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Defect formation and thermal stability of H in high dose H implanted ZnO

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We studied the structural properties, defect formation, and thermal stability of H in hydrothermally grown ZnO single crystals implanted with H⁺ dose ranging from 2.5×10^{16} to 1×10^{17} cm⁻². H implantation is found to create deformed layers with a uniaxial strain of 0.5–2.4% along the c-axis in ZnO, for the low and high dose, respectively. About 0.2–0.4% of the original implanted H concentration can still be detected in the samples by secondary ion mass spectrometry after annealing at a temperature up to 800 °C. The thermally stable H is tentatively attributed to H related defect complexes involving the substitutional H that are bound to O vacancies and/or the highly mobile interstitial H that are bound to substitutional Li occupying Zn vacancies as the samples are cooled slowly from high temperature annealing. H implantation to a dose of 1×10^{17} cm⁻² and followed by annealing at 800 °C, is found to result in the formation of vacancy clusters that evolved into faceted voids with diameter varying from 2 to 30 nm. The truncations around the voids form more favorably on the O-terminated surface than on the Zn-terminated surface, suggesting that O is a preferred surface polarity for the internal facets of the voids in the presence of H. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4819216>]

I. INTRODUCTION

ZnO is a direct wide bandgap (~3.4 eV) semiconductor with promising applications in a wide variety of devices, such as transparent conducting oxides for photovoltaics, optoelectronics operating in the blue to deep UV region, spintronics, sensors, and piezoelectric devices. ZnO has a large free exciton binding energy of ~60 meV, high radiation hardness, mature crystal growth processes, and is non-toxic. However, it is still difficult to achieve stable and reproducible p-type conductivity in ZnO. The reason for the inherently n-type conductivity in as grown ZnO still remains controversial. Intrinsic defects, in particular, O vacancies and Zn interstitials, have long been debated as the dominant donors in as grown ZnO.¹ On the other hand, first principles calculations by Van de Walle have shown that the n-type conductivity in as grown ZnO can arise from hydrogen.² ZnO has always found to be incorporated with H during growth and processing.^{2,3} Intentional doping of H is also reported to increase the free electron concentration in ZnO.^{4–7} Although H is generally not believed to be the only source of the persistent n-type conductivity that is found in as grown ZnO, it may increase the n-type conductivity in ZnO by behaving either as a shallow donor in an interstitial position and/or the substitutional oxygen site,^{2,8} or passivate compensating acceptors by forming neutral hydrogen-acceptor complexes.^{9–13}

Hydrogen has been introduced into ZnO by plasma treatments or by heat treatment in H₂ gas filled ampoules for the

investigation of H related defects and complexes.^{4–7,10,14–26} Ion implantation can also be used to introduce H into ZnO with the benefit of this technique having a precise control over depth and dose. In addition, structural damage created by ion implantation also provides the opportunity to study the interaction between the implanted species and the intrinsic defects created. More importantly, H implantation in semiconductors has been used to transfer very thin and high quality layers with the SmartCut^{TM} technology.²⁷ H implanted ZnO has been studied by photoluminescence (PL) spectroscopy,^{28,29} Fourier transform infrared spectroscopy,^{28,30} Rutherford backscattering spectrometry,²⁹ secondary ion mass spectrometry (SIMS),^{29,31,32} scanning spreading resistance microscopy (SSRM),³¹ Hall effect technique,³³ Raman scattering spectroscopy,³⁴ transmission electron microscopy (TEM),³⁵ scanning electron microscopy,³⁵ and positron annihilation spectroscopy (PAS).³⁶ Monakhov *et al.*³¹ have studied the effect of annealing on the electrical properties and H concentration profiles in ZnO implanted with H doses of 5×10^{16} and 2×10^{17} cm⁻². Their SSRM measurement showed that the implanted H resulted in a highly conductive layer with 3–7 orders of magnitude lower in resistance compared with the background. The H concentration profiles also became shallower after heat treatment, which was attributed to the release of trapped H from immobile complexes upon heat treatment. The highly conductive layer was stable up to 600 °C annealing temperature when H outdiffused from the implanted region after heat treatment. Ip *et al.*²⁹ have investigated the thermal stability of H in ZnO implanted with a lower H dose of 1×10^{15} to 1×10^{16} cm⁻². Implanted H was found to outdiffuse from the

