Zinc Oxide Whiskers with Intense Ultraviolet Emission

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強い紫外線発光を示す酸化亜鉛ウイスカー

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Well-organized ZnO whiskers were grown on the sapphire single crystalline substrate with a relatively high growth rate using the chemical-vapor-deposition technique. The ZnO whiskers showed ultraviolet emission on the photoluminescence and cathodoluminescence spectra. The intensity of the ultraviolet emission was comparable to the blue emission obtained from the commercial blue phosphor.

[Received November 5, 2002; Accepted December 19, 2002]

Key-words : Orientation, Whisker, ZnO, CVD, Photoluminescence, Cathodoluminescence, SEM

1. Introduction

The luminescence from ZnO crystallites is important in many technological photonic applications. Zu et al. reported room-temperature free exciton absorption and photoluminescence observed in ZnO thin films grown on sapphire substrates by a laser molecular beam epitaxy technique.¹⁾ Ogata et al. obtained the ZnO films with a source gas combination of diethylzinc and nitrous oxide using metalorganic vapor phase epitaxy. The films maintained *c*-axis orientation and exhibited a bound exciton emission as well as a free exciton emission on the photoluminescence spectrum at 9 K.²⁾ On the other hand, cathodoluminescence spectra were also evaluated from several samples. Sekiguchi et al. synthesized ZnO crystals using a flux method. They found that hydrogen plasma treatment strongly inhibited the green emission at 560 nm and promoted excitonic cathodoluminescence at 380 nm in ZnO.³⁾ Haga et al. successfully prepared the ZnO films using remote-enhanced chemical-vapor-deposition (CVD) of diethylzinc and carbon dioxide. The cathodoluminescence spectrum consisted of a sharp band at 380 nm and a broad band centered at 560 nm.⁴⁾ These reports suggest that ZnO is thought to be an important candidate for applications to ultraviolet (UV) emitters and diode lasers.

We have developed a CVD apparatus in which operation is possible at atmospheric pressure.^{5),6)} Fundamentally, this technique is thermal CVD. However, one major advantage is that the epitaxial growth of metal oxides at a high rate is possible. We already reported the formation of highly oriented ZnO whiskers formed on a (0001) sapphire single crystal by this CVD technique with zinc 2,4-pentanedionate, $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$.^{7),8)} 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 $[\bar{1}010](0001)//\text{sapphire} [\bar{1}2\bar{1}0](0001)$. The structure of epitaxially grown whiskers may offer many possibilities for application in the fields of electronic and optical technologies.

Several applications on the ZnO whisker technology have been proposed up to now. For example, a new type of the ceramic field emitter was designed using the combination of

the electrically conductive Al:ZnO whisker with an extremely sharp tip and the amorphous carbon and related coating having relatively low work function.^{9)–11)} In addition, highly oriented europium-doped yttria ($\text{Eu:Y}_2\text{O}_3$) whiskers showing highly intensity of red photoluminescence were obtained using the atmospheric CVD technique.¹²⁾ These results motivate us to use ZnO whiskers for obtaining intense UV emission. In this letter, the photoluminescence and cathodoluminescence properties of ZnO are described. Furthermore, defect-induced ZnO was also prepared by introducing Al incorporation into the ZnO whiskers. The luminescence intensities of these samples are compared.

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 $5 \times 10 \times 0.5 \text{ mm}^3$ and then ultrasonically cleaned sequentially with trichloroethane, acetone, and methanol. After treatment, the single crystal was washed with deionized water for 30 minutes. On the (0001) sapphire substrate, having a lattice constant of $a_0 = 0.47587 \text{ nm}$ at a temperature of 25°C , ZnO, having a lattice constant of $a_0 = 0.32497 \text{ nm}$ at a temperature of 25°C , grows along the *c*-axis with $\langle 0001 \rangle$ orientation. There is a relatively large lattice mismatch of 31.7% between two crystals, when the crystalline direction of sapphire is parallel to that of ZnO. However, regarding atomic configuration, the position of every 14th zinc ion of ZnO overlaps with the position of every 11th oxide ion of sapphire with a lattice mismatch of less than 0.4%, by the 30° rotation of ZnO relative to sapphire in the *c*-plane. Therefore, the 30° rotational epitaxy of ZnO whiskers is expected.

