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Crystal growth on ZnO ceramics heated by direct current

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A new and intriguing phenomenon related to ZnO crystal growth was recently discovered by the authors. Without large system and high electric power, ZnO crystals were grown by very simple and easy methode. When a direct current flowed through a sample of pure ZnO ceramics bar in air at room temperature, the sample was heated by joule heating, and the crystal growth occurred at the sample surface immediately. The grown crystals had various forms, i.e. hexagonal prism, hollow prism and whisker. A novel form, double hollow, was also obtained. With increasing current the form of grown crystals changed from hexagonal prism to hollow prism. When a direct current in the range of 7.6 - 91 A/cm^2 flowed through a sample, temperature at the sample surface covered 300 - 1300 ℃. The mechanism of the crystal growth was considered as vapor phase crystal growth in the supersaturated vapor of ZnO and Zn generated by elevated temperature. New functional devices including ultraviolet laser might be realized by using obtained novel crystals.

Key words: ZnO, crystal growth, whisker, hexagonal prism, hollow prism, double hollow

1. INTRODUCTION

Nowadays a great many people obtain various information, even at home, thanks to the development of information transmitting technology and medium as internet. Needless to say, further development of information technology is essential. Efficient use of light is the key to support the development. The high performance optoelectronic devices are necessary to be realized.

It is widely known that the wurtzite type of ZnO has many functions including, photoconductivity, piezoelectricity, pyroelectricity and fluorescence. Zinc oxide is also one of the very attractive materials for solid-state ultraviolet lasers. Recently, stimulated emission due to excitonic recombination was observed at room temperature by optically pumping ZnO nanocrystalline thin films grown on sapphire substrates by the laser molecular beam epitaxy (MBE) technique.[1, 2] Furthermore the lasing of the exciton took place using naturally occurring grain boundaries as cavity mirrors.

We recently discovered many kinds of ZnO crystals were grown at the ZnO ceramics bar heated by direct current. Obtained novel double hexagonal hollow crystals had smooth facets. It may be possible to use the facets as cavity mirrors for the lasing of ring cavity mode travelling along a hexagonal optical path.

We report intriguing ZnO crystals including the novel crystals grown by the very simple and easy technique. This method was based on self-substrating, self-heating, self-sourcing and self-organization. The aim of present work is to investigate the relation between the form of crystals and the growth conditions.

2. EXPERIMENTAL

Zinc oxide ceramics bars were prepared by conventional solid-state reaction. The ZnO starting powder (Soekawa Chemicals, 99.999 % purity) was pressed at 20 MPa in plate of 20 mm×50 mm×5 mm, sintered at 750 ℃ in air for 1 h and cut into bars (about 1 mm×1 mm×15 mm). The outer edges of each bar were electroded by using Ag or Pt paste. A direct current flowed through the sample by using a regulated dc power supply (Kikusui Electronics, PAD500-1.2A). Temperature of the sample surface was measured by using an infrared camera (NEC San-ei, TH3101MR). The morphology of obtained crystals were observed by using a scanning electron microscope (SEM, JEOL, JSM-T220A).

3. RESULTS AND DISCUSSION

When a direct current flowed through a sample at room temperature in air, the sample was heated by joule heating, and crystal growth occurred at the sample surface immediately. It was found that a sample was burned at certain position on the sample after a direct current continued flowing through the sample for a certain time. Figure 1 shows a burning sample with current of 161 A/cm^2.

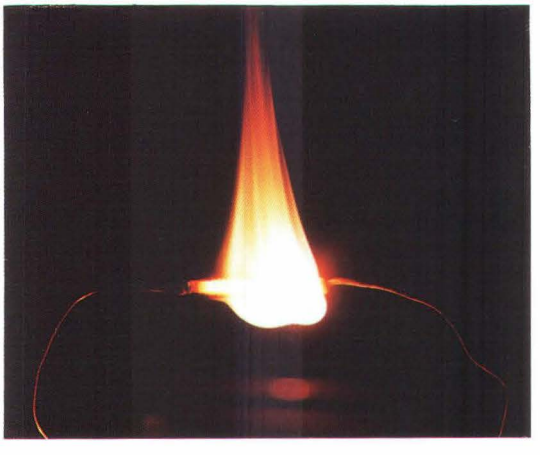


Fig. 1. Photograph of burning sample when a direct current continued flowing through ZnO ceramics bar.

