Defects Studies of ZnO Single Crystals Prepared by Various Techniques

F. Lukáč, J. Čížek, I. Procházka, O. Melikhova, W. Anwand and G. Brauer

1. Introduction

Zinc oxide (ZnO) is a perspective wide band gap semiconductor for blue/UV light emitters, detectors, and optoelectronic devices [1]. Despite the great progress in growth of high quality ZnO crystals [2], the preparation and characterization of ZnO single crystals is still a challenging task since various methods provide samples with various defects introduced by the method. A detailed characterization of these defects is crucial since they often strongly influence electrical, magnetic, and optical properties of ZnO crystals [3].

Positron lifetime (LT) spectroscopy [4] provides unique tools for characterization of point defects present in a material. In case of ZnO, the LT results available in literature show different lifetimes for as-grown crystals from various suppliers [5–9]. There is also a controversy in the interpretation of LT results. Therefore, a systematic investigation of ZnO crystals prepared by various methods is desirable in order to clarify the kinds of defects introduced by different methods of crystal growth. These experimental results were compared with ab initio theoretical calculations of positron annihilation characteristics for various defect configurations in ZnO-lattice performed in Ref. [8].

2. Experimental

Single crystals with dimensions of $10 \times 10 \times 0.5 \text{ mm}^3$ have been investigated. Hydrothermal (HT) grown samples were supplied by MaTecK GmbH (Jülich), CrystTec GmbH (Berlin), University Wafers (South Boston/MA), MTI (Richmond/CA) and Altra (Atomergic Chemetals Corp., Farmingdale/NY). Pressurized melt (PM) grown crystals were fabricated by Cermet Inc. (Atlanta/GA) and crystals prepared by Bridgman growth (BG) method were grown at the Institut für Kristallzüchtung (IKZ, Berlin).

A digital LT spectrometer [10] with excellent time resolution of $145 \text{ ps}$ (FWHM $^{22}\text{Na}$) was employed for the LT investigations. A $^{22}\text{Na}_2\text{CO}_3$ positron source with activity of $1.5 \text{ MBq}$ deposited on a $2 \mu\text{m}$ thick Mylar foil was sandwiched between a pair of ZnO crystals. At least $10^7$ positron annihilation events were accumulated in the LT spectra which were decomposed using a maximum likelihood based procedure [11]. The source contribution consisted of two weak components which come from positrons annihilated in the source spot and the covering Mylar foil and exhibit lifetimes of $\approx 368 \text{ ps}$ and $\approx 1.5 \text{ ns}$ and intensities of $\approx 7\%$ and $\approx 1\%$, respectively.

Variable energy positron annihilation spectroscopy (VEPAS) investigations were performed on a magnetically guided variable energy slow positron beam SPONSOR [12] at Helmholtz Zentrum Dresden-Rossendorf. Energy of incident positrons was varied in the range from 0.03 to 36 keV. Doppler broadening of annihilation profile was measured by HPGe detector with energy resolution of $(1.09 \pm 0.01) \text{ keV}$ at 511 keV and analyzed using $S$ and $W$ line shape parameters.

3. Results and discussion

Results of the LT investigations of the HT, PM, BG, and vapor phase (VP) grown ZnO single crystals obtained in this work and collected from literature are listed in Table. Each LT spectrum after the source contribution correction consisted of a single component only. The lifetimes measured on various ZnO crystals are plotted in Fig. 1. From inspection of Fig. 1, it becomes clear that the positron lifetimes fall into two groups: (i) HT grown...
samples exhibit higher positron lifetimes in the range of 179–182 ps, while (ii) ZnO crystals grown by the other techniques (PM, BG, VP) exhibit shorter lifetimes falling into the range of 160–173 ps. There is only one exception from this division: Sarkar et al. [7] reported the lifetime of 164 ps for a HT grown ZnO crystal supplied by the MTI (Richmond, CA). To clarify this inconsistency, we purchased a HT grown ZnO crystal fabricated by the MTI company and re-measured it in our laboratory. One can see in Table that this crystal exhibits the positron lifetime of (179.6 ± 0.5) ps which belongs to the group (i) and is consistent with the lifetimes measured in HT grown crystals in our laboratory and also by other authors [5, 6]. For this reason, the value of 164 ps reported by Sarkar et al. [7] was not considered further in this work and is not plotted in Fig. 1.