ZnO whiskers were prepared using an atmospheric CVD apparatus that was previously employed in obtaining epitaxial anatase films,⁵⁾ with titanium tetra-isopropoxide as the source complex. The reactant, $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$ (Soekawa Chemical Co., quoted purity of 99.9%), was loaded into a vaporizer and vaporized using an electric heater. In order to synthesize Al:ZnO whiskers, $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$ (Soekawa Chemical Co., quoted purity of 99.9%), was also loaded into the vaporizer. The amount of doping of Al was changed with the amount of $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$ loaded into the vaporizer. 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 rate of $1.2 \text{ dm}^3/\text{min}$ and then sprayed from the metallic

nozzle directly onto the single crystalline (0001) sapphire substrate mounted on the electric heater. The surface temperature measured using the *K*-type thermocouple is defined as the substrate temperature. The reactant vapor, $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$, was immediately decomposed by the heat from the substrate heater to form whiskers. The deposition duration of ZnO was maintained between 60 and 90 min for each experiment using a metallic shutter placed below the nozzle. The substrate was heated to 550°C using the electric heater. The distance between the nozzle and the substrate was maintained at 15 mm throughout the experiments.

The metal composition of the samples was determined using inductive coupled plasma-atomic emission spectroscopy (ICP-AES) with a spectrometer, SPS-400, Seiko Instruments Co. The surface morphology and the cathodoluminescence spectrum of the sample were measured at room temperature using a scanning electron microscope (SEM; T-300, JEOL with a cathodoluminescence spectrometer). The photoluminescence spectrum of the sample was also obtained room temperature using a spectrometer (FP 6500DS, JASCO Co.). Transmission electron microscopy (TEM; using JEM-2010F, JEOL) was also conducted.

3. Results and discussion

In this experiment, not only non-doped ZnO whiskers but also whisker samples with 0.5, 0.8 and 2.0 mol% Al were synthesized. Note that the samples for Al doping evaluation were dissolved into acid solution. Therefore, the Al doping evaluation was carried out after cathodoluminescence measurement. Figure 1 shows a set of SEM images of the specimens obtained with growth durations of 90, 75 and 60 min. A series of growths were performed at various amounts of doped Al ranging from 0 to 2.0 mol%. Typical SEM images were taken of the center region of each sample synthesized for the SEM observation. For the non-doped ZnO whiskers as shown in (a), a whisker diameter of approximately 2.5 μm and a whisker length of approximately 27 μm were observed, implying an aspect ratio of 10.8. The number density of the whiskers was $9 \times 10^4 \text{ mm}^{-2}$. These values were unchanged with the concentration of Al. For the 0.8 mol% Al: ZnO and 2.0 mol% Al: ZnO whiskers, the whisker length was reduced to 22 μm and 17 μm as shown in (b) and (c), respectively, while the diameter and the density unchanged. The epitaxial relationship between the whisker and the substrate has already discussed in Ref. 13). Figure 2 shows the TEM image of the intrinsic ZnO whisker cut in round slice. The lattice image shows no disturbance of the atomic order. The free exciton luminescence or UV emission is emitted at room temperature from the ZnO crystal with high atomic ordering.¹⁾

Figure 3 shows the photoluminescence properties for ZnO and Al: ZnO whiskers grown on the sapphire substrate. The spectra were obtained from the typical ZnO whisker and several Al-doped samples at room temperature, where the 258 nm line of the normal UV radiation lamp was used as an excitation source. For the ZnO whiskers, the main features of the photoluminescence spectra can be divide into three categories: dominant emission at UV region, low energy tail extending from the dominant emission and a weak violet-blue peak. The dominant emission peak is identified as the I9 line at 390 nm.¹⁴⁾ This line has previously assigned to the recombination of excitons bound to neutral donors or acceptors.¹⁵⁾ For the Al: ZnO whiskers, a broad emission was seen around 410 nm, superimposed to the long emission tail of the near band edge emission. The intensity of the dominant emission obtained from the ZnO whiskers decreased with incorporation of Al into the whisker, suggesting that the UV emission was attributable to that obtained from ordered crystalline configuration.

Fig. 1. A set of SEM images of the specimens obtained with growth durations of (a) 90 min, (b) 75 min and (c) 60 min. The concentration of Al is 0.5 mol%, 0.8 mol% and 2.0 mol% for samples (a), (b) and (c), respectively.

Fig. 2. TEM images of intrinsic ZnO whisker cut in round slice.

The cathodoluminescence spectra of the ZnO whisker and several Al-doped samples at room temperature, where the electron beam at an accelerating voltage of 30 keV, used as

Fig. 3. Photoluminescence properties for ZnO and Al:ZnO whiskers grown on the sapphire substrate.

Fig. 4. Cathodoluminescence properties for ZnO and Al:ZnO whiskers grown on the sapphire substrate.

an excitation source are shown in Fig. 4. The spectrum has a strong peak that is attributable to the band edge luminescence at 379 nm and a low energy tail extending from the main emission. A broad emission around 560 nm which is so-called green emission was not seen at any samples. With the increase of the Al concentration, the intensity of UV luminescence significantly decreases. In contrast, the broad peak around 410 nm appeared. The 410 nm emission is very weak and 10–30 times less than that of the band edge emission. It is noted that the broad emission might be assigned to the donor-acceptor recombination induced by the incorporation of Al. This is consistent with the photoluminescence property. However, for accurate identification, further investigation is needed.

