Author(s): Tuomisto, Filip & Look, David C.

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Vacancy defect distributions in bulk ZnO crystals

Filip Tuomisto*[a] and David C. Look[b,c]
[a]Laboratory of Physics, Helsinki University of Technology, POB 1100, FI-02015 TKK, Finland;
[b]Semiconductor Research Center, Wright State University, Dayton, OH USA 45435;
[c]Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH USA 45433

ABSTRACT

We have used positron annihilation spectroscopy to study vacancy defects in ZnO single crystals grown by various methods from both commercial and academic sources. The combination of positron lifetime and Doppler broadening techniques with theoretical calculations provides the means to deduce both the identities and the concentrations of the vacancies. The annihilation characteristics of the Zn and O vacancies have been determined by studying electron-irradiated ZnO grown by the seeded vapor phase technique. The different ZnO samples were grown with the following techniques: the hydrothermal growth method, the seeded vapor phase technique, growth from melt (skull melting technique), and both conventional and contactless chemical vapor transport. We present a comparison of the vacancy defects and their concentrations in these materials.

Keywords: ZnO, vacancy, positron annihilation, single crystal

1. INTRODUCTION

Point defects have an important effect on the electronic and optoelectronic properties of semiconductor materials. Both their identification and quantification are necessary in order to understand the microscopic processes leading to the specific properties. Point defects are created in semiconductors during growth, where their formation is governed by thermodynamics and growth kinetics. Different growth methods naturally lead to different point defect distributions due to different temperatures, pressures, and in the case of compound semiconductors, the stoichiometry of the growth environment. Also the nature of the impurities present and their final concentrations vary from one growth method to another.

In this work we apply positron annihilation spectroscopy to study the vacancy defects in bulk ZnO crystals. Positrons are sensitive to open volume (i.e., vacancy-type) defects, at which they can get trapped. The trapping of positrons at vacancy defects is observed as changes in the positron-electron annihilation characteristics. The positron lifetime reflects the size of the open volume of the defect, while the Doppler broadening of the 511-keV annihilation radiation gives information about the electron momentum distribution at the annihilation site and is sensitive to the atomic environment of the vacancy. The combination of these techniques can thus be used to identify both the open volume and the sublattice of the defect in compound semiconductors.

We show that the bulk ZnO crystals grown by the seeded vapor phase and melt techniques have very low concentrations of vacancy defects, but still the dominant defects observed by positrons are the Zn vacancies. On the other hand, in addition to Zn vacancies, relatively high concentrations of O vacancies are observed in ZnO bulk crystals grown by the hydrothermal and conventional chemical vapor transport methods. The contactless chemical vapor transport produces material with a high concentration of Zn vacancies, but no O vacancies are observed, as in the ZnO grown by the seeded vapor phase and skull-melt techniques.

Our paper is organized as follows. In Sec. 2 we give details on the measured ZnO samples and give a short introduction to positron annihilation spectroscopy. In Sec. 3 we show how the vacancy defects on both the Zn and O lattices are identified. We present the results obtained in the bulk ZnO crystals in Sec. 4 and discuss the differences and similarities of the different growth techniques in Sec. 5. Finally we summarize the work in Sec. 6.

*filip.tuomisto@tkk.fi; phone +358-9-4513144; fax +358-9-4513116; http://www.fyslab.hut.fi

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2. METHOD

2.1 ZnO samples

The original identification of the Zn and O vacancies in ZnO[1–3] was performed in ZnO samples grown by Eagle-Picher (E-P) with the seeded vapor phase technique,[4] and then irradiated with 2-MeV electrons at room temperature. The samples grown with the same technique by ZN-Technologies (ZNT) are in principle identical to those grown by E-P. ZnO bulk crystals grown from the melt (the skull-melt method[5]) were obtained from Cermet. In all three materials, the concentrations of all impurities (except hydrogen) are below 10^{17} cm^{-3}. ZnO bulk crystals grown by the hydrothermal technique (see *e.g.* Ref. 6) were obtained from two different manufacturers: Tokyo Denpa (TD) and Scientific Production Company (SPC). The concentration of the most abundant impurity, lithium, is in the 10^{18} cm^{-3} range in these samples. This is a general property of hydrothermally grown ZnO. The conventional and contactless chemical vapor transport techniques were applied to the growth of bulk ZnO crystals at the Institute of Physics of the Polish Academy of Sciences.[7,8] These materials are also characterized by low (below 10^{17} cm^{-3}) impurity concentrations. All the measured samples were nominally undoped. ZnO grown by the hydrothermal method had high resitivity, while the other materials were all slightly *n*-type due to residual impurities or intrinsic defects.

