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Towards p-type doping of ZnO by ion implantation

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ABSTRACT

Zinc oxide is a very attractive material for a range of optoelectronic devices including blue light-emitting diodes and laser diodes. Though n-type doping has been successfully achieved, p-type doping of ZnO is still a challenge that must be overcome before p-n junction devices can be realized. Ion implantation is widely used in the microelectronics industry for selective area doping and device isolation. Understanding damage accumulation and recrystallization processes is important for achieving selective area doping. In this study, As (potential p-type dopant) ion implantation and annealing studies were carried out. ZnO samples were implanted with high dose (1.4×10^{17} ions/cm²) 300 keV As ions at room temperature. Furnace annealing of samples in the range of 900°C to 1200°C was employed to achieve recrystallization of amorphous layers and electrical activation of the dopant. Rutherford backscattering/channeling spectrometry, transmission electron microscopy and cathodoluminescence spectroscopy were used to monitor damage accumulation and annihilation behavior in ZnO. Results of this study have significant implications for p-type doping of ZnO by ion implantation.

INTRODUCTION

Zinc Oxide (ZnO) is increasingly attracting more and more interest as a material for a range of optoelectronic devices including blue and UV light-emitting diodes and laser diodes [1]. With a large exciton binding energy of 60 meV at room temperature, a wide band gap of 3.4 eV [1] and resistance to radiation damage [2], it is the perfect candidate for such devices. Devices incorporating a p-n junction have yet to be realized, however, because p-type doping of ZnO is still proving to be a major challenge [3]. Currently, there is still much to be understood about the issues of dopant incorporation and activation in ZnO [4].

Ion implantation is widely used in the microelectronics industry for selective area doping and device isolation [5]. Ion implantation of potential p-type dopants [6] and co-implantation studies [7] are beginning to show promising results for producing p-type ZnO. A thorough understanding of damage accumulation and recrystallization processes is thus important for

achieving consistent and controllable selective area doping. In this study, we address some of these issues by monitoring the damage accumulation and annihilation behavior in single crystal ZnO that has been implanted with very high-doses. We have chosen to conduct the high-dose implants with arsenic ions, due to the potential for arsenic to act as a p-type dopant in ZnO [6, 8]. Following implantation, samples were annealed in the range of 900°C to 1200°C to achieve recrystallization of amorphous layers and try to electrically activate arsenic. Rutherford backscattering/channeling (RBS/C) spectrometry, and cross-sectional transmission electron microscopy (XTEM) were used to monitor damage accumulation and recrystallization processes in ZnO. Cathodoluminescence (CL) spectroscopy was used to monitor the annihilation behaviour and check for evidence of dopant activation.

EXPERIMENTAL DETAILS

The samples used in this study were high quality single crystal n-ZnO (0001) from Cermet Inc. and were nominally undoped and single sided polished (O-face). Prior to all experiments the samples were chemically degreased in boiling trichloroethylene and isopropanol for 5 minutes, before rinsing in de-ionized water and blow-drying under N₂. Samples were then implanted with 300 keV As⁺ at room temperature to a dose of 1.4×10^{17} As⁺cm⁻² with the ANU 1.7 MV tandem accelerator (NEC, 5SDH-4). All samples were tilted by ~7° relative to the incident beam to minimize channelling.

Following implantation, samples were characterized *ex situ* by RBS/C in the ANU 1.7 MV tandem NEC accelerator at room temperature with a 2 MeV ⁴He⁺ beam to monitor the extent of damage present. The He beam was incident along the (0001) direction and was backscattered into detector at a backscattering angle of ~168°.

Selected samples were then furnace annealed for 15 minutes under Ar ambient in a quartz tube within the 900 – 1200°C range. In all cases, during annealing, the samples were proximity capped with undoped ZnO epilayers to inhibit surface degradation. After annealing, the samples were again characterized by RBS/C to monitor the extent of recrystallization.

Implanted samples, both before and after annealing, were studied by XTEM to further examine their microstructure and extent of amorphization/ recrystallization. XTEM specimens were prepared by mechanical grinding/polishing using the tripod technique and followed by ion-beam thinning in a Gatan precision ion polishing system operating at 3 kV. These TEM specimens were investigated in a FEI F20 TEM operating at 200 keV.

