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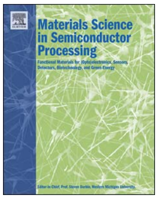

# Subsurface damage in polishing–annealing processed ZnO substrates

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## ABSTRACT

Positron annihilation spectroscopy and secondary ion mass spectrometry have been applied to study the evolution of polishing-induced defects in hydrothermally grown ZnO samples depending on the annealing temperature. Annealing of the as-grown ZnO wafer at 1200–1500 °C is found to lead to Li accumulation in the sub-surface layer, and significant reduction of Li content in the bulk. Polishing is shown to introduce vacancy complexes involving both $V_{Zn}$ and $V_O$. Post-polishing annealing of hydrothermally grown ZnO with removed Li layer at 800 °C reduces the concentration of polishing-induced defects below the detection limit.

## 1. Introduction

The boom in energy-efficient lighting and sustainable energy technology created strong research interest in ZnO as a potential substitute for GaN thanks to its superior properties [1–5]. Among others, hydrothermal (HT) growth has been proven to be the most efficient method in the light of scale-to-cost ratio for manufacturing large-area bulk ZnO [3]. Its application as a substrate in ZnO homo- and III-nitrides heteroepitaxy has the advantage of almost no or low lattice and thermal mismatch along with the polarity control [6–9].

The large fractions of incorporated Li originating from the mineralizer during hydrothermal growth is one of the dominating defects controlling the electrical and optical properties of the material [2,3,7,10]. High temperature annealing has been shown to lead to Li accumulation in the sub-surface region [11]: within a few tens of micrometers in the O-face and a couple of micrometers on the Zn-face from the surface [12]. Consequently, polishing is required after the high temperature processing of HT ZnO in order to remove Li from the material. Polishing and post-polishing treatment are also essential to prepare ZnO substrates for epitaxial growth.

Polishing required for substrate preparation induces subsurface damage and has been shown to influence the crystalline quality and electrically active defects dramatically [6,13]. However, a deeper understanding of the prevailing defects and defect complexes as well as their thermal evolution are missing despite being of high scientific and technological importance. Recent work [14,15] provides an insight on how to distinguish between various kinds of defect complexes involving $V_{Zn}$, $V_O$, H and Li using positron annihilation spectroscopy.

In this work, positron annihilation spectroscopy and secondary ion mass spectrometry have been employed to study the thermal evolution of polishing-induced defects close to the sample surface in HT ZnO. We show that the Li accumulation in the sub-surface region (and its corresponding depletion from the bulk) at high annealing temperatures strongly affects the thermal evolution of polishing-induced sub-surface damage.

## 2. Material and methods

We have investigated HT-grown ZnO substrates purchased from SPC Goodwill. These substrates were then subjected to thermal annealing and mechanical polishing processing steps. The mechanical polishing was performed on as-received substrates as well as on substrates annealed at 1200 °C and 1500 °C. After polishing, the substrates were either left as they were or annealed at 600 °C, 800 °C and 1000 °C. The polished samples are denoted by X/P/Y, where X and Y stand for the pre- and post-polishing annealing temperatures. RT indicates no thermal annealing. Samples labelled X/U/Y have undergone the same thermal processing, but without polishing in between the annealings. As an example, sample RT/U/RT is the as-received substrate and sample 1200/P/600 was first thermally annealed at 1200 °C, then polished and finally annealed at 600 °C. All of the annealings were performed in air for one hour. The samples are listed in Table 1.

Mechanical polishing (0.25 μm particle size) was performed in order

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**Table 1**
Surface treatment and annealing conditions of hydrothermally grown ZnO samples. U stands for unpolished and P stands for polished samples. RT denotes room temperature (no annealing). The near-surface damage and trapping by $Li_{Zn}$ are identified in positron experiments. Number of fitted layers corresponds to the number of layers used in the VEPFIT model. The presence or the absence of near-surface damage and/or $Li_{Zn}$ is marked with × and – signs, respectively.

| $T_{pre}$ (°C) | Surface treatment | $T_{post}$ (°C) | Near-surface damage | Number of fitted layers | $Li_{Zn}$ |
|---|---|---|---|---|---|
| RT | U | RT | × | 2 | × |
| RT | U | 600 | – | 1 | × |
| RT | U | 800 | – | 1 | × |
| RT | U | 1100 | – | 1 | × |
| 1200 | U | RT | – | 1 | – |
| 1200 | U | 600 | – | 1 | – |
| 1200 | U | 800 | – | 1 | – |
| 1200 | U | 1100 | – | 1 | × |
| 1500 | U | RT | × | 2 | × |
| 1500 | U | 600 | × | 2 | × |
| 1500 | U | 800 | × | 2 | × |
| 1500 | U | 1100 | × | 2 | × |
| RT | P | RT | × | 3 | × |
| RT | P | 600 | × | 2 | × |
| RT | P | 800 | × | 2 | × |
| RT | P | 1100 | × | 2 | × |
| 1200 | P | RT | × | 2 | – |
| 1200 | P | 600 | × | 2 | – |
| 1200 | P | 800 | × | 2 | – |
| 1200 | P | 1100 | – | 1 | – |
| 1500 | P | RT | × | 2 | – |
| 1500 | P | 600 | × | 2 | – |
| 1500 | P | 800 | × | 2 | – |
| 1500 | P | 1100 | – | 1 | – |

to remove the Li accumulated at the surface. Li diffusion is known to start below 600 °C [10,16,17] and its concentration reduces from $10^{17}$ to $10^{15}$ $cm^{-3}$ in the temperature range from 900 to 1400 °C [11].