2.2 Experimental details

The positron lifetimes were measured with a conventional fast-fast coincidence spectrometer with a time resolution of 250 ps.[9] Two identical sample pieces were sandwiched with a 20 μCi positron source (^{22}Na deposited on 1.5 μm Al foil). Typically 2×10^6 annihilation events were collected in each positron lifetime spectrum. The lifetime spectrum $n(t)= \Sigma_i I_i \exp(-t\ /\ \tau_i)$ was analyzed as the sum of exponential decay components convoluted with the Gaussian resolution function of the spectrometer, after subtracting the constant background and annihilations in the source material (typically a few percent, for details see e.g. Refs. 1, 2) The positron in state *i* annihilates with a lifetime τ_i and an intensity I_i. The state in question can be the delocalized state in the lattice or the localized state at a vacancy defect. The increase of the average lifetime $\tau_{\mathrm{ave}} = \Sigma_i I_i\ \tau_i$ above the bulk lattice lifetime τ_B shows that vacancy defects are present in the material. This parameter is insensitive to the decomposition procedure, and even as small a change as 1 ps in its value can be reliably measured.

In the case of one type of vacancy defect with specific lifetime t_V, the decomposition of the lifetime spectrum into two components τ_1 and τ_2 is straightforward to interpret. The second lifetime component $\tau_2 = \tau_V$ gives directly the vacancy specific lifetime and the first lifetime component is $\tau_1 = (\tau_B^{-1} + \kappa_V)^{-1} < \tau_B$, where τ_B is the positron lifetime in the delocalized state in the lattice and κ_V the positron trapping rate into the vacancy defects.

The Doppler broadening of the annihilation radiation was measured simultaneously with the positron lifetime using a Ge detector with an energy resolution of 1.3 keV. The conventional valence (*S*, low momenta: $|p_z| < 3 \times 10^{-3}\ m_0c$) and core (*W*, high momenta: $10 \times 10^{-3}\ m_0c < |p_z| < 30 \times 10^{-3}\ m_0c$) annihilation parameters were determined from the measured data after background subtraction as the fractions of annihilations in the corresponding momentum ranges. The parameters are presented here as relative to the parameters specific to the annihilation from the delocalized state in the perfect ZnO lattice. The coincidence detection of both 511 keV photons emitted from the positron-electron annihilation was accomplished with a NaI detector providing the gate signal. The peak-to-background ratio was 10^4 and 3×10^6 counts were collected in the spectrum in the coincidence mode.

2.3 Data analysis

The temperature dependence of the positron annihilation parameters (τ_{ave}, *S*, and *W*) is analyzed with the model of trapping and escape rates of positrons, explained in detail in earlier works.[9–12] In this model, the trapping coefficient μ_V to a neutral vacancy is independent of temperature and to a negatively charged vacancy it varies as $T^{-0.5}$. The trapping rate of positrons into the vacancies (concentration c_V) is $\kappa_V = \mu_V\ c_V$. Positrons can get trapped also at hydrogen-like Rydberg states surrounding negative-ion-type defects (shallow traps for positrons). The positron trapping rate at the Rydberg state μ_R varies also as $T^{-0.5}$, which is the result predicted by theory for the transition from a free state to a bound state in a Coulomb potential.[12] The thermal escape rate from the Rydberg state can be written as

$$\delta_{\mathrm{st}} = \mu_R \left(\frac{m_+ k_B T}{2\pi\hbar^2} \right)^{3/2} e^{-E_{b,\mathrm{st}} / k_B T}, \tag{1}$$

where μ_R is the positron trapping coefficient to the lowest hydrogenlike Rydberg state, $E_{b,\mathrm{st}}$ is the positron binding energy of the lowest Rydberg state (typically < 0.1 eV), and $m_+ \cong m_0$ is the effective mass of the positron. In principle, positrons can also escape from the Rydberg states around negatively charged vacancies, but we assume that the transition from the Rydberg state to the ground state in the vacancy is fast enough so that this effect can be neglected. This is supported by the results obtained in both ZnO[1] and GaN.[13] An effective trapping rate of the shallow traps can thus be defined as

$$\kappa_{\mathrm{st}}^{\mathrm{eff}} = \frac{\kappa_{\mathrm{st}}}{1 + \delta_{\mathrm{st}} / \lambda_{\mathrm{st}}}, \tag{2}$$

where $\lambda_{\mathrm{st}} \cong \lambda_B$ is the annihilation rate of positrons trapped at the Rydberg state, which coincides with the annihilation rate λ_B from the delocalized state in the bulk lattice, and $\kappa_{\mathrm{st}} = \mu_R\, c_{\mathrm{st}}$ is directly related to the concentration of the negative ions.

Finally, the decomposition of the lifetime spectra into several lifetime components gives the possibility to determine experimentally the fractions of positrons annihilating in various states. The average lifetime can be written as

$$\tau_{ave} = \eta_B \tau_B + \sum_j \eta_{D,j} \tau_{D,j}, \tag{3}$$

where η_B and τ_B are the annihilation fraction and positron lifetime in the free state in the lattice, and $\eta_{D,j}$ and $\tau_{D,j}$ are the corresponding values in bound states at the defect D_j. The annihilation fractions are related to the trapping rates through

$$\eta_B = \frac{\lambda_B}{\lambda_B + \sum_j \kappa_{D,j}^{\mathrm{eff}}}, \qquad \eta_{D,j} = \frac{\kappa_{D,j}^{\mathrm{eff}}}{\lambda_B + \sum_{j'} \kappa_{D,j'}^{\mathrm{eff}}}. \tag{4}$$

