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Electron irradiation-induced defects in ZnO studied by positron annihilation

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Abstract

ZnO crystals were subjected to 3 MeV electron irradiation up to a high dose of $5.5 \times 10^{18}\,cm^{-2}$. The production and recovery of vacancy defects were studied by positron annihilation spectroscopy. The increase of positron lifetime and Doppler broadening S parameter after irradiation indicates introduction of V_{Zn} related defects. Most of these vacancies are annealed at temperatures below 200 °C. However, after annealing at around 400 °C, secondary defects are produced. All the vacancy defects are annealed out at around 700 °C.

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Keywords: Positron annihilation; Defect; ZnO; Electron irradiation

1. Introduction

In recent years there is a growing interest in ZnO [1–3] because of its wide band gap (3.4 eV) and large-exciton binding energy (60 meV), which enable its potential applications in the short wavelength light-emitting devices [4]. Among those investigations, the study of defects is one of the most important subjects because of their strong influence on the electrical and optical properties.

Positron Annihilation Spectroscopy (PAS) has been proved to be a powerful tool for the study of vacancy-type defects in semiconductors [5]. The annihilation characteristics of positron at the defects are different from the defect-free bulk state, thus it provides a direct method for the identification of vacancy defects. Up to now a few works have been conducted on the study of defects in ZnO by PAS [6–9]. In this paper, we studied the vacancy defects and their thermal recovery process in the 3 MeV electron irradiated ZnO through positron annihilation measurements.

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2. Experiment

ZnO samples are hydrothermal grown single crystals obtained from the Scientific Production Company (SPC goodwill). Electron irradiation was performed at room temperature on the Zn face of the sample. The energy of electrons was 3 MeV and the electron dose ranged from 5×10^{17} to $5.5 \times 10^{18}\,cm^{-2}$. The irradiated samples were isochronally annealed from 100 to 700 °C in nitrogen ambient for 30 min.

Positron lifetime measurement was performed using a fast–fast coincidence system with time resolution of about 210 ps. Doppler broadening spectra were measured using a high purity Ge detector with energy resolution of about 1.3 keV at 511 keV. The Doppler spectra are characterized by the S and W parameters, which are defined as the ratio of the central region (511 ± 0.85 keV) and wing region (511 ± 3.4 to 511 ± 6.8 keV) to the total area of the 511 keV annihilation peak, respectively. In this work, they were normalized to the defect free bulk value. Therefore $S > 1$ or $W < 1$ shows existence of vacancy defects. Micro-Raman-scattering measurements were performed using the NANOFINDER spectrometer. The 488.0 nm-line of an Ar^+-ion laser was used for excitation.

3. Results and discussion

Fig. 1 shows the average positron lifetime τ_{av} as a function of the electron irradiation dose. Before irradiation, the positron lifetime shows only a single component of about 183 ± 1 ps, which is very close to the bulk positron lifetime reported in our earlier work [9]. Therefore, we believe that no or very few defects trap positrons in the unirradiated sample.

After electron irradiation, the average positron lifetime shows monotonous increase up to about 212 ps at a dose of $5.5 \times 10^{18}\,cm^{-2}$. The S parameter also increases to about 1.016 ± 0.001. This means that vacancy defects are introduced by electron irradiation. Fig. 2 shows the decomposed positron lifetime τ_1, τ_2, intensity I_2 and the positron-trapping rate κ as a function of the electron dose. The lifetime $\tau_{1,mod}$ calculated according to the trapping model coincides with the experiment value, suggesting that the decomposition is reliable. τ_2 corresponds to the positron lifetime at vacancy defects. With electron dose increases to above $2 \times 10^{18}\,cm^{-2}$, the decomposition becomes relatively stable, and τ_2 is stabilized at about 230 ps. This value is in agreement with that reported by Tuomisto et al. [10], which corresponds to monovacancies. In ZnO, V_O is essentially invisible to positrons [9,10]. Therefore, the vacancies observed by positrons are V_{Zn} related defects.

As seen in Fig. 2, the positron-trapping rate κ shows linear increase with electron dose. As $\kappa = \mu C_d$, where μ is the specific positron trapping rate, C_d is the vacancy concentration, this suggests that the vacancy concentration increases linearly with the electron dose. Taking $\mu = 3 \times 10^{15}\,s^{-1}$ for V_{Zn} [10], the vacancy introduction rate is about $0.05\,cm^{-1}$.