Selected samples were also studied with CL performed at 77K using an Oxford Instruments MonoCL2 system installed on a JEOL35C scanning electron microscope (SEM). The CL spectra were measured using a Hamamatsu R943-02 Peltier cooled photomultiplier tube and a 1200 lines/mm grating blazed at 500nm. The SEM was operated at 15 keV and the electron beam current was kept fixed at ~80 nA. All CL spectra were corrected for system response.

RESULTS AND DISCUSSION

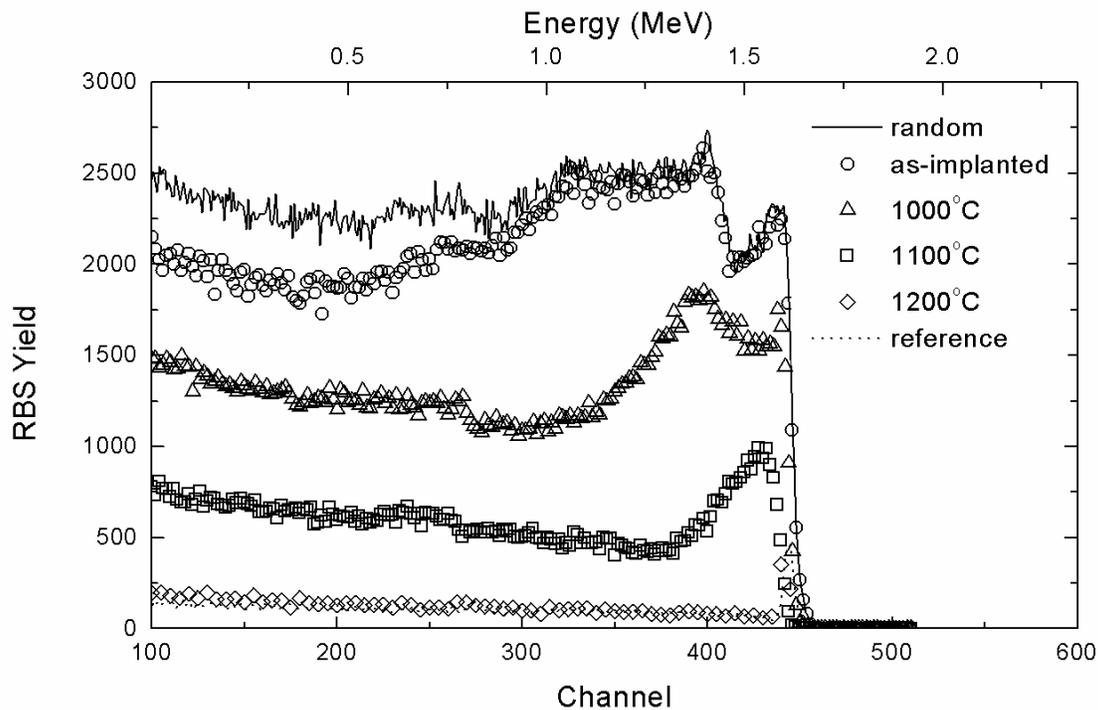


Figure 1. RBS/C spectra of single crystal ZnO implanted with $1.4 \times 10^{17} \text{ As}^+/\text{cm}^2$ at an energy of 300 keV, showing the evolution of recrystallization with increasing annealing temperature. These data suggest that annealing at 1200°C completely recovers ion-produced damage.

Figure 1 shows RBS/C spectra of ZnO implanted with 300 keV As^+ to a dose of 1.4×10^{17} ions/ cm^2 , illustrating the evolution of recrystallization with increasing annealing temperature. It can be seen that following implantation, the channelled spectra of the as-implanted sample closely matches the random spectrum taken from the same sample (from channel 300 and above). This is suggestive of a continuous amorphous layer formed to a depth of $\sim 190\text{nm}$ below the surface. This depth corresponds to the damage profile calculated using Monte-Carlo TRIM [9] simulations for 300 keV As ions implanted into ZnO. With annealing, it can be seen that the damage peak in RBS/C spectra becomes increasingly less pronounced, until at 1200°C it is almost completely gone, and the spectra closely resembles that of the spectra taken from an unimplanted ZnO reference sample. Thus from the RBS/C spectra it would appear that complete recrystallization of ZnO implanted with very high dose arsenic ions is achieved by annealing at 1200°C for 15 minutes. There are other features of these spectra that are worthy of note. However, these will be discussed elsewhere [10].