3. IDENTIFICATION OF THE VACANCY DEFECTS

The results of the positron lifetime and Doppler broadening measurements in both the as-grown and irradiated E-P ZnO samples[1–3] are presented as a function of measurement temperature in Fig. 1. The increase of the average positron lifetime τ_{ave} with decreasing temperature is a clear indication of the presence of negatively charged vacancy defects. In the as-grown material, the monotonous behavior of the lifetime below 300 K indicates that these vacancy defects are the dominant negatively charged defect. On the other hand, in the electron-irradiated samples the decrease of the positron lifetime with decreasing temperature is typical of negative-ion-type defects that compete in trapping of positrons with the negative vacancies. This is observed also as the increase of the first lifetime component τ_1, where the increased trapping in the negative-ion-type defects brings the component closer to the bulk lifetime. The Doppler broadening parameters S and W behave as a function of temperature similarly to the positron lifetime.

A higher lifetime component of $\tau_V = \tau_2 = 230 \pm 10$ ps could be extracted from the exponential lifetime spectra below 300 K, while the data measured in the as-grown ZnO sample above 300 K exhibited only one component. The higher lifetime component is constant as a function of temperature, which implies that it represents positrons annihilating in one bound state. In our previous study, we have identified this higher lifetime component as that specific to the Zn vacancy and the lifetime $\tau_B = 170$ ps to the annihilation from the delocalized state in the ZnO lattice at 300 K.[1] Also the Doppler broadening parameters ($S_D = 1.039$ and $W_D = 0.87$) specific to the Zn vacancy were determined in that work. By comparing the positron results to temperature-dependent Hall measurements, the Zn vacancy in the double-negative charge state was identified as the dominant compensating defect (concentration $[V_{\mathrm{Zn}}] = 2 \times 10^{15}$ cm^{-3}) in as-grown ZnO and co-dominant together with the so-far-unidentified negative-ion-type defect in the irradiated material, where the concentrations of both defects were obtained as $[V_{\mathrm{Zn}}] = c_{st} = 2 \times 10^{16}$ cm^{-3}. The identification was based on both positron lifetime and Doppler broadening coincidence measurements together with comparison to theoretical positron calculations. In addition, the Zn vacancies were the main defect observed by positron annihilation spectroscopy. The Doppler broadening parameters S and W fall on a line when plotted against each other with temperature as the running parameter, which typically indicates the presence of only two distinguishable positron states (bulk and vacancy). The negative-ion-type defects do not cause deviations from the straight line, since the annihilation parameters of positrons trapped at these shallow traps coincide with those of the bulk parameters.

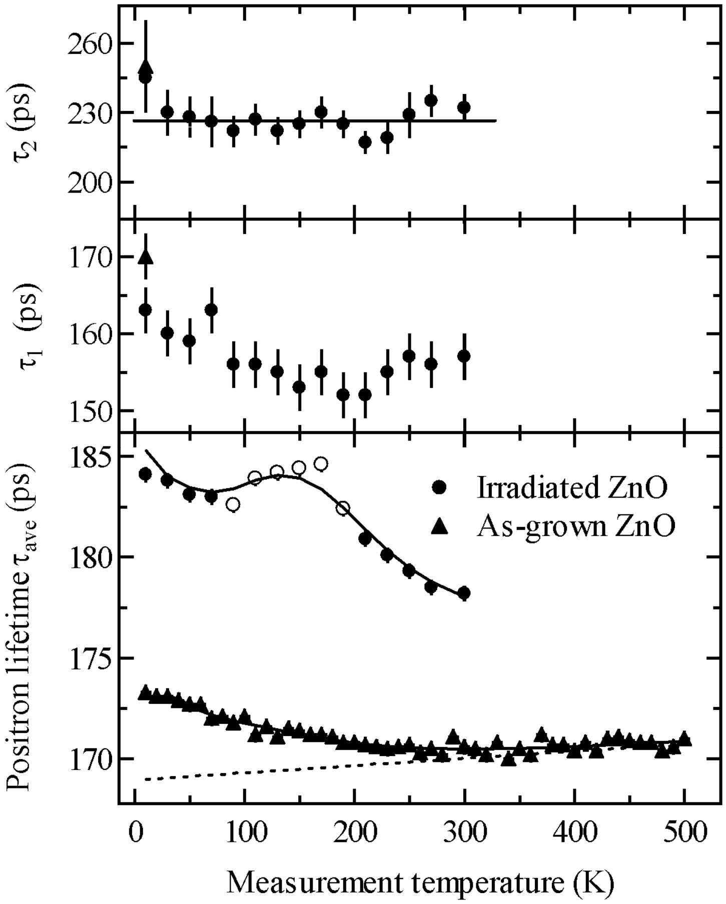

Fig. 1. The positron lifetime parameters of the as-grown and irradiated samples plotted as a function of measurement temperature. The solid curves represent the parameters obtained by fitting the temperature-dependent trapping model to the data. The dashed line shows the fitted bulk lifetime, where the temperature dependence is due to the thermal expansion of the lattice. The circles are drawn as open in the temperature range 90–190 K, where the effect of the oxygen vacancies is most visible.

