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Effect of annealing in an O_2 atmosphere on the electrical properties of high-quality ZnO single crystals grown by seeded chemical vapor transport

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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 2.8×10^{17} cm^{-3}. After heat treatment in the O_2 atmosphere at 1000 °C for 5 h, the color of the crystal changed from an orange color to transparent, and the N_D value decreased to 4.3×10^{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 a Zn_i, and its E_D is 30 meV in bulk ZnO grown from the vapor-transport (VT) and SCVT methods, whereas Auret *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 °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_h) should be higher than T_s, so the growth condition was set to be $\Delta T'$ (T_h–T_s) = 2 K. The growth time was three weeks. After growth, the ampoule was air cooled to room

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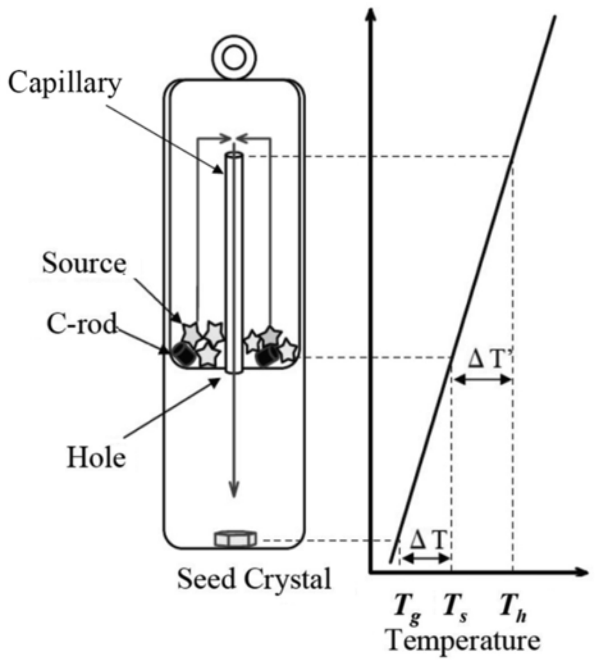

Fig. 1. Schematic diagram of the newly-designed ampoule and the temperature profile of the furnace.

temperature.

Single ZnO crystals with large natural facet planes, about 5 × 5 × 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 × 3 × 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) :

$$n = \sqrt{\gamma_D N_D N_C}\exp\left(\left(-\frac{E_D}{2\kappa_B T}\right), \right) \quad (1)$$

where $\gamma_D = 1/2$.

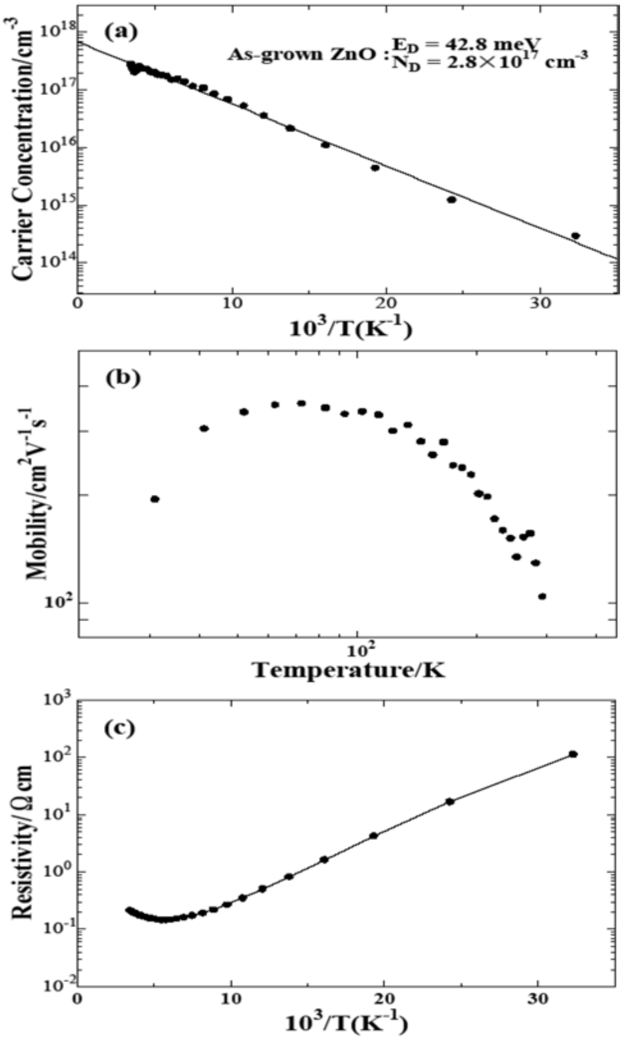

Fig. 2. Temperature dependencies of (a) carrier concentration, (b) carrier mobility and (c) resistivity of a ZnO single crystal.

