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Zn precipitation and Li depletion in Zn implanted ZnO

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Ion implantation of Zn substituting elements in ZnO has been shown to result in a dramatic Li depletion of several microns in hydrothermally grown ZnO. This has been ascribed to a burst of mobile Zn interstitials. In this study, we seek to understand the reason behind this interstitial mediated transient enhanced diffusion in Li-containing ZnO samples after Zn implantation. ZnO wafers were implanted with Zn to two doses, $5 \times 10^{15} \text{ cm}^{-2}$ and $1 \times 10^{17} \text{ cm}^{-2}$. Secondary ion mass spectrometry was carried out to profile the Li depletion depth for different annealing temperatures between 600 and 800 °C. The 800 °C annealing had the most significant Li depletion of close to 60 μm . Transmission electron microscopy (TEM) was carried out in selected samples to identify the reason behind the Li depletion. In particular, TEM investigations of samples annealed at 750 °C show significant Zn precipitation just below the depth of the projected range of the implanted ions. We propose that the Zn precipitation is indicative of Zn supersaturation. Both the Li depletion and Zn precipitation are competing synchronous processes aimed at reducing the excess Zn interstitials.

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The incorporation of Li during hydrothermal growth of ZnO produces high quality ZnO crystals with a carrier concentration as low as 10^{14} cm^{-3} . Indeed, Li acts as a compensating dopant and reduces the unintentional n-type doping observed in ZnO. Ion implantation is useful for incorporating dopants with both lateral and in depth control. Recently, Neuvonen *et al.*¹ reported that for Zn implantation in Li-containing ZnO samples, upon annealing at >600 °C, Li was drastically depleted from the surface to several microns depth. This was ascribed to the displacement of Li from Zn sites (Li_{Zn}) by mobile Zn interstitials (Zn_i) via a “kick-out” mechanism. The high mobility of both the Zn_i and Li interstitials (Li_i),^{2,3} as well as the low energy barrier for Li to switch between interstitial and substitutional sites,⁴ was useful in explaining the significant Li depleted region.¹

It is well known that transient enhanced diffusion (TED) can occur in Si after ion implantation.^{5,6} After heat treatments, excess ion implantation-induced point defects are observed to displace substitutional dopants such as B and P through a “kick-out” mechanism.^{5,6} This results in a broadening of the dopant profiles, a challenge in device technology. The TED phenomenon is attributed to the dissolution of “{311}” defects with a release of Si interstitials which displace substitutional dopants.^{5,6} In this letter, we show that there is significant Zn precipitation during Zn implantation of ZnO and this process occurs in parallel with the Li depletion. We attribute both transient processes to a huge supersaturation of Zn_i .

The wafers used were hydrothermally grown (0001) ZnO supplied by Tokyo Denpa Co. Japan, unintentionally doped with a Li concentration of $\sim 2\text{--}4 \times 10^{17} \text{ cm}^{-3}$ during

growth. 400 keV and 500 keV $^{64}\text{Zn}^+$ ions were implanted into the (0001) Zn polar face to doses of $5 \times 10^{15} \text{ cm}^{-2}$ and $1 \times 10^{17} \text{ cm}^{-2}$, respectively, at room temperature. The implantation was carried out with an NEC 5SDH-4 tandem accelerator. A 10° beam tilt angle was used during the implantation to minimize channeling.⁷ The nominal projected range of 400 keV and 500 keV Zn ions R_p in ZnO is $\sim 158 \text{ nm}$ and 201 nm , respectively, as calculated by Stopping and Range of Ions in Matter (SRIM) code.⁸ The samples were then processed in a rapid thermal annealing system at 600–800 °C in O_2 for 30 s. The cooling rate was initially fast, about 70 °C per second until the temperature reached 300 °C. Li concentration profiles were measured by secondary ion mass spectrometry (SIMS) using a Cameca IMS 7f instrument. The SIMS detection limit for Li is $\sim 1 \times 10^{13} \text{ cm}^{-3}$. Cross-section transmission electron microscopy (XTEM) samples were prepared either by mechanical polishing followed by further thinning to electron transparency using a Gatan Model 691 Precision Ion Polishing System or focused ion beam using a Ga beam in an FEI Helios 600 NanoLab instrument. Both transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) analyses were carried out using a JEOL2100F instrument operating at 200 kV with a field emission gun and an energy dispersive x-ray (EDX) JEOL silicon drift detector.