However, as can be seen in Fig. 3, the points measured at 90–190 K in the irradiated samples fall off the straight line determined by the annihilations in the bulk lattice and the Zn vacancy. This implies that a third positron state can be distinguished in the lifetime versus Doppler parameter data although the Doppler data themselves are linear. In order to cause a deviation from the straight line, the localization to this defect needs to be strong, implying that the defect has a distinguishable open volume. On the other hand, the open volume of this defect cannot be very large, since, as pointed out above, the independence of temperature of the higher lifetime component τ_2 shows no evidence of the mixing of several lifetime components. Hence, the lifetime specific to this defect needs to be sufficiently far from τ_2 (and closer to τ_1), i.e., below about 200 ps. In addition, in order to produce the deviation observed in Fig. 3, the defect-specific lifetime needs to be above τ_{ave} over the whole temperature range — i.e., above about 185 ps. This defect has been identified as the O vacancy in a previous study.[3]

Results of positron measurements in E-P bulk ZnO crystals, have been reported also by two other groups.[14,15] The conclusions in these works coincide with ours: the vacancy defect concentration in this material is below the detection limit of positron annihilation spectroscopy at room temperature and only one lifetime component can be fitted to the spectrum, thus giving directly the bulk lifetime. The bulk lifetime values reported by the two other groups are about 10 ps lower than that reported in our previous works.[1–3] However, slight differences in the positron lifetime spectrometers, such as scintillators, geometry, and electronic settings influence the absolute values of the positron lifetimes. Also electron-irradiated E-P ZnO samples were investigated in Ref. 14. In terms of the most important comparable parameter, namely the ratio between the positron lifetimes at the Zn vacancies and in the bulk, the agreement between that work and our work in Refs. 1–3 is excellent.

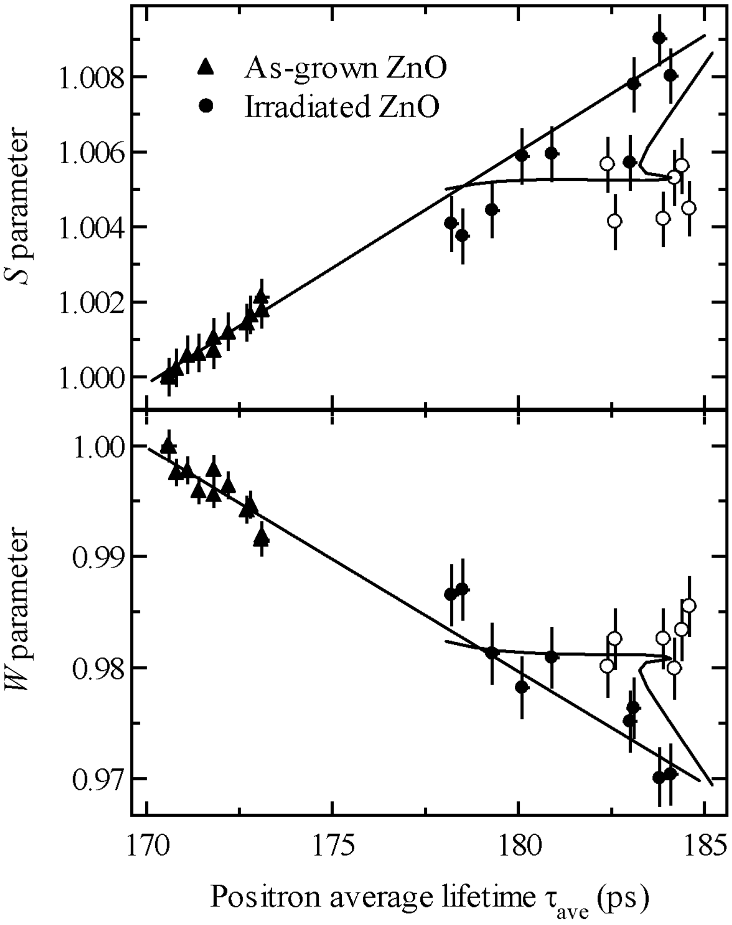

Fig. 2. The S and W parameters plotted as a function of τ_{ave}. The parameters depend linearly on each other in the temperature range where the low-binding-energy positron traps do not contribute significantly. The open circles were measured at T=90–190 K. The solid lines connect the parameters of the bulk lattice to those (not shown) of the Zn vacancy. The solid curves are obtained from the fits to the S vs T, W vs T, and τ_{ave} vs T data.

In summary, we have determined the bulk lifetime of positrons in ZnO as 170 ps and have identified the vacancy defects on both sublattices in ZnO. The positron lifetime at a Zn vacancy V_{Zn} is $\tau_{V,Zn}$ =230 ± 10 ps, while it is $\tau_{V,O}$ =195 ± 5 ps at an O vacancy (V_O). The latter is typically inseparable from the annihilation spectra, as it is very close to the bulk lifetime. The Zn vacancies have also a clear effect on the Doppler broadening of the annihilation radiation, with vacancy-specific parameters (S_D = 1.039 and W_D = 0.87). The O vacancies produce Doppler parameters very close to those of the ZnO lattice.