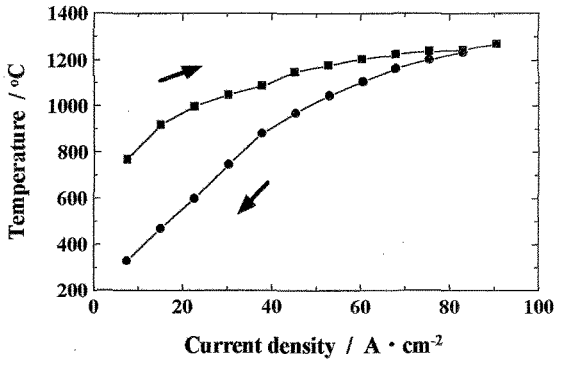


Fig. 2. Current density-temperature characteristics in air. A direct current was changed every 30 s with 7.6 A/cm^2. The current was increased up to 91 A/cm^2 and decreased to 7.6 A/cm^2.

Table I. Schematic diagram of the relation between form of ZnO crystal and growth conditions. A direct current flowed through ZnO ceramics bar within 60 min.

Current density / A·cm^{-2}	11	22	33	40	47	91
Time to the break down / min	—	—	—	28	15	5
Form of grown crystal	Hexagonal prism					Hollow prism

Figure 2 shows the relation between current density and temperature. A direct current was changed every 30 s with 7.6 A/cm^2. An increase up to 91 A/cm^2 and a decrease to 7.6 A/cm^2 was regarded as one cycle. Three cycles were performed on the same sample. Temperature for the first cycle is shown in this figure. Temperature was increased by increasing current. When a current density in the range of 7.6 - 91 A/cm^2 flowed through a sample, temperature at a sample surface covered 300 - 1300 ℃. Temperature in current decrease process was lower than that in increase process. A temperature change for the second and third cycle was the same as current decrease process of first cycle, which may be caused by the decrease in resistance due to the sintering.

A sample was burned when a current density of higher than about 40 A/cm^2 flowed through the sample for a certain time. The relation between electric current condition and the form of grown crystals at the sample surface is shown in Table I. With increasing a direct current the form changed from hexagonal prism to hollow prism. This phenomenon is revealed clearly in SEM images (Fig. 3).

Kuroda et al.[3, 4] reported that the morphological instability of polyhedral snow crystals bounded by two basal (0001) and six prism (10$\bar{1}$0) occurs with an increase in the degree of supersaturation. In this study, with increasing current the form of grown crystals