Fig. 1 shows the SIMS Li profiles and SRIM simulated Zn profile in the sample implanted with 400 keV $^{64}\text{Zn}^+$ to a dose of $5 \times 10^{15} \text{ cm}^{-2}$, before and after annealing. The same ZnO piece was annealed for the SIMS annealing study. As illustrated in Fig. 1(a), in the as-implanted sample (solid black line), there is a small drop in Li concentration from the surface to $\sim 200 \text{ nm}$. This suggests that Li already starts to

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FIG. 1. SIMS Li profile and SRIM simulated Zn profile in hydrothermally grown single crystal ZnO implanted with 400 keV $^{64}\text{Zn}^+$ of dose $5 \times 10^{15} \text{ cm}^{-2}$, before and after annealing.

redistribute right after implantation. Annealing at 600 °C does not produce any noticeable changes to the Li profile. TEM analysis of this sample shows very little contrast, clearly indicating a small change in microstructure after the 600 °C annealing. After 700 °C annealing, Li depletion starts to occur. Furthermore, the width of the Li depleted region also increases with annealing temperature, in good agreement with previous reports.¹ As shown in Fig. 1(b), after 800 °C, the Li depletion is substantial, reaching almost 60 μm from the surface. This is deeper than the one reported by Neuvonen *et al.*,¹ although they used a similar dose but a longer annealing time. In addition, at the same temperature (800 °C), Li also appears to diffuse back into the depleted region. As illustrated in the inset of Fig. 1(b), a shoulder of $\sim 2 \mu\text{m}$ wide emerges on the boundary of the Li depleted region at $\sim 59 \mu\text{m}$. Interestingly, the same sample shows a Li peak close to $R_p \approx 200 \text{ nm}$ with a maximum concentration of $\sim 2 \times 10^{15} \text{ cm}^{-3}$ (see dark green line in Fig. 1(a)).

Fig. 2 illustrates a typical cross-section TEM (XTEM) image along the $[11\bar{2}0]$ direction after 750 °C annealing compared with the SIMS and SRIM results. We observe long streaks parallel to the surface close to the projected range of the ion R_p amongst with smaller defects. These long streaks are planar defects on the basal plane and are found in the implanted region of all the samples annealed from 600 to 800 °C. Interestingly, these defects are clearly visible when

FIG. 2. XTEM image of hydrothermally grown ZnO implanted with 400 keV $5 \times 10^{15} \text{ cm}^{-2}$ $^{64}\text{Zn}^+$ and annealed at 750 °C for 30 s, compared to the SRIM simulated implanted Zn profile and the SIMS Li profiles before and after annealing.

viewed along the $[11\bar{2}0]$ direction but not so easy to distinguish along the $[10\bar{1}0]$ direction. Within the literature,^{9–12} there are four possible variants of Burgers vectors for planar defects (a) $1/3\langle 10\bar{1}0 \rangle$ also known as **p** (b) $1/3\langle 11\bar{2}0 \rangle$ also as **a** (c) $\langle 0001 \rangle$ also known as **c** (d) $\mathbf{c}/2 + \mathbf{p}$. Out of these, we expect the last two variants to be interstitial in nature. Diffraction contrast experiments show these defects to be visible especially when $\mathbf{g} = [10\bar{1}0]$ but invisible when $\mathbf{g} = [0002]$ and $[1\bar{2}10]$. Using the invisibility criteria of $\mathbf{g} \cdot \mathbf{b} = 0$, these defects are consistent with an in-plane Burgers vector parallel to $\langle 10\bar{1}0 \rangle$ ¹³ and hence consistent with the (a) variant. This variant was calculated to be the most stable of all the stacking faults in GaN.¹⁴ We note that the diffraction contrast observed by Kucheyev *et al.*¹⁰ is consistent with our large defects. These defects are not expected to be a source of interstitials and cannot explain the transient diffusion process. These stacking faults were also reported in ZnO nanowires and nanobelts.¹²

XTEM images of the implanted region near R_p of the 750 °C sample are illustrated in Fig. 3 along (a) $[10\bar{1}0]$ and (b) $[11\bar{2}0]$ directions. Interestingly, apart from the SFs, circular features with a fringe-like pattern (as indicated by the red arrows) with diameter around $\sim 5\text{--}15 \text{ nm}$ are also found near R_p . These are moiré fringes indicating the formation/precipitation of a different crystalline phase. Figs. 3(c)–3(d) show a magnified image of the moiré fringes viewed along two different orientations. The moiré fringes are observable in both a and m axes. The images in Fig. 3 show moiré fringes oriented in different directions. Figs. 3(a) and 3(c) were taken close to the $[10\bar{1}0]$ direction and show fringes parallel to the c-plane. The moiré fringes observed in Fig. 3(b) along the a-axis are almost perpendicular to the c-plane. In fact, the magnified image in Fig. 3 shows a slight rotation of