4. RESULTS IN BULK ZNO CRYSTALS

4.1 Seeded-vapor-phase and melt-growth techniques

The average positron lifetimes measured as a function of temperature in bulk ZnO crystals grown by the seeded vapor phase (E-P and ZNT) and skull-melt (Cermet) techniques are shown in Fig. 3. As explained above, the E-P material contains Zn vacancies in the double negative charge state at a concentration of $[V_{Zn}] = 2 \times 10^{15}$ cm^{-3}, evident from the separation of the lifetime components (not shown in Fig. 3) and the increase of the average lifetime with decreasing temperature. The positron lifetime representative of the pure ZnO lattice was fitted to the data obtained above 300 K, and is shown as the dotted line in Fig. 3. The slight increase with increasing temperature is due to the thermal expansion of the lattice. The material grown by ZN-Technologies (labeled ZNT) is nominally identical to that grown by Eagle-Picher (E-P). Figure 3 shows that the average positron lifetimes in these two materials coincide above 300 K, but at lower temperatures the average lifetime is lower in the ZNT ZnO (about 171 ps at 20 K compared to 173 ps in E-P ZnO), but still slightly above the fitted ZnO lattice lifetime. This indicates that a very small but measurable fraction of positrons annihilates at vacancy defects (concentration lower than in E-P ZnO, about 10^{15} cm^{-3}), which are presumably Zn vacancies. However, the fraction is too small for the lifetimes to be separable from the lifetime spectrum and hence the defects cannot be conclusively identified.

Interestingly, the average positron lifetime measured in Cermet ZnO coincides with the lifetime of the ZnO lattice estimated from the E-P ZnO data in the whole temperature range of the measurement, and no higher components could be separated from the lifetime spectra at any temperature. This indicates that the concentration of vacancy defects in this material is below the detection limit of positron annihilation spectroscopy, i.e. well below 10^{15} cm^{-3}. Another positron annihilation study[16] has reported a very high vacancy concentration (about 10^{17} cm^{-3}) in a Cermet bulk ZnO crystal. However, in this case the material was purchased much earlier, while we performed measurements on very recent ZnO material.

The results presented above support the estimation of positron lifetime in the ZnO lattice as 170 ps at room temperature. As the positron lifetimes measured in these samples coincide at room temperature, our results show that any of these three bulk ZnO crystals (E-P, ZNT, or Cermet) qualify as good reference samples (i.e., providing defect-free parameters) for accurate and reliable positron measurements in ZnO.

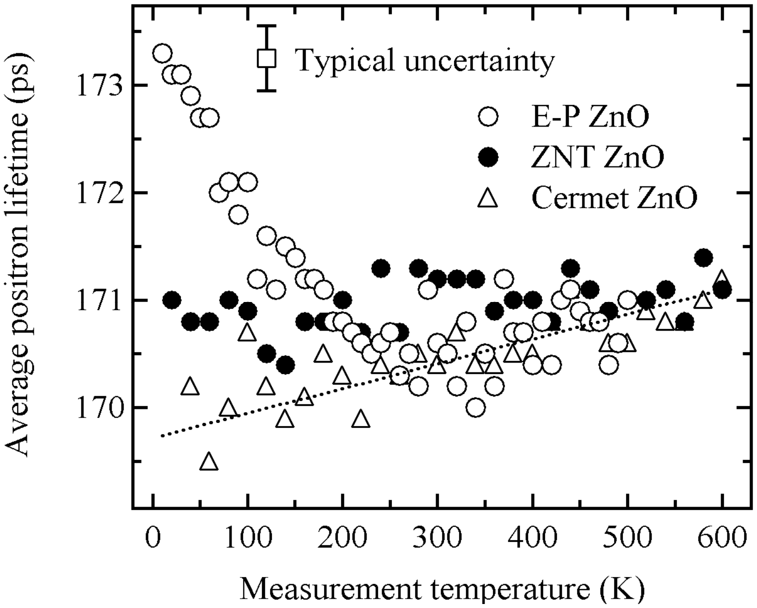

Fig. 3. The average positron lifetimes measured in the bulk ZnO crystals grown by the seeded vapor phase technique (E-P and ZNT) and the skull-melt technique (Cermet). The dashed line shows the bulk lifetime in the ZnO lattice originally fitted to the E-P data. The temperature dependence of the bulk lifetime reflects the thermal expansion of the lattice.

4.2 Hydrothermal growth

Results from bulk ZnO crystals grown by the hydrothermal method (TD and SPC) are shown in Fig. 4. The data obtained in E-P ZnO are shown as a reference together with the fitted lattice ZnO lifetime. The average positron lifetime is of similar magnitude (180-185 ps) in the TD and SPC ZnO crystals, about 10-15 ps above the lattice ZnO lifetime measured in the E-P ZnO. This is in excellent agreement with earlier reports of positron lifetimes in ZnO crystals grown by the hydrothermal method.[14,17] The main difference between the TD and SPC ZnO crystals is in the behavior of the average positron lifetime with measurement temperature: the average positron lifetime decreases with increasing temperature in TD ZnO, while it increases slightly in SPC ZnO. This indicates that positrons are trapped at negatively charged vacancy defects in TD ZnO, while the data in SPC ZnO suggest that the vacancy defects are neutral and that positrons are also trapped at negatively charged non-open volume defects (negative ions) in SPC ZnO. The negatively charged vacancy defects in TD ZnO are likely to be Zn vacancies.