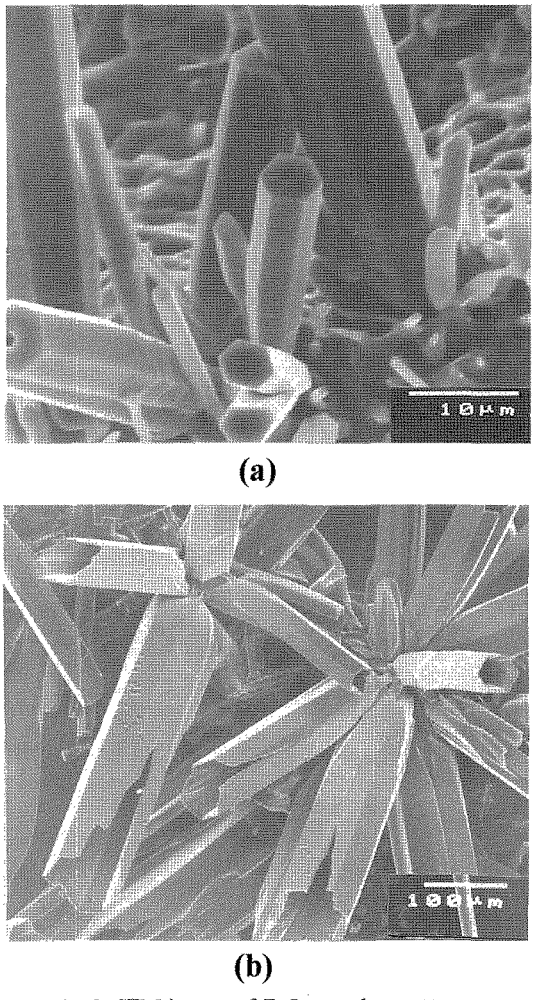


Fig. 3. SEM images of ZnO crystals. (a) Hexagonal prisms were grown at the surface of ZnO ceramics bar. The growth condition was current of 22 A/cm^2 for 60 min in air. (b) Hollow prisms were grown at the surface of ZnO ceramics bar. The growth condition was current of 33 A/cm^2 for 60 min in air.

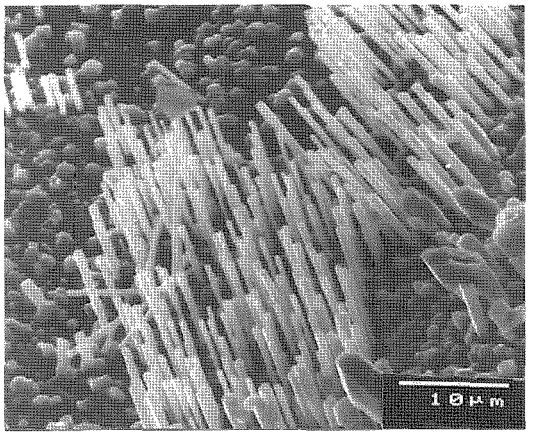


Fig. 4. SEM image of ZnO whiskers. Whiskers were grown at the surface nearby break down point of burned ZnO ceramics bar. The growth condition was current of 91 A/cm^2 for 5 min in air.

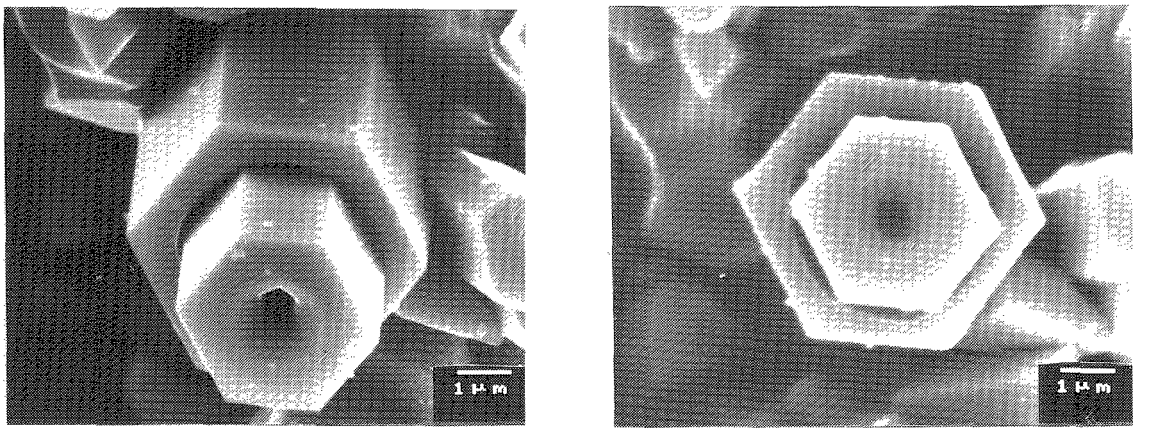


Fig. 5. SEM images of ZnO double holow. It was grown at the surface nearby break down point of burned ZnO ceramics bar. The growth condition was current of 91 A/cm^2 for 5 min in air.

Table II. Relation between typical form of grown crystal at the sample surface and O_2 concentration. The growth condition was current of 45 A/cm^2 for 4 min.