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implanted region to a concentration below the SIMS detection limit at annealing temperatures $\geq 700^\circ\text{C}$. Singh *et al.*³⁵ observed exfoliations on the surface of ZnO implanted with H dose higher than $2.5 \times 10^{17} \text{ cm}^{-2}$. They also found that the defect band in the as implanted samples was filled with nanovoids with size from 3 to 10 nm. These nanovoids disappeared after annealing at 960°C for 1 h in air. Chen *et al.*³⁶ studied the thermal evolution of defects in H implanted ZnO with positron annihilation spectroscopy. They suggested that upon annealing at $200\text{--}500^\circ\text{C}$, Zn vacancies created by H implantation in ZnO will coalesce into H-filled bubbles. Further annealing at higher temperatures releases the H from the H-filled bubbles, hence turning the H-filled bubbles into microvoids, which will eventually be annealed out at 1000°C .

In this work, X-ray diffraction (XRD) and TEM are used to analyze the evolution of the structural defects and deformation in hydrothermally grown ZnO single crystals implanted with H dose up to $1 \times 10^{17} \text{ cm}^{-2}$. Vacancy type defects or voids are observed in the H implanted region after annealing. The possible configurations of the thermally stable implanted H in the samples, as revealed by SIMS, after heat treatment at temperatures up to 800°C are also discussed.

II. EXPERIMENT

The samples used in this study were high quality hydrothermally grown single crystal n-type ZnO purchased from Tokyo Denpa Co. (Japan). 100 keV of H^+ ions with doses ranging from 2.5×10^{16} to $1 \times 10^{17} \text{ cm}^{-2}$ were implanted into the (0001) Zn face of the samples at room temperature. The implantation was carried out in a tandem accelerator (NEC, 5SDH-4) with a maximum terminal voltage of 1.7 MeV . During implantation, the samples were tilted 10° relative to the incident beam to minimize channelling.³⁷ The beam flux was recorded to be between 5.14×10^{11} and $1.16 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. The estimated projected range of the ions is 624 nm as calculated by Stopping and Range of Ions in Matter (SRIM).³⁸ Displacement energies of 34 eV for Zn and 44 eV for O are used for the SRIM simulation.^{39,40} After implantation, the samples were subsequently annealed isochronally at temperatures between 600°C and 800°C for 1 h in air. High resolution XRD measurements were carried out with a PANalytical X'pert Pro MRD diffractometer using $\text{Cu K}\alpha$ radiation ($1.540598 \text{ \AA}$). TEM analysis of selected samples was carried out using a Philips CM300 instrument with a LaB_6 filament operating at 300 kV . TEM samples were prepared by mechanical polishing with a tripod polisher followed by 1–2 h ion beam thinning at -168°C with a Gatan 691 Precision Ion Polishing System (PIPS) operating at $3.0\text{--}3.5 \text{ keV}$. H and Li concentration–depth profiles were measured by SIMS using a Cameca IMS 7f instrument. A primary beam of 15 keV Cs^+ or 10 keV O_2^+ ions was used to monitor H and Li, respectively, and rastered over a $125 \times 125 \mu\text{m}^2$ surface area where the secondary ions were collected from the central region of the crater. Crater depth was measured with a Dektak 8 stylus profilometer, and a constant erosion rate was assumed for converting the sputtering time into sample depth. Implanted reference samples

were used to convert the H and Li signals into impurity concentrations. SSRM measurements were obtained from a Digital Instrument's Nanoscope Dimension 3100 microscope. A DC voltage of -4 V was applied to a conductive Ti-Pt-coated tip (MikroMasch) for the SSRM measurement. Surface swelling on the samples after implantation was measured with a Veeco Wyko® NT9100 optical profiling system.

III. RESULTS

A. Redistribution of H and Li during annealing

Fig. 1 shows typical H and Li concentration versus depth profiles measured by SIMS for the samples implanted with H dose of $5 \times 10^{16} \text{ cm}^{-2}$ before and after annealing. In the as implanted samples, the H profile shows a Gaussian distribution with peak position at a depth of about 700 nm from the surface (R_p). This observation is consistent with the SRIM simulation which shows a slightly shallower projected range at 624 nm . Maximum H concentrations of $1 \times 10^{21}\text{--}4 \times 10^{21} \text{ cm}^{-3}$ in the implanted region were obtained for doses of $2.5 \times 10^{16}\text{--}1 \times 10^{17} \text{ cm}^{-2}$, respectively. Interestingly, before annealing, Li is found to already redistribute and peak at the end of the implanted region at around $0.9 \mu\text{m}$. The Li profile shows a constant concentration of about 10^{17} cm^{-3} from the surface to a depth of about $0.8 \mu\text{m}$, which corresponds to the implanted region of the sample. This is similar to the Li concentration incorporated in the as grown samples during the hydrothermal growth process, which is measured by SIMS to be between 2 and $3 \times 10^{17} \text{ cm}^{-3}$.

