Positron annihilation study of defects in electron-irradiated single crystal zinc oxide

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Abstract. Pressurized melt grown zinc oxide (ZnO) single crystals purchased from Cermet Inc. were irradiated by 2MeV electrons with fluence of 6x10¹⁷cm⁻². Isochronal annealing from 100 °C - 800 °C was performed on the crystals under argon and air ambience. Variable Energy Doppler Broadening Spectroscopy (VEDBS) was carried out on both the as-grown and the irradiated samples at each annealing step. The migration, agglomeration and annealing of grown-in and irradiated-introduced defects were studied. It was observed that the grown-in vacancy-type defects concentration decreased at 300 °C and 600 °C. For the irradiated sample annealed in argon, the positron trapping vacancy-type defect concentration decreased at 300 °C and 600 °C. Further annealing the as-grown and irradiated samples in argon increased the S parameter further. For the irradiated sample annealed in air, the vacancy-type defect concentration decreases at 300 °C and 700 °C.

1. Introduction

ZnO is a II-VI semiconductor possessing a direct wide band gap of ~3.3eV. It has a large exciton binding energy of 60meV. It is a potential candidate for making novel chemical sensors, piezoelectric transducers, short wavelength optoelectronic devices and spintronic devices.¹-³ The presence of defects strongly degrades the optical and electrical properties of ZnO devices. A better understanding of the identity, quantity and stability of the defects is required to fabricate high quality devices. Defects are inevitably introduced to semiconductors during their growth processes. The impurities and types of defects introduced to ZnO are different in different crystal growth method. Tuomisto et al. performed a comprehensive study of recovery of point defects induced in vapour phase grown crystals.⁴ Chen et al. and Lu et al. carried out positron annihilation studies on hydrothermal grown ZnO crystal.⁵,⁶ ZnO is a irradiation-hard material.⁷,⁸ With a high electron dosage of 6x10¹⁷cm⁻², the vacancy introduction rate is 0.03cm⁻¹ ²⁻¹ and the rate is 30 times lower than that of V_Ga in GaN.¹¹ Thus, ZnO devices can be used in high-irradiation environment.

Positron is a powerful non-destructive probe for vacancy type defects such as V_Zn and V_Zn related defect and complexes in ZnO. In the present study, the thermal evolution of defects under both equilibrium (i.e. as-grown) and non-equilibrium conditions (electron-irradiated) were studied by Variable Energy Doppler Broadening Spectroscopy (VEDBS) to obtain the bulk S parameter, positron diffusion length for analysis.
2. Experimental

Pressurized melt grown (MG) ZnO single crystals terminated with Zn face (0001) were purchased from Cermet, inc.. The as-grown samples are n type. The crystals were irradiated by 2MeV electron with a fluence of $6 \times 10^{17} \text{cm}^{-2}$. The current density for the irradiation was $6\text{mA}/200\text{cm}^{-2}$. The VEDBS measurement was performed using the slow positron beam facility of the University of Hong Kong. The Doppler Broadened gamma photons were detected by high purity Ge detector. The energy resolution of the electronic data acquisition system was $1.3\text{keV}$ at the $514\text{keV}$ photon peak. The Doppler Broadening spectrum was characterized by the valence annihilation S parameter and the core annihilation W parameter. The energy window for the S parameter was $511\pm0.76\text{keV}$ and that for the W parameter was from $511\pm3.4\text{keV}$ to $511\pm6.8\text{keV}$. Depth profiling was done by measuring the S and W parameter against the different positron incident energy from 0.35 to 22keV. The S-E data was analyzed by the program VEPFIT. Isochronal annealing was carried out for the samples from 100°C to 800°C. The samples were heated in a tube furnace in argon and air ambience for 30min.

3. Results

![Figure 1](image1.png)

**Figure 1.** Variation of bulk S parameter and positron diffusion length in as-grown ZnO annealed in argon.

![Figure 2](image2.png)

**Figure 2.** Variation of bulk S parameter and positron diffusion length in electron irradiated ZnO annealed in argon.

![Figure 3](image3.png)

