Point defects in ZnO crystals grown by various techniques

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Abstract. In the present work point defects in ZnO crystals were characterized by positron lifetime spectroscopy combined with back-diffusion measurement of slow positrons. Defects in ZnO crystals grown by various techniques were compared. Hydrothermally grown ZnO crystals contain defects characterized by lifetime of ≈181 ps. These defects were attributed to Zn vacancies associated with hydrogen. ZnO crystals prepared by other techniques (Bridgman, pressurized melt growth, and seeded chemical vapour transport) exhibit shorter lifetime of ≈165 ps. Positron back-diffusion studies revealed that hydrothermally grown ZnO crystals contain higher density of defects than the crystals grown by other techniques. The lowest concentration of defects was detected in the crystal grown by seeded chemical vapor transport.

1. Introduction
Zinc oxide (ZnO) is a wide band gap (3.4 keV) semiconductor with a high exciton binding energy of 60 meV. Nowadays ZnO attracts large interest as a promising material for blue/UV light emitters and optoelectronic devices [1]. Because of the progress in the growth techniques high quality ZnO crystals became available [2]. At present there are several techniques capable of production of high quality ZnO crystals, namely seeded chemical vapor transport growth (CVT) [3], pressurized melt growth (PMG) [4], Bridgman growth (BG) [5] and hydrothermal growth (HTG) [6].

The main obstacle for widespread use of ZnO consists in doping asymmetry [1]: practically all ZnO crystals exhibit n-type conductivity but it is hard to achieve stable and reproducible p-type doping. A solution of this problem requires understanding of point defects which govern optical and electrical properties of ZnO crystals and ability to control their population. To contribute to this research in the present work point defects in ZnO crystals grown by various methods were characterized by positron lifetime spectroscopy combined with positron back-diffusion measurement.

2. Experimental details
A variety of ZnO single crystals were studied, namely (i) HTG ZnO crystals supplied by the following producers: MaTecK (Germany), Crystec (Germany), MTI (USA), Altramek (USA); (ii) PMG crystals
provided by Cermet (USA), (iii) BG crystals grown at the Institut für Kristallzüchtung (IKZ) in Berlin (Germany); and (iv) CVT crystals grown at the Oak Ridge National Laboratory (ORNL) in USA.

Bulk positron lifetime investigations were performed using a 1.5 MBq $^{22}$Na radioisotope deposited on a 2 $\mu$m thick mylar foil employing a digital positron lifetime spectrometer [7] with time resolution of 145 ps (FWHM of resolution function). The source contribution consisted of two components with lifetimes of 368 ps and 1.5 ns and relative intensities of 7 and 1%. Measurement of back-diffusion of slow positrons was carried out on a continuous magnetically guided slow positron beam [8] with energy of incident positrons adjustable in the range from 0.03 up to 35 keV. Doppler broadening of annihilation peak was measured by a HPGe detector with energy resolution of 1.09 keV at 511 keV and was evaluated using the line-shape $S$ parameter. Selected samples were investigated on a pulsed slow positron beam PLEPS [9] at the intense positron source NEPOMUC. The energy of incident positrons in PLEPS was varied in the range 0.5-18 keV and the time resolution was 300 ps.

3. Results and discussion

3.1. As-grown crystals

All as-grown ZnO single crystals studied exhibited a single component positron lifetime spectrum (except of the source contribution). Chemical analysis revealed different concentrations of impurities not only in ZnO crystals provided by various producers but also in crystals from the same producer but supplied in different years [10]. It is therefore important to check whether crystals provided by single supplier in various years can be considered to be the same from the point of view of intrinsic defects. Hence, at first we compared batches of crystals fabricated by MaTecK and Cermet companies in various periods. Figure 1 shows that lifetimes measured for HTG ZnO crystals supplied by MaTecK in various years are practically the same. Similarly lifetimes for PMG ZnO crystals provided by Cermet in different years are close to each other. Thus, regarding defects, the crystals prepared in various periods are comparable. However there is a striking difference between HTG and PMG crystals.

![Figure 1](image1.png)

Figure 1. Results of bulk positron lifetime measurements for batches of HTG and PMG ZnO crystals supplied by MaTecK and Cermet companies in various years.

Figure 2 shows results of bulk positron lifetime measurements of ZnO crystals prepared by various methods. All HTG crystals exhibit similar lifetime around 181 ps independently on the supplier. On the other hand, crystals prepared by other techniques (PMG, BG and CVT) are characterized by a remarkably shorter lifetime around 165 ps. Positron lifetimes reported for ZnO crystals in literature [11-15] are plotted in the figure as well. Positron lifetimes measured on various setups may slightly differ. Scatter of literature data is, therefore, higher due to systematic errors but the literature data are basically in accordance with the aforementioned picture.
Examples of $S$ parameter curves for as-grown ZnO crystals prepared by various techniques are plotted in Figure 3a. The $S(E)$ curves were fitted by VEPFIT code [16] using a single layer model. The mean positron diffusion length $L_+$ and the $S$ parameter for ZnO bulk obtained from fitting are plotted in Figure 3b and in the inset of Figure 3a, respectively. The CVT ZnO crystal exhibits the longest $L_+$ among all samples studied. PMG crystals are characterized by shorter $L_+$ and the shortest $L_+$ values were measured for HTG ones. The $S$ parameters exhibit opposite behavior. It indicates that the CVT crystal contains the lowest density of defects among the samples studied; the concentration of defects in PMG crystals is slightly higher and HTG crystals exhibit the highest density of defects. Note that in contrast to other samples CVT ZnO crystals are completely colorless indicating very low level of impurities.