After annealing at 600°C , the maximum H concentration in the implanted region is found to decrease to about $1.4\text{--}4.5\%$ of the initial concentration for the 2.5×10^{16} to $1 \times 10^{17} \text{ cm}^{-2}$ implanted H doses before annealing. The peak of the H profile also shifts by $50\text{--}100 \text{ nm}$ towards the surface of the sample, which in addition to diffusion and retrapping of the implanted H, may also be caused by slight variations in the erosion rates during the SIMS profiling due to a lower density in the H peak region relative to the substrate. After annealing, the H profile also becomes significantly narrower for all the samples. Two residual shallower peaks are observed

FIG. 1. SIMS profiles of implanted H (100 keV at RT) and Li with respect to different annealing temperatures (600°C and 800°C for 1 h in air) in single crystal ZnO implanted with H dose of $5 \times 10^{16} \text{ cm}^{-2}$.

at depths of about $0.2\ \mu\text{m}$ and $0.35\ \mu\text{m}$ for the samples implanted with $5 \times 10^{16}\ \text{cm}^{-2}$ H dose (see R_1 and R_2 in Fig. 1, respectively). Interestingly, after annealing at 600°C , there is also an enhancement of the Li concentration in the region close to the peak of the H profile. In particular, the Li profile is found to match the H profile in shape. Similar peaks close to R_1 and R_2 of the H profile in Fig. 1 are also observed in the Li profile. The similarity in shape and features between the Li and H profiles after annealing at 600°C is also observed in the samples implanted with other H doses (not shown).

Heat treatment at 800°C results in further outdiffusion of H from the samples. The maximum H concentration decreases to about 0.2–0.4% of the initial concentration for the 2.5×10^{16} to $1 \times 10^{17}\ \text{cm}^{-2}$ implanted H doses before annealing. This concentration is at around 3.6×10^{18} – $6.8 \times 10^{18}\ \text{cm}^{-3}$, which is still well above the SIMS detection limit. Most significantly, the implanted profile has evolved into a two-peak profile as illustrated in Fig. 1 (brown solid line). The deeper, less prominent peak is actually a broad shoulder centered at a depth of around $0.8\ \mu\text{m}$ (see R_3 in Fig. 1). The most prominent peak centered at around $0.65\ \mu\text{m}$ seems to correspond to the projected range of the implanted H ions (Fig. 1). Again, the Li profile shows a close similarity to the H profile with two peaks also located at identical locations at about $0.65\ \mu\text{m}$ and $0.8\ \mu\text{m}$. The two peaks feature in the H and Li profiles are also observed in the samples implanted with other H doses and annealed at 800°C (not shown).

B. Deformation in the implanted layer, swelling and recovery after annealing

Fig. 2(a) shows the X-ray rocking curves for the as implanted samples of different H doses along the symmetrical (0002) reflection, i.e., normal to the implanted surface. After H implantation, interference fringes are observed on the lower 2θ value of a sharp diffraction peak located at 34.4° . The sharp peak is the ZnO Bragg peak arising from the unperturbed part of the implanted substrates. The number of oscillating fringes is a measure of the strain in the implanted layer and as will be discussed, it is found to increase with increasing dose. No amorphous layers are detected even for the sample implanted with the highest dose ($1 \times 10^{17}\ \text{cm}^{-2}$). Fig. 2(b) shows the reciprocal space mapping (RSM) of the sample implanted with $5 \times 10^{16}\ \text{cm}^{-2}$ H in the asymmetrical (11 $\bar{2}$ 4) reflection. Here, Q_x and Q_z are expressed as $Q_x = 2\pi[\cos(\omega) - \cos(2\theta - \omega)]/\lambda$ and $Q_z = 2\pi[\sin(\omega) + \sin(2\theta - \omega)]/\lambda$.^{41,42} The RSM peak is found to elongate towards the lower values of the RSM coordinate Q_z . The presence of fringes to the left of the ZnO Bragg peak in the rocking curves and the elongation of the RSM peak show that H implantation creates deformed layers in ZnO that are dilated predominantly along the c-axis. The tail of the RSM peak in Fig. 2(b) is also observed to bent slightly towards larger Q_x value, indicating that the implanted layers with higher strains experience a slight in-plane strain relaxation in a similar manner described by Moram and Vickers for completely relaxed epilayers.⁴¹

Figs. 2(c) and 2(d) show the X-ray rocking curves along the (0002) reflection after annealing at 600°C and 800°C .