**Figure 3.** Variation of bulk S parameter and positron diffusion length in electron irradiated ZnO annealed in air.

For the as-grown sample (Fig.1), the S parameter increased sharply from 0.394 at 100°C to 0.400 at 200°C while there was an abnormal slight increase in positron diffusion length ($L_+$). The change was tentatively attributed to the decrease in positron scattering centre concentration together with an
increase in the positron trapping vacancy-type defect concentration. From 200°C to 300°C, there was a sudden decrease in S parameter from 0.400 to 0.393 with the increase in \( L_+ \). This might be due to the decrease of deep positron trap concentration. The S parameter rose from 0.393 at 300°C to 0.395 at 500°C. The increases were accompanied with decreases in \( L_+ \), indicating that the positron trapping centre concentration increases. Another S parameter slight decrease from 0.3950 to 0.3946 was observed from 500°C to 600°C with the decrease in \( L_+ \). This might be explained by the formation of positron scattering centres. The S parameter peaked at 200°C and 500°C respectively indicating that defect reactions and agglomeration of defects might have taken place in two annealing temperatures. The S parameter reached a minimum at 300°C and 600°C respectively indicating that a recovery process occurred with 2 annealing stages.

For the irradiated sample annealed in argon (Fig. 2), from room temperature to 100°C, the S parameter increased drastically from 0.393 to 0.399 while the \( L_+ \) decreased slightly. The anti-correlation showed the increase of vacancy-type concentration. From 100°C to 300°C, the S parameter dropped considerably from 0.399 to 0.394. Together with the increase of \( L_+ \), it was revealed that some vacancy-type defects began to anneal out. From 300°C to 400°C, the S parameter rose and peaked at 0.397 with a slight decrease in \( L_+ \), indicating that more vacancy-type defects were formed. From 400°C to 600°C, the S parameter decreased from 0.397 to a local minimum of 0.394 and at the same time the \( L_+ \) was decreasing steadily. This might implied that the vacancy-type defect concentration decreased but the positron scattering defect concentration increased at the same time. The S parameter peaked at 100°C and 400°C respectively indicating that defect reactions and agglomeration of defects might have taken place at the two annealing temperatures. The S parameter approached a minimum at 300°C and 600°C respectively signifying that the annealing out of positron-trapping defects occurred in 2 stages.

For the irradiated sample annealed in air (Fig. 3), from room temperature to 200°C, the S parameter increased from 0.394 to 0.400 while the \( L_+ \) remained unchanged. This indicated the increase of vacancy-type defect concentration. From 200°C to 300°C, the S parameter decreased drastically to a minimum value of 0.394 with a small increase in \( L_+ \). This could be explained by the decrease of vacancy-type defect concentration. From 300°C to 500°C, the S parameter rose from 0.394 to 0.395 while the \( L_+ \) increases. This showed that secondary vacancy defects were formed and some of the positron scattering centres were annealed out. From 500°C to 700°C, there was a small decrease of S parameter from 0.3955 to 0.3946. \( L_+ \) increased in the above temperature range indicating the decrease of vacancy-type defects concentration. In short, the S parameter arrived at a maximum at 200°C and 500°C implying that defect reactions and agglomeration of defects might have taken place at the two temperatures. The S parameter attained a minimum at 300°C and at around 700°C indicating that vacancy-type defects positron-trapping vacancy defects annealed out in 2 stages.

4. Discussions

\( V_o \) and/or \( Zn_i \) are the possible defects which could act as positron scattering centres since they were the common types of defects which were present in single crystal ZnO. At room temperature, \( V_o \) was positively charged and might scatter the positrons by distorting the lattice around its open volumes. The positron binding energy of positron to \( V_o \) was very small. Therefore, \( V_o \) and/or \( Zn_i \) were considered to be the main positron scattering species which could decrease the positron diffusion length in the present study. On the other hand, the rise of S parameter was due to \( V_{Zn} \) or \( V_{Zn} \) related defects since they were the dominant positron trapping centres in as-grown and irradiated n-type ZnO. Lu et al. and Chen et al. reported the presence of positron defect lifetime 230ps and 231ps respectively in electron irradiated ZnO single crystal. They both concluded that \( V_{Zn} \) were introduced to the ZnO single crystals by electron irradiation. Their conclusion were consistent with the theoretical and experimental positron lifetime results by Tuomisto et al. Therefore the rise and fall in the S
parameter in the present study were mainly due to increase and decrease of \( V_{Zn} \) and \( V_{Zn} \) related defects and complexes concentration.