![Figure 2. Positron lifetimes for various ZnO crystals. Data measured in the present work and taken from the literature [11-15] are plotted by full and open symbols, respectively.](image)

![Figure 3. Results of positron back-diffusion measurements of as-grown ZnO crystals: (a) examples of $S(E)$ curves; solid lines are model curves calculated by VEPFIT. The inset shows the $S$ parameters for ZnO bulk obtained from fitting; (b) the mean positron diffusion lengths $L_+$ obtained from fitting.](image)

*Ab-initio* theoretical calculations of positron lifetimes were employed in order to identify defects in ZnO crystals [10]. Calculated positron lifetimes depend on the approximation of electron-positron correlation used. Hence, Table 1 shows not only the calculated lifetimes but also their ratios to the bulk lifetime $\tau_B$ calculated with the same approach that depend only slightly on the approximation used. Our calculations are in a satisfactory agreement with $\tau/\tau_B$ ratios calculated in Ref. [14], see Table 1. The oxygen vacancy ($V_O$) is only a shallow trap incapable of positron confinement. On the
other hand, zinc vacancy ($V_{Zn}$) is a deep positron trap (positron binding energy $> 1$ eV) characterized by positron lifetime exceeding 200 ps. Zinc and oxygen di-vacancy ($V_{Zn}V_{O}$) is a deep trap as well.

**Table 1.** Lifetimes $\tau$ for various positron states in ZnO obtained by *ab-initio* theoretical calculations and their ratios to the bulk lifetime $\tau / \tau_B$. Detailed description of the calculations is given in Ref. [10].

| Positron state | bulk | $V_{O}$ | $V_{Zn}$ | $V_{Zn}V_{O}$ | $V_{Zn+H}$ |
|---------------|------|---------|----------|--------------|------------|
| Lifetime $\tau$ (ps) | 154 | 154 | 207 | 253 | 179 |
| $\tau / \tau_B$ | 1 | 1 | 1.34 | 1.64 | 1.16 |
| Ref. [14] | 1 | 1 | 1.34 | 1.53 | |

From comparison of experimental data with theoretical calculations one can conclude that the lifetime of 165 ps measured for PMG, BG and CVT crystals is $\approx 10$ ps longer than the calculated bulk lifetime $\tau_B = 154$ ps. This indicates that PMG, BG and CVT crystals exhibit relatively low density of defects and the majority of positrons is annihilated in the free state. Experimental lifetimes slightly higher than the calculated $\tau_B$ might be caused by lattice expansion due to absorbed hydrogen. It supports analysis of CVT crystal which revealed hydrogen concentration as high as 1.03 wt.%. HTG crystals, however, exhibit lifetime which is on one hand remarkably higher than the bulk ZnO lifetime but on the other hand smaller than the lifetime calculated for positrons trapped at $V_{Zn}$. Hence, HTG crystals contain defects with open volume smaller than $V_{Zn}$ and the concentration of these defects is so high that virtually all positrons are annihilated in the trapped state (saturated positron trapping).

| Figure 4. | Positron lifetimes for radiation-induced defects in electron and proton irradiated ZnO crystals. Results measured in the present work and data taken from literature are plotted by full and open symbols, respectively. The labels in the figure denote energies of bombarding electrons or protons (in MeV). Solid lines indicate calculated lifetimes for various positron states, see Table 1. |

The most probable candidates for defects in HTG ZnO crystals are $V_{Zn}$ associated with some impurities. It has been demonstrated that hydrogen is the most important impurity in ZnO crystals because its concentration is roughly two orders of magnitude higher than the concentration of any other impurity [10]. Thus, it is natural to consider $V_{Zn}$ associated with hydrogen ($V_{Zn+H}$). Theoretical calculations revealed that there is attractive interaction between H and $V_{Zn}$, and the calculated lifetime of positrons trapped at $V_{Zn+H}$ was found to be 179 ps [10]. This value is in excellent agreement with the lifetime of $\approx 181$ ps measured in HTG crystals.

