In this work, H is deliberately introduced by shallow ion implantation and subsequent annealing (in diffusion), and its interaction with Li\textsubscript{Zn} and V\textsubscript{Zn} is studied by positron annihilation spectroscopy (PAS) and SIMS. Both Li-rich and Li-poor HT ZnO samples have been employed. In the former case, H is found to predominantly passivate the Li\textsubscript{Zn} acceptor leaving V\textsubscript{Zn} as the main positron trap, while in the latter case an apparent reduction in the concentration of V\textsubscript{Zn} occurs. V\textsubscript{Zn} is anticipated to be in a double negative charge state in n-type material,\textsuperscript{17} and the results from the Li-poor samples suggest the formation of a neutral V\textsubscript{Zn}H\textsubscript{2} complex.

II. METHODOLOGY

Two n-type HT ZnO wafers (labeled A and B) with a size of 10 × 10 × 0.5 mm\textsuperscript{3} were used in this study and supplied by SPC-Goodwill. A concentration of 2 × 10\textsuperscript{17} Li/cm\textsuperscript{3} was found in wafer A, as measured by SIMS employing a Cameca IMS\textsubscript{7f} microanalyzer (details about the SIMS analysis can be found in Ref.\textsuperscript{16}). Wafer B was postgrowth annealed in air at 1500 °C (1 h) in order to reduce the Li content, followed by mechanical polishing of the O face to restore the surface smoothness.\textsuperscript{14} After polishing, wafer B was further annealed in air at 1100 °C (1 h) to minimize the polishing damage in the near-surface region and its influence on PAS Doppler-broadening measurements.\textsuperscript{18} The resulting concentration of Li in wafer B, as measured by SIMS, was below 3 × 10\textsuperscript{15} cm\textsuperscript{-3}; see Fig. 1. The resistivities of wafer A and wafer B (after the postgrowth treatment) were found by four-point probe measurements to be 2 kΩ cm and 0.6 Ω cm, respectively. One quarter of wafer A and of wafer B (A-2 and B-2) were then implanted on the O face at room temperature (RT) with 35-keV H\textsuperscript{-} ions to a dose of 1 × 10\textsuperscript{16} cm\textsuperscript{-2}, while two quarters (A-1 and B-1) were kept as is. The projected range \begin{math} R_p \end{math} was 265 nm, as estimated by SRIM.\textsuperscript{19} A-2 and B-2 were subsequently heat treated at 350 °C (30 min) for diffusion of H into the bulk of the samples.\textsuperscript{9} Monoe energetic positrons with energies in the 0.5–38 keV range, giving mean penetration depths of 0.05–2.4 μm, were implanted into the O face of the samples at RT in order to conduct depth-resolved PAS Doppler-broadening.
exceeding ∼×1–2 Li has been rearranged in the peak region but still reaches about HT sample A and the post-treated HT sample B contain 2 applying the conventional resolution of 1.24 keV at 511 keV. The data were analyzed experiments. The Doppler broadening of the annihilation and 3
fractions of counts in the central and 3 of annihilating electron-positron (e-p) pairs. These changes can be modeled with the positron lifetime and narrows the momentum distribution due to a locally reduced Coulomb repulsion. This increases negatively charged open-volume sites in the crystal lattice material were accounted for.

FIG. 1. (Color online) Li concentration vs depth profiles for samples A-1, A-2, B-1, and B-2 as measured by SIMS. The as-grown HT sample A and the post-treated HT sample B contain 2 × 10¹⁷ and 3 × 10¹⁵ Li/cm³, respectively. After implantation and diffusion, Li has been rearranged in the peak region but still reaches about 1–2 × 10¹⁷ cm⁻³ for A-2 and 6 × 10¹⁴ cm⁻³ for B-2 at depths exceeding ∼1 and ∼2 μm, respectively.

Our main focus is the region probed by positron implantation energy (0.5–38 keV) for the A-1, A-2, B-1, and B-2. A-1 and B-1 have uniform Li concentrations of 2 × 10¹⁷ and 3 × 10¹⁵ cm⁻³, respectively. However, in A-2 and B-2, Li has redistributed and accumulated in the implantation peak region at the expense of the concentration in the bulk. This process is very similar to that reported by Børseth et al., who found Li to be trapped by implantation-induced vacancy clusters. It should also be noted that, despite the accumulation in the implanted region, the Li concentration in sample A-2 remains close to 2 × 10¹⁷ cm⁻³ for depths >1 μm, while in B-2 it is in the 10¹⁴ cm⁻³ range for depths at least up to ∼3–4 μm.

