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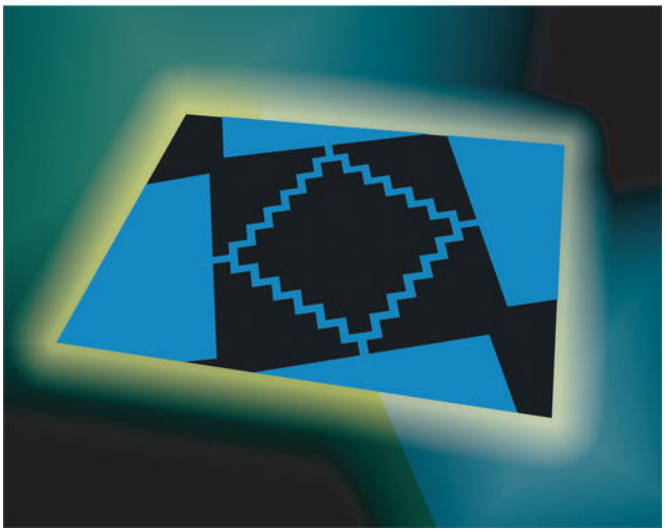

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Comparative characterization of differently grown ZnO single crystals by positron annihilation and Hall effect

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Abstract

High-quality ZnO single crystals of dimensions $10 \times 10 \times 0.3$ mm^3, grown either using a pressurized melt or a hydrothermal growth approach, have been investigated in their as-received state and are compared regarding their properties revealed by positron annihilation and Hall effect measurements. By positron annihilation performed at room temperature it is found that the pressurized melt grown crystals contain a certain amount of Zn + O divacancies, but no Zn vacancies are detected, whereas the hydrothermally grown crystals contain a dominating defect yet unknown in its structure but possibly connected to the Zn vacancy. Furthermore, the influence of an additional refined chemical–mechanical polishing of the crystal surface by a special procedure on the depth distribution of vacancy-type defects is demonstrated. Hall measurements, performed in the temperature range 20–325 K, showed that the crystal growth method has a strong influence on the carrier mobility, and the estimated acceptor densities also differ significantly in both types of crystal.

Keywords: ZnO single crystal; Vacancy-type defects; Slow positron implantation spectroscopy; Hall effect; Charge balance equation

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1. Introduction

Zinc oxide has drawn interest in recent years due to its suitability for visible and UV light emitters and detectors as well as high-temperature electronics [1,2]. It is certain that all types of applications rely on a full understanding of the role of lattice defects, which largely control the optical and electrical properties of semiconductors, and provision of high-quality bulk material and films. Both needs are not yet achieved but there is rapid development in these fields.

Positron **A**nnihilation **S**pectroscopy (PAS) [3,4], especially in the form of **S**low **P**ositron **I**mplantation **S**pectroscopy (SPIS) using mono-energetic positrons [5,6], is now a well-established tool for the study of electronic and defect properties of bulk solids and thin films. Recently, PAS studies of ZnO from the literature have been summarized and theoretical calculations of the positron lifetime for selected defects, including lattice relaxations around these defects, have been published [7]. Thus, for the first time, a consistent theoretical modeling of bulk and defect positron properties of ZnO has been given which allowed the estimation of a defect concentration. On the other hand, this can serve as a basis to have a more careful and systematic look to a suspected influence of the growth method of ZnO on grown-in lattice defects and their electrical and optical properties.

In the present study, two differently grown ZnO single crystals are investigated by PAS and **t**emperature-**d**ependent **H**all (TDH) measurements, and compared regarding their defect properties.

2. Experimental

High-quality ZnO single crystals of dimensions $10 \times 10 \times 0.3$ mm^3, grown using a **p**ressurized **m**elt **g**rowth (PMG) approach, were supplied by Cermet Inc. (Atlanta/GA). Each crystal had the Zn-face lapped and the O-face polished. Other, **h**ydro**t**hermally **g**rown (HTG) high-quality ZnO single crystals, of dimensions $10 \times 10 \times 0.5$ mm^3, were supplied by MaTecK GmbH (Jülich) with the O-face polished. For purposes of comparison, one crystal of each kind was given an additional refined chemical–mechanical polishing on both faces [8].

PAS studies were here performed by **p**ositron **l**ifetime (PL) measurements using a fast–fast PL spectrometer with a timing resolution of 160 ps [9] collecting up to 10^7 events per spectrum. Any measured PL spectrum can be described as a sum of exponential components smeared by the resolution function of the spectrometer. The lifetimes of the exponential components allow for the identification of defect types, whereas relative intensities of the components are related to defect densities. SPIS studies were performed with a positron energy adjustable from 0.03 to 36 keV, accumulating about 10^6 events per spectrum [10]. The energy resolution of the Ge detector used is (1.09 ± 0.01) keV at 511 keV, resulting in a high sensitivity to changes in material properties from surface to depth.

