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Positron lifetimes in ZnO single crystals

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Abstract

Analysis of positron lifetime data for ZnO single crystals suggests that four well-separated lifetime levels exist between those for the bulk and the Zn vacancy. Due to the hydrothermal growth conditions of most ZnO single crystals studied so far, it is postulated that a hydrogen–defect interaction could be responsible for this finding.

Keywords: ZnO; Positron lifetime; Vacancy defects; Hydrogen–defect interaction

1. Introduction

Future applications of ZnO, e.g. in visible and UV light emission, in detectors or high-temperature electronics, rely on a full understanding of the role of lattice defects, which largely control the optical and electrical properties of semiconductors [1,2].

Positron annihilation spectroscopy (PAS) [3,4] is now among the established research tools in materials science, and in particular positron lifetime measurements are used to study defect properties of bulk solids. Whereas for metals and many alloys the defect properties have already been investigated in detail and are rather well understood, the situation for elemental and compound semiconductors is comparatively less clear. This is mainly connected with the fact that native defects may exist—in the case of compound semiconductors on both sub-lattices and in different charge states—and that impurity atoms play a much greater role. ZnO has already been investigated by positron lifetime spectroscopy but the interpretation of results differs depending on the research groups—for a recent summary see Ref. [5]. Also in paper [5], theoretical calculations are presented for the first time of positron-related defect properties of ZnO, which include Zn and O vacancies and the Zn + O divacancy, and take into account lattice relaxations around these defects.

In the present work, positron lifetime data available from the literature—together with some of the latest results from the authors' laboratory—are collected and related to the values recently calculated for bulk and defect configurations within the same scheme [5]. These findings are then discussed and suggestions for their understanding and an improved interpretation are concluded.

2. Results and discussion

If the recent theoretical calculations [5] are used to scale the positron lifetimes observed and published to date [6–16], their collection in Table 1 shows two features. The first is that positron lifetimes at open volumes of size larger than the Zn + O divacancy have been calculated up to now only in the frame of a rigid lattice, and indeed such long lifetimes have been observed either in sintered powders [15] or following post-irradiation annealing [6,7]. The second, more interesting feature is that seemingly four well-separated lifetime levels exist between the bulk and Zn vacancy (V_{Zn}) lifetimes. In Fig. 1, this is illustrated more clearly as a function of the supposed number of n hydrogen atoms attached to a Zn vacancy. Such a successive decrease of the positron lifetime from the value of a vacancy

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Table 1
Positron lifetimes (τ) in various ZnO single crystals

Positron location	τ_{theory} (ps)	$\tau_{\text{experiment}}$ (ps)	Reference	Remarks
Larger open volume				
6Zn + O	~375		[14]	Rigid lattice
5Zn + O	~360		[14]	Rigid lattice
4Zn + O	~350		[14]	Rigid lattice
3Zn + O	~310		[14]	Rigid lattice
2Zn + O	~265		[14]	Rigid lattice
		370 ± 20	[6,7]	PIA
		300–340	[15]	Sintered powder
Zn + O4	294 (294)		This work	Rigid (relaxed) lattice
Zn + O (1)	224 (286)		[5]	Rigid (relaxed) lattice
Zn + O (2)	223 (276)		[5]	Rigid (relaxed) lattice
1Zn + O	~220		[14]	Rigid lattice
		257 ± 2	[5]	PMG
		260 ± 7	[6,7]	Electron/proton irradiation
V_{Zn}	194 (229)		[5]	Rigid (relaxed) lattice
	~188		[14]	Rigid lattice
	217		[12]	
		209 ± 6	[6,7]	Electron/proton irradiation
		214.2 ± 0.6	This work	HTG, electron irradiation
		230 ± 10	[8,9]	HTG, electron irradiation
V_{Zn} + 1H?	185–207			This work
		198.5	[10]	HTG
		203 ± 3	[11]	FG
		203	[8]	
		189	[13]	HTG
V_{Zn} + 2H?		182.1 ± 0.4	[16]	HTG
		182 ± 3	[11]	
		181 ± 1	[11]	CVTG
		179 ± 1	[11]	CVTG
		181	[13]	HTG, after annealing
		183 (180)	[6,7]	As received (annealed)
		176	[6,7]	HTG
V_{Zn} + 3H?		170.4	[8,9]	HTG
		169 ± 2	[11]	FG + TCR
		169 ± 1	[11]	CVTG + TCR
		173 ± 1	[11]	CVTG + TCR
		171 ± 1	[13]	HTG
V_{Zn} + 4H?		158–162	[6,7]	HTG
V_O		159 (160)	[5]	Rigid (relaxed) lattice
Bulk		159	[5]	
		158	[14]	
		153	[12]	
		151 ± 2	[5]	PMG
		~145	[15]	Sintered powder

