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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)	$\tau_{experiment}$ (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