The change of the average positron lifetime and S parameter after annealing is shown in Fig. 3. A fast decrease of both positron lifetime and S parameter is seen below 200 °C. After that, both of them begin to increase, and reach a maximum value at 400 °C. Above 400 °C, the positron lifetime and S parameter decrease again, and approach the bulk value at 700 °C. The decrease of positron lifetime and S parameter below 200 °C might be due to the recombination of V_{Zn}–Zn_i close Frenkel pairs. Tomiyama et al. [6] observed similar annealing stage at around 150–200 °C for the 28 MeV electron irradiated ZnO. Brunner et al. [7] also observed such annealing stage at 50–150 °C in the 2 MeV electron irradiated ZnO, and it was attributed to the annealing of Zn monovacancies.

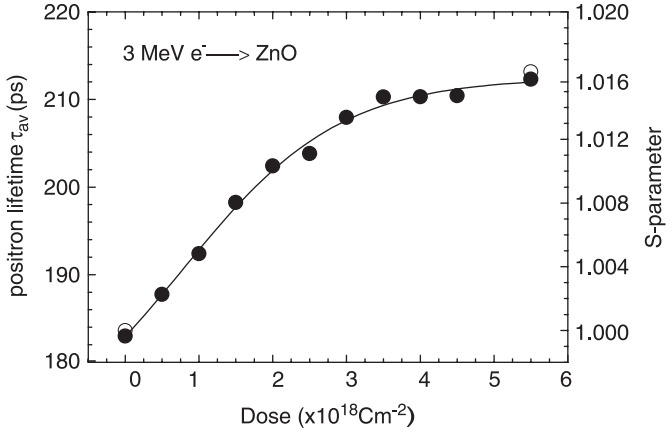

Fig. 1. Average positron lifetime τ_{av} and S parameter as a function of electron irradiation dose.

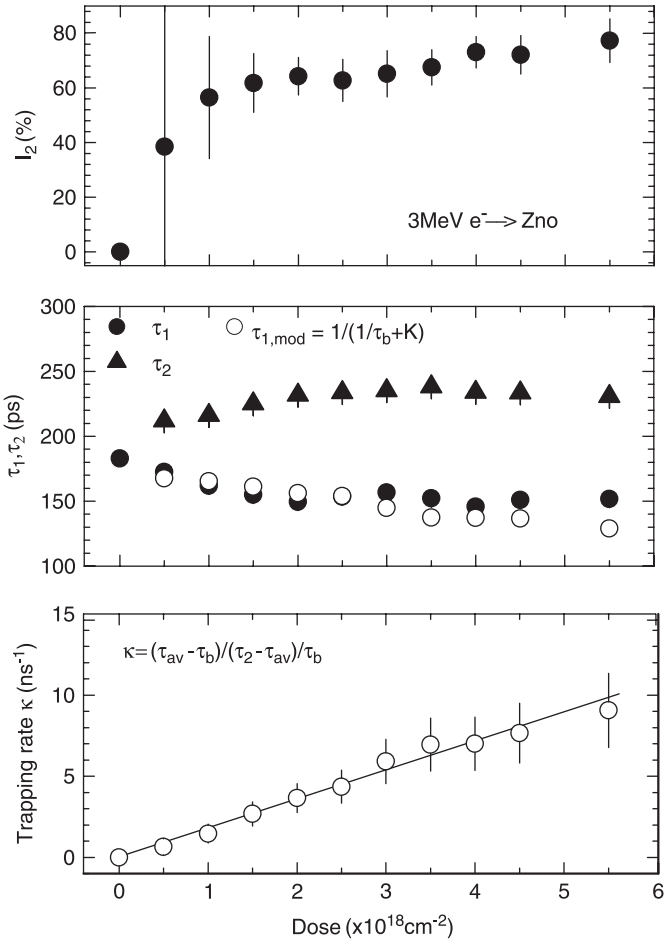

Fig. 2. Decomposed positron lifetime τ_1, τ_2, intensity I_2 and the positron-trapping rate κ as a function of electron irradiation dose.

As for the increase of the positron lifetime and S parameter after annealing at 400 °C, there are two possible reasons. First, the vacancy defects might become more negatively charged, therefore it leads to the increase of positron trapping rate. Second, some additional defects are created. Our Hall measurements show that the sample becomes semi-insulating after irradiation with dose of $5.5 \times 10^{18}\,cm^{-2}$. Even after 400 °C annealing, it still keeps high resistivity. This means that the Fermi level does not move after annealing up to 400 °C. Therefore, the first possibility can be excluded. Some secondary defects are probably produced by the thermal treatment.