The motion of the electron–positron pair prior to annihilation causes a Doppler broadening of the 511 keV annihilation line and can be characterized by the line-shape parameters S and W. The usefulness of these parameters may be illustrated further by an S–W plot, which allows one to conclude whether the changes are due to a change in concentration or type of a defect. For a more general discussion of these parameters we refer to the literature [3,4]. The depth information was obtained from the correlation of S and W with positron energy E using the versatile program package VEPFIT [11], in which a density of 5.605 g cm^{-3} for ZnO was used.

TDH measurements were performed in the temperature range 20–325 K at Leipzig using an automated Hall setup (Keithley 220 programmable current source, Keithley 7001 switch

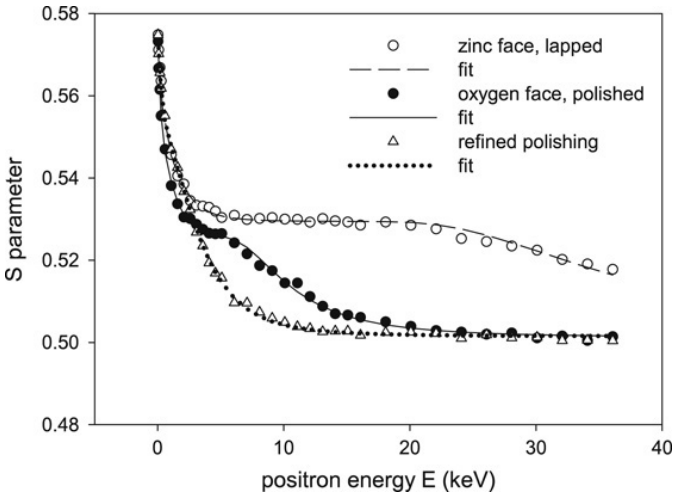

Fig. 1. Doppler broadening parameter S of a virgin PMG ZnO single crystal as a function of incident positron energy E in the as-received state (lapped, polished) and with improved surface quality (refined polishing). The best fit to the data is shown. Figure taken from Ref. [7].

equipped with a 7065 Hall card, Keithley multimeter 2000, a Lakeshore 330 temperature controller, and an HP 6030A power supply for the magnetic coils).

3. Results and discussion

The PMG samples have already been investigated in their virgin and ion-implanted states by PAS, TDH and **d**eep **l**evel **t**ransient **s**pectroscopy (DLTS), with the results being extensively discussed in the context of various theoretical considerations [7]. Free fitting of the PL measurements showed the existence of a two-component spectrum, and the following positron lifetimes and intensities were found: $\tau_1 = (93 \pm 3)$ ps, $\tau_2 = (257 \pm 2)$ ps, $I_1 = (39.9 \pm 0.7)\%$, and $I_2 = (60.1 \pm 0.7)\%$. From these results a bulk lifetime of (151 ± 2) ps was derived, and the longer lifetime was attributed to neutral Zn+O divacancies of a concentration $\sim 3.7 \times 10^{17}$ cm^{-3}. The positron lifetime in Zn vacancies has been calculated to fall into the range (194–229) ps, with the lower and upper limit representing the case of a rigid and relaxed lattice, respectively [7], which compares to an earlier experimental value of (209 ± 6) ps interpreted to represent the negatively charged Zn vacancy [12,13].

The HTG ZnO samples investigated here are found to exhibit a single-component positron lifetime spectrum of (182.1 ± 0.4) ps, i.e. all positrons are trapped in a defect exhibiting an obviously smaller open volume than the Zn vacancy. The decrease of the positron lifetime, compared to that for a Zn vacancy in ZnO, could be due to the 'attachment of hydrogen' – an effect known to exist in metals [14] – but this needs further investigation and clarification.

SPIS investigations of the PMG samples revealed the presence of near-surface damage in the as-received samples which could be removed by a refined polishing (Fig. 1), whereas in the HTG samples neither such damage nor any improvement of the surface quality due to a refined polishing could be observed (Fig. 2). This will not necessarily mean that such damage does not exist in the as-received samples. Due to preferential trapping in the defects characterized by the 182.1 ps lifetime it might be 'invisible' to positrons and thus cannot be judged here. A direct comparison of both types of samples – after application of the refined surface polishing – is presented in Fig. 3. As expected from the PL results, the bulk S for the HTG sample is found at higher value due to the saturation trapping in a defect yet unknown in its structure but possibly connected to the Zn vacancy, and this sample also exhibits a shorter positron diffusion length L_+.

