5 h.

Table 1. The surface and optical properties of ZnO thin films as a function of immersion time into an aqueous solution

Immersion time	RMS roughness (nm)	Contact angle (degree)	Transmittance at 550 nm (%)
1.0 h	151.3	161	89.5
1.5 h	155.1	158	43.5
2.0 h	86.8	145	42.3
2.5 h	108.6	148	38.9

substrates into an aqueous solution for 1.0 or 1.5 h and these films showed superhydrophobic properties after the modification of the ZnO surface using FAS. Among ZnO thin films fabricated with different immersion times, a transparent superhydrophobic ZnO thin film was fabricated by immersing into an aqueous solution for 10 minutes. This film would be useful for applications requiring a high transmittance such as a self-cleaning window, water-repellent glass for automobiles and a solar cell cover glass.

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