Homogeneous Growth of Aggregation of Al : ZnO Whiskers by Scanning Chemical-Vapor Deposition

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走査型化学気相析出法による Al : ZnO ウイスカー群の均一合成
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Interests in the use of conductive whiskers for development of large-area cold emitters require fabrication of well-organized aluminum-doped zinc oxide (Al:ZnO) whiskers with uniform length and growth axis aligned in the out-of-plane direction of the substrate. In this study, a chemical-vapor deposition apparatus with a scanning nozzle, operating under atmospheric pressure was employed to achieve homogeneous growth of aggregation of Al:ZnO whiskers. The 0.5 x 50 mm² slit-type nozzle was designed and scanned on single crystalline substrates of (100) silicon for 7.5 h. Homogeneous Al:ZnO whiskers were grown on the substrate with an area of 50 x 50 mm².

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1. Introduction

A chemical-vapor deposition (CVD) technique under atmospheric pressure was developed for growth of metal oxide amorphous and crystalline structures formed by ZnO,1–3) aluminum-doped ZnO (Al:ZnO),4) yttria-based phosphor,5) MgO6) and TiO2.7)–9) Our CVD setup is fundamentally a thermal CVD type. However this setup enables the design of microarchitectures of metal oxide crystallites, epitaxy and non-epitaxy processes with high growth rate, and operation without a vacuum system.

The CVD technique operated under atmospheric pressure uses β-diketone or metal-alkoxides as the source material. For example, when Zn 2.4-pentanedionate was used as the source, ZnO homogenous polycrystalline films and ZnO whiskers grow on the solid-state substrate at low and high supersaturating conditions of the precursor, respectively. On the substrate of single crystalline Si, the whiskers grow nearly normal to the substrate within a deviation of ±5°. On the other hand, on the substrate of single crystalline (0001) sapphire, the whiskers grow epitaxially.10) As the epitaxial relationship is ZnO [110] || (0001) || sapphire [101] || (0001), the ZnO whiskers crowd together and align to ⟨0001⟩ direction. The conductive whiskers of Al:ZnO, are also obtained with a combination of Al- and Zn-complexes.2)

Our research group develops the ceramic field emitter formed by the electrically conductive whisker with combination of two features: sharp tip and amorphous carbon and related coating with relatively low-work function,11)–14) For example, a performance of the diode display operated by the cold emitter formed from the Al:ZnO whiskers coated with amorphous hydrogenated carbon nitride (α-CN₃H; C₃N₃H) films was reported. The europium-doped yttria (Eu:Y₂O₃) phosphor film was excited by the field emitted electrons at an operating voltage of ~600 V. Very strong luminescence was observed entirely the area in which the red phosphor film was deposited.

Although the cold emitter needs the large-area whisker aggregation, fixed slit-type nozzle, with an opening of 0.5 x 25 mm², settled on our CVD apparatus fabricates small-area whisker aggregation up to 8 x 15 mm². In this experiment, we designed and operated a new type of scanning slit-type nozzle to achieve homogeneous growth of the aggregation of the Al:ZnO whiskers to use the ceramic cold emitter. The performance of the scanning CVD apparatus will be described.

2. Experimental

Figure 1 shows a schematic diagram of the CVD apparatus with a scanning nozzle, operated under atmospheric pressure. The reactants, 8 g of Zn(C₅H₅O₂)₂ (Soekawa Chemical Co., quoted purity of 99.9%) and 2 g of Al(C₃H₅O₂)₃ (Soekawa Chemical Co., quoted purity of 99.9%), were loaded into two vaporizers and vaporized at 115 and 80°C, respectively. The inside temperature of the vaporizer measured using a K-type thermocouple is defined as the vaporizing temperature. The reactant vapor was first carried by nitrogen gas flowing at a total rate of 3.5 dm³/min and then sprayed from the slit-type nozzle directly onto the n-type silicon (Shin-Etsu Semiconductor Co., resistivity of 2.00–50.0 Ω·cm) substrate mounted on the electric heat-

Fig. 1. Schematic diagram of the CVD apparatus with the scanning nozzle, operated under atmospheric pressure.
er. The nozzle has a slit sized of $0.5 \times 50$ mm$^2$, and supplies
the precursors to the area $50 \times 50$ mm$^2$ with a scan speed of
10 mm/min. The substrate was heated to 550$^\circ$C using the
electric heater. The surface temperature measured using
the $K$-type thermocouple is defined as the substrate tempera-
ture. The reactants, $\text{Zn(C}_2\text{H}_4\text{O}_2)_2$ and $\text{Al(C}_2\text{H}_4\text{O}_2)_3$, were
immediately decomposed by the heat from the substrate heater
to form whiskers. The distance between the nozzle and
the substrate was maintained at 15 mm throughout the
experiments. Deposition duration was fixed at 7.5 h.

