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Thermal stability of ion-implanted ZnO

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Abstract

Zinc oxide single crystals implanted at room temperature with high-dose ($1.4 \times 10^{17} \text{ cm}^{-2}$) 300 keV As⁺ ions are annealed at 1000 – 1200 °C. Damage recovery is studied by a combination of Rutherford backscattering/channeling spectrometry (RBS/C), cross-sectional transmission electron microscopy (XTEM), and atomic force microscopy (AFM). Results show that such a thermal treatment leads to the decomposition and evaporation of the heavily-damaged layer instead of apparent defect recovery and recrystallization that could be inferred from RBS/C and XTEM data alone. Such a relatively poor thermal stability of heavily-damaged ZnO has significant implications for understanding results on thermal annealing of ion-implanted ZnO.

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With a wide bandgap of ~ 3.4 eV and a large excitonic binding energy of ~ 60 meV at room temperature (RT), ZnO is a very strong candidate for a range of blue and ultra-violet optoelectronic devices.¹⁻⁴ These properties, combined with other physical characteristics of ZnO such as the ability to grow single crystals, a low-power threshold for optical pumping, many possibilities for wet-chemical etching, and resistance to radiation damage,¹⁻⁷ further strengthen the device-based interest in this material. Important aspects of device fabrication include electrical isolation and selective-area doping, which are commonly achieved in the microelectronic industry by ion implantation.^{3,7} Recent studies on ion implantation of potential *p*-type dopants such as arsenic^{8,9} and nitrogen¹⁰ into ZnO are showing promise as a viable method of achieving *p*-type conductivity in ZnO.

In order for *p*-type doping of ZnO by ion implantation to be successful and reproducible, a thorough understanding of damage accumulation and thermal stability of implantation-produced defects in ZnO is highly desirable.⁶ A number of previous studies of thermal annealing exist, both for as-grown ZnO films and crystals¹¹⁻¹³ and for ion-implanted ZnO.^{9,14,15} None of these studies, however, deal directly with the recrystallization of heavily-damaged ZnO at high temperatures. Jeong et al.⁹ recently presented an annealing study of low-energy As⁺ implants into ZnO at RT involving relatively low doses (10^{15} cm⁻²). They annealed their samples at various temperatures and reported that an anneal at 800 °C for 1 hour produced an optimum recovery of crystallinity.⁹

In this letter, we study the thermal stability of ZnO implanted with As⁺ ions to high doses. To examine the microstructure of the as-implanted and annealed samples, we use a combination of Rutherford backscattering/channeling (RBS/C) spectrometry, cross-sectional transmission electron microscopy (XTEM), and atomic force microscopy (AFM). Our results reveal relatively poor thermal stability of heavily-damaged ZnO, with almost complete decomposition of the implanted layer during anneals at 1200 °C.

The samples used in this study were high quality single crystal *n*-type ZnO (000 $\bar{1}$) purchased from Cermet Inc. They were nominally undoped and single-side (O-face) polished. These samples were implanted with 300 keV As⁺ ions at RT to a dose of 1.4×10^{17} cm⁻² using a 1.7 MV tandem accelerator (NEC, 5SDH-4). The ion beam flux was $\sim 2.5 \times 10^{12}$ cm⁻² s⁻¹. During implantation, samples were tilted 7° relative to the incident beam to minimize channeling. A piece of Si was used to mask a part of each sample to create an implanted/unimplanted interface for further analysis. Arsenic ions were chosen due to their potential to act as *p*-type dopants in ZnO.⁸

Following implantation, selected samples were furnace annealed in the range of 1000 – 1200

°C for 15 minutes under Ar ambient. During annealing, the samples were proximity capped with ZnO epilayers (grown on sapphire substrates) to minimize surface degradation. All samples were then characterized *ex-situ* by RBS/C, XTEM, and AFM. RBS/C was conducted in a 1.7 MV tandem accelerator (NEC, 5SDH) at RT with 2 MeV $^4\text{He}^+$ beam to monitor the extent of lattice damage. The He beam was incident along the [0001] direction, and backscattered ions were collected by a detector positioned at a glancing angle of 10° . Specimens for XTEM were prepared by mechanical grinding/polishing using the tripod technique, followed by Ar ion-beam thinning in a Gatan precision ion polishing system operating at 3 kV. These XTEM specimens were then investigated in a FEI F20 microscope operating at 200 kV. Finally, AFM was conducted under ambient conditions in tapping mode with a Digital Instruments Nanoscope III scanning probe microscope. The cantilever was a commercially available Si tip with force constants of $30 - 120 \text{ N m}^{-1}$.