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

$$E_D = 2\kappa_B \frac{\Delta \ln n}{\Delta \frac{1}{T}}, \quad (2)$$

where κ_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 × 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 5.0×10^{-1} Ωcm at 80 K and 2.1×10^{-1} Ωcm at 290 K (with the minimum of 1.5×10^{-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 ºC for 5 h under 0.1 MPa oxygen atmosphere.

After annealing one of the as-grown crystals at 1000 ºC 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

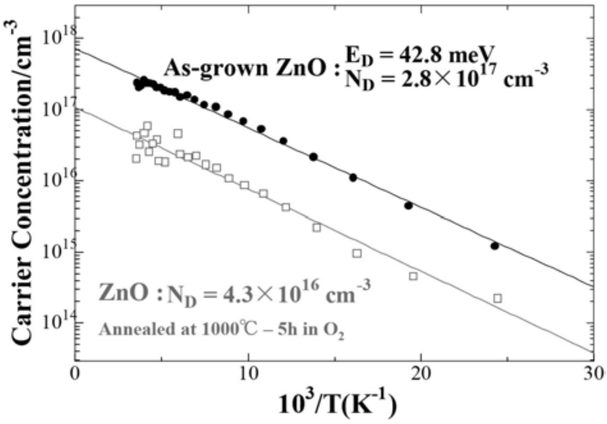

Fig. 4. Carrier concentration of an as-grown (black), and crystal annealed at 1000 ºC (blank) for 5 h in an 0.1 MPa O_2, as a function of inverse temperature.

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 $\mu \propto T^{-3/2}$ 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 date 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.

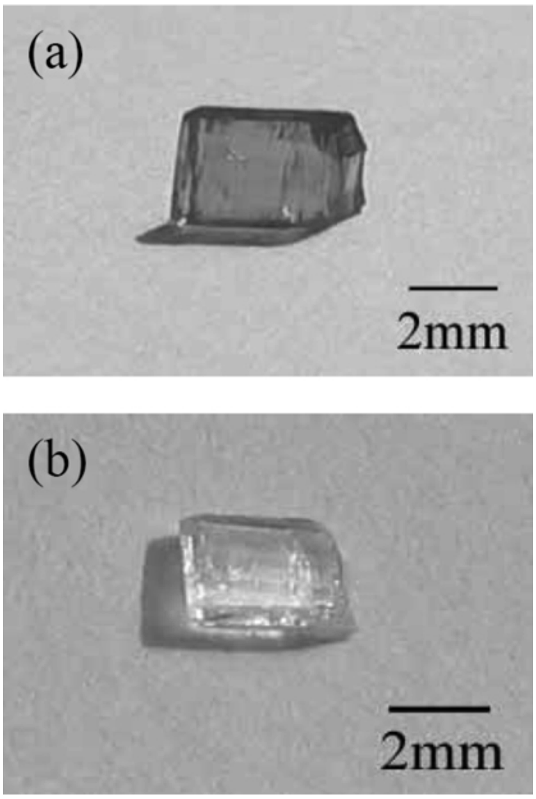

Fig. 3. As-grown crystal (a) and the crystal annealed at 1000 for 5h uder an 0.1 MPa oxygen atmosphere (b).

Table 1. Comparison of electrical properties for as-grown and annealed ZnO bulk single crystals

Condition	Temperature (K)	N (cm^{-3})	μ ($cm^2V^{-1}s^{-1}$)	ρ_s (Ù cm)	Conductivity type
As-grown	280	2.4×10^{17}	120	2.0×10^{-1}	n
	70	2.1×10^{16}	358	8.2×10^{-1}	n
Annealed in O_2	280	4.3×10^{16}	159	9.3×10^{-1}	n
	70	2.2×10^{15}	765	3.7	n

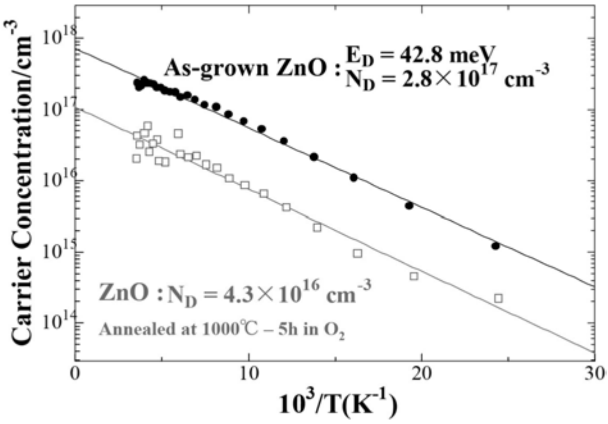

Fig. 4. Carrier concentration of an as-grown (black), and crystal annealed at 1000 °C (blank) for 5 h in an 0.1 MPa O_2, as a function of inverse temperature.