Most of the fringes disappear after heat treatments, suggesting that the strain introduced by implantation is significantly reduced by annealing. However, the (0002) Bragg peak of the annealed samples is still broader than in the as grown samples, with residual broadening still persistent at lower 2θ values in the rocking curves. Therefore, annealing at a temperature up to 800°C is not enough to completely anneal out the lattice distortions caused by H implantation in ZnO. Interestingly, the residual strain after annealing is most significant in the samples implanted with the lowest dose compared with the other higher doses. This suggests that the damage recovery process is more efficient in the samples implanted with H doses higher than $2.5 \times 10^{16}\ \text{cm}^{-2}$. This unexpected easier recovery for the higher dose samples is possibly due to a nucleation threshold dose for stable larger defects, such as voids, which may show a lower residual strain as detected by XRD. Below this threshold dose, a higher density of defects clusters will distort the lattice more and hence explains the larger strain detected. Our XRD rocking curve simulation shows that about 0.05–0.08% residual strain still remains in the annealed samples.

Simulation of the XRD rocking curves of the as implanted samples was carried out with the X'pert Epitaxy

FIG. 2. (a) XRD rocking curves on symmetrical (0002) reflection of single crystal ZnO before implantation and after implanted with 100 keV H^+ doses of $2.5 \times 10^{16}\ \text{cm}^{-2}$, $5 \times 10^{16}\ \text{cm}^{-2}$, $7.5 \times 10^{16}\ \text{cm}^{-2}$, and $1 \times 10^{17}\ \text{cm}^{-2}$. (b) RSM of the sample implanted with $5 \times 10^{16}\ \text{cm}^{-2}$ H in the asymmetrical (11 $\bar{2}$ 4) reflection. (c) XRD rocking curves for the samples in (a) after annealing at 600°C . (d) XRD rocking curves for the samples in (a) after annealing at 800°C .

software, which employs the Takagi-Taupin diffraction theory.⁴³ Fig. 3(a) shows a comparison between the best-fit simulated and the experimental X-ray rocking curve for the sample implanted with H dose of $5 \times 10^{16} \text{ cm}^{-2}$. Fig. 3(b) shows the strain distribution used in the simulation in Fig. 3(a), along with the H profile measured by SIMS, the corresponding SRIM simulated H profile and the SRIM simulated energy loss by the implanted ions to nuclear collisions profile. For comparison purpose, the SRIM simulated H profile and the energy loss to nuclear collision profile are normalised to the SIMS H profile with scale ratios of 0.87 and 0.031, respectively. As shown in Fig. 3(b), the strain distribution along the c-axis of the as implanted samples exhibits

FIG. 3. (a) Simulated and experimental XRD rocking curve along the (0002) reflection of single crystal ZnO implanted with 100 keV H⁻ dose of $5 \times 10^{16} \text{ cm}^{-2}$. (b) Strain profile compared with the implanted H profiles and the profile of the energy loss to nuclear collision, in single crystal ZnO implanted with 100 keV H⁻ dose of $5 \times 10^{16} \text{ cm}^{-2}$. The SRIM simulated H profile and the energy loss to nuclear collision profile are normalised to the SIMS H profile with scale ratios of 0.87 and 0.031, respectively. (c) Maximum strain and average swelling versus dose for single crystal ZnO implanted with 100 keV H⁻.

a near-Gaussian distribution that matches most closely the H implantation profile measured by SIMS and simulated by SRIM. The maximum strain was extracted from the simulation of the XRD rocking curves for different implantation doses and plotted as a function of the implanted dose in Fig. 3(c). Swelling observed on the surface of the samples due to implantation is also illustrated in Fig. 3(c) as a function of implantation dose. The maximum strain varies from 2.4% for the dose of $1 \times 10^{17} \text{ cm}^{-2}$ to 0.5% for the dose of $2.5 \times 10^{16} \text{ cm}^{-2}$. The average swelling varies from 6.8 nm for the dose of $1 \times 10^{17} \text{ cm}^{-2}$ to 2.7 nm for the dose of $2.5 \times 10^{16} \text{ cm}^{-2}$. Both the maximum strain and the average swelling increase linearly with the implantation dose.