FIG. 3. Magnified XTEM image of the sample in Fig. 2 along (a) and (c) $[10\bar{1}0]$ direction and (b) and (d) $[11\bar{2}0]$ direction.

the moiré fringes, i.e., they are not perfectly perpendicular to the stacking faults which are guidelines for the basal planes. In some cases, there are slight distortions of the moiré fringes indicative of strain and defects making accurate measurements of these fringe spacings subject to large errors. The moiré fringes measured in the two respective images (c) and (d) show fringe spacings of about 2.3 and 1.3 nm, respectively. A detailed analysis of the moiré spacings will be discussed later.

In the sample implanted with $5 \times 10^{15} \text{ cm}^{-2}$ Zn dose, it was difficult to obtain good diffraction patterns to identify the nature of the precipitates. In addition, the size of these precipitates relative to the TEM foil made it very difficult to obtain relevant chemical information by EDX mapping. With this in mind, a higher Zn dose of $1 \times 10^{17} \text{ cm}^{-2}$ was implanted to identify the origin of these precipitates and the sample annealed at 750°C for 30 s. A typical XTEM image is shown in Fig. 4(a) along the $[11\bar{2}0]$ direction and shows some precipitation as evidenced by the moiré fringes. These

precipitates have a larger diameter compared to the low dose case with diameters ranging from 8 to 19 nm. In addition, there was a band of voids in this sample close to the surface, also visible in the high angle annular dark field (HAADF) images collected in STEM mode (see Figs. S1 and S3 in [supplementary material](#)). EDX mapping shows that these precipitates are Zn rich and O poor (see Fig. S2 in [supplementary material](#)). Selected area diffraction (SAD) pattern of the sample shows extra spots (see red circles) in addition to the ZnO spots (see Fig. 4(b)). These reflections are parallel to the $(2\bar{2}00)$ reflections of ZnO. As shown, these d-spacings match nicely to the literature values of the hexagonal Zn phase (see Table I). The correlation of data extracted from the spacings of the moiré fringes and the SAD patterns is consistent with a $(11\bar{2}0)\text{Zn} \parallel (11\bar{2}0)\text{ZnO}$ relationship and the same orientation for all the planes.

There are no reports of Zn precipitation in ZnO. The identification of Zn precipitation in ZnO is clear for the high dose sample. To correlate the information between the low and high dose samples, the spacings of the moiré fringes were measured for both. On a first approximation, the moiré fringes in Figs. 3(c) and 3(d) are assumed to be translational, i.e., the two crystal planes are parallel to each other. Because of the distortions in the moiré fringes, several sets of moiré fringes were measured. Details of this analysis are listed in Table S1 of the [supplementary material](#) and compared to the calculated moiré fringe spacings for the hexagonal Zn phase with a relationship to the ZnO matrix consistent with the SAD. Interestingly, the moiré fringes for both implantation doses are consistent for the $(1\bar{1}00)$ and the $(1\bar{2}10)$ planes and strongly support the argument that the precipitates are of the same nature for both doses. In addition, they are consistent with the calculated values expected for the $(1\bar{1}00)$ and the $(1\bar{2}10)$ Zn planes. This is further supported by the results extracted from the SAD patterns for these two reflections as shown in Table I. The SAD did not show any spots parallel to the (0002) ZnO reflections which could be linked to Zn precipitates.

The moiré fringes start to be visible in the samples after annealing at $\geq 700^\circ\text{C}$ at low density with significantly higher density observed at 750°C . We note that TEM investigations have a detection limit $\approx 1 \times 10^8 \text{ cm}^{-2}$ for defects. It can be seen here that the Zn precipitates (marked by yellow arrows) are spread around R_p after 750°C annealing, but only observed in the region shallower than R_p after 800°C annealing (see Fig. S4 in [supplementary material](#)). This comparison suggests the dissolution of Zn precipitates beyond the R_p region.

As discussed earlier, Neuvonen *et al.*¹ attributed the Li depletion to Zn_I injection from the implanted layer. Zn_I is calculated to have a low migration energy of $\sim 0.6 \text{ eV}$ and is

FIG. 4. (a) Cross sectional TEM image along the a-axis of hydrothermally grown single crystal ZnO implanted with 500 keV $1 \times 10^{17} \text{ cm}^{-2}$ $^{64}\text{Zn}^+$ and annealed for 30 s at (a) 750°C (b) SAD pattern of corresponding ZnO showing extra spots highlighted with red circles.