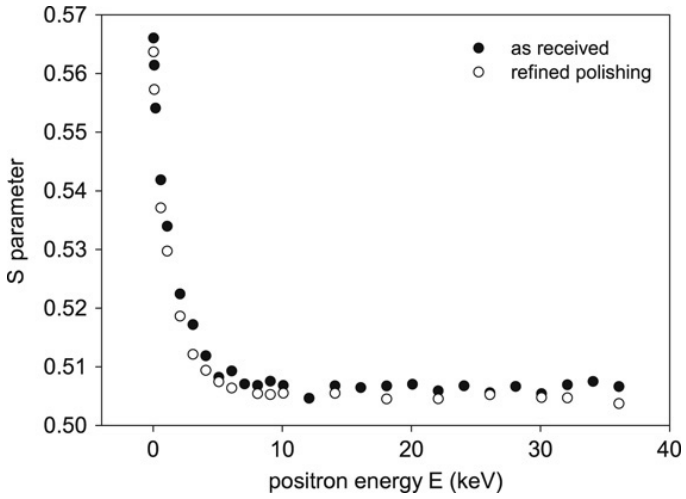

Fig. 2. Doppler broadening parameter S of a virgin HTG ZnO single crystal as a function of incident positron energy E in the as-received state and with improved surface quality (refined polishing).

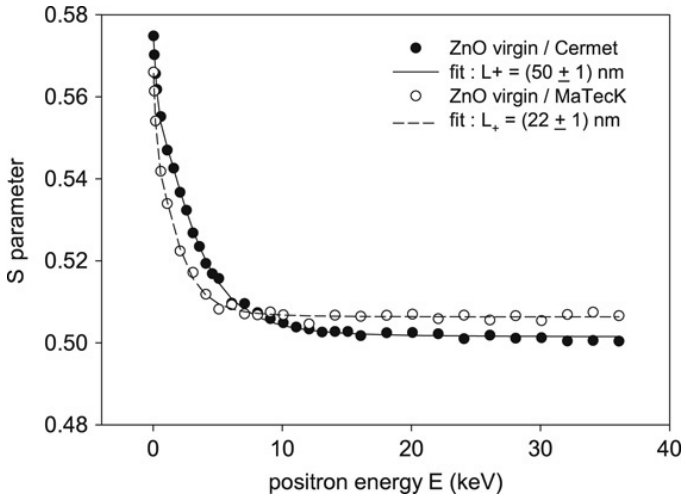

Fig. 3. Doppler broadening parameter S of differently grown ZnO single crystals after refined surface polishing as a function of incident positron energy E. The best fit to the data and the estimated positron diffusion length L_+ for each sample are also given.

The electrical properties of PMG and HTG ZnO single crystals are found to differ significantly. The HTG sample has a resistivity ρ of about 80 Ω cm at room temperature (RT) which is more than two orders of magnitude higher than for the PMG sample. The dependence on temperature of the free-electron concentration n is depicted in Fig. 4. The HTG sample becomes insulating for temperatures lower than about 200 K. It is supposed that large amounts of group I elements are incorporated on Zn sites during the HTG, causing a high degree of compensation. This is also reflected by the comparatively low Hall mobility μ_H (RT) (see Table 1) which cannot be explained by intrinsic scattering mechanisms alone. This implies that the concentration of ionized impurities is so large that ionized impurity scattering is effective even at RT. Due to the high degree of compensation of the HTG sample the evaluation of the TDH data (especially the mobility data) yields only rough estimates. The results are summarized for both types of sample in Table 1.

The density of compensating acceptors N_a is obtained by fitting the temperature dependence of μ_H (see Fig. 5) considering intrinsic (deformation potential, piezoelectric potential, polar

Table 1
Electrical properties of ZnO single crystals grown by pressurized melt growth (PMG) or hydrothermal approach (HTG), respectively

	n(RT) (cm^{-3})	μ_H(RT) (cm^2/Vs)	N_{d1} (cm^{-3})	E_{d1} (meV)	N_{d2} (cm^{-3})	E_{d2} (meV)	N_a (cm^{-3})
PMG	4×10^{16}	231	4.8×10^{16}	51	4×10^{15}	16	3.9×10^{15}
HTG	10^{13}	157	4.5×10^{17}	353	–	–	4.4×10^{16}

See text for explanation of symbols.