C. Microstructures in H implanted ZnO after annealing

Fig. 4(a) shows a bright field cross-sectional TEM micrograph for the sample implanted with $1 \times 10^{17} \text{ cm}^{-2}$ H and annealed at 800 °C for 1 h in air. A dense network of defects is observed from the sample surface to a depth of about 1 μm into the sample. When the sample was tilted slightly off the zone axis to minimise the contrast arising from the defects, a typical micrograph as shown in Fig. 4(b)

FIG. 4. (a) Cross-sectional TEM image along the [1100] zone axis of single crystal ZnO implanted with $1 \times 10^{17} \text{ cm}^{-2}$ H⁻ at 100 keV and annealed at 800 °C. (b) Cross-sectional TEM image of the H implanted sample in (a), taken when the sample is tilted slightly off the zone axis. (c) H and Li SIMS profiles in single crystal ZnO implanted with $1 \times 10^{17} \text{ cm}^{-2}$ H⁻ and annealed at 800 °C. Resistance measured by SSRM on the sample is also shown.

is obtained. Fig. 4(b) shows a band of nanovoids which corresponds to the peak of the H implantation profile as shown in Fig. 4(c). The nanovoids were identified by performing a through focal series experiment where a dark Fresnel fringe and a bright Fresnel fringe were observed on the voids boundaries when viewed in an underfocus and overfocus condition, respectively. The voids are most likely formed from the clustering of vacancies that are created by H implantation and subsequent heat treatments. These voids have a diameter ranging from 2 to 30 nm. The larger voids are found to be surrounded by sharply defined facets and concentrate around the peak of the H implantation profile at about 600–700 nm as measured by SIMS. The smaller voids are also distributed at depths around the peak of the implantation profile but have a more rounded shape.

As mentioned earlier, the SIMS profiles of the annealed samples show an interesting two-peaks feature (see Fig. 4(c)) in both the H and Li profiles. The void distribution does not seem to have any correlation with the two peaks profile, possibly suggesting that the deeper peak may be related to the formation of Li–H complexes rather than H and Li trapped at the large voids. Another interesting correlation between the SIMS profiles and the defect distribution is that the dislocation profile in Fig. 4(a) drops sharply at about 1 μm depth where the Li concentration also reaches the background concentration. Furthermore, from the resistance measured by SSRM as shown in Fig. 4(c), there is no significant change in conductivity of the layer containing voids compared with the background.

Fig. 5(a) shows a magnified cross-sectional TEM image of the voids in the implanted region. The facets of the voids are found to be formed on the non-polar $\{11\bar{2}0\}$ planes and

FIG. 5. (a) Higher magnification cross-sectional TEM image of the defect band in Fig. 4(b). (b) Magnified cross-sectional TEM image of a large void, showing truncations on the O and Zn internal surfaces of the void.

slightly different inclined semi-polar planes. Some large voids such as voids A and B in Fig. 5(a) and the void in Fig. 5(b) also show truncations on the polar $\{0001\}$ planes, where the O-terminated truncation is found to be longer than the Zn-terminated one. The O-terminated truncations also occur more often than the Zn-terminated truncations, such as void C in Fig. 5(a), where only O-terminated truncation can be clearly seen. In addition, the angle between the semi-polar facets and the non-polar $\{11\bar{2}0\}$ facets is also found to vary depending whether they are formed adjacent to the O-terminated or Zn-terminated truncation of the void. From the analysis of a total of 40 large voids, we found that the planes of the semi-polar facets that are formed adjacent to the O-terminated truncation are $\{11\bar{2}4\}$ (53%), $\{11\bar{2}5\}$ (41%), and $\{11\bar{2}6\}$ (6%). On the other hand, the planes of the semi-polar facets that are formed adjacent to Zn-terminated truncation are $\{11\bar{2}6\}$ (28%), $\{11\bar{2}7\}$ (40%), and $\{11\bar{2}8\}$ (32%). It is important to note here that since the angle between each possible semi-polar planes of the facets is small (which varies from only 2.8° between the $\{11\bar{2}7\}$ and $\{11\bar{2}8\}$ planes to 6° between the $\{11\bar{2}4\}$ and $\{11\bar{2}5\}$ planes), some errors are expected especially when it is not possible to have all the voids in the right focus condition for cross-sectional TEM imaging. As the voids are at different depths within the foil of the samples, it is very hard to capture all the voids within one frame at optimum focus with the TEM.