As explained above, an average lifetime higher than that in the pure ZnO lattice indicates that a fraction of the annihilating positrons must be trapped at vacancy defects. An average-lifetime value 10-15 ps different than that in the bulk is typically enough for the separation of lifetimes, as in e.g. the case of electron irradiated E-P ZnO (see Sec. 3). However, in these hydrothermal samples the separation was possible only in SPC ZnO at 250-300 K (not shown in Fig. 4), giving $\tau_2 \cong 230$ ps, indicating that Zn vacancies are present in the SPC ZnO as well. The problems in the separation of the lifetime components suggest that there is a relatively high intensity of some additional lifetime between the bulk and Zn vacancy lifetimes in the lifetime spectrum. Larger vacancy defects with higher lifetimes than those of the Zn vacancy are not present, as there would then be no problems in the separation. A natural cause for these problems would the presence of a relatively high concentration of neutral O vacancies (whose specific positron lifetimes is $\tau_{V,O} = 195 \pm 5$ ps). In order to create such problems in the separation of the lifetimes, the concentration of these O vacancy related defects needs to be in the $[V_O] \cong 10^{17}$ cm^{-3} range. On the other hand, the concentrations of the Zn vacancy related defects causing the increase of the average positron lifetime with decreasing temperature in TD ZnO and evident from the separation of the lifetime components in SPC ZnO, must be in the low 10^{16} cm^{-3} range.

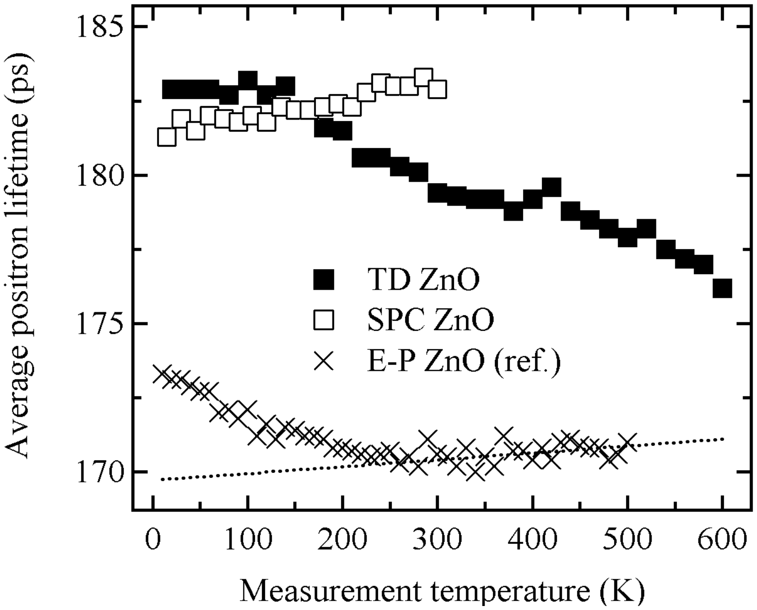

Fig. 4. The average positron lifetimes measured in the bulk ZnO crystals grown by the hydrothermal technique (TD and SPC). The dashed line shows the bulk lifetime in the ZnO lattice originally fitted to the E-P data. The temperature dependence of the bulk lifetime reflects the thermal expansion of the lattice

4.3 Chemical vapor transport

Figure 5a shows the average positron lifetime measured as a function of temperature in the ZnO samples grown by the conventional chemical vapor transport (CVT) and contactless chemical vapor transport (CCVT) methods.[18,19] The data obtained in an E-P ZnO are shown for comparison. The average lifetime is above the bulk lifetime $\tau_B = 170$ ps in both the CVT and CCVT grown samples throughout the whole temperature range, indicating the trapping of positrons at vacancy defects. The lifetime spectra measured in both materials could be separated into two components, of which the higher (average value $\tau_2 = 230 \pm 15$ ps) is shown in Fig. 5b. This component can be attributed to positrons annihilating as trapped at Zn vacancies. The increase of the average lifetime with decreasing temperature CCVT ZnO is a clear indication that the Zn vacancies are in the negative charge state. On the other hand, the independence on temperature of the average positron lifetime in CVT-grown ZnO in the range 100–500 K indicates that the observed vacancies are in the neutral charge state.

