Epitaxial Growth of Wurtzite ZnO Crystals in an Aqueous Solution System

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Vertical and in-plane crystallographic orientation of ZnO rods was preferentially achieved through epitaxial growth on a Zn-face single-crystalline ZnO(001) substrate in an aqueous solution of $ZnSO_4$ under basic conditions at 60 °C.

Wurtzite-type zinc oxide (ZnO) is an attractive material because of its excellent properties, such as optical transparency, conductivity, piezoelectricity, and near-UV emission. The arrays of ZnO nanorods and nanocolumns have been prepared on substrates using vapor- and liquid-phase routes to produce thin films consisting of oriented ZnO crystals. Epitaxial growth, which is generally required for the exact control of the crystallographic orientation in the films, has been performed on sapphire,[1] gallium nitride (GaN),[2] and single-crystalline ZnO,[3,4] using physical vapor deposition techniques. In recent years, solution processing[5–12] has been developed for the fabrication of crystalline ZnO films because of their advantages, such as low cost, low energy consumption, and the ease of large-scale production. Wurtzite ZnO rods with a *c* axis normal to the surface were grown on polycrystalline ZnO in various solution systems at a low temperature.[5,8,9] In these cases, however, the *c*-axis orientation was achieved through geometric selection, and the in-plane orientation of the crystals in the films was not ordered. On the other hand, the epitaxial growth in the solution systems would be more difficult than that in the vapor phase since the existence of water molecules and various ions adsorbed on the surface prevents the ordered assembly of the ZnO lattice. Whereas the epitaxial growth of hexagonal ZnO rods was performed on a GaN single crystal by electrodeposition,[11] the electrochemical reaction on a conductive surface was required for the ordered growth. Highly *c*-axis-oriented ZnO rods were fabricated on silver films from an aqueous solution containing zinc nitrate and sodium citrate.[12] However, the detailed conditions of the epitaxial growth in the solution systems have not been clarified. The realization of homoepitaxial growth of ZnO crystals on a single-crystalline ZnO substrate in an aqueous solution is a meaningful challenge for understanding the epitaxial growth mechanism in the solution and the development of wet chemical processes for functional oxide materials. This letter describes a successful approach for the homoepitaxial growth of ZnO crystals and the face dependence of the growth mode in an aqueous solution system.

A stock solution containing 0.01 mol/dm^3 zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$, 99.5%; Kanto Chemical) as a zinc source and 0.2 mol/dm^3 ammonium chloride (NH_4Cl; Junsei Chemical) as a complexing agent was adjusted to pH 9.50 by the addition of 5 mol/dm^3 sodium hydroxide aqueous solution.[8] One-side mirror-polished (Zn- and O-face) single-crystalline ZnO(001) wafers (Earth Chemical) and a glass slide coated with a polycrystalline ZnO thin film[8] were used as substrates. The

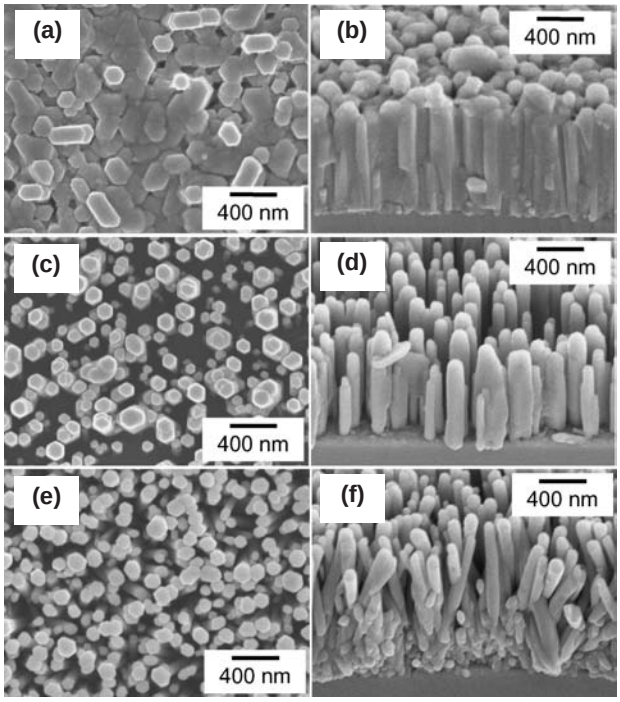

Figure 1. SEM images of ZnO rods grown on a Zn-face ZnO(001) substrate (a and b), an O-face substrate (c and d), and a polycrystalline ZnO film (e and f).

