

Positron Annihilation Study of Radiation Defects in Zinc Oxide

Noriyuki TOMIYAMA, Minoru TAKENAKA* and Eiichi KURAMOTO*

Dep. of Phys., Fac. of Educ., Nagasaki University, Nagasaki 852, Japan

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Abstract

Positron annihilation studies have been carried out to clarify the radiation induced defects in ZnO single crystals. Vapor-grown ZnO crystals were irradiated at 77 K with 28 MeV electrons. Before irradiation as-grown specimens showed the mean positron lifetime in the range of 160–195 ps. Electron irradiation increased the mean positron lifetime up to 205–210 ps. This long-lifetime disappeared until 473 K during successive isochronal annealing steps. The radiation-induced coloration was annealed out around 523 K. During this stage, the radiation induced oxygen vacancies are thought to be moved away and disappeared. The second recovery stage at around 823 K is thought to be caused by the recovery of small ZnO interstitial clusters formed through clustering of interstitial atoms.

1. Introduction

Zinc oxide, known as an n-type semiconductor of the wurzite structure, is a practical material providing a variety of characteristics such as semiconducting, piezoelectric and optical conductivity. The effect of electron irradiation on ZnO crystals has been studied through optical absorption measurement¹⁾, EPR measurement²⁾, *in-situ* observation in a high voltage electron microscope^{3,4)} and other methods. However, these researches could have not reached a satisfactory level, because there is a difficulty in obtaining materials satisfying the required specifications in purity, homogeneity and size. Vehse *et al.*¹⁾ irradiated ZnO with 0.6 and 1.7 MeV electrons, and succeeded to observe absorption spectra of 410 nm in case of the latter radiation energy. The radiation-induced coloration indicates the potentiality of existence of neutral interstitial zinc atoms. Locker *et al.*²⁾ measured the production rate of F⁺ center and EPR spectrum while varying irradiation energy. As a result, they found that; the threshold of displacement energy is 310

* Research Institute for Applied Mechanics, Kyushu University, Kasuga, Fukuoka 816 Japan

keV for O-atom and 900 keV for Zn-atom; and radiation induced coloration is caused by singly ionized oxygen vacancies. Iwanaga *et al.*³⁾ and Yoshiie *et al.*⁴⁾ observed that dislocation loops are formed at acceleration voltage of 300 kV and above by excess zinc atoms originally existed interstitially in the crystals and by oxygen atoms produced by irradiation. These loops can be disappeared by high-temperature annealing. However, they estimated that zinc vacancies cannot be disappeared even at 973 K and above.

On the other hand, the positron annihilation techniques have proved most useful in the investigation of vacancy-like defects in solids. This techniques have been applied to analyze the sintering characteristics of compressed ZnO powder⁵⁾. However, the crystal behavior of disappearance internal defects has not been demonstrated. In this paper results of positron annihilation lifetime measurements performed for vapor-grown ZnO single crystals irradiated by 28 MeV electrons at 77 K will be presented.

2. Experimental

ZnO single crystals used in this investigation were grown by the vapor-phase method⁶⁾. Dozens of yellowish-white granular crystals each measuring about $2 \times 4 \times 1 \text{ mm}^3$ were prepared. The low-temperature electron irradiations were performed by KURRI-LINAC (Kyoto University Reactor Research Institute, LINAC, 28 MeV electron) at 77 K to the dose of $4 \times 10^{18} \text{ e/cm}^2$. The positron annihilation lifetime spectra were obtained at room temperature by the conventional fast-slow coincidence apparatus which facilitates the measurement with resolution 250 to 260 ps in FWHM ($^{22}\text{NaCl}$ source, plastic scintillator KL236 and C31024 RCA phototubes). The measurement was conducted both before and after irradiation. Isochronal annealing was conducted in vacuum ($< 1.3 \times 10^{-3} \text{ Pa}$) while varying the temperature every after 20 min of measurement by 50 K step from a room temperature to 1273 K. In each step, the positron lifetime was measured. The lifetime spectra obtained were decomposed into one component by 'Resolution Program' developed at Risø Institute. Two component analyses were also applied to some data.