In addition, Fig. 1 shows not only the experimental positron lifetimes but also the results of ab initio theoretical calculations of positron lifetimes for free positrons (bulk), positrons trapped at zinc vacancies (V_{Zn}), and positrons trapped at (V_{Zn}−H) complexes calculated in Ref. [8] using the self-consistent electron density and considering ion relaxation around defects and positron induced forces.

The theoretical calculations of point defects in ZnO available in literature consistently show that an oxygen vacancy is too shallow to trap positrons. On the other hand, a zinc vacancy is a deep positron trap and defects found in the ZnO crystals should be related to zinc vacancies. However, the lifetime of positrons trapped at zinc vacancy calculated using the self-consistent electron density and taking into account ion relaxation and positron induced forces is 207 ps [8] and the lifetimes calculated in other less accurate approaches are even higher, see Fig. 1. Hence, the lifetimes measured in as-grown ZnO single crystals are remarkably smaller than those calculated for the zinc vacancy. This can be caused by impurities bound to zinc vacancies which cause a shortening of the lifetime of trapped positron. In Refs. [8, 15] it was shown that hydrogen is the most important impurity in ZnO crystals and its concentration in ZnO crystals is more than one order of magnitude higher than the concentration of any other impurity. Moreover, hydrogen atoms are attracted to open-volume defects and form complexes with zinc vacancies (V_{Zn}−H). The lifetime of the positrons trapped at (V_{Zn}−H) complexes calculated in Ref. [8] using the self-consistent electron density and taking into account the ion relaxation and positron induced forces is 179 ps, see dashed line in Fig. 1, which agrees well with the life-

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\begin{array}{|c|c|c|c|}
\hline
\text{Method of growth} & \text{Supplier} & \tau_1 [\text{ps}] & \text{Reference} \\
\hline
HT & MTI, USA & 164 (1) & [7] \\
HT & MTI, USA & 164 (2) & [8] \\
P M & Cermet, USA & 166.2 (1) & [9] \\
P M & Cermet, USA & 166.4 (3) & [9] \\
BG & IKZ, Germany & 166.0 (3) & [9] \\
VP & Eagle-Picher, USA & 173 (2) & [9] \\
VP & Eagle-Picher, USA & 161 (2) & [9] \\
\hline
\end{array}
\]
times measured in HT grown ZnO crystals. ZnO crystals grown by other techniques exhibit shorter positron lifetimes which are, however, still higher than the ZnO bulk lifetime. Hence, in the ZnO crystals grown by the other techniques, the positrons are trapped at the defects with smaller open volume than the \((V \text{Zn}_0 \text{-H})\) complexes. Since a high density of stacking faults (SF) was found in BG grown ZnO crystals by X-ray diffraction combined with transmission electron microscopy, it has been suggested that in the ZnO crystals grown by BG and PM techniques positrons are trapped at open-volume misfit defects associated with stacking faults [13]. High density of SFs in these crystals can be attributed to thermal gradients existing in the melt.

\[ L_0 = \frac{kT}{m^*\tau_{ph}} \]  

(1)

where \( k \) is the Boltzmann constant, \( T \) is thermodynamical temperature, \( m^* \approx 1.5m_0 \) is the effective positron mass in the units of the rest electron mass \( m_0 \) and \( \tau_{ph} \) is the relaxation time for the positron scattering process. For thermalized positrons in ZnO, the acoustic longitudinal phonon scattering dominates and the relaxation time for this process \( \tau_{ph} \) can be calculated using the deformation-potential approximation [17, 18]:

\[ \tau_{ph} = \sqrt{\frac{8\pi}{9}} \frac{\hbar^3\langle \epsilon_{ii} \rangle}{(m^*kT)^2E_d^2}, \]