O_2 concentration / %	Ar atmosphere	20	40	60	80	100
Form of grown crystal	Whisker Tetrapod-like crystal	Hexagonal prism Hollow prism				

changed from hexagonal prism to hollow prism. It is considered that the morphological instability of polyhedral crystals occurred by supersaturated vapor of ZnO and Zn generated by the elevated temperature.

Whiskers were grown at sample surface nearby break down point of burned sample as shown in Fig. 4. The growth condition was current of 91 A/cm^2 for 5 min in air. Burning temperature reached about 1700 ℃. The growth condition employed here meets that of whisker reported by Suyama et al.[5], namely, reaction temperature of higher than 850 ℃, Zn concentration of 2.5 % and O_2 concentration of approximately 20 %. As regards Zn, it is considered that the Zn vapor was generated from the bar, because the bar was burned (Fig. 1) due to oxidation of Zn vapor.

Figure 5 shows a novel growth form, double hollow. It was grown at the sample surface nearby break down point. The growth condition was current of 91 A/cm^2 in air for 5 min. Outer and inner hollow grew to the same direction. Each face of outer hollow was parallel with that of inner hollow. Kuroda et al.[3, 6] reported that the complicated habit change of snow crystals occurred at certain temperature. The growth mechanism of the double hollow in ZnO crystal may be thought that result of the morphological instability of polyhedral crystals occurred with an increase in the degree of supersaturation at higher current, and the complicated habit change of polyhedral ZnO crystal occurred.

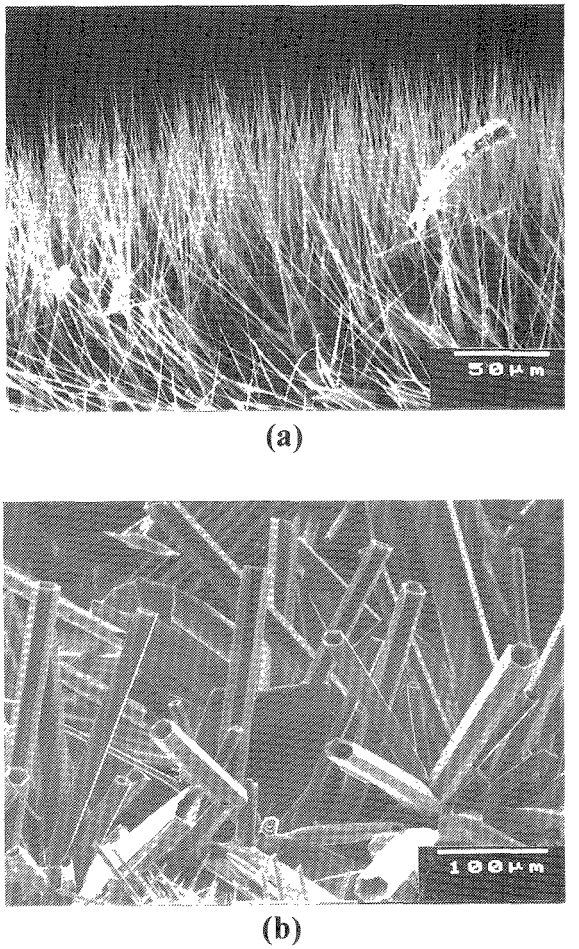


Fig. 6. SEM images of grown crystals on ZnO ceramics. The growth condition was current of 45 A/cm^2 for 4 min (a) in Ar atmosphere (b) in O_2 concentration of 40 %.