Figure 1 shows RBS/C spectra of as-implanted and annealed samples. It can be seen from Fig. 1 that, following implantation, the channeled and random spectra of the as-implanted sample match for a depth up to $\sim 200 \text{ nm}$, indicating the formation of a heavily damaged layer. From TRIM code calculations,¹⁶ the broad nuclear energy-loss profile peaks at $\sim 70 \text{ nm}$, and the end of range is $\sim 200 \text{ nm}$. Hence, the thickness of the heavily damaged layer revealed in Fig. 1 is consistent with what is expected based on ballistic simulations such as the TRIM code.¹⁶ In Fig. 1, the distorted shape of both random and channeled RBS/C spectra of the as-implanted sample (i.e., a dip and a shoulder at ~ 30 and 60 nm , respectively) can be attributed to the large concentration of implanted As atoms as well as possible ion-beam-induced stoichiometric changes discussed in more detail below.

To better illustrate the nature of lattice defects produced by implantation, Fig. 2(a) shows a XTEM image of the as-implanted sample. Examination of this image reveals that the implanted region consists of a heavily damaged layer extending $\sim 200 \text{ nm}$ into the bulk, which is consistent with RBS/C data from Fig. 1. Figure 2(a) also reveals a band of small cavities $\sim 15 \text{ nm}$ in size (as confirmed by monitoring the change in contrast while varying focusing conditions) centered at $\sim 130 \text{ nm}$ below the surface. Further studies are needed to identify whether these cavities are voids or gas bubbles. The dark grains visible in Fig. 2(a) are caused by diffraction contrast arising from strain fields. Finally, there are two bands of contrast evident in Fig. 2(a): a lighter contrast band extending from the surface to $\sim 30 \text{ nm}$ and a band of darker contrast between the lighter band and the region with cavities. The location of these two bands of different contrast corresponds well to the depth of the dip and the shoulder observed in the RBS/C spectrum from this sample (Fig. 1).

We attribute these features to ion-beam-induced stoichiometric changes, and this effect deserves additional studies.

The RBS/C spectra in Fig. 1 also show that thermal annealing in the range of 1000 – 1200 °C appears to effectively recover the crystallinity of the implanted layer. In particular, the level of lattice disorder progressively decreases with increasing annealing temperature, and the spectrum from the sample annealed at 1200 °C is almost identical to that of the virgin sample, suggesting a complete recovery of implantation damage.

Figures 2(b) – 2(d) show XTEM images taken from annealed samples. Figure 2(b) reveals large cavities of ~ 60 nm in size in the sample annealed at 1000 °C. After annealing at 1100 °C [Fig. 2(c)], further cavity growth is evident, and these cavities are now open to the surface. Although the material surrounding these cavities is highly crystalline, some dislocations in the surface layer can also be seen from Fig. 2(c). Finally, Fig. 2(d) shows that most implantation-induced damage has effectively been removed by annealing at 1200 °C. However, a significant number of dislocations can still be seen in Fig. 2(d).

The thermally-induced damage recovery revealed by RBS/C (Fig. 1) and XTEM (Fig. 2) data can be due to either lattice recrystallization or a decomposition and evaporation of the implanted layer. To clarify this, we have studied the surface morphology of as-implanted and annealed samples (Fig. 3). It is seen from Fig. 3(a) that, after annealing at 1000 °C, the surface is relatively smooth, having a rms roughness of ~ 3.5 nm.²⁰ This is, however, rougher than both the unimplanted ZnO that has been annealed at 1000 °C and the as-implanted sample, which have rms roughness values of ~ 0.6 and ~ 2.5 nm, respectively. Note that the rms roughness of the annealed, unimplanted ZnO is the same as that of the as-received ZnO (i.e., ~ 0.6 nm). In addition, there is a negligible height difference between the implanted and unimplanted regions of the sample annealed at 1000 °C.

Interestingly, after annealing at 1000 °C, the surface of the implanted region is covered in cracks, as clearly illustrated in the optical image in Fig. 3(d). The pattern of surface cracks in Fig. 3(d) reflects the low index crystallographic directions of the wurtzite structure of ZnO. Such cracking suggests that tensile stress develops in the implanted layer during annealing, which could be related to local changes in stoichiometry in the near-surface region, discussed above. Moreover, the presence of stress also explains the observation of (stress-induced) dislocations in XTEM images of annealed samples [Figs. 2(c) and 2(d)].^{17,18}

Figure 3(b) shows that the surface of the sample annealed at 1100 °C exhibits cavities, which

is also consistent with XTEM data from Fig. 2(c). For this sample, the interface between the implanted and unimplanted regions has a step height of ~ 30 nm, indicating some material loss from the implanted region during annealing. At 1200 °C, these effects are further exacerbated. Indeed, Fig. 3(c) shows that the surface is covered by ridges and troughs. For this sample, the step height between the implanted and unimplanted regions ranges from $\sim 50 - 100$ nm. Note that the roughness of the unimplanted region remains essentially unchanged after annealing at 1200 °C. Thus, instead of the apparent recovery of heavily-damaged ZnO, decomposition and evaporation of the implanted layer occurs during the high-temperature heat treatment, rather than defect recovery and recrystallization. After such a thermally-induced decomposition (into Zn-rich ZnO_x and O_2), material evaporation is not unexpected since Zn metal has relatively low melting and boiling points of ~ 420 and ~ 910 °C, respectively.¹⁹

In conclusion, we have found that, upon annealing at high temperatures (1000 – 1200 °C), the heavily damaged layer formed by high-dose ion bombardment of ZnO exhibits decomposition and evaporation. In contrast, unimplanted ZnO does not undergo any detectable decomposition for such annealing conditions. This finding is significant for understanding the behavior of damage recovery in ion-implanted ZnO.