(2)

where \( \hbar \) is the reduced Planck constant, \( \langle \epsilon_{ii} \rangle \) is the averaged elastic constant associated with longitudinal waves [19], and \( E_d = 3.9 \text{ eV} \) is the deformation potential [20]. The positron diffusion coefficient \( D_+ = 5.2 \text{ cm}^2 \text{s}^{-1} \) was obtained for a perfect ZnO crystal using Eqs. (1), (2). The mean positron diffusion length in a perfect ZnO crystal \( L_{+B} \) can be then calculated as

\[ L_{+B} = \sqrt{D_+\tau_{B}}. \]

(3)

Using \( \tau_B = 154 \text{ ps} \) as bulk positron lifetime, Eq. (3) yields \( L_{+B} = 280 \) nm. This value is comparable with the positron diffusion lengths measured on well annealed semiconductors which usually fall into the range of 200-300 nm [21].

Figure 2 shows dependences of the \( S \)-parameter on the energy \( E \) for HT (full points) and PM (open points) grown ZnO crystals. Model curves calculated by VEPFIT [16] are plotted by solid lines.

\[ S = \frac{S_0}{E} \]

\[ E \]

(4)

The symbol \( \nu \) stands for the specific positron trapping rate for cation vacancies. Using \( \nu = 1.7 \times 10^{13} \text{s}^{-1} \) [21], which is a typical value for a double charge negative vacancy, Eq. (4) yields \( c_V = (1.4 \pm 0.1) \times 10^{-4} \) \( ((1.1 \pm 0.1) \times 10^{19} \text{ cm}^{-3}) \) and \( c_V = (0.8 \pm 0.1) \times 10^{-4} \) \( ((0.7 \pm 0.1) \times 10^{15} \text{ cm}^{-3}) \) for the HT and PM grown ZnO crystal, respectively.

The concentration of defects is given also by the two-state trapping model (STM) [23]:
\[ c_v = \frac{1}{\nu} \frac{I_2}{I_1} \left( \frac{1}{\tau_B} - \frac{1}{\tau_D} \right), \]

where \( I_1 \) and \( I_2 \) is the intensity of free positron component and the component which comes from positrons trapped at defects, respectively. The symbol \( \tau_D \) denotes the lifetime of trapped positrons, i.e. \( \tau_D \approx 180 \) ps and \( 165 \) ps for HT and PM grown ZnO crystals, respectively. Using Eq. (5) and the defect concentration determined in ZnO crystals by Eq. (4), one can easily calculate that STM predicts extremely low intensity of the free positron component \( I_1 \leq 1\% \). In practice, it is not possible to resolve the free positron component when its intensity becomes as small as \( \approx 1\% \). Hence, the density of cation vacancies in ZnO crystals is so high that it leads to saturated positron trapping which is in accordance with LT results. Measurement of positron diffusion length by VEPAS is more sensitive than LT spectroscopy to variations of defect density in materials where the concentration of defects becomes very high [24]. Hence, VEPAS enables to obtain reliable estimate of defect concentrations in the materials with very high density of defects where LT spectroscopy cannot be used due to saturated trapping.

4. Conclusions

An investigation of positron lifetimes for high quality ZnO single crystals from various suppliers was performed in this work. All ZnO crystals studied exhibit a single component LT spectrum with lifetime remarkably higher than the bulk ZnO lifetime due to saturated positron trapping at defects. Two groups of ZnO crystals can be distinguished: (i) HT grown samples contain zinc vacancies associated with hydrogen and characterized by lifetimes falling in the range 179-182 ps, (ii) crystals grown by other techniques (PM, BG, and VP) contain vacancy-like open volume defects located at SFs and characterized by shorter lifetimes falling in the interval 160-173 ps. This phenomenon can be explained by different nature of the growing methods. In HT method, ZnO are grown from concentrated aqueous solutions of hydroxides and presence of relatively high amount of hydrogen leads to formation of \( \text{Zn}_x\text{H}_y \)-complexes. PM and BG techniques utilizing melting of ZnO induce stacking faults due to unavoidable temperature gradients in the melt. Similarly, VP growth technique likely introduces SFs into the crystal due to unequal solidification rate. VEPAS investigations revealed that HT grown crystal exhibits higher defect density than PM grown sample.

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References