IV. DISCUSSION

A. Strain in H implanted ZnO

From the XRD measurements in Fig. 2(a), the elongation of the lattice constant normal to the surface, as created by H implantation in the ZnO samples can also be found in N implanted ZnO,⁴⁴ and in other implanted Wurtzite semiconductors, such as Eu implanted AlN⁴⁵ and He implanted 4H-SiC,⁴⁶ as well as in implanted cubic semiconductors.⁴⁷ In Fig. 3(b), XRD simulation shows that the strain distribution in the as implanted samples is closer to the implantation profile than the distribution of the energy deposited in nuclear (damage) collisions. In contrast, the strain profiles are reported to follow the distribution of the energy deposited by nuclear collisions in low dose ion implanted GaAs⁴⁸ and He implanted 4H-SiC.⁴⁶ This result suggests that the implantation-induced strain in H implanted ZnO may be caused specifically by the interaction between the implanted H and the ZnO lattice, and/or by the defects with distribution that follows the H implantation profile, but not from atomic displacements or point defects as generally observed in implanted GaAs and SiC. The weak connection between the atomic displacements and strain formation in H implanted ZnO may be due to the high radiation hardness and dynamic annealing of ZnO,^{1,49} where less atomic displacements are created by ion bombardment in ZnO compared with the other semiconductors. Defect annihilation already occurs rapidly at 200 K for Zn sublattices and at 400 K for O sublattices.⁵⁰

After heat treatment at 800 $^\circ\text{C}$ for 1 h in air, residual strain of about 0.05–0.08% remains in the samples. This

result is similar to what has been reported in N implanted ZnO, which is annealed for a shorter time (15 min) but at a higher temperature (900 °C).⁴⁴ Thus, annealing at a temperature higher than 800 °C to 900 °C or a longer annealing duration may be needed to completely recover the lattice distortions caused by H implantation. This is especially important for doping of ZnO based devices and structures using ion implantation as the damage could be detrimental for the optical and electrical device properties.

B. Thermal stability of H in hydrothermally grown ZnO

As shown in Fig. 1, after annealing at 800 °C, H concentrations from 3.6×10^{18} to $6.8 \times 10^{18} \text{ cm}^{-3}$ or equivalent to 0.2–0.4% of the initial implanted H concentration, respectively, can still be detected in the implanted layer. Ip *et al.*²⁹ have previously shown that the implanted H outdiffused to a concentration below the detection limit of SIMS at annealing temperatures ≥ 700 °C. However, the result from Ip *et al.* may not be comparable with ours because they used a lower implanted H dose, shorter annealing time and ZnO substrates that were grown differently than ours. The XRD rocking curves in Fig. 2(d) reveal that some deformations still remain in the samples after heat treatment at 800 °C. Cross-sectional TEM images in Figs. 4(a) and 4(b) also show the presence of extended defects in the implanted region of the samples after annealing at 800 °C. Preliminary studies of these defects unveil that they are not simple interstitial defects involving a plane of interstitials as observed in ion implanted Si and SiC.^{51,52} Detailed investigations are underway to fully characterize the nature of these defects, but it appears that the apparent high thermal stability of H could be due to trapping by the extended defects that remain after annealing at 800 °C.

A possible atomic configuration of the thermally stable H that is found in the annealed samples is the substitutional H that is bound to an O vacancy (H_O). Based on theoretical investigation by Janotti and Van de Walle, H_O is found to be a highly stable shallow donor in n-type ZnO with a binding energy of 3.8 eV and a lower formation energy compared with the O vacancy in n-type ZnO by at least 0.5 eV.⁸ They have shown that in oxygen-rich conditions, interstitial H (H_i) is found to be the highly dominant species. On the other hand, in oxygen-poor conditions, the difference between the formation energy of H_O and H_i is only about 0.1 eV. As H_i is mobile at modest temperatures, H_O is expected to exist predominantly in annealed ZnO.^{8,53} As a result, H_O may be a possible configuration of the thermally stable H detected in the annealed samples. Moreover, from SRIM simulation, about 2×10^{21} to $8 \times 10^{21} \text{ cm}^{-3}$ of O vacancies are generated in the samples by H implantation for doses from 2.5×10^{16} to $1 \times 10^{17} \text{ cm}^{-2}$, respectively, when self-annihilation is neglected. However, although defect recombination between O interstitials and O vacancies is anticipated to already occur during implantation and modest annealing at 100 °C,⁵⁰ the presence of voids in the cross-sectional TEM image in Fig. 4(b) shows that not all the vacancies created by H implantation are being annihilated. These vacancies could be stabilised by the implanted H that