After annealing at above 400 °C, the positron lifetime and S parameter show decrease again. It can be inferred that the remaining V_{Zn} are removed in this stage, possibly through migration into the sinks. The secondary defects

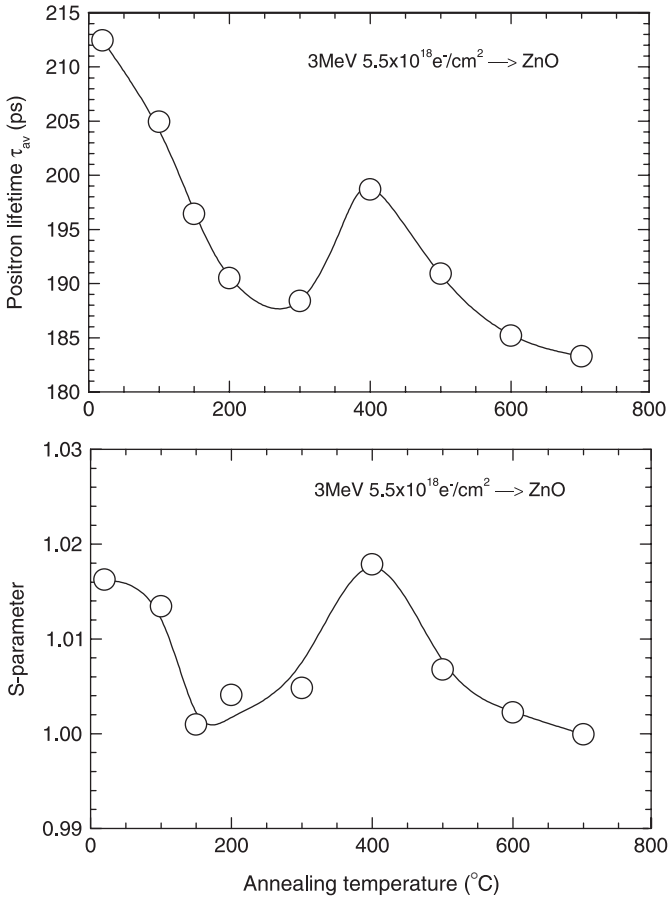

Fig. 3. Average positron lifetime and S parameter as a function of annealing temperature in the electron-irradiated ZnO with a dose of $5.5 \times 10^{18}\,\mathrm{cm}^{-2}$. The annealing time was 30 min.

created at around 400 °C are also annealed out, as both the positron lifetime and S parameter decrease to the bulk value at 700 °C.

Fig. 4 shows the change of S versus W parameter during the annealing process. The S–W data are concentrated on two different lines, which corresponds to two different types of defects, i.e., the electron irradiation induced V_{Zn} (defect 1) and the annealing produced secondary defects (defect 2). Therefore, this confirms that annealing at 400 °C produces additional vacancy defects that are different from V_{Zn}.

Fig. 5 shows the Raman spectra for the electron irradiated ZnO before and after annealing. The primary peak at $437\,\mathrm{cm}^{-1}$ is the high-frequency E_2 phonon mode, which represents the wurtzite structure of ZnO [11,12]. After electron irradiation, a broad peak at $575\,\mathrm{cm}^{-1}$ appears. This is obviously induced by the defects produced by electron irradiation. The broad peak shows very small decrease after annealing up to 200 °C. Only at 300 °C, it becomes much weaker, and at 400 °C, it decreases to the level of the as-grown sample. As the positron measurements show that most of V_{Zn} disappear below 200 °C, the broad Raman peak is apparently not due to V_{Zn} related defects. The possible candidate for this defect might be