Doppler-broadening experiments were conducted for all the samples, and Fig. 2 shows the S parameter as a function of positron implantation energy with the corresponding mean positron penetration depth depicted on the upper x axis. The peak at ∼10 keV for samples A-2 and B-2 is related to the damage induced by the implantation of H (R_p ∼300 nm). Our main focus is the region probed by >25-keV positrons (depths >1 μm), and Fig. 3 displays the W parameter versus the S parameter as measured for energies of 25–38 keV. The parameter values are normalized to those of the delocalized positron implantation energy (0.5–38 keV) for the A-1, A-2, B-1, and B-2 samples. Positrons implanted with an energy ≤5 keV may reach the surface by diffusion and annihilate, leading to the increased S-parameter values observed for low energies. The observed peaks in S-parameter value at ∼10 keV for samples A-2 and B-2 are caused by the end-of-range defects induced by the H implantation.
bulk annihilation in the VP-reference specimen, labeled “ZnO-Bulk.” Values for $V_{Zn}$ saturation trapping (not shown) are established from previous studies employing electron and oxygen irradiated samples and taking into account the detector resolution used in the present experiment, giving $S/S_\text{ref} = 1.049(3)$ and $W/W_\text{ref} = 0.79(1)$.

The line connecting the ZnO-Bulk value with the value for $V_{Zn}$ saturation trapping is referred to as the $V_{Zn}$ line. In samples where the $V_{Zn}$ is the dominant positron trap, the $S$- and $W$-parameter values will obey the $V_{Zn}$ line, and the position along the line is determined by the $V_{Zn}$ concentration.

The black circle in Fig. 3 represents experimental $S$- and $W$-parameter values previously found for Li$_{Zn}$ in Li-rich ZnO. The difference found between sample A-1 and B-1 is close to $2 \times 10^{17}$ cm$^{-3}$ for sample A-2, the $W$- and $S$-parameter values in Fig. 3 follow the $V_{Zn}$ line. This indicates that after hydrogenation Li$_{Zn}$ is not the dominant positron trap, but rather $V_{Zn}$ is.

To gain additional insight into the passivation process, fast positron lifetime measurements were conducted, giving average information over depths up to 100 $\mu$m from the sample surface using samples A-1, B-1, A-3, and B-3. Samples A-3 and B-3 were both hydrogenated by heating in a sealed quartz ampoule filled with 0.5 bar of wet $^2$H gas for 1 h at 700 $^\circ$C, expected to give a uniform concentration of $^2$H in the $10^{17}$ cm$^{-3}$ range throughout the samples.

For sample A-1, an average lifetime $\tau_{ave}$ of 187 ps is recorded, consistent with that typically found for as-grown (Li-rich) HT ZnO. However, for sample A-3 (Li rich, hydrogenated) $\tau_{ave}$ is reduced to 176–177 ps, similar to that for sample B-1 (Li poor, not hydrogenated), while for sample B-3 $\tau_{ave}$ is even further reduced to 171 ps, close to the bulk value of $\sim 170$ ps ($\tau_0$) for ZnO. These results are fully consistent with those obtained by the Doppler-broadening experiments and support a scenario where $H$ primarily interacts with (passivates) the Li$_{Zn}$ acceptor in Li-rich samples and has only a minor effect on the background concentration of $V_{Zn}$ ($\sim 5 \times 10^{16}$ cm$^{-3}$). On the other hand, in Li-poor samples $V_{Zn}$ prevails as a major trap for $H$, and the apparent $V_{Zn}$ concentration deduced by PAS is reduced by a factor of $\geq 5$ to $\leq 1 \times 10^{16}$ cm$^{-3}$. An overview of the estimated values for the bulk $V_{Zn}$ concentration in samples A-2, A-3, B-1, B-2, and B-3 is given in Table I.

In principle, one could argue that the disappearance of Li$_{Zn}$ as the main positron trap in Li-rich samples after hydrogenation (sample A-2) is not due to passivation but is caused by a change of configuration to Li. However, local density functional calculations of formation energies performed by Wardle et al. show that the abundance of Li$_{Zn}$ exceeds that of Li by many orders of magnitude in $n$-type samples prepared under normal conditions. Hence, the formation of Li$_i$ is ruled out as a likely explanation, and in addition, the results in Ref. 6 demonstrate that OH-Li$_{Zn}$ is a highly preferred defect in the presence of hydrogen. Here it should also be mentioned that OH-Li$_{Zn}$ has theoretically been shown to exhibit a similar positron annihilation signature to Li$_{Zn}$. However, in the neutral charge state of Li$_{Zn}$ the trapping coefficient is significantly reduced compared to the negative charge state due to the decreased Coulomb attraction and relatively small open volume of the defect.