Figure 2 indicates a measuring map for evaluation of
homogeneous growth of aggregation of Al:ZnO whiskers.
The silicon substrate with an area of $50 \times 50$ mm$^2$ was divid-
ed into four parts. At 40 measurement points, cross-section-
al morphology, X-ray diffraction (XRD) and Al concentra-
tion of the Al:ZnO whiskers were evaluated. XRD analysis
(using M03XHF, Mac Science Co.) was performed to re-
veal the crystal structure and the growth direction. The
cross-sectional morphology of the whiskers was observed by
field-emission scanning electron microscopy (FE-SEM; using
JSM 6700F, JEOL). The metal composition of the sam-
ple was determined using inductive coupled plasma-atomic
emission spectroscopy (ICP-AES) with a spectrometer,
SPS-400, Seiko Instruments Co.

3. Results and discussion

Figure 3 indicates a series of SEM micrographs of the
cross-sectional image of the aggregation of the Al:ZnO
whiskers grown on the substrate. The series from #1 to #20
is in order of the position from the edge of the substrate to
the center along to the nozzle slit. At the point #1, whisker
image is recognized. However, the length and the diameter
of the whisker are small. At the points #3 and higher, clear
whisker images were obtained. The micrographs showed
achieving homogeneous growth of the aggregation of the
Al:ZnO whiskers. The length and the diameter of the
whisker are almost unchanged with the observation pos-
tion. As the edge of the substrate corresponds to the posi-
tion of the end of the slit, supplying amount of the precursor
might be less than that at the slit center. It has been already
clear that (1) the fixed slit nozzle with an opening of $0.5 \times
50$ mm$^2$ offers the plateau of the growth rate: 8 mm in per-
pendicular to slit and 25 mm along slit and (2) the growth
rate of the whisker over the plateau is suddenly decreased to
the half of the rate at the slit center. Therefore, the results
as shown in Fig. 3 are explained as the supplying rate of
the precursor. The length of the whiskers was summarized in
Fig. 4. There is a plateau between 10 mm and 35 mm,
showing the length of 21–23 $\mu$m. At out of this region, the
length was suddenly decreased to the half of the length at
the plateau. At any point on the substrate, the precursor is
supplied for approximately 1 min for one scan, calculated by
a combination of the plateau width of 8 mm of the fixed slit
and the scan speed of 10 mm/min. As one scan interval is
5 min, accumulated total growth duration at any point is 90
min for 7.5 h scan. This corresponds to the growth rate of
4 nm/s, which is similar to the growth rate of the whisker
obtained by the fixed slit.9 The whisker diameter was also
summarized in Fig. 5. The diameter distribution is in the
range of 1.8–3.3 $\mu$m, and homogeneous at the center region.

Figure 6 also demonstrates a series of SEM micrographs
of the cross-sectional image of the aggregation of the Al:
ZnO whiskers grown on the substrate. The series from #21 to #40 is in order of the position from the edge of the substrate to the center along the direction perpendicular to the nozzle slit. At the point #21, no clear whisker image is recognized. The length and the diameter of the whisker are small at the positions from #23 to #26. At the points #29 and higher, clear whisker images were obtained. The micrographs showed achieving homogeneous growth of the aggregation of the Al:ZnO whiskers near the center. The edge of the substrate corresponds to the position of the end of slit scanning. The length of the whiskers was summarized in Fig. 7. There is a plateau between 15 mm and 35 mm, showing the length of 21–23 μm. At out of this region, the length was suddenly decreased. Figure 8 indicates the whisker diameter distribution showing the range of 1.0–3.3 μm, and homogeneous at the center region. Figure 9 demonstrates the SEM image of the structure of the Al:ZnO whiskers: (a) enlarged side view and (b) top view. The number of density of the whisker has reached $1 \times 10^5$ mm$^{-2}$. The whisker lengths are within $20 \pm 5$ μm.

Figure 10 demonstrates the distribution of the full width at half maximum (FWHM) value of the Rocking curve of the ZnO (0002) XRD line. The silicon substrate was divided into 9 pieces. The FWHM value is in the range of 1.8°–2.9°, which is smaller than that obtained using fixed slit nozzle. All whiskers were grown perpendicularly to the substrate. This is strong advantage for application of the whisker to the cold emitter array. Figure 11 demonstrates the distribution of the aluminum concentration of the Al:ZnO whiskers. The distribution was obtained from the ICP-AES data determined using the sample divided into 9 pieces for XRD experiment. The aluminum concentration is in the range of 0.80–0.86 at.%. All whiskers possessed optimum concentration to maintain enough conduction to emit the electrons. This is also strong advantage for application of the whisker to the cold emitter array.

4. Conclusion

We designed and operated the new type of scanning slit-type nozzle to achieve homogeneous growth of the aggregation of the Al:ZnO whiskers to use the ceramic cold emitter. On the silicon substrate with a size of 50 × 50 mm$^2$, a plateau region showing homogeneous distribution of length, di-
Fig. 9. SEM image of the Al:ZnO whiskers: (a) enlarged side view (b) top view.

Fig. 10. Distribution of the FWHM value of the Rocking curve of the ZnO (0002) XRD line.

Fig. 11. Distribution of the aluminum concentration of the Al:ZnO whiskers.

ameter, inclination deviation and aluminum concentration exists. These results suggest the advantage for application of the whisker obtained using scanning CVD to the cold emitter array.

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Reference