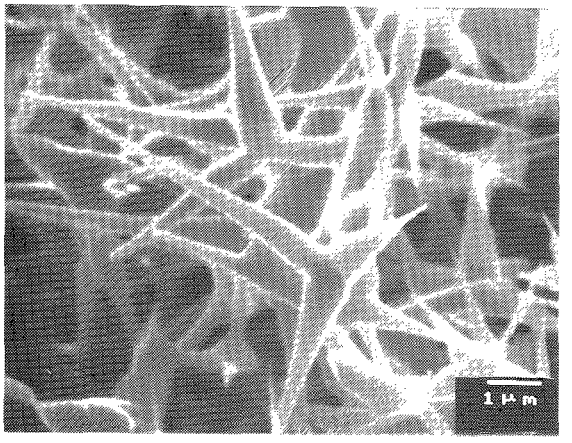
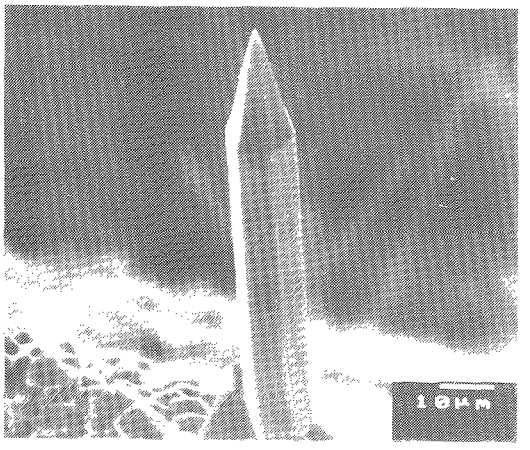


Fig. 7. SEM image of tetrapod-like crystals. The growth condition was current of 23 A/cm^2 for 5 min in Ar atmosphere.



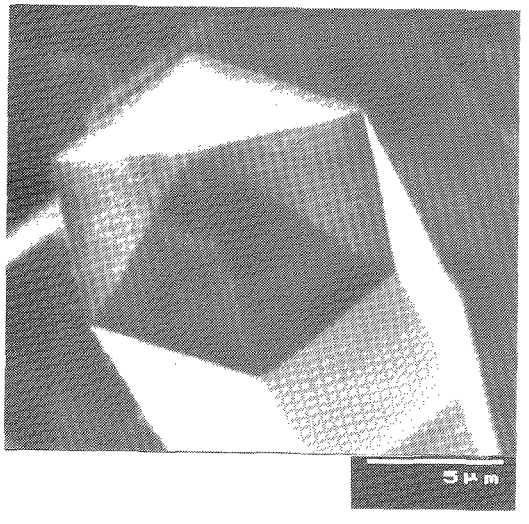


Fig. 8. SEM images of hexagonal prism with a sharp tip. The growth condition was current of 45 A/cm^2 for 4 min in O_2 concentration of 60%.

Table II and Fig. 6 show the effect of O_2 concentration in atmosphere on the form of grown crystal at the sample surface. It was found that the growth form tended to be whisker in Ar atmosphere, and hexagonal prism or hollow prism in O_2 containing atomosphere.

Tetrapod-like crystals are shown in Fig. 7. The growth condition was current of 23 A/cm^2 for 5 min in Ar atmosphere. A leg length was approximately 1 - 10 μm and an edge size of centering nucleus was approximately 1 μm. Kitano et al.[7] and Suyama et al.[5] also fabricated tetrapod-like crystals by oxidation of Zn vapor.

Hexagonal prism with a sharp tip are shown in Fig. 8. Its growth condition was current of 45 A/cm^2 for 4 min in O_2 concentration of 60 %. The crystal had clear facets and represented the typical structural characteristic of ZnO.

4. CONCLUSIONS

Zinc Oxide crystals with various forms were grown by on electric current heating method.

(1) When a direct current in the range of 7.6 - 91 A/cm^2 flowed through a sample, temperature at the sample surface covered 300 - 1300 ℃. With increasing current the form of grown crystals changed from hexagonal prism to hollow prism.

(2) A sample was burned at certain position on the sample after a direct current density of higher than 40 A/cm^2 flowed through the sample in air for a certain time. Burning temperature reached at approximately 1700 ℃. The crystals on the break down point had various growth forms, e.g. whisker and double hollow.

(3) Form of grown crystal depending on O_2 concentration was investigated. It was found that the growth form tended to be whisker in Ar atmosphere, and hexagonal prism or hollow prism in O_2 containing atomosphere.

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