Effect of annealing in an O$_2$ atmosphere on the electrical properties of high-quality ZnO single crystals grown by seeded chemical vapor transport

Sang-Hwui Hong$^{a,b}$*, Ji-Hun Mun$^a$, Kouji Mimura$^a$, Makoto Mikami$^a$, Masahito Uchikoshi$^b$ and Mino ru Iishi ki$^b$

$^a$Gyeongbuk Hybrid Technology Institute, 36 Goyeong-Dong, Yeongcheon Gyeongbuk, 770-170, Korea
$^b$Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

We have investigated the effect of annealing in an O$_2$ atmosphere on the electrical properties of high-quality ZnO single crystals grown by seeded chemical vapor transport (SCVT). A temperature dependent Hall-effect technique indicates that the dominant donor in as-grown ZnO crystals has an $E_D$ of 42.8 meV and $N_D$ value of $2.8 \times 10^{17}$ cm$^{-3}$. After heat treatment in the O$_2$ atmosphere at 1000$^\circ$C for 5 h, the color of the crystal changed from an orange color to transparent, and the $N_D$ value decreased to $4.3 \times 10^{16}$ cm$^{-3}$, while the $E_D$ value did not change. It can be deduced that the dominant donor in as-grown ZnO single crystals is a donor-type native defect, which has a donor binding energy of about 42.8 meV.

Key words: II-VI semiconductors, Hall measurements, Donor binding energy, Zinc oxide.

Introduction

Zinc oxide (ZnO) is one of the most promising materials for fabricating ultraviolet light emitting devices with high efficiency [1]. However, few successful techniques have been developed for growing p-type ZnO crystals [2, 3], because it is very difficult to prepare a p-type ZnO crystals due to the strong self-compensation effect caused by the residual donor type impurities and native defects. For the preparation of a p-type crystal, high-purity ZnO single crystals with extremely low donor concentration should be grown and then the doping effect of acceptor-type impurities should be examined. Therefore, clarification of the role of dopant impurities and native defects is important in ZnO. To elucidate the behaviors of native defects, high purity and good crystallinity ZnO bulk single crystals are required to minimize the influence of the residual impurities. From this point of view, high-purity and good-crystallinity ZnO single crystals have been grown by seeded chemical vapor transport (SCVT) using carbon as a transport agent in a previous study [4].

A recent theoretical investigation [5] has found that the dominant donor in ZnO was generally assumed to be a native defect, either an O vacancy ($V_O$) or a Zn interstitial (Zn$_i$). Zhang et al. [6] have reported that $V_O$ and Zn$_i$ behave as a deep donor and a shallow donor, respectively. Correspondingly, Hofmann $et$ $al.$ [7], Kohan $et$ $al.$ [8] and Kröger [9] argued that $V_O$ us as the dominant donor, while Look $et$ $al.$ [10] and Mohanty and Azaroff [11] insisted it was Zn$_i$. Thus, the dominant native defect and their donor binding energy ($E_D$) are still controversial.

Several experiments have indicated the dominant defect and the donor binding energy ($E_D$) in as-grown ZnO. For example, Look $et$ $al.$ [10, 12] reported that the dominant donor is assigned as Zn$_i$, and its $E_D$ is 30 meV in bulk ZnO grown from the vapor-transport (VT) and SCVT method whereas Aur et $et$ $al.$ [13] have revealed that the main defect is the $V_O$ in bulk ZnO grown from SCVT and the pressurized melt growth (PMG) technique. The activation energy is about 12 and 29 meV, respectively. As mentioned above, the reported values on the $E_D$ are scattered. This lack of precise information on the native defect of ZnO suggests that we have to examine the electrical properties of ZnO crystals of a very high purity.

In the present study, the main efforts are focused on measuring the electrical properties of high-purity and good-crystallinity ZnO single crystals and on clarifying the donor binding energy of donor type native defects in ZnO.

Experimental

To improve the single crystal growth of ZnO by the CVT method, our group has developed an ampoule with a unique configuration as shown in Fig. 1. In a previous study [4], the new ampoule had a symmetric structure with a capillary, resulting in improving the reproducibility of making the ampoule, and in homogenizing the vapor species transport. The single crystal growth was carried out according to the temperature gradient in a vertical furnace. The growth temperature ($T_g$) was fixed at 965$^\circ$C and the difference between the growth ($T_g$) and source ($T_s$) temperatures was $\Delta T = 5$ K. The temperature of the capillary ($T_c$) should be higher than $T_g$ so the growth condition was set to be $\Delta T$ ($T_c$−$T_g$) = 2 K. The growth time was three weeks. After growth, the ampoule was air cooled to room
temperature.

Single ZnO crystals with large natural facet planes, about $5 \times 5 \times 5$ mm$^3$ in size, could be grown under the present conditions [4]. The secondary ion mass spectrometry (SIMS) analysis, X-ray rocking curve and photoluminescence measurements demonstrate that the single crystals grown are of high-purity and good-crystallinity [4]. To examine the dominant donor in as-grown ZnO crystals, thermal annealing of them at 1000 °C for 5 h under a 0.1 MPa oxygen atmosphere was carried out.

The Hall effect of the single crystals was measured as a function of temperature by the Van der Pauw method using indium electrodes. The temperature dependence of the carrier concentrations, resistivity and mobility were measured between 30 and 300 K using a $4 \times 3 \times 1.0$ mm$^3$ sample, which was cut from a high-purity and high-crystallinity ZnO single crystal.

Results and Discussion

In Fig. 2, the measured carrier concentration, mobility and resistivity are plotted against and a linear relationship between the carrier concentration and is clearly observed.