3. Results and Discussion

Fig. 1 shows the positron annihilation spectra of as-grown ZnO specimens. Crystal (2) shows a slightly smaller slope; a longer lifetime. The mean lifetime of crystals (1) and (2) is 158 and 196 ps, respectively. These values are the shortest and the longest lifetime among vapor-grown specimens. The lifetime elongation is caused by the annihilation of the positrons trapped by excess zinc atoms and impurities, produced in the process of vapor-growing. Such structural defects

seem to be an original feature of this type of crystals. The vapor-grown ZnO crystals are known to be n-type semiconducting oxide with non-stoichiometric (excess) zinc atoms⁷).

Figs. 2 and 3 show a comparison between positron annihilation lifetime spectra before and after electron irradiation. Both spectra show the lifetime elongation due to irradiation. This is caused by the annihilation of the positrons trapped in vacancies produced by irradiation.

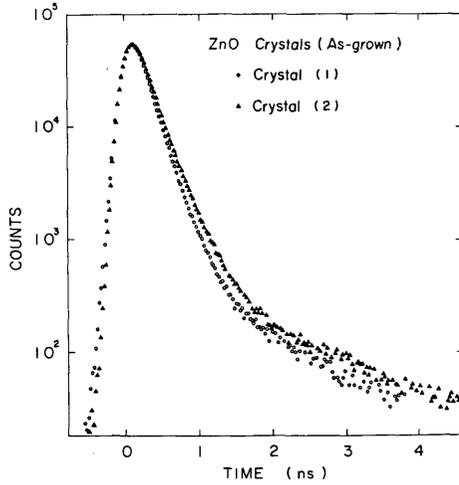


Fig. 1. Positron annihilation lifetime spectra for two as-grown ZnO specimens.

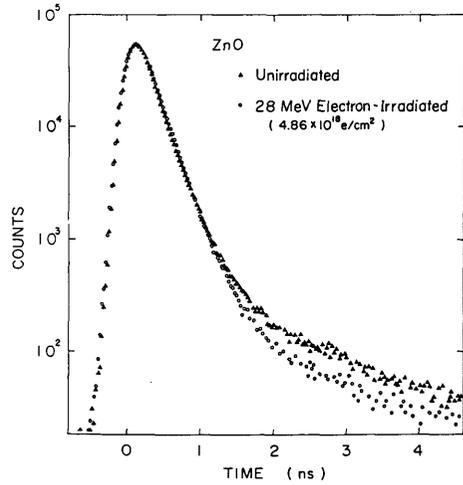


Fig. 2. Positron annihilation lifetime spectra (before and after irradiation) for ZnO specimens.

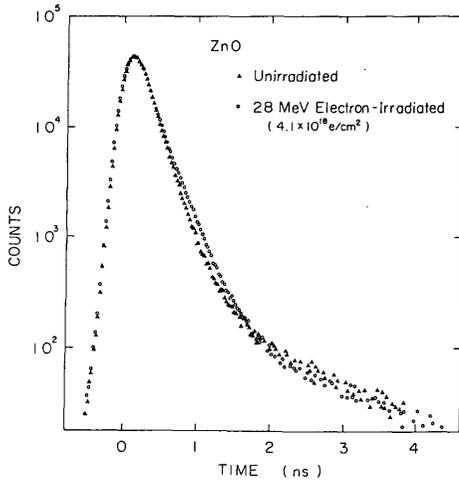


Fig. 3. Positron annihilation lifetime spectra (before and after irradiation) for ZnO specimens.

Fig. 4 shows the isochronal annealing results of the unirradiated and electron irradiated specimens obtained by the positron annihilation lifetime measurements. The lifetime unirradiated crystals (1) and (2) is 167 and 196 ps, respectively. In both crystals, the lifetime stabilizes up to 723 K. Between 723 and 923 K, the lifetime decreased. The long-lifetime specimens, which tend to give off gases, showed decrease in lifetime by about 30 ps. The short-lifetime specimens less give off gases. The lifetime degradation is thought to be caused by becoming difficult in positron trapping due to the disappearance of precipitations comprising excess zinc atoms and impurity atoms which have been originally contained in the specimens. The lifetime of long-lifetime specimens and short-lifetime specimens decreased to about 160 and 155 ps, respectively, in the course of temperature rise from 923 to 1273 K. High-temperature annealing seems to cause disappearance of structural defects. After annealing in vacuum conditions at 1273 K, annealing was conducted for 20 min in air at the same temperature. As a result, no significant change was observed in lifetime.