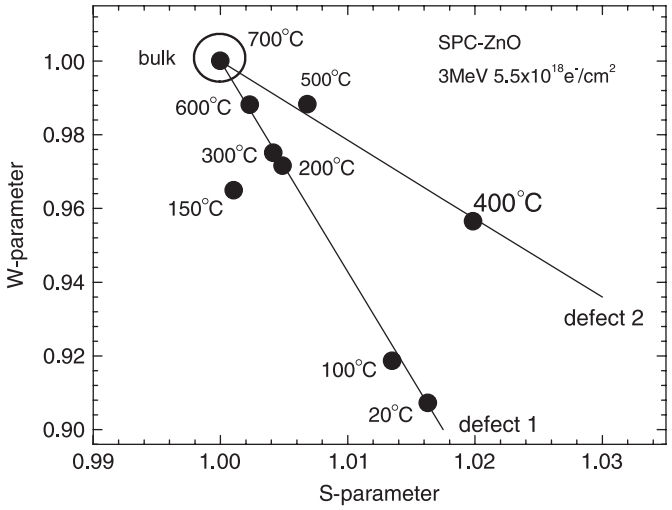

Fig. 4. S–W plot measured for the electron-irradiated ZnO during annealing process.

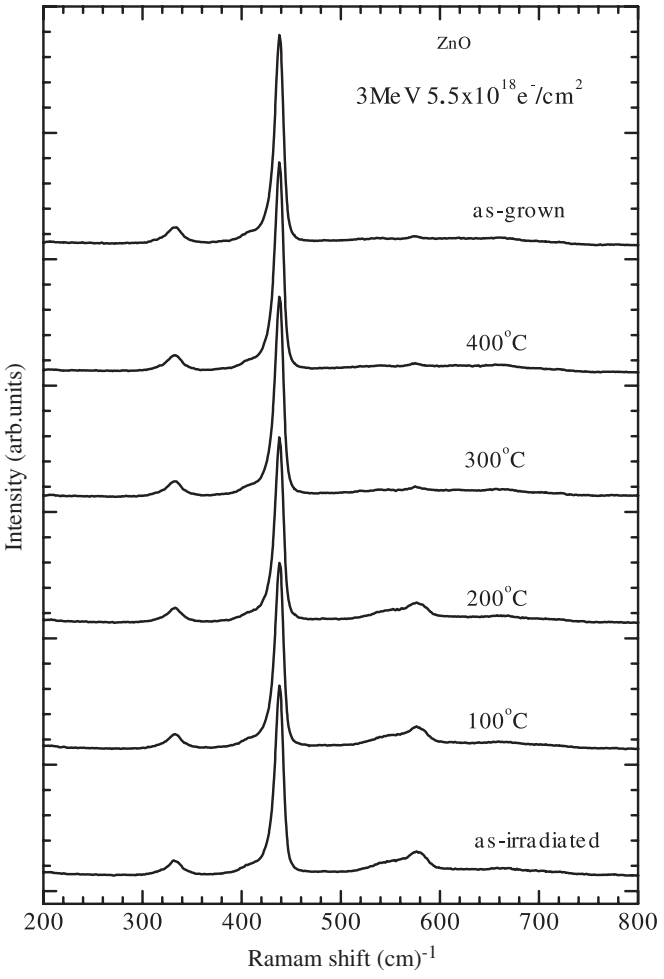

Fig. 5. Annealing effect on the Raman spectra measured for the electron-irradiated ZnO with dose of $5.5 \times 10^{18}\,\mathrm{cm}^{-2}$.

oxygen vacancy. This has been confirmed by many other researchers [13,14], as they found that such broad peak will be enhanced in a oxygen deficient condition.

The Raman measurements thus show that V_O disappears at around 400 °C. This is also in good agreement with the recent measurements by Vlasenko and Watkins [15]. This means that V_O becomes mobile between 200 and 400 °C, which coincides with the temperature for the production of secondary defects. Thus we may assume that while some of the V_O disappear through recombination with their interstitials or migration into sinks, many other of them might also take part in the following defect reactions:

$$V_{Zn} + V_O \rightarrow V_{Zn}V_O,$$
$$Zn_{Zn} + V_O \rightarrow (V_{Zn} - Zn_O).$$

Therefore, the divacancies or V_{Zn}–Zn_O complexes might be the candidates for the secondary defects formed at 400 °C. Further study is still needed to confirm this possibility.

4. Conclusion

Defects in the electron irradiated ZnO crystals were studied by positron annihilation spectroscopy. The irradiation-induced defects detected by positrons are Zn monovacancies. Most of them are annealed at 0–200 °C. However, after annealing at around 400 °C, additional vacancy defects are produced. The *S*–*W* correlation study reveals that these two vacancy defects are not the same category. The secondary defects might be divacancies or V_{Zn}–Zn_O complexes. All the vacancy defects are annealed out at around 700 °C.

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