prevent them from being annihilated by mobile interstitials during annealing.

Weber and Lynn have studied H in ZnO and suggested that the introduction of H leads to the expansion of lattice caused by H_O .⁵⁴ Their samples went from being transparent towards a red coloration as a result of the hydrogenation of ZnO substrates in sealed ampoules with an oxygen deficient environment. Weber and Lynn claimed that the red coloration of their samples is a complex behavior related to the thermochromic properties of ZnO and a lattice expansion attributed to the formation of H_O in the ZnO lattices.⁵⁴ In our experiment, the ZnO substrates became yellowish in color after implantation, with the samples implanted with higher H dose having slightly darker color. The samples become transparent again just after annealing at 600 °C. While we cannot conclude that the strain in the as implanted samples is solely caused by H_O , H_O may contribute to some of the residual strain in the samples after annealing at 800 °C as shown by the XRD measurements in Fig. 2(d), and therefore also account for some of the thermally stable H in the samples, as discussed previously.

Another possible configuration of the thermally stable H is a complex involving substitutional Li in a Zn vacancy (Li_Zn) that is bonded to an OH^- ion at an adjacent O site, or simply the Li_Zn –OH complex.¹⁶ As shown by the SIMS data in Fig. 1, there is a good correlation between the Li and H profiles after annealing, both in terms of shape and the location of the concentration peaks. It is a distinct possibility that the overlapping of the SIMS profiles is due to the recapturing of H by Li_Zn to form Li_Zn –OH complexes when the samples are cooled down slowly after annealing.³⁰ Li_Zn –OH gives rise to a dominant 3577 cm^{-1} infrared absorption band which remains in ZnO only after slow cooling down from annealing at 1200 °C.³⁰ Hydrothermally grown ZnO substrates are known to be incorporated with Li impurities during growth.^{55,56} Therefore, the possibility of H getting retrapped by Li_Zn antisites to form related complexes in the hydrothermally grown substrates used in our experiments is expected to be higher than in the vapour phase grown materials used by Ip *et al.*²⁹ These trapped H in the Li_Zn –OH complexes may also explain why the concentration of the remaining H detected in our samples is higher than the samples prepared by Ip *et al.* However, it should be emphasized here that in our annealed samples, it is also possible that both the H and Li are trapped by the same defects that are not necessarily the Li_Zn –OH complexes.

The evolution of H profiles with annealing temperature as measured by SIMS in Fig. 1 is in good agreement with the previous study by Monakhov *et al.*³¹ Monakhov *et al.* suggested that the narrowing of H profiles upon annealing, which is also observed in the samples in Fig. 1, is caused by the release of trapped H from immobile complexes. Monakhov *et al.*³¹ also observed a decrease in 3–7 orders of magnitude in SSRM resistance in the implanted region for H implanted ZnO annealed up to 600 °C. However, they did not investigate the SSRM profiles of the samples annealed at a temperature higher than 600 °C. The SSRM result in Fig. 4(c) shows no significant change in resistance (<1 order of magnitude) in the implanted region compared with the background for the

samples annealed at 800 °C, while the samples annealed at lower temperatures qualitatively follow that of Monakhov *et al.* This suggests that at an annealing temperature >600 °C, the conductive region (n^+ layer) created by H implantation in the samples as observed by Monakhov *et al.* may have annealed out together with the less thermally stable H at temperatures >600 °C. The remaining thermally stable H does not contribute to any change in the conductivity as measured by SSRM. This is a possible indication that the remaining thermally stable H related complexes are electrically inactive. Calculations by Wardle *et al.*¹² have shown that all the possible $\text{Li}_{\text{Zn}}\text{-H}$ configurations are electrically inactive.