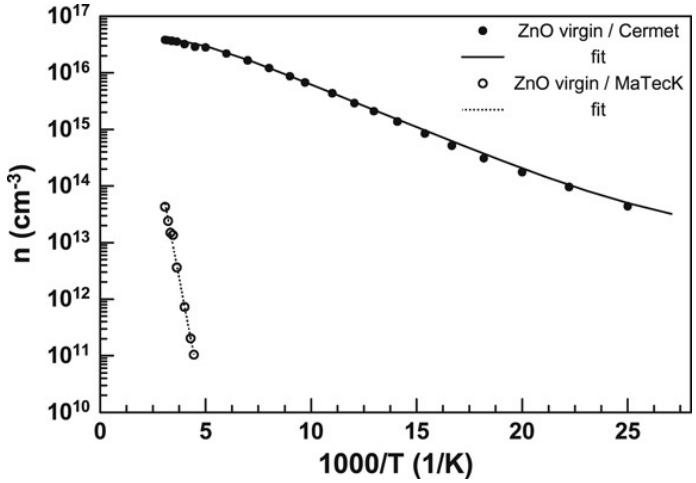

Fig. 4. Free-electron concentration n (symbols) and corresponding fits (lines) of differently grown ZnO single crystals after refined surface polishing as a function of the reciprocal temperature $1/T$.

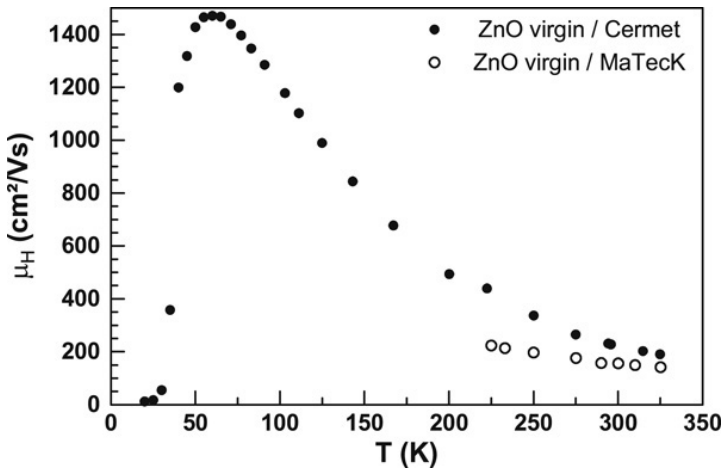

Fig. 5. Hall mobility μ_H of differently grown ZnO single crystals observed after refined surface polishing as a function of temperature T.

optical scattering) and ionized impurity scattering. The Hall factor is set to unity and the individual scattering mechanisms are summed according to Matthiessen's rule. N_a is about an order of magnitude larger in the HTG sample, explaining the lower Hall mobility and the full compensation for temperatures lower than 200 K. Due to the large N_a value, shallow donors – such as for instance hydrogen, which is contained in HTG samples as concluded from the existence of the I4 transition in the recombination spectrum (not shown) – are ionized for all temperatures, and hence their concentration must be lower than N_a. This implies that the fit of

the temperature dependence of n does not yield the density N_d of the dominant donor but the sum $(N_d + N_{d,sh})$ with $N_{d,sh}$ describing the density of ionized shallow donors.

The temperature dependence of n is modelled by solving the one- or two-donor charge balance equation considering compensation for the HTG and the PMG sample, respectively. In the temperature regime investigated, the dominant donor of the HTG sample has a thermal activation energy $E_{d1} = 353$ meV. Its density is estimated to be $N_{d1} = 4.5 \times 10^{17}$ cm^{-3}. For the PMG sample [7], two donors have to be considered to model $n(T)$ over the entire temperature interval, i.e. a shallow donor ($E_{d2} = 16$ meV) with a concentration $N_{d2} = 4 \times 10^{15}$ cm^{-3} governs $n(T)$ for $T < 70$ K, and a second donor ($E_{d1} = 51$ meV) with a concentration $N_{d1} = 5 \times 10^{16}$ cm^{-3} dominates $n(T)$ for $T > 100$ K. The chemical nature of these donors cannot yet be identified.

4. Conclusions

The grown-in open volume lattice defects differ significantly in differently grown (PMG, HTG) single crystals of ZnO. Furthermore, the existence of subsurface damage due to original polishing and lapping has been demonstrated in PMG crystals. However, it was shown that this damage can be removed by application of a refined polishing.

Regarding electrical properties, it is found that HTG samples are insulating for $T < 200$ K due to a high degree of compensation, whereas the PMG samples contain two shallow donors with thermal activation energy of 16 and 51 meV, respectively. In contrast to this, the thermal activation energy of HTG samples (353 meV) is found to be comparatively large. Furthermore, the concentration of shallow donors in the HTG samples is found to be lower than the concentration of compensating acceptors.

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