Tuomisto et al. found that \( V_{Zn} \) annealed out of ZnO crystal in 2 annealing stages at about 400K and 600K\(^4\). Chen et al. observed that \( V_{Zn} \) were recovered at 200\(^\circ\)C and 700\(^\circ\)C from ZnO\(^5\). At 400\(^\circ\)C, additional vacancy-type defects were formed\(^5\). Our results were different from the above studies.

5. Conclusions
Recovery of \( V_{Zn} \) and/or \( V_{Zn} \) related defects in as-grown and electron irradiated ZnO crystal occurred with 2 stages at 300\(^\circ\)C and at around 600\(^\circ\)C to 700\(^\circ\)C. Annealing in air or in argon ambience did not affect the recovery temperature.

References
[1] S. J. Pearton, D. P. Norton, R. Frazier, S. Y. Han, C. R. Abernathy and J. M. Zavada, Iee P-Circ Dev Syst 152 (4), 312-322 (2005).
[2] U. Ozgur, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho and H. Morkoc, J Appl Phys 98 (4), 041301 (2005).
[3] D. C. Look, Mat Sci Eng B-Solid 80 (1-3), 383-387 (2001).
[4] F. Tuomisto, K. Saarinen, D. C. Look and G. C. Farlow, Phys Rev B 72 (8), 085206 (2005).
[5] Z. Q. Chen, S. J. Wang, M. Maekawa, A. Kawasuso, H. Naramoto, X. L. Yuan and T. Sekiguchi, Phys Rev B 75 (24), 245206 (2007).
[6] L. W. Lu, C. K. So, C. Y. Zhu, Q. L. Gu, C. J. Li, S. Fung, G. Brauer, W. Anwand, W. Skorupa and C. C. Ling, Semicond Sci Tech 23 (9), 095028 (2008).
[7] D. C. Look, D. C. Reynolds, J. W. Hemsky, R. L. Jones and J. R. Sizelove, Appl Phys Lett 75 (6), 811-813 (1999).
[8] S. O. Kucheyev, P. N. K. Deenapanray, C. Jagadish, J. S. Williams, M. Yano, K. Koike, S. Sasa, M. Inoue and K. Ogata, Appl Phys Lett 81 (18), 3350-3352 (2002).
[9] C. Coskun, D. C. Look, G. C. Farlow and J. R. Sizelove, Semicond Sci Tech 19 (6), 752-754 (2004).
[10] F. Tuomisto, V. Ranki, K. Saarinen and D. C. Look, Phys Rev Lett 91 (20), 205502 (2003).
[11] J. Oila, V. Ranki, J. Kivioja, K. Saarinen, P. Hautojarvi, J. Likonen, J. M. Baranowski, K. Pakula, T. Suski, M. Leszczynski and I. Grzegory, Phys Rev B 63 (4), art. no.-045205 (2001).
[12] G. Brauer, W. Anwand, W. Skorupa, J. Kurilplach, O. Melikhova, C. Moisson, H. von Wenckstern, H. Schmidt, M. Lorenz and M. Grundmann, Phys Rev B 74 (4), 045208 (2006).
[13] T. Koida, S. F. Chichibu, A. Uedono, A. Tsukazaki, M. Kawasaki, T. Sota, Y. Segawa and H. Koinuma, Appl Phys Lett 82 (4), 532-534 (2003).
[14] S. Brunner, W. Puff, A. G. Balogh and P. Mascher, Positron Annihilation - Icpa-12 363-3, 141-143 (2001).
[15] Z. Q. Chen, M. Maekawa, S. Yamamoto, A. Kawasuso, X. L. Yuan, T. Sekiguchi, R. Suzuki and T. Ohdaira, Phys Rev B 69 (3), 035210 (2004).
[16] A. Uedono, T. Koida, A. Tsukazaki, M. Kawasaki, Z. Q. Chen, S. Chichibu and H. Koinuma, J Appl Phys 93 (5), 2481-2485 (2003).
[17] K. I. Hagemark, J Solid State Chem 16 (3-4), 293-299 (1976).
[18] G. D. Mahan, J Appl Phys 54 (7), 3825-3832 (1983).
[19] C. C. Ling, C. K. Cheung, Q. L. Gu, X. M. Dai, S. J. Xu, C. Y. Zhu, J. M. Luo, C. Y. Zhu, K. H. Tam, A. B. Djurisic, C. D. Beling, S. Fung, L. W. Lu, G. Brauer, W. Anwand, W. Skorupa and H. C. Ong, Appl Surf Sci 255 (1), 58-62 (2008).