ZnO crystals were prepared by immersing the substrates into the stock solution in a sealed glass tube at 60 °C for 12 h. After the reaction, the substrates were withdrawn from the solution, rinsed with purified water, and dried at room temperature. X-ray diffractometery (XRD) was performed with a Rigaku RAD-C in a $2\theta/\theta$ configuration using Cu Kα radiation. Morphologies and detailed structures of the crystals grown on the substrates were observed with a Hitachi S-4700 field emission scanning electron microscope (SEM) and a Philips TECNAI F20 field emission transmission electron microscope (TEM).

Figure 1 shows typical SEM images of rod-shaped crystals grown on a Zn-face ZnO(001) substrate, an O-face ZnO(001) substrate, and a polycrystalline ZnO film. A lattice image with a spacing of 0.26 nm for the ZnO(002) plane (Figure 2) indicates that the rods were wurtzite-type ZnO crystals elongated along the *c* axis. Therefore, upright hexagonal ZnO rods with a height of ca. 1 μm and a diameter of 60–350 nm were grown on the single-crystalline ZnO(001) substrates. In contrast, the orientation of the crystal growth on the polycrystalline substrate was random near the surface, whereas the rods were roughly aligned at the top of the films. The presence of an intense peak due to (103) and weak signals assignable to (101), (102), and (112) of the wurtzite structure in the XRD pattern suggests the disorder

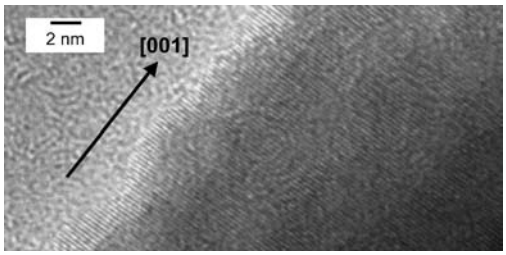

Figure 2. A lattice image of a ZnO rod. The spacing with a value of 0.26 nm was consistent with the (002) plane of wurtzite ZnO structure. The rods grew in the *c*-axis direction.

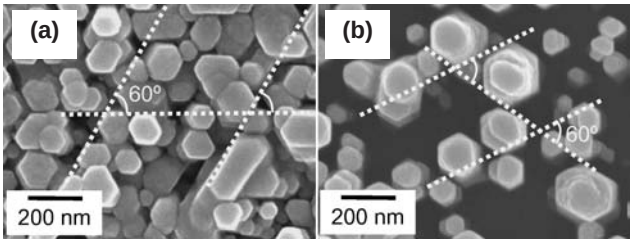

Figure 3. (a) Enlarged SEM images of the top of ZnO rods grown on (a) a Zn-face ZnO and (b) an O-face ZnO substrate. As marked with dotted lines, hexagonal ZnO rods were oriented in the same direction.

of the crystallographic orientation near the polycrystalline substrate (see Figure S1 in Supporting Information). The deficient crystallographic arrangement was achieved through the geometrical selection.[13] On the other hand, the *c* axis of the ZnO rods was perfectly vertical to the (001) face of the single crystals because only the (002) reflection was observed.

As shown in Figure 3, the sixfold facets (e.g. (100) face) of individual rods were well oriented in the same directions on the (001) planes of single-crystalline ZnO substrates. This means that in-plane alignment of ZnO crystals was achieved on the substrates. Therefore, the epitaxial growth of wurtzite ZnO crystals was successfully performed on a mirror-polished single-crystalline ZnO wafer in this solution system under a basic condition. The fresh surface prepared by mechanical and mechanochemical polishing would be important for the specific growth mode. However, the density of the ZnO rods depended on the chemical structure and the polarity of the ZnO surface. Although a dense film consisting of oriented grains was obtained on the Zn-face substrate, hexagonal rods grew sparsely on the O-face one, as shown in Figures 1 and 3. Thus, the chemical structure of the Zn-face would be suitable for the ordered assembly of the ZnO lattice from the soluble precursor, $Zn(OH)_2$, in the solution system at pH 9.50.[8]

The amount of adsorbed water layers on the O-face was estimated to be greater than that on the Zn-face on the basis of an atomic force microscopic characterization.[14] In previous trials, epitaxial growth was observed on a GaN layer[11] and a silver film.[12] Consequently, the presence of a less interactive surface with water molecules is required for the epitaxy of wurtzite ZnO crystals. In an ultrahigh vacuum, a flat surface of ZnO crystal was epitaxially produced on a Zn-face substrate through the two-dimensional growth mode using a molecular beam epitaxy (MBE) method.[3] On the other hand, only hexagonal grains were grown in an aqueous solution through the spiral step-flow mode even on an atomically flat Zn-face substrate owing to the coverage with water molecules.

In conclusion, homoepitaxial growth of upright ZnO rods was successfully achieved in a simple aqueous solution system. Oriented films of densely packed columnar ZnO crystals were fabricated on a mirror-polished Zn-face on a single-crystalline ZnO(001) substrate. The chemical structure of the surface of a substrate is essential for the ordered growth of oxide crystals in aqueous systems.

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