Although RBS/C provides information about the gross amount of ion-produced damage, in order to determine the nature of defects produced we have analysed samples with XTEM. Figure

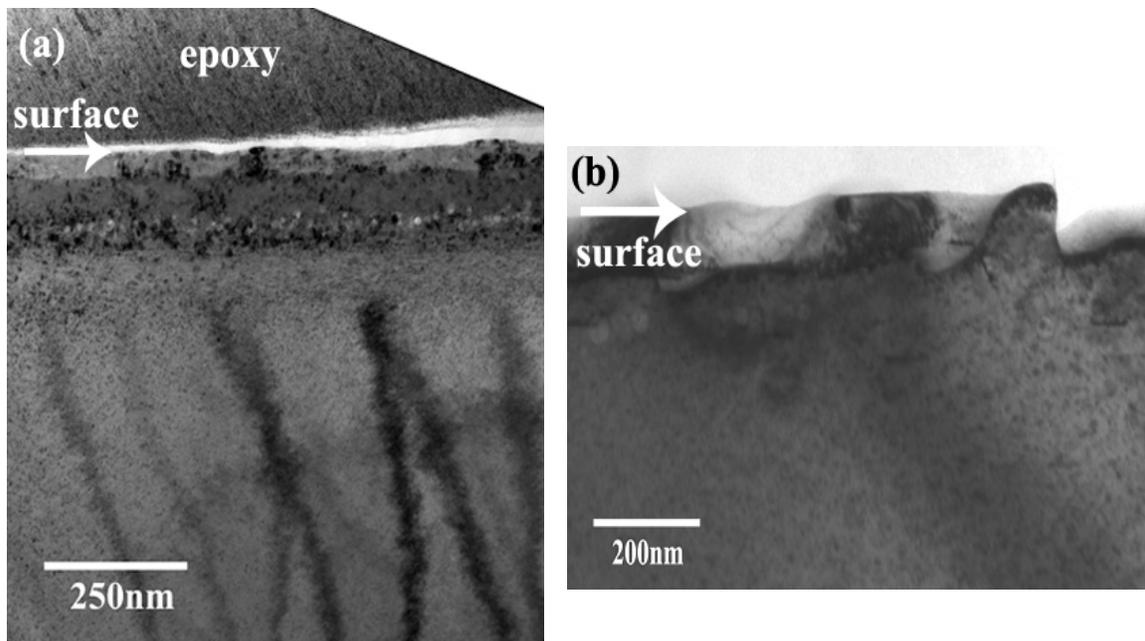


Figure 2. (a) Bright Field (BF) XTEM image taken from the as-implanted sample irradiated with $1.4 \times 10^{17} \text{ As}^+/\text{cm}^2$ at 300 keV. The image shows a heavily damaged region with amorphous zones extending $\sim 190\text{nm}$ into the sample. There is a layer of voids at $\sim 150\text{nm}$. (b) BF XTEM image of an implanted sample annealed at 1100°C for 15 minutes. Note that the voids have apparently agglomerated and migrate to the surface. The underlying ZnO is of excellent crystallinity.

2(a) shows an XTEM image from the as-implanted sample. Firstly, the image indicates that contrary to what RBS/C suggests, the ZnO is not completely amorphous following implantation. Rather, it shows the formation of a heavily damaged layer extending to $\sim 190\text{nm}$ below the surface which contains some amorphous zones, as well as what appear to be voids $\sim 20\text{nm}$ in size. The nature of the voids was confirmed by comparing dark-field and bright-field images. The absence of amorphization even for such high dose implants (well over $\sim 10 \text{ at.}\%$ of As has been added) is, however, not unexpected given a high ionicity of Zn-O bonds [5].

Following annealing at 1000°C , XTEM analysis shows that the voids have begun to agglomerate and move toward the surface. At this temperature, the voids are $\sim 60 \text{ nm}$ in size and are located towards the surface of the ZnO. At 1100°C , there is further void agglomeration and a definite migration to the surface as can be seen in Figure 2(b). The ZnO surrounding the voids is crystalline. Some evidence of dislocations can, however, be seen within the implantation region. The underlying bulk material is of good crystalline quality. At 1200°C , XTEM analysis shows that nearly all of the voids have apparently migrated to the surface, and most of the implantation-induced damage is no longer present. The ZnO is crystalline; however, there appear to be a large number of dislocations in ZnO, not only in the region adjacent to the surface. It is uncertain at present as to whether these dislocations derive as a result of the implantation process or because of possible plastic deformation during the high temperature annealing step. Overall at this temperature (1200°C), however, it can be considered that the majority of the defects created by

As ion implantation have been removed from the implanted layer leaving behind reasonably high quality crystalline ZnO.