Secondary ion mass spectrometry (SIMS) using a Cameca IMS7f microanalyzer was employed to study the dominant impurities in the samples. A beam of 10 keV $O_2^+$ ions was rastered over a surface area of 150×150 $\mu m^2$ and secondary ions were collected from the central part of the sputtered crater. Crater depths were measured with a Dektak 8 stylus profilometer, and a constant erosion rate was assumed when converting sputtering time to sample depth. Calibration of the Al, Na and Li signals was performed using implanted reference samples with the detection limit for all three signals in the $10^{14}$ $cm^{-3}$ range.

Depth-resolved positron annihilation spectroscopy measurements were performed at room temperature with variable energy slow positron beams. The positron implantation energy varied from 0.5 keV up to 24/38 keV depending on the setup used. The resolution of HPGe detectors used for measuring the Doppler broadening of the 511 keV annihilation line was 1.2 keV. The peak lineshape was analysed using conventional low momentum parameter *S* corresponding to longitudinal electron momenta [−0.4 to 0.4] a.u., and ± [1.6–4.0] a.u. window was applied for high momentum *W* parameter. The momentum distribution is different depending on whether the positron is in the delocalized state or trapped at a vacancy-type defect. The latter results in narrowing of the annihilation line mainly due to the reduced overlap of the positron wavefunction with core electron wavefunctions. The signal is also affected by the type of atoms surrounding the annihilation site [18]. The known dependence of the Doppler broadening spectrum and, consequently, of the *S* and *W* lineshape parameters on the detector resolution and on the width of the energy windows has been taken into account during the positron data analysis. In order to compare the results obtained with both slow positron beams, the data were scaled taking into account the aforementioned factors as described in detail in Ref. [19].

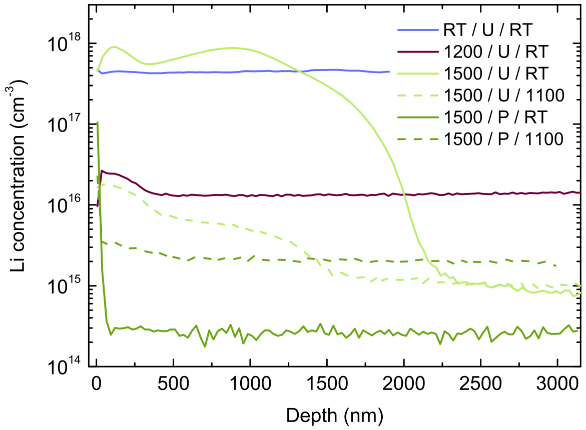

**Fig. 1.** Li concentration versus depth profiles for a selected set of samples.

## 3. Results and discussion

Aluminium and lithium were identified as the dominant impurities by SIMS. All samples show a uniform distribution of Al in the range of 0.8–2×$10^{17}$ $cm^{-3}$, except for the 1500/U/Y series, where Al is found in the near-surface region down to about 500 nm (not shown), potentially originating from surface contamination. Fig. 1 presents Li concentration versus depth profiles for a selected set of samples. In the RT/U/RT sample a uniform concentration of Li of ~4×$10^{17}$ $cm^{-3}$ is observed, but the bulk concentration is significantly reduced after thermal treatments. In the unpolished samples a near-surface region is evident and strongest in the 1500/U/RT sample. In addition to Al and Li, Na is also found close to the sample surface, most probably due to in-diffusion from surface contamination in some of the samples.

The results of conventional Doppler broadening measurements at room temperature for selected samples are presented in Figs. 2 and 3. Keeping in mind that the signal at any given point is broadened by the positron implantation profile and positron diffusion [20], the *S* parameter can be displayed as a function of positron implantation energy and mean implantation depth. These two figures are not directly comparable due to two different detector systems used for the measurements. At low implantation energies (less than 3–10 keV depending on the sample) a fraction of the thermalized positrons diffuses back to the surface and annihilates there. This phenomenon is discussed in more details in e.g. Ref. [15]. At higher implantation

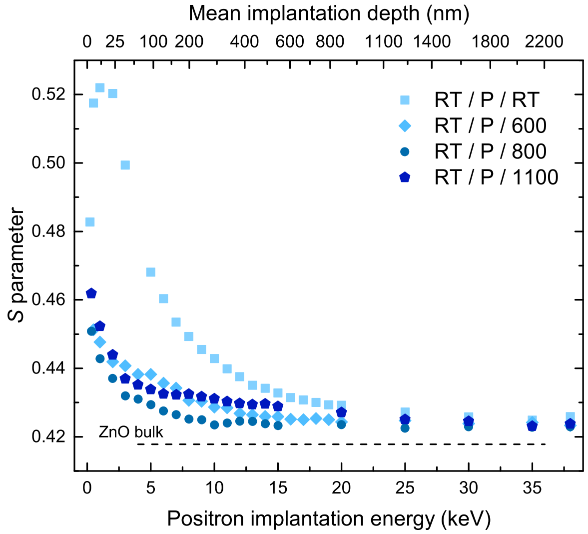

**Fig. 2.** *S* parameter as a function of positron implantation energy and mean implantation depth for polished ZnO sample series RT/P/Y. The dashed line indicates the bulk ZnO value obtained in the defect-free reference [21].