The concentration of $V_{Zn+H}$ can be estimated from positron back-diffusion measurement using the formula $[V_{Zn+H}] = \nu^{-1} \tau_{BB}^{-1} (L_{\tau_{BB}}^2 / L_{\tau}^2 - 1)$, where $\tau_B$ is the bulk ZnO lifetime and $\nu \approx 10^{15}$ s$^{-1}$ is the...
specific positron trapping rate typical for negatively charged vacancies in semiconductors [17]. Assuming that positron diffusion length determined for CVT crystal is the value corresponding to a perfect ZnO lattice, i.e. $L_{+B} \approx 100$ nm, one gets $[V_{Zn+H}] \approx 2 \times 10^{-2}$ at. $^{-1}$ $(10^{18}$ cm$^{-3}$) with $L_{+} = 54$ nm. Using the two-state simple trapping model [17] one can easily calculate that such a concentration of defects corresponds to the free positron component with lifetime of $\approx 20$ ps and intensity of $\approx 3\%$ only. It is too weak to be resolved in positron lifetime spectrum. Thus, the estimated $[V_{Zn+H}]$ in HTG crystals is consistent with saturated positron trapping. Note that hydrogen content in HTG crystals determined by nuclear reaction analysis [10] is roughly 20 times higher than $[V_{Zn+H}]$. Hence, all $V_{Zn}$ available in HTG crystals were coupled with H and remaining hydrogen occupies interstitial sites in ZnO lattice.

Recently it has been proposed that positrons in HTG crystals are trapped by negatively charged substitutional Li impurities [18]. Although this might be a plausible explanation, the concentration of Li in some of our HTG crystals is lower than $[V_{Zn+H}]$. More importantly there are strong variations of Li content in HTG crystals (e.g. MaTecK sample exhibits $[Li] = 3 \times 10^{16}$ cm$^{-3}$ while crystal from Altramet has $[Li] = 6 \times 10^{16}$ cm$^{-3}$) but no variations of positron lifetimes were observed. Thus, we propose that in HTG crystals positrons are trapped at $V_{Zn+H}$.

**Figure 5.** Results of positron annihilation studies of HTG ZnO crystals supplied by MaTecK in the as-grown state and after irradiation by 2.5 MeV protons: (a) $S(E)$ curves, solid lines are model curves calculated by VEPFIT; (b) the dependence of the mean positron lifetime on the energy of incident positrons. Dashed lines indicate the mean lifetimes obtained by bulk positron lifetime spectroscopy.

### 3.2. Irradiated crystals

Additional knowledge about defects in ZnO crystals can be obtained from irradiation experiments. Irradiated ZnO crystals exhibit typically two-component positron lifetime spectra. The longer component represents a contribution of positrons trapped at defects created by irradiation. Figure 4 shows the lifetime of radiation-induced defects for ZnO crystals irradiated by electrons (diamonds) and protons (stars). Lifetimes for irradiation-induced defects reported in literature are plotted in the figure as well (open symbols). The energies of bombarding electrons or protons (in MeV) are indicated by labels in the figure. The points for the same energies are ordered according to increasing fluence. The investigations of irradiated samples supported the calculated positron lifetimes for $V_{Zn}$ of 207 ps and for $V_{Zn}V_{O}$ of 253 ps. One can conclude that electron irradiation introduced a mixture of $V_{Zn}$ and $V_{Zn}V_{O}$. The fraction of $V_{Zn}V_{O}$ increases with increasing electron energy and increasing fluence. Irradiation by protons with energy exceeding 1 MeV introduced always $V_{Zn}V_{O}$ as dominating defects. Recently it has been reported [20] that lifetime of positrons trapped at $V_{Zn}V_{O}$ is practically the same as that for $V_{Zn}$. This, however, contradicts not only our calculations but also the calculations in Ref. [14].

Figure 5a shows a comparison of $S(E)$ curves for virgin and 2.5 MeV proton irradiated HTG crystals. Proton irradiation led to shortening of $L_{+}$ and increase of the $S$ parameter inside ZnO due to $V_{Zn}V_{O}$ created by irradiation. Figure 5b shows a comparison of the mean positron lifetime measured on a pulsed slow positron beam in a HTG crystal in the virgin state and after irradiation by 2.5 MeV...
protons. The mean lifetime gradually decreases from the surface value at very low energies down to a value corresponding to the situation when virtually all positrons are annihilated inside the ZnO crystal. This value is in good agreement with the lifetime around 181 ps obtained in the bulk positron lifetime measurements as indicated by the red dashed line in the figure. The sample irradiated by 2.5 MeV protons exhibits an enhanced lifetime inside the crystal due to defects created by irradiation. Again this value is in good agreement with the mean lifetime obtained in the bulk positron lifetime measurement. This testifies that depth concentration profile of radiation-induced defects is rather flat.

4. Conclusions
Defects in ZnO single crystals grown by various methods were characterized by positron annihilation spectroscopy. ZnO crystals prepared by melt growth, Bridgman growth and chemically assisted vapor phase are characterized by positron lifetime of 165 ps which is close to the calculated bulk ZnO lifetime of 154 ps. These crystals exhibit a low concentration of defects and the majority of positrons are annihilated in the free state. Hydrothermally grown ZnO crystals exhibit saturated positron trapping at defects characterized by the lifetime of 181 ps. We propose that these defects are $V_{\text{Zn}}$ associated with H. Irradiation experiments revealed that $V_{\text{Zn}}$ and $V_{\text{Zn}}V_{\text{O}}$ are characterized by lifetimes of $\approx 210$ ps and $\approx 255$ ps. These values are in good agreement with theoretical calculations.

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