Finally, to study the optical properties of the ZnO layers following implantation and annealing, and also the possibility of p-type activation of the implanted As^+ , CL was conducted on the samples at 77 K. The CL spectra taken from the 1000°C and 1200°C annealed samples are shown in Figure 3, along with a reference ZnO spectrum (from ZnO not exposed to either implantation or annealing) for comparison. Keeping in mind that the incident beam power was kept fixed for these measurements, we see that following implantation and annealing at 1200°C the optical properties of the ZnO are completely recovered, and the CL intensity is also slightly enhanced. At 1000°C in comparison, there is a significant decrease in CL intensity and a red shift of the near-gap CL band, which can be attributed to the effect of light absorption by defects present within the damaged surface region. No characteristic peak related to acceptor transition (p-type) was seen in the annealed samples. However, it may be necessary to re-conduct the measurements at 4 K to decisively verify whether or not any dopant activation has occurred.

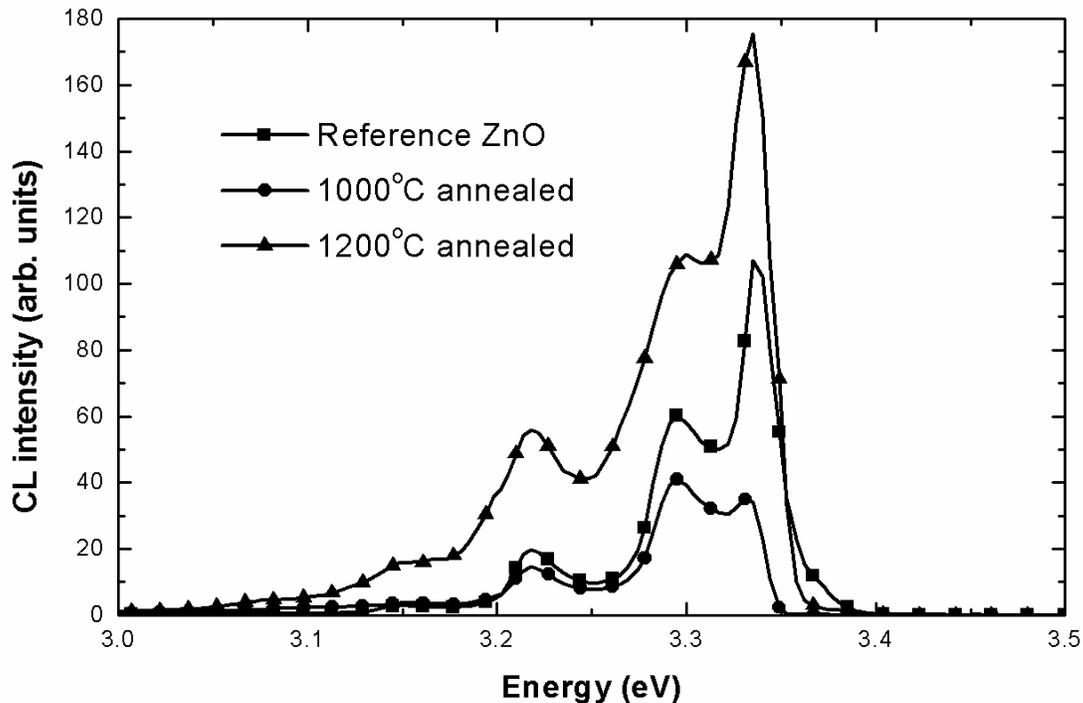


Figure 3. CL spectra of implanted and annealed samples compared with a ZnO reference sample. Spectra were taken using a 15 keV electron beam at 77 K with fixed incident beam power. No obvious p-type activation is evident. However, recovery and a possible improvement of optical properties of ZnO can be seen following annealing at 1200°C.

CONCLUSIONS

Single crystal ZnO is not completely amorphized by high-dose (1.4×10^{17} ions/cm²) 300 keV arsenic implants at room temperature. However a heavily damaged region that extends ~200nm below the surface is created, consisting of voids and pockets of amorphous regions. Upon annealing, it is found that the damage to the ZnO can be almost completely recovered at high temperatures (1200°C). Damage recovery is attributed to defect migration to the sample surface. The optical properties of ZnO are completely restored after high temperature annealing. No clear indication of dopant activation was seen in the CL spectra at 77 K.

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