PMG: pressurized melt grown; HTG: hydrothermally grown; FG: flux grown; CVTG: chemical vapor transport grown; TCR: thermochemical reduction at higher temperatures; PIA: post-irradiation annealing. In the case of the Zn + O divacancy, two non-equivalent configurations denoted Zn + O (1) and Zn + O (2) were considered in the calculations [5].

towards the bulk lifetime due to the attachment of hydrogen is an effect known to exist in metals [17].

The theoretical calculation of positron lifetimes for intrinsic defects larger in open volume than the Zn + O divacancy is not easy, especially if lattice relaxations are taken into account. The assumption that larger defects are made up of multiples of the Zn + O divacancy [14] might have been chosen in analogy to a previous work on SiC [18] but it is not certain if this viewpoint is realistic in ZnO. Complementary to the clustering of Zn + O divacancies [14], preliminary results obtained here for the case of a missing ZnO_4 tetrahedron are presented in Table 1 which show no difference with respect to a rigid lattice or a possible relaxation. This case needs further investigation

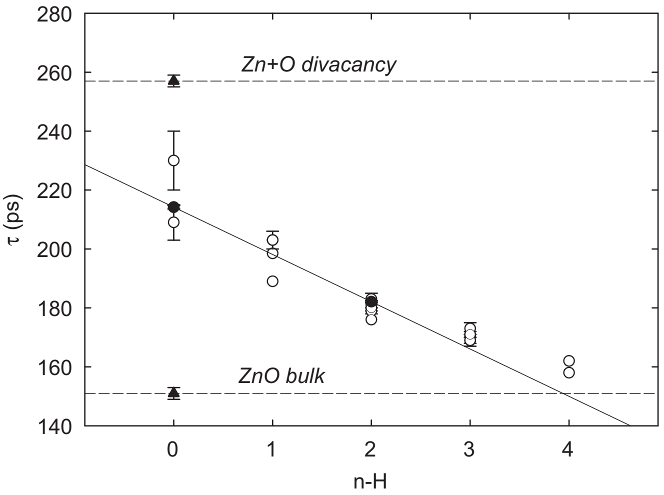

Fig. 1. Experimentally observed positron lifetimes τ in ZnO (see also Table 1) sorted by a supposed number of n hydrogen atoms attached to a Zn vacancy. The straight line is drawn to guide the eye only, using our results to define its slope.

and clarification, but the larger open volume of this possible defect is reflected in a longer lifetime compared to that of the Zn + O divacancy.

The theoretical calculation of positron lifetimes for defects decorated with an impurity is also a difficult task. In the case of hydrothermally grown ZnO, the decorating impurity of a Zn vacancy is most probably hydrogen. Hydrogen as a cause of doping has been extensively considered in a recent paper [19], and various positions for interstitial hydrogen incorporation into the ZnO lattice have been considered there. In order to achieve an initial estimate of the decrease in positron lifetime for one H atom attached to a Zn vacancy, two extreme cases are considered here: (a) the H atom is placed directly into the center of the Zn vacancy, and (b) the H atom occupies a so-called perpendicular bond-center position [19]. Case (b) means that the H atom position remains unchanged when a vacancy is created at the nearest-neighbor Zn site, while case (a) means that the H atom is attracted by the vacancy and becomes trapped directly in its center. It is clear that case (a) leads to a maximum shortening of the positron lifetime, whereas a smaller shortening is expected in case (b). A very first and still rough calculation using the atomic superposition method [20] gives the following positron lifetimes (relaxed lattice) for the two cases mentioned: (a) $\tau_{\mathrm{defect}} = 185\,\mathrm{ps}$, (b) $\tau_{\mathrm{defect}} = 207\,\mathrm{ps}$. Note that the electron–positron correlation was treated using the corrected Boronski–Nieminen approach in the same way as in Ref. [5]. In reality, the lifetime of positrons trapped at a Zn vacancy–1H complex should be expected at some value between these extreme cases (a) and (b), i.e. $185\,\mathrm{ps} < \tau(V_{\mathrm{Zn}}\text{–H}) < 207\,\mathrm{ps}$. Thus, the assignment of the experimental lifetime 198.5 ps [10] to a Zn vacancy connected with 1H atom seems to be supported.