The temperature dependence of electron density in an n-type semiconductor, if the temperature region is extremely low and the electron density ($n$) can be presented as $N_D >> n >> N_A$, is represented as the following equation (1):

$$n = \sqrt[3]{N_D N_A} \exp \left( \frac{E_D}{2k_B T} \right),$$

(1)

where $\gamma_D = 1/2$.

According to it only one electron is emitted from the one donor (Pauli’s principle). $E_D$ can be expressed as, Eq. (2):

$$E_D = 2k_B \frac{\Delta \ln n}{\Delta T},$$

(2)

where $k_B$ is the Boltzmann constant. From Eq. (2), the values of $E_D$ may be estimated from the slope of the $(\ln n)$ versus $(1/T)$ plot.

A single donor model was used to fit the data between about 30 and 300 K. From the dependence of the carrier concentration on plotted in Fig. 2(a), the as-grown ZnO crystal gives an $E_D$ of 42.8 meV and $N_D$ value of $2.8 \times 10^{17}$ cm$^{-3}$. The Hall mobility data are shown in Fig. 2(b). The higher mobility ($358$ cm$^2$V$^{-1}$s$^{-1}$ at 70 K and about $120$ cm$^2$V$^{-1}$s$^{-1}$ at 280 K) is comparable to the 298 cm$^2$V$^{-1}$s$^{-1}$ at 78 K measured on the ZnO single crystal grown with
the PMG method, reported by Nause and Nemeth et al. [14]. As seen in Fig. 2(c), the electrical resistivities are about $5.0 \times 10^{-1}$ Ωcm at 80 K and $2.1 \times 10^{-1}$ Ωcm at 290 K (with the minimum of $1.5 \times 10^{-1}$ Ωcm at 175 K).

The dominant donor in a ZnO crystal could be a native defect, either the zinc interstitials or oxygen vacancies [5]. Therefore, thermal annealing was carried out to understand the details of the dominant donor in ZnO crystals. The as-grown sample (Fig. 3(a)) was annealed at 1000 °C for 5 h under 0.1 MPa oxygen atmosphere.

After annealing one of the as-grown crystals at 1000 °C for 5 h under an 0.1 MPa oxygen atmosphere, the sample became colorless and transparent as seen in Fig. 3(b). SIMS measurements revealed that the impurity peaks detected in our ZnO single crystals were Li, Al and K with very low intensities [4]. These results demonstrate that the purity of the ZnO single crystals grown is remarkably high and carbon contamination does not exist. Therefore, the orange-red color of the crystals was not affected by impurities. Further annealing under a zinc vapor changes the sample into an orange-red color. The details are described in our previous report [15]. These result demonstrated that the orange-red color of the crystals must be caused by native defects, either the zinc interstitials or oxygen vacancies.

The measured carrier concentrations of both as-grown and annealed ZnO crystals were plotted against $1/T$ and linear fitted as indicated in Fig. 4. The data obtained on the as-grown sample was also plotted (black color) for comparison. The result obtained for the ZnO crystal annealed in an oxygen atmosphere was that both $E_D$ values are nearly equal; however, the carrier concentration of ZnO single crystals after the oxygen annealing markedly decreased. This result indicates that the dominant donor is the same for both the as-grown crystal and the annealed crystal, and annealing in an oxygen atmosphere decreases the concentration.

Therefore, it is expected that the number of oxygen vacancies or zinc interstitials would be reduced by the oxygen annealing. The origin of native defects has not been specified yet by only Hall effect measurements. However, our results suggest clearly that the dominant donor-type native defect has a donor binding energy of about 42.8 meV.

After annealing of as-grown crystals, the resistivity and mobility increase as shown in Fig. 5 and Table 1.

There are some known scattering mechanisms of charge carriers such as ionized impurity scattering, neutral impurity scattering and lattice vibration scattering [16]. Generally, ionized impurity scattering shows a temperature dependence of $T^{3/2}$ [17] and the solid line in Fig. 5(a), at 30-70 K is present with a temperature dependence of $T^{3/2}$. This means that ionized impurity scattering was dominant to limit the mobility at 30-70 K. So, the native defect (oxygen vacancies or zinc interstitial) may be inhibiting the mobility in as-grown ZnO crystals at a low temperature. On the other hand, the mobility begins to decrease from its highest value of 765 cm$^2$V$^{-1}$s$^{-1}$ at 70 K through another dominant scattering mechanism. In Fig. 5(a), the mobility of ZnO follows the relation of $\mu \propto T^{-2}$ in the temperature range from 70 K to 290 K. It can be deduced that the electron transport seems to be dominated by lattice vibration scattering [18]. The data obtained on the as-grown sample was also plotted (black color) for comparison. The result obtained in the ZnO crystal annealed in an oxygen atmosphere suggests that the scattering mechanism is nearly the same.
Conclusions

We have investigated the electrical properties of high-purity and high-quality ZnO single crystals grown by seeded chemical vapor transport (SCVT), using a temperature dependent Hall-effect technique. As to the dominant donor in as-grown ZnO crystal, an $E_D$ of 42.8 meV and a $N_D$ value of $2.8 \times 10^{17} \text{cm}^{-3}$ were obtained. After annealing in an $O_2$ atmosphere at 1000 °C for 5 h, the color of the crystal changed from an orange color to colorless transparent, and the $N_D$ value decreased to $4.3 \times 10^{16} \text{cm}^{-3}$, while the $E_D$ value did not change. From the results, the dominant defect in as-grown ZnO single crystals must be a donor-type native defect, which has a donor binding energy of about 42.8 meV.

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References

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