The decrease in the average lifetime below 100 K in the CVT-ZnO sample and the flat region at 50–100 K in the CCVT-ZnO sample is interpreted as positrons trapping at negative ion type defects, which have no open volume and hence produce the annihilation characteristics of the bulk lattice. This is observed only at low temperatures, since the negative ion type defects act as shallow traps for positrons, and the escape rate at elevated temperatures is faster than the annihilation rate. The effect of the negative ion type defects is small in the CCVT ZnO sample, and hence the Zn vacancies are the dominant negatively charged (acceptor-type) defect. Using the kinetic temperature-dependent trapping model, the concentration of the negative Zn vacancies (or related complexes) in CCVT ZnO can be estimated as $[V_{Zn}] \cong 1.5 \times 10^{16}$ cm^{-3}. The concentration of the negative ion type defects can be estimated to be roughly one order of magnitude lower.

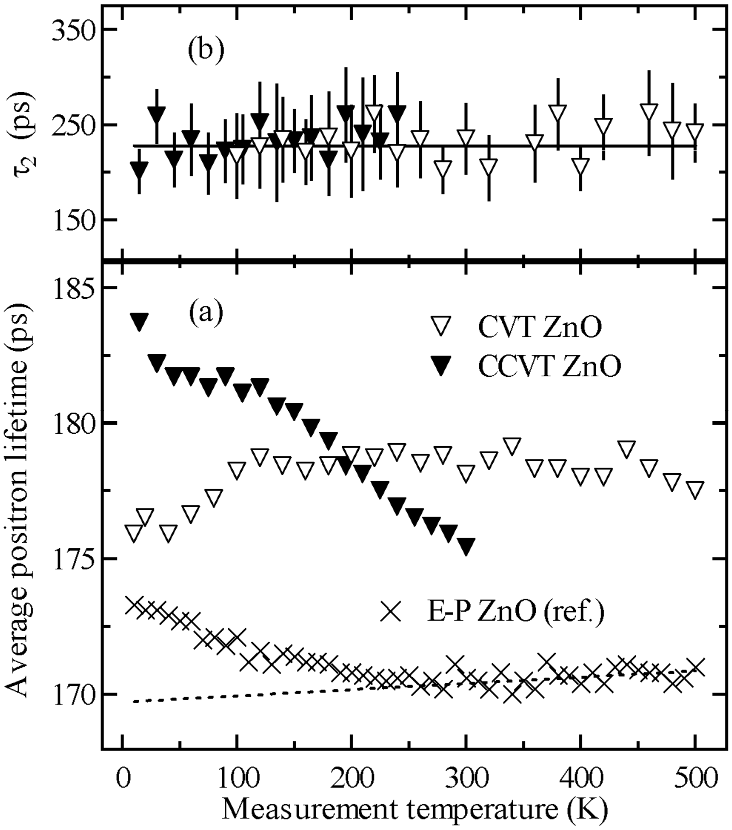

Fig. 5. The average positron lifetime (a) and the higher lifetime components separated from the annihilation spectra (b) as a function of measurement temperature in the CVT and CCVT ZnO samples.

The first lifetime component τ_1 (not shown) is well below the bulk lifetime τ_B in CCVT-grown ZnO, indicating that the one-defect trapping model works. However, in CVT-grown ZnO the first lifetime component coincides with τ_B, indicating the mixing of the bulk component with a defect-specific component with a lifetime close to (but higher than) the bulk lifetime. This can be interpreted as positrons trapping at O vacancies. The concentrations of the neutral Zn vacancy related complexes in CVT-grown ZnO can be estimated as $[V_{Zn}] \cong 2 \times 10^{16}$ cm^{-3}, and the negative ion concentration can be estimated to be of the same order of magnitude. The concentration of the O vacancies in CVT-grown ZnO can be estimated with trapping rate analysis as $[V_O] \cong 10^{17}$ cm^{-3}.

5. COMPARISON AND DISCUSSION

For easy comparison of the average positron lifetimes, the data from all the different measured bulk ZnO crystals are collected in Fig. 6. As seen in the figure, the materials can be roughly divided to two groups, where the vacancy concentrations observed with positrons are either in the low 10^{15} cm^{-3} range or below, or in the low 10^{16} cm^{-3} range or above. The ZnO crystals grown by Eagle-Picher, ZN-Technology or Cermet belong to the former and the crystals grown by Tokyo Denpa, Scientific Production Company or the Institute of Physics of the Polish Academy of Sciences (CVT and CCVT) belong to the latter. Recent measurement in bulk ZnO crystals grown by CVT in the University of Valencia show that also this material contains Zn vacancy related defects with a concentration in the low 10^{16} cm^{-3} range.[20]

Interestingly, the Zn vacancy concentrations in the bulk ZnO crystals grown by the chemical vapor transport and hydrothermal methods are very similar, in spite of the growth environment being Zn-rich in the former and O-rich in the latter. Further, the presence of a rather high concentration of O vacancy related defects in the ZnO crystals grown by the hydrothermal method is surprising, and is likely to be connected to the high Li concentration in the material. On the other hand, the O-rich skull-melt and Zn-rich seeded vapor transport methods also produce ZnO crystals that are very much alike from the vacancy point of view. Hence it seems that in the case of the bulk growth techniques, the formation of the vacancy defects is not that much affected by the stoichiometry or the partial pressures of the growth environment, but rather by the residual impurites and other intrinsic defects.