If the—in detail yet unknown—attachment of n hydrogen atoms ($n \geqslant 1$) to V_{Zn} is considered to be responsible for the measured shortening of the positron lifetime, the interpretation of experimental results collected in Table 1 still appears contradictory. One example concerns an observed decrease of the positron lifetime from 182 ± 3 ps in the as-grown state [11] to a value of ∼169 ps following thermochemical reduction at various higher temperatures—without further change in this number despite extended heat treatment once it is reached. In one sample pair, being slightly green colored, the longer lifetime of 203 ps has been considered most likely to correspond to some trapped positron state from defects associated with an impurity—without being more specific. Compared to this, a positron lifetime of ∼180 ps has been observed in as-grown colorless crystals [11].

In another paper [13], the positron lifetime decreases upon annealing in the temperature range (400–600) °C from ∼189 to ∼181 ps although measurements of cathodoluminescence on the same samples suggest that hydrogen is released from defects, resulting in a visible emission observed over 700 °C. Normally, one would have expected to see an increase in positron lifetime due to the release of hydrogen from the defects.

Recently, saturation positron trapping has been reported in an hydrothermally grown sample which is characterized by a positron lifetime of (182.1 ± 0.4) ps [16]. In order to see if it is possible to produce in this material plain zinc vacancies V_{Zn} by electron irradiation, first experiments have been performed (electron energy: 10 MeV; fluence: $1 \times 10^{18}\,\mathrm{cm}^2$; irradiation temperature: $< 100\,^{\circ}\mathrm{C}$). The preliminary evaluation of positron lifetime measurements shows the presence of a second component having a positron lifetime $\tau_2 = 214.2 \pm 0.6\,\mathrm{ps}$. Such a value nicely corresponds with previous results from other irradiation experiments in the literature [6,7] where a positron lifetime (209 ± 6) ps is reported to be connected with the negatively charged zinc vacancy. This finding caused us to start with some new and more comprehensive electron irradiation experiments, and their results will be published in due time elsewhere.

As expected, due to the variety of possible defects in compound semiconductors like ZnO, and the fact that native defects may exist on both sub-lattices and in different charge states, the interpretation of experimental results is not trivial. Neutral or negatively charged defects connected with a free volume (vacancies and related defects) are attractive for positrons and thus can be detected using PAS, in principle. As for the position of the defect-related energy level in the band gap of an n-type material, the temperature-dependent Hall (TDH) method can be used to examine shallow donors (i.e. donors having their corresponding levels close to the conduction band edge) and all compensating acceptors. Furthermore, the deep-level transient spectroscopy (DLTS) technique allows the study of defects with corresponding levels positioned deep in the band gap. Finally, it has to be mentioned that there is no obvious relation between the free volume of a defect and the position of the corresponding energy level or the defect charge state. This complicates the making of a direct correlation between the results of PAS measurements and these other techniques. The application of a combination of the three methods has recently been demonstrated [5].

The usefulness of further methods in the characterization of defects in ZnO has also been demonstrated, like Raman scattering, cathodoluminescence, electromagnetic paramagnetic resonance, photoluminescence and X-ray diffraction—see e.g. Refs. [13,21,22].

3. Conclusions

From the analysis of existing literature positron lifetime data for ZnO single crystals, the grouping of positron lifetimes in four well-separated lifetime levels between that of the bulk and the Zn vacancy is noticed. Because most of the ZnO single crystals studied so far were produced at hydrothermal growth conditions, it is supposed that hydrogen–defect interactions could be responsible for this finding.

Very first results of theoretical calculations are presented for a defect complex consisting of one hydrogen atom attached to a Zn vacancy. However, not only are further improvements of these calculations highly desirable, but also the inclusion of more than one hydrogen atom is required in order to see whether or not the experimentally observed positron lifetimes may really be modeled in the manner suggested here.

It has to be emphasized that the proposed idea of Zn vacancy–hydrogen complexes to explain experimentally observed positron lifetimes represents a challenge not only to further experimental and theoretical PAS studies but requires the inclusion of results from many other methods for final clarification.

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