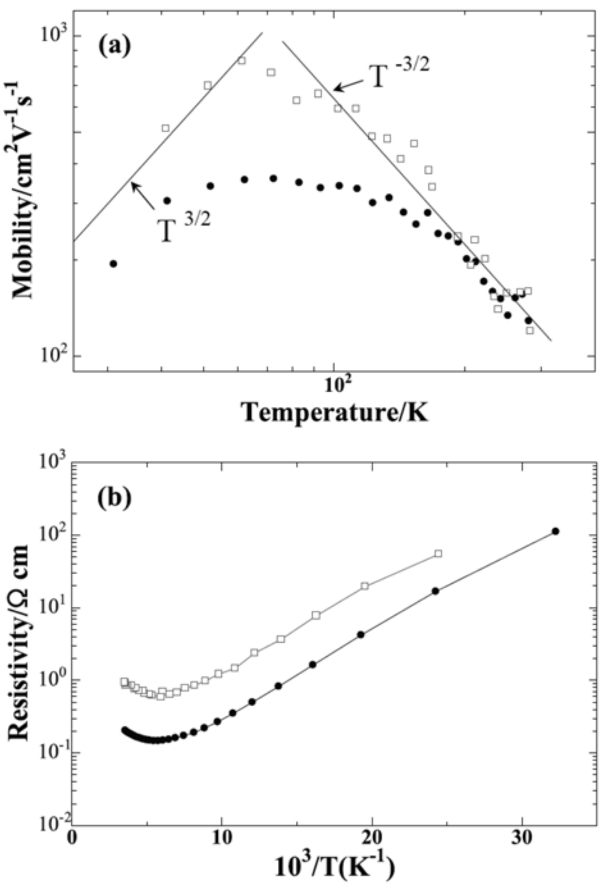

Fig. 5. Mobility (a) and resistivity (b) as a function of inverse temperature for as-grown (black), and annealed crystal at 1000 °C (blank) in 0.1 MPa O_2.

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 2.8×10^{17} 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 4.3×10^{16} 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.

Acknowledgements

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References

1. D. Bagnal, Y. Chen, Z. Zhu, T. Yao, S. Koyama, M. Shen and T. Goto, Appl. Phys. Lett. 70 (1997) 2230.
2. D.C. Look and B. Claflin, Phys. Status Solidi B 241 (2004) 624.
3. A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma and M. Kawasaki, Nature Mater. 4 (2005) 42.
4. S.H. Hong, M. Mikami, K. Mimura, M. Uchikoshi, A. Yasuo, S. Abe, K. Masumoto and M. Isshiki, J. Crystal Growth 311 (2009) 3609.
5. F. Oba, S.R. Nishitani, S. Isotani, H. Adachi and I. Tanaka, J. Appl. Phys. 90 (2001) 824.
6. S.B. Zhang, S.H. Wei and A. Zunger, Phys. Rev. B 63 (2001) 075205.
7. D.M. Hofmann, D. Pfisterer, J. Sann, B.K. Meyer, R. Tena-zaera, V. Munoz-sanjose, T. Frank and G. Pensl, Appl. Phys. A 88 (2007) 147.
8. A.F. Kohan, G. Ceder, D. Morgan and C.G. Van de Walle, Phys. Rev. B 61 (2000) 15019.
9. F.A. Kröger, *The Chemistry of Imperfect Crystals* (North-Holland, Amsterdam, 1974).
10. D.C. Look, J.W. Hemsky and J.R. Sizelove, Phys. Rev. Lett.82 (1999) 2552.
11. G.P. Mohanty and L.V. Azaroff, J. Chem. Phys. 35 (1961) 1268.
12. D.C. Look, G.C. Farlow, P. Reunchan, S. Limpijumnong,

S.B. Zhang and K. Nordlund, Phys. Rev. Lett. 95 (2005) 225502.
13. F.D. Auret, J.M. Nel, M. Hayes, L. Wu, W. Wesch and E. Wendler, Superlattices and Microstructures 39 (2006) 17.
14. J. Nause and B. Nemeth, Semicond. Sci. Technol. 20 (2005) 45.
15. M. Mikami, T. Eto, J. Wang, Y. Masa and M. Isshiki, J. Crystal Growth 276 (2005) 389.
16. Z.L. Pei, C. Sun, M.H. Tan, J.Q. Xiao, D.H. Guan, R.F. Huang and L.S. Wen, J. Appl. Phys. 90 (2001) 3432.
17. Handbook on Semiconductors - Materials, Properties and Preparation, Series editor, T.S. Moss and Volume editor, S. Mahajan (Amsterdam, Tokyo, North-Holland, Volume 3a).
18. E. Gür, S Tüzemen and S. Doğan, Phys. Scr. 79 (2009) 035701.