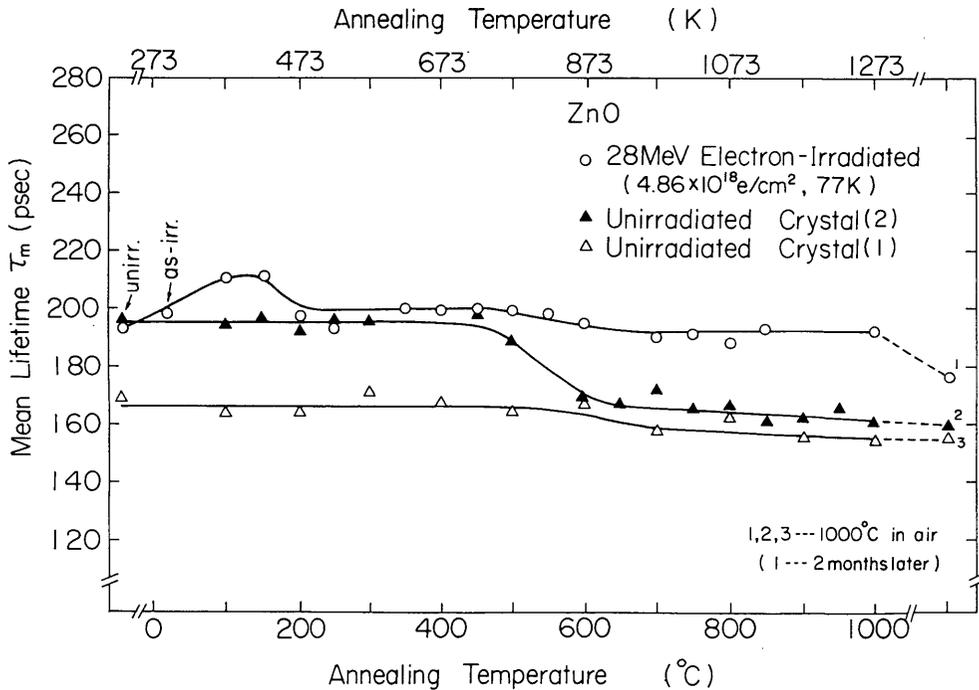


Fig. 4. Temperature dependence of the mean positron lifetime for the ZnO specimens. The open circles represent data on electron-irradiated specimens while the triangle symbols are for data on unirradiated specimens.

Figs. 4 (open circles represent data) and 5 show the annealing behavior of electron-irradiated specimens. In both specimens, irradiation turned the crystals orange from yellowish-white. In Fig. 4 the open circles representing the data shows that the lifetime of 193 ps increases to 198 ps by irradiation (see Fig. 2). But it further increased to about 210 ps. Subsequent isochronal annealing in vacuum condition restored the original color and stabilized the lifetime at around 523 K. Between 723 and 923 K, the lifetime decreases from 200 to 193 ps. During this period, the crystal surface turned from black to grey. The black color might have come from arriving of excess Zn atoms to the crystal surface at this high temperature. Vaporization from crystal inside caused the increase in pressure vacuum degradation for several minutes at the start of annealing; and grey sub-structure part of a quartz glass tube in which samples were loaded for annealing. As a result of analyzing the substance with energy dispersive X-ray spectroscopy (EDS), it was found that the substance contains Zn and Na, which is contained in the major component of the crystal and the starting raw material (ZnF_2). The vaporization seems to be caused by the disappearance of; extract containing excess zinc atoms and sodium atoms, which have originally existed in the crystals; and the dislocation loops formed by migration of radiation induced Zn and