Table I. Estimated apparent $V_{Zn}$ concentration [$V_{Zn}$] for samples A-2, A-3, B-1, B-2, and B-3 in bulk (beyond the implanted peak). The value for A-1 could not be determined because of the dominant trapping of by Li$_{Zn}$. The values for B-2 and B-3 are effectively estimated values, not accounting for possible $V_{Zn}$-$H_2$ complexes. The vacancy concentrations were determined from the $S$ and $W$ parameters for samples A-2, B-1, and B-2 and from the positron lifetime in A-3 and B-3, using a positron trapping coefficient typical of negative vacancies $\mu_V = 3 \times 10^{15}$ s$^{-1}$ (see Ref. 20).

<table>
<thead>
<tr>
<th>Sample</th>
<th>[$V_{Zn}$] (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>B-1</td>
</tr>
<tr>
<td>A-2</td>
<td>5 $\times$ 10$^{16}$</td>
</tr>
<tr>
<td>A-3</td>
<td>5 $\times$ 10$^{16}$</td>
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<td></td>
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</table>

FIG. 3. (Color online) The normalized $W$ parameter vs the $S$ parameter obtained for positron implantation energies ranging from 25 to 38 keV for the Li-rich (A) and the Li-poor (B) HT samples before and after hydrogenation. The black circle represents previously obtained experimental values of the $W$ and $S$ parameters for Li$_{Zn}$ in Li-rich ZnO.
\( \sim 5 \times 10^{16} \text{ cm}^{-3} \), but not entirely; assuming diffusion-limited reactions and equal capture radii of H by Li\(_{Zn}\) and V\(_{Zn}\), only a difference of a factor of \( \sim 4 \) in trapping rate is expected, while, experimentally, a factor of \( \geq 20 \) is obtained. On the other hand, if the relative content of Li is sufficiently reduced, V\(_{Zn}\) becomes the dominant H trap despite its limited efficiency. The formation of V\(_{Zn}\)H\(_2\) requires consecutive trapping of two H atoms, and hence, a low rate of decrease of the apparent V\(_{Zn}\) concentration occurs. Further, the formation of the V\(_{Zn}\)H\(_2\) complex fully explains the apparent low V\(_{Zn}\) concentration in samples B-2 and B-3. The effect of adding two H atoms into the Ga vacancy in GaN (with very similar positron characteristics to the Zn vacancy in ZnO) results in a reduction of the difference between \( \tau_v \) and \( \tau_0 \) by 45 ps (from 70 ps).\(^{27}\) A similar lifetime reduction is likely for the V\(_{Zn}\)H\(_2\) complex and is enough to explain the decrease of the average lifetime as seen for B-3 as compared to B-1. Similarly, the addition of two H atoms into the vacancy draws the \( S \) and \( W \) parameters of the vacancy defect much closer to the ZnO bulk value, explaining the apparent low V\(_{Zn}\) concentration obtained for B-2. Hence it can be concluded that the hydrogenation does not truly reduce the Zn vacancy concentration but reduces the open volume in the Zn vacancies by hydrogen filling.

**IV. CONCLUSION**

In as-grown HT ZnO samples the Li\(_{Zn}\) acceptor is found to be efficiently passivated by hydrogen, introduced via diffusion from the O face, and its characteristic PAS signal disappears while forming the neutral OH-Li\(_{Zn}\) complex. For V\(_{Zn}\), the opposite holds, and it emerges as the dominant positron trap after the hydrogenation with a concentration similar to that detected in postgrowth-annealed Li-poor HT samples. However, in the latter samples, where the Li content is about two orders of magnitude lower than the V\(_{Zn}\) content and Li does not truly compete for H trapping, hydrogenation leads to a decrease in the PAS signal of V\(_{Zn}\). This decrease is presumably due to formation of the neutral V\(_{Zn}\)H\(_2\) complex, and the apparent V\(_{Zn}\) concentration, as detected by PAS, approaches the bulk value of high-purity VP samples (\( \leq 1 \times 10^{16} \text{ cm}^{-3} \)).

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