The results of the photoluminescence and cathodoluminescence spectra indicate that high crystalline ordering is obtained in the non-doped ZnO whisker. Figure 5 indicates the cathodoluminescence spectra of the non-doped ZnO whiskers and the commercial blue phosphor. The commercial blue phosphor is the crystalline particles of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$, obtained from Nicha Chemical Co. This indicates very intense visible blue emission. The intensities of these two samples are placed on the same sample holder in the cathodoluminescence spectrometer and compared each other. The peak intensity of the UV emission obtained from the ZnO whiskers is comparable to that obtained from the commercial blue phosphor.

4. Conclusion

The well-organized ZnO and Al:ZnO whiskers were prepared on the (0001) sapphire single crystal by the

Fig. 5. Cathodoluminescence of ZnO whisker and $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ blue phosphor.

atmospheric CVD technique. The photoluminescence and cathodoluminescence spectra obtained from the ZnO whiskers had the structure consisted of the dominant UV emission, the low energy tail extending from the UV emission and the weak violet-blue peak. With the increase of the Al concentration, the intensity of the UV emission significantly decreases. In contrast, the violet-blue peak around 410 nm appeared. The peak intensity of the UV emission obtained from the ZnO whiskers is comparable to that obtained from the commercial blue phosphor.

Acknowledgments The authors thank to JEOL Co., Ltd. for TEM operation. This study partially supported by 21st century COE program at Nagaoka University of Technology.

References

- 1) Zu, P., Tang, Z. K., Wong, G. K. L., Kawasaki, M., Ohtomo, A., Koinuma, H. and Segawa, Y., *Solid State Commun.*, Vol. 103, pp. 459–463 (1997).
- 2) Ogata, K., Kim, S.-W., Fujita, Sz. and Fujita, Sg., *J. Cryst. Growth*, Vol. 240, pp. 112–116 (2002).
- 3) Sekiguchi, T., Ohashi, N. and Terada, Y., *Jpn. J. Appl. Phys.*, Vol. 36, L289–L291 (1997).
- 4) Haga, K., Kamidaira, M., Kashiwaba, Y., Sekiguchi, T. and Watanabe, H., *J. Cryst. Growth*, Vol. 214/215, pp. 77–80 (2000).
- 5) Tanaka, N., Ohshio, S. and Saitoh, H., *J. Ceram. Soc. Japan*, Vol. 105, pp. 551–555 (1997).
- 6) Saitoh, H., Sunayama, H., Tanaka, N. and Ohshio, S., *J. Ceram. Soc. Japan*, Vol. 106, pp. 1051–1055 (1998).
- 7) Satoh, M., Tanaka, N., Ueda, Y., Ohshio, S. and Saitoh, H., *Jpn. J. Appl. Phys.*, Vol. 38, L586–L589 (1999).
- 8) Saitoh, H., Satoh, M., Tanaka, N., Ueda, Y. and Ohshio, S., *Jpn. J. Appl. Phys.*, Vol. 38, pp. 6873–6877 (1999).
- 9) Ohkawara, Y., Naijo, T., Washio, T., Ohshio, S., Ito, H. and Saitoh, H., *Jpn. J. Appl. Phys.*, Vol. 40, pp. 7013–7017 (2001).
- 10) Ohkawara, Y., Akasaka, H., Namiki, K. C., Ohshio, S., Ito, H. and Saitoh, H., *Jpn. J. Appl. Phys.*, in press.
- 11) Washio, T., Ohkawara, Y., Ohshio, S., Ito, H. and Saitoh, H., *New Diam. Frontier Carbon Technol.*, Vol. 12, pp. 157–160 (2002).
- 12) Satoh, Y., Ohshio, S. and Saitoh, H., *Jpn. J. Appl. Phys.*, Vol. 41, pp. L1250–L1252 (2002).
- 13) Saitoh, H., Namioka, Y., Sugata, H. and Ohshio, S., *Jpn. J. Appl. Phys.*, Vol. 40, pp. 6024–6028 (2001).
- 14) Bagnall, D. M., Chen, Y. F., Shen, M. Y., Zhu, Z., Goto, T. and Yao, T., *J. Cryst. Growth*, Vol. 184/185, pp. 605–609 (1998).
- 15) Reynolds, D. C., Look, D. C., Jogai, J., Litton, C. W., Collins, T. C., Harsch, W. and Cantwell, G., *Phys. Rev. B*, Vol. 57, pp. 12151–12155 (1998).