Dendritic Side-Branching Observed on ZnO Epitaxial Whiskers

Hidetoshi SAITOH, Minoru SATOH and Shigeo OHSHIO

Department of Chemistry, Nagaoka University of Technology, 1603-1, Kamitomioka, Nagaoka-shi, Niigata 940-2188

Several common modes of crystal growth provide particularly simple and elegant examples of spontaneous pattern formation in not only nature but also artificial circumstance. ZnO whiskers epitaxially grown using a chemical vapor deposition technique often show remarkable secondary growth. This growth develops the elegant side-branch on the edge of the hexagonal columnar structure.

Key-words: ZnO, Dendrite, Whisker, CVD, SEM

1. Introduction

We already reported the formation of highly oriented ZnO whiskers formed on (0001) sapphire single crystal by an atmospheric chemical-vapor deposition (CVD) technique with zinc 2,4-pentanedionate, Zn(C_{5}H_{7}O_{2})_{2}.\(^{1,2}\) The experimental ZnO whiskers of micrometer scale grow from the atomically flat surface of the single crystal. Therefore, all whiskers are perpendicularly oriented to the substrate. The whiskers have the following features: (1) the length and shape of the whiskers are almost uniform throughout the structure; (2) the growth rate of the whiskers remains constant with time; and (3) the epitaxial relationship between the whiskers and the substrate is determined to be ZnO [10\overline{1}0] (0001)//sapphire [12\overline{1}0] (0001). The structure of epitaxially grown whiskers may offer many possibilities for application in the fields of electronic and optical technologies.

A CVD apparatus we used in this study is fundamentally thermal CVD. This apparatus has a major advantage that the epitaxial growth of metal oxides at a high rate is possible. We have previously reported the epitaxy of the ZnO whiskers on single crystalline (0001) sapphire substrates with various growth rates.\(^{2,3}\) Recently, extraordinary growth of the ZnO whisker was seen near the edge region of the substrate. These whiskers show remarkable secondary growth. This growth develops the elegant side-branch on the edge of the hexagonal columnar structure. In this communication, the growth mechanism of the ZnO whisker was discussed using morphology of the secondary growth.

2. Experimental

The single crystalline (0001) sapphire substrates were obtained from Dowa Co., and polished with a mis-cut value of within 0.1°. The substrate was cut into a size of 5 × 5 × 0.5 mm\(^{3}\) and then ultrasonically cleaned sequentially with trichloroethane, acetone, and methanol. After treatment, the single crystal was washed with deionized water for 30 min. The ZnO whiskers were prepared using an air-opened atmospheric CVD apparatus that was previously employed in obtaining epitaxial anatase films,\(^{5,6}\) with titanium tetra-isopropoxide as the source complex. The reactant, Zn(C\_{5}H\_{7}O\_{2})\_{2} (Soekawa Chemical Co., quoted purity of 99.9\%), was loaded into a vaporizer and vaporized using an electric heater. The inside temperature of the vaporizer measured using a K-type thermocouple is defined as the vaporizing temperature. The reactant vapor, Zn(C\_{5}H\_{7}O\_{2})\_{2}, was immediately decomposed by the heat from the substrate heater to form whiskers. The whiskers grow uniformly under the slit at an area of 40 × 20 mm\(^{2}\). However, the sapphire substrate was located out of this area in this study. The deposition duration of ZnO was maintained for 500 minutes using a metallic shutter placed below the nozzle. The substrate and vaporizer were heated to 550 and 115°C using the electric heater, respectively. The distance between the nozzle and the substrate was maintained at 15 mm throughout the experiments. The surface morphology of the whiskers was observed by scanning electron microscopy (SEM; using JSM T–300, JEOL).