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Figures

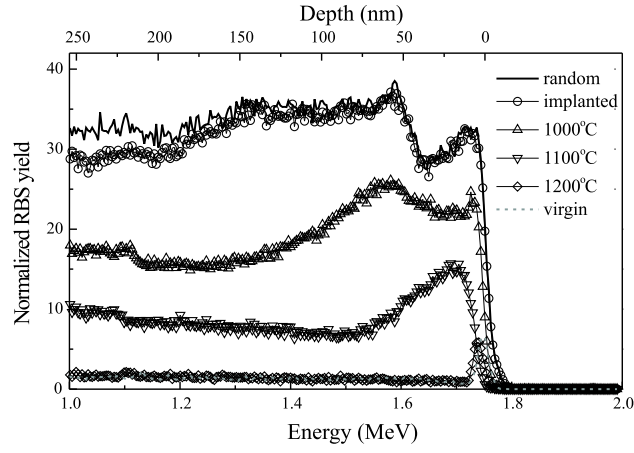


FIG. 1: RBS/C spectra showing effective damage recovery upon annealing of ZnO bombarded at room temperature with 300 keV As^+ ions to a dose of $1.4 \times 10^{17} \text{ cm}^{-2}$. Annealing temperatures are indicated in the legend. Note that the random spectrum was taken from the as-implanted sample.

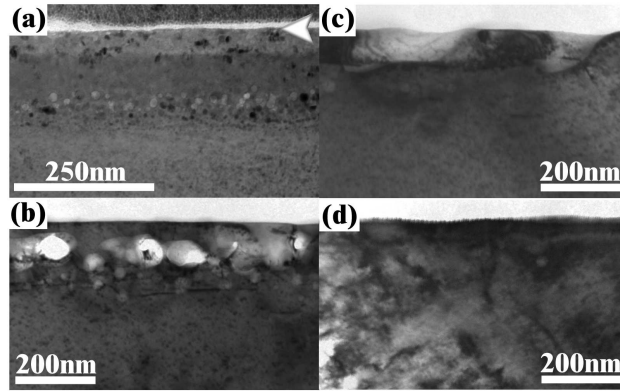


FIG. 2: Bright-field XTEM images of ZnO implanted at room temperature with 300 keV As^+ ions to a dose of $1.4 \times 10^{17} \text{ cm}^{-2}$. Image (a) is the as-implanted sample. Images (b) – (d) are implanted samples annealed at 1000, 1100, and 1200 °C, respectively. The arrow in (a) indicates the sample surface.

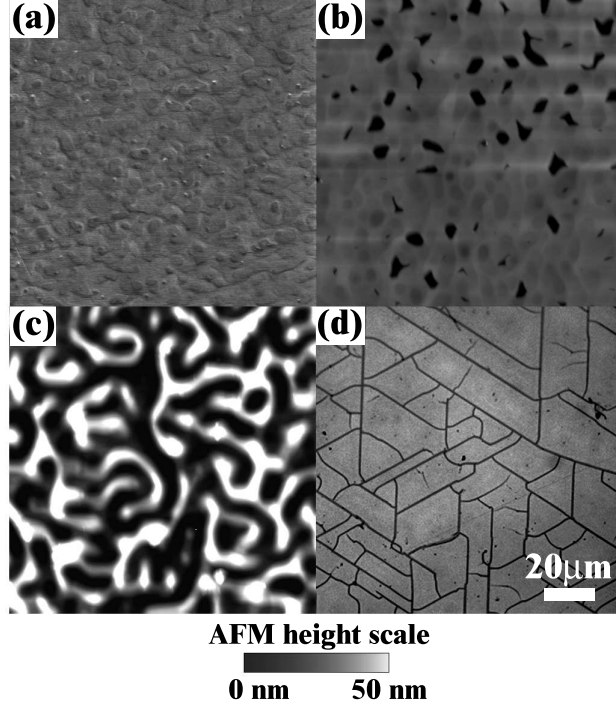


FIG. 3: AFM [(a) – (c)] and optical (d) images of ZnO samples implanted at room temperature with 300 keV As^+ ions at a dose of $1.4 \times 10^{17} \text{ cm}^{-2}$ and annealed at 1000 °C [(a),(d)], 1100 °C (b), and 1200 °C (c). All AFM images were taken with the same height scale (as shown) and are for a field of view of $5 \times 5 \mu\text{m}^2$.