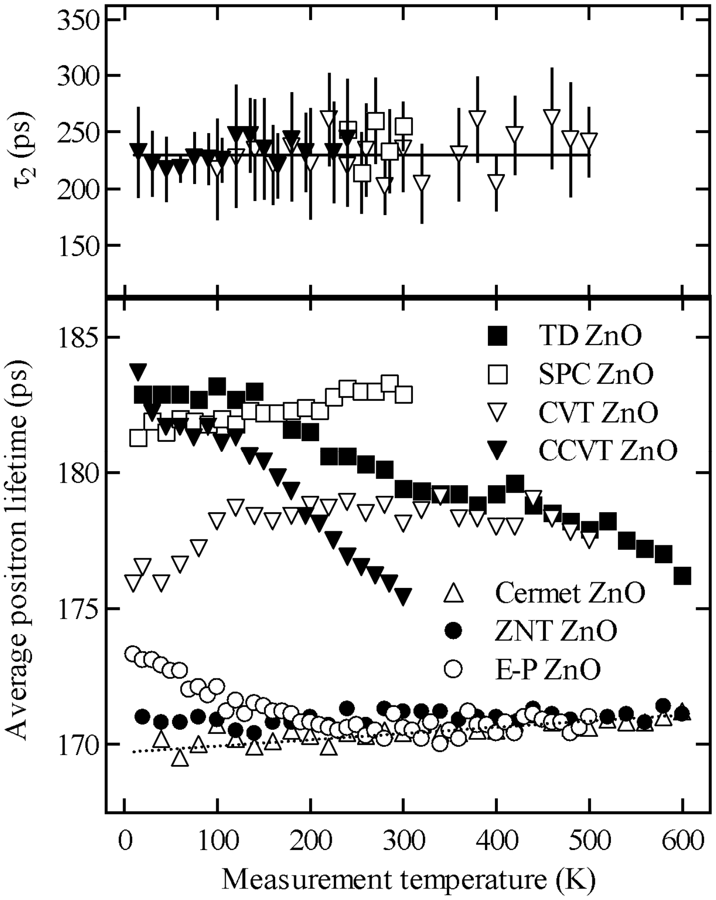

Fig. 6. The average positron lifetime (lower panel) and the higher lifetime components separated from the annihilation spectra (upper panel) as a function of measurement temperature in all the measured ZnO samples.

An important observation to be made from Fig. 6 is that the higher lifetime component separated from the measured lifetime spectra (where it could be performed) is the same in all the samples over the whole measurement temperature range, i.e. $\tau_2 \cong 230$ ps. It also coincides with that obtained in electron-irradiated material, hence demonstrating that the Zn vacancies are important defects in ZnO and supporting the determination of their lifetime value. In as-grown ZnO, it is very likely that the Zn vacancies are complexed either with residual impurities or other intrinsic defects, as the irradiation-induced (likely isolated) vacancies have been shown to anneal out from the material already at rather low temperatures of about 500-600 K. This applies to the O vacancies as well.

The results obtained in the E-P ZnO and CCVT ZnO show that the Zn vacancies act as dominant acceptors in *n*-type ZnO, similarly as the Ga vacancies do in *n*-type GaN.[21] The situation is more difficult in the ZnO crystals grown by the other techniques due to either too low a concentration of vacancies in general, or too high a concentration of other types of vacancies, such as O vacancies. The Zn vacancies are most likely complexed with donor-type defects, and as they survive the cooling down from the high growth temperatures of about 1000 ºC, the stabilizing donors are likely to be located on the O sublattice. In the case of cation vacancies complexed with cation-sublattice-substitutional donor defects, the binding energy is prone to be too low for the vacancies to be effectively stabilized, as in the case of Si donors in GaN.[22] As the total open volume of the in-grown Zn vacancies is the same as that of the irradiated Zn vacancies, we suggest that these donor defects are residual impurities, the concentrations of which are of the same order of magnitude as that of the Zn vacancies. On the other hand, the possibility of the Zn vacancies being bound to O vacancies as $V_{\mathrm{Zn}} - V_{\mathrm{O}}$ complexes cannot be completely ruled out, as the latter are very difficult to distinguish from the isolated Zn vacancies with positrons.[1] It is important, however, to understand that the O vacancies observed in the hydrothermal and CVT grown bulk ZnO crystals are not complexed with the Zn vacancies, as the positrons are sensitive to the total open volume of the defect.

6. SUMMARY

We have applied positron annihilation spectroscopy to study the vacancy defects in bulk ZnO crystals grown by various methods. We show that the bulk ZnO crystals grown by the seeded vapor phase and melt techniques have very low concentrations of vacancy defects, and the dominant defects observed by positrons are the Zn vacancies. On the other hand, in addition to Zn vacancies, relatively high concentrations of O vacancies are observed in ZnO bulk crystals grown by the hydrothermal and conventional chemical vapor transport methods. The contactless chemical vapor transport method produces material with a high concentration of Zn vacancies, but no O vacancies are observed. The latter holds for ZnO crystals grown by the seeded vapor phase and skull-melt techniques as well.

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