Figure 1 shows an SEM image of the specimen after deposition. The edge direction of each crystallite was completely aligned. The diameter of the crystallites is divided

Fig. 1. SEM image of the specimen after deposition.
into two sizes, 1 μm with point image and 60 μm with star-like image. The extraordinary growth of the ZnO whisker was seen near the edge region of the substrate. The precursors needed to grow the whisker are formed by hydrolysis with water in air. At the edge of the substrate, more amounts of water promote the growth of the ZnO whisker. As shown in Fig. 2, these crystallites were whisker with the growth rates of 7 and 150 nm/s for small and large crystallites, respectively. This implies that atmospheric air is needed for high-rate growth of the ZnO crystal. The number density of small crystals was reduced around the large whiskers, suggesting that the precursors in the gas phase were preferentially consumed by the star-like whiskers. However, the nucleation density on the substrate was uniform at the initial stage of the crystal growth. Figures 3 (a) and (b) indicate the enlarged SEM images of the star-like whisker that possesses the side-branching with holds six-fold symmetry. The whisker growth develops the elegant side-branch structure on the edge of the hexagonal column.

Three growth mechanisms have been mainly proposed to understand steady-state growth of the whisker with the dendrite structure: VSL process, Frank mechanism and Kossel mechanism. Morphology of ZnO whiskers is compared with the peculiar morphologies observed on each growth mechanism. Then, the optimum growth mechanism will be determined.

For the VLS process, the liquid phase is a preferred site for deposition of feed from the vapor that causes the liquid to become supersaturated. Crystal growth occurs by precipitation from the supersaturated liquid at the liquid-solid interface. Therefore, a morphological characteristic of the VLS whisker is that there is a spherical lump, formed by solidification of liquid phase, on the tip of the whisker after cooling. However, the whiskers obtained in this study have the sharp tip but no spherical topping, suggesting that the VLS growth mechanism is not dominant in this study.

Next, the Frank mechanism is examined. For the Frank mechanism, high-density steps mainly capture a large number of precursors supplied form the vapor phase. These steps promote anisotropic growth of the crystal. Continuous step supplying mechanism is required for prevention of lack of the step density or disappear of steps, resulting to continue anisotropic growth preferentially. For this mechanism, a screw dislocation or spiral stacking of the crystal planes is necessary. If the whisker growth occurs according to the Frank mechanism, the screw steps should be observed on the surface of the growth front. However, the microphotograph displayed no evidence of the presence of the screw steps. These facts suggest that the Frank mechanism is not the candidate for the whisker growth mechanism in this

Fig. 2. SEM images of the (a) small whiskers with a growth rate of 7 nm/s and (b) large whisker with a growth rate of 150 nm/s. Bar represents 1 μm.

Fig. 3. Enlarged SEM images of the star-like whisker that holds six-fold symmetry: (a) whole image and (b) side-branching. Bars represent 10 and 1 μm, respectively.
study.

Finally, the Kossel mechanism is also examined. For the Kossel mechanism,\textsuperscript{6) }kinked faces mainly absorb a large number of precursors supplied from the vapor phase. These kinks also promote anisotropic growth of the crystal. In this mechanism, continuous kink supplying mechanism is required for prevention of lack of the kink density or disappearance of kinks, resulting in continuous anisotropic growth preferentially. If the whisker growth occurs according to the Kossel mechanism, extremely high supersaturating condition is necessary to generate high-density kinks. The air-opened atmospheric CVD technique is the one of the strong methods in obtaining extremely large degree of supersaturation under constant condition of the total gas pressure. Therefore, the Kossel mechanism is one of the strong candidates for the mechanism of the extraordinary growth of the whisker and side-branch.

4. Conclusion

ZnO whiskers were prepared on the single crystalline (0001) sapphire substrates using the air-opened atmospheric CVD apparatus. The extraordinary growth of the star-like whiskers was observed. The Kossel mechanism is one of the strong candidates for the mechanism of the star-like whisker growth.

Acknowledgment
This work was supported by the Grant-in-Aid for Scientific Research (B) from the Ministry of Education, Culture, Sports, Science and Technology, under contract No. 11450247.

References