TABLE I. Summary of the lattice spacings extracted from SAD patterns d_p and compared to the literature Zn lattice spacings d_{Zn} for the respective planes.

Zone axis	ZnO plane	d_{ZnO} (nm)	d_p (nm)	d_{Zn} (nm)/plane
$[11\bar{2}0]$	$(2\bar{2}00)$	0.1405	0.1167	0.1150/ $(2\bar{2}00)$
$[10\bar{1}0]$	$(1\bar{2}10)$	0.1610	0.1351	0.1340/ $(1\bar{2}10)$

expected to be mobile at room temperature.² These highly mobile Zn_I rapidly convert substitutional Li in Zn sites (Li_{Zn}) into Li interstitials (Li_I) via a “kick-out” mechanism at temperatures above 700 °C

As Li_I are also highly mobile,³ they diffuse towards the surface or the bulk producing a significant Li depletion. However, the Li depletion phenomenon is not limited to Zn implantation. Azarov *et al.*¹⁵ show that this is observed for B, Mg, P, Ag, Cd, and Sb. If the Li depletion is purely driven by Zn_I generated by collision cascades during implantation, we would expect a mass dependence effect where the Li depletion would be least significant for light elements like B. Yet, Azarov *et al.*¹⁵ show significant depletion for B implanted sample and that Li depletion is suppressed with co-implantation of O.

We propose the following scenario. In the initial stages of ion implantation, the collision cascades result in generation of interstitials and vacancies, both Zn and O defects. During the annealing process, at temperatures ≥ 700 °C, the implantation species favouring Zn sites will displace Zn and create a net Zn_I excess. There is suddenly a Zn_I supersaturation which will be dissipated through competing processes which consume Zn_I . Amongst these, we have the transient processes of Zn precipitation and Li depletion. Both processes reach a maximum somewhere between 750 °C and 800 °C. From Fig. 1(b), the background Li concentration in the bulk is $\sim 1 \times 10^{17} \text{ cm}^{-3}$, while the maximum width of the Li depleted region is $\sim 60 \mu\text{m}$. Thus, the maximum amount of Li depleted is estimated to be $\sim 6 \times 10^{14} \text{ cm}^{-2}$. This is almost 10 times less than the implanted Zn dose of $5 \times 10^{15} \text{ cm}^{-2}$. The result suggests that of all the implanted Zn, only $\sim 15\%$ are involved in the Li_{Zn} “kick-out” process. The “missing” implanted Zn, some of which could be the highly mobile Zn_I , may be trapped in defect complexes or migrated towards the sample surface.

From an atomic density perspective, the atomic density of zinc is $0.065 \text{ \AA}^{-3}$ compared to the atomic density of Zn in ZnO of $0.042 \text{ \AA}^{-3}$. It is a significant change because for every 2 Zn atoms in the crystal you can accommodate an extra one. Hence, Zn precipitation is an effective way to reduce Zn_I . Both the Li depletion and Zn precipitation are maximised somewhere between 750 °C and 800 °C. It is clear that at 800 °C, some Zn precipitates start to dissolve while the Li starts to diffuse back in the depleted layer in an attempt to restore equilibrium. Any injected Zn_I will diffuse to the nearest sink, which is most likely the sample surface. We can also explain why in the case of O or inert gas implantation

(e.g., Ar), there is no depletion observed. These implanted species do not have the affinity to occupy Zn sites and do not “kick-out” Zn_I responsible for Li depletion.

In conclusion, the Zn interstitial mediated process in Zn implanted samples is investigated. Both the Li depletion and Zn precipitation occur at the same time and are signs of a Zn interstitials oversupply which is triggered at temperatures higher than 700 °C. The fast diffusing Zn interstitials displace Li resulting in a Li depletion region. Zn precipitation is another effective competitive process to condense the Zn interstitials in a smaller volume. Zn precipitation and Li depletion are maximised sometime between 750 °C and 800 °C annealing, respectively, and both processes are transient in nature. We propose that the Li depletion and Zn precipitation are competing processes to reduce the Zn supersaturation arising from implantation of species favouring the occupation of Zn sites.

See [supplementary material](#) for detailed TEM, STEM and EDS analysis of Zn precipitates.

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