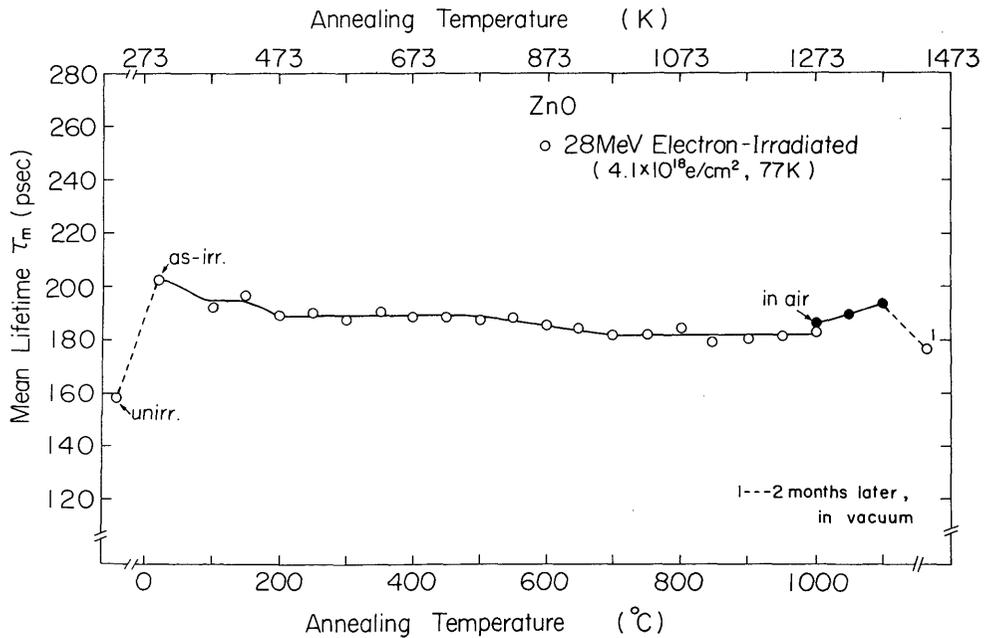


Fig. 5. Temperature dependence of the mean positron lifetime for the electron-irradiated ZnO specimens.

O interstitial atoms. The vaporization causes the difficulty in positron trapping, which results in lifetime degradation. Between 923 and 1273 K, the lifetime is stable at 193 ps. The rather longer lifetime (193 ps) seems to be caused by the annihilation of positrons trapped in zinc vacancies or small clusters of them, which can remain even in a high-temperature zone. The lifetime after exposure to an atmosphere for two months decreased to 176 ps. After another two months, the lifetime decreased to 168 ps. This might be due to some circumstance effect, *e.g.*, invasion of hydrogen atoms from the air.

Fig. 5 shows a case that the lifetime increases from 158 to 202 ps by irradiation (see Fig. 3). As a result of two-component analysis, it was found that the lifetime and intensity of a long-lifetime component of the radiation-induced vacancies is 212 ± 2 ps and $79.8 \pm 2.1\%$, respectively. A lifetime recovery stage and radiation-induced coloration exist in the same temperature region as that in the before-mentioned case, and the lifetime decreases to 190 ps at 523 K. In the next stage, the lifetime further decreases to 180 ps. However, vaporization is not significant. This seems to be caused by originally less excess zinc atoms. After a series of annealing in vacuum conditions, isochronal annealing was carried out in air, while varying the temperature every after 20 min by 50 K step from 1273 to 1373 K. As a result, the lifetime increased from 180 to 195 ps. The lifetime then decreased to 176 ps after two months exposure in a low-vacuum chamber.

The recovery stage at around 473 K can be explained using the theory proposed Locker *et al.*²⁾; the movement and disappearance of radiation-induced oxygen-ion vacancies causes a recovery stage. The recovery stage at around 823 K is thought to be caused by; the disappearance of structural defects which have originally existed in the crystals; and the disappearance of dislocation loops, which have been observed by Yoshiie *et al.*⁴⁾. The subsequent longer and stable lifetime in a high temperature region seems to be caused by the annihilation of positrons trapped in zinc vacancies produced by irradiation.

4. Conclusion

Summarizing the results of the positron lifetime studies of electron irradiated ZnO crystals the following statements have to be made. Electron-irradiation causes interstitial defects which function as color centers to absorb visible radiation. Vapor-grown yellowish-white crystals turned orange by irradiation. A long-lifetime component of about 210 ps arisen from irradiation seems to be caused by the positrons trapped in oxygen vacancies. Subsequent isochronal annealing decreased the lifetime at around 523 K and restored the crystals in color. Ionized oxygen vacancies seem to be disappeared resulting from moving away. The second recovery stage appears at around 823 K: this stage corresponds to evaporation

of excess zinc atoms and impurity atoms, which are originally contained in the specimens, and some amount of dislocation loops produced by irradiation. This recovery stage was also observed in the unirradiated specimens. Electron irradiated specimens could not be restored in the initial value even at 1273 K. This seems to be caused by positrons trapped in zinc vacancies or small clusters of them. The lifetime value in the matrix was evaluated as about 160 ps.

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