C. Microstructures in H implanted ZnO after annealing

Nanovoids that are observed in the samples after annealing as shown in Figs. 4(b) and 5 are also reported to form in other H implanted semiconductors after annealing, such as H implanted GaN,^{57–59} GaAs,⁶⁰ and Si.⁶¹ We found that there is a tendency for the polar truncations around the voids to form more favorably on the O-terminated surface than on the Zn-terminated surface. This result suggests that under the coverage of the implanted H, the O-terminated surface is more stable than the Zn-terminated surface. In ZnO, H-terminated O surface has always found to be very stable, as the exposure of H to clean O surface will result in the rapid formation of O-H species that stabilise the O-terminated ZnO surface.^{62,63} On the contrary, He-atom scattering experiments have shown that prolonged exposure to H can cause the Zn-terminated ZnO surface to reconstruct and become disordered.^{62,64} In the annealed samples, Li may also play a role in stabilising the O-terminated truncation of the void as both the Li and H concentration profiles measured by SIMS in these samples also exhibit the same trend, as shown in Fig. 4(c). However, as shown by the voids in Figs. 5(a) and 5(b), the stable O-terminated surface only forms truncation around the void while long facets are formed on the non-polar $\{11\bar{2}0\}$ planes and the semi-polar planes. This observation may be due to the lower surface formation energy of the non-polar planes compared with the polar planes in ZnO. Indeed, as calculated from first principles density functional theory, the formation energy of the polar surfaces in ZnO is significantly higher (2 times) than the non-polar surfaces, such as $\{11\bar{2}0\}$.^{65,66} We note that the orientation of the semi-polar facets also shows this predisposition towards the O polar surfaces, where higher index semipolar planes are observed for “Zn polar” semi-polar facets (adjacent to the Zn truncations) compared with “O polar” semi-polar facets.

The presence of nanovoids in the cross-sectional TEM images in Figs. 4(b) and 5 also agrees well with the PAS studies in H implanted ZnO by Chen *et al.*³⁶ Chen *et al.* observed that the S parameter of the Doppler broadening spectra in the implanted region increased upon annealing at 300 °C, reaching a maximum value at 700 °C and decreased to the background intensity at 1100 °C. They attributed this observation to the formation of vacancies filled by implanted H. The annealing causes the agglomeration of the H-filled vacancies into H-filled bubbles. Further annealing at higher temperatures causes the implanted H to diffuse out from the

bubbles, leaving behind a large amount of empty volumes that increase the S-parameter. We believe that some implanted H still remains in the voids in the samples after annealing at 800 °C, and this causes the truncations and facets of the voids to form more favorably on the O-polar surfaces, as discussed in the previous paragraph. In addition, during annealing, the implanted H may also help to stabilise the implantation-induced vacancies, causing them to coalesce and grow to the size observable by TEM instead of recombining with mobile interstitials. The size of the voids is also dependent on the implanted H dose, as Chen *et al.* suggested that the H implantation dose that they used ($\sim 4.4 \times 10^{15} \text{ cm}^{-2}$) might be too low to create voids that are large enough for direct observation with TEM, compared with $1 \times 10^{17} \text{ cm}^{-2}$ used in Figs. 4(b) and 5(a). To prove whether the evolution of the H-filled bubbles/microvoids with respect to temperature can be correlated exactly to the change in S-parameter as observed by Chen *et al.*, a detailed TEM study of implanted samples annealed at a wider range of temperatures than the one used in this work is needed. This is beyond the scope of this paper.

V. CONCLUSION

XRD, SIMS, SSRM, and TEM were used to characterize the evolution of structural and microstructural properties in H implanted ZnO with respect to annealing temperatures and dose. H implantation is found to create deformed layers with their crystal lattices elongated along the c-axis in ZnO. Most of the strain in the deformed layers is annealed out after heat treatment at 600 °C and 800 °C. The concentration of implanted H is observed to decrease by an order of magnitude and nearly 3 orders of magnitude after annealing at 600 °C and 800 °C, respectively. H can still be detected in the implanted region after annealing at 800 °C. The high thermal stability of the implanted H can possibly be associated with H related defect complexes, such as H_O and/or $\text{Li}_{\text{Zn}}\text{-OH}$. Faceted voids are also observed to form in the implanted region of the samples after annealing at 800 °C for 1 h. There is a polarity preferred termination of the voids' facets, where the polar truncations and the semi-polar facets are found to form more favorably on the O-terminated surface than on the Zn-terminated surface.

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