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Electrical characterization of 1.8 MeV proton-bombarded ZnO

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We report on the electrical characterization of single-crystal ZnO and Au Schottky contacts formed thereon before and after bombarding them with 1.8 MeV protons. From capacitance–voltage measurements, we found that ZnO is remarkably resistant to high-energy proton bombardment and that each incident proton removes about two orders of magnitude less carriers than in GaN. Deep level transient spectroscopy indicates a similar effect: the two electron traps detected are introduced in extremely low rates. One possible interpretation of these results is that the primary radiation-induced defects in ZnO may be unstable at room temperature and anneal out without leaving harmful defects that are responsible for carrier compensation. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1415050]

ZnO is presently used in many diverse products, including facial powders, phosphors, paints, piezoelectric transducers, varistors, and transparent conducting films, the latter being important for the photovoltaic industry. However, from a recent review, where the properties of ZnO are summarized,[1] it is clear that ZnO can be used for several other, more sophisticated, electro-optical applications. Based on the fact that ZnO has an experimental direct band gap of 3.4 eV, it can play an important role in realizing blue and ultraviolet (UV) light-emitting devices, such as light-emitting diodes and lasers, as well as daylight-blind UV detectors, as is the case for GaN with a similar band gap. Furthermore, the large band gap of ZnO renders it suitable for the fabrication of solar cells, catalysts, and as a substrate or buffer layer for the group III-nitride based devices. For space applications, these devices often have to operate at elevated temperatures, typically above 200 °C, in harsh radiation conditions comprising energetic particles. Further practical advantages of ZnO include bulk-growth capability, amenability to conventional wet chemistry etching, which is compatible with Si technology[2] (unlike the case for GaN), and convenient cleavage planes.

An important consideration for space applications is that the material should be as radiation hard as possible in order for it to reliably operate for extended periods. Presently, the main wide band gap materials for space applications are considered to be the III–V nitrides, SiC, and diamond. Whereas the effect of high-energy electron irradiation has been reported for ZnO,[3] GaN,[4,5] and SiC,[6] no data are yet available regarding the exposure of ZnO to heavier particles such as protons and He-ions, as was reported for GaN.[7,8] In particular, to our knowledge, data pertaining to radiation- and implantation-induced deep level defects in ZnO are not yet available. In a report on the effect of high-energy electrons on ZnO, Look *et al.*[3] concluded, from variable temperature Hall measurements, that the effect of these electrons on ZnO is significantly lower than that on GaN, GaAs, and Si.

In this letter, we report on the electrical characterization of high-energy proton bombarded single-crystal ZnO, fabricated with Au Schottky contacts. The most significant observation was that ZnO is extremely radiation hard against high-energy protons; i.e., the free carrier removal rate by 1.8 MeV protons in ZnO is about 100 times less than that in GaN. In addition, deep level transient spectroscopy (DLTS) reveals that proton implantation introduces two electron trap defects, but at extraordinary low rates compared to those of radiation induced defects in GaN.

The ZnO used for this study was *n*-type material grown by a vapor-phase technique, making use of a nearly horizontal tube.[9] Following the cleaning procedure described before,[10] circular Au contacts, 0.7 mm in diameter and 200 nm thick, were resistively deposited onto the (000−1) O face of the ZnO crystal through a mechanical mask. Thereafter, InGa ohmic contacts were applied to the opposite side (Zn face) of the sample. The Au/ZnO Schottky barrier diode (SBD) structures were characterized by standard room temperature (297 K) current–voltage ($I-V$) and capacitance-voltage ($C-V$) measurements, and the defects in the ZnO by DLTS using a lock-in amplifier based system in the temperature range 25–330 K. $I-V$ measurements showed that the SBD had an ideality factor $n=1.19$ (calculated by assuming that charge is predominantly transferred by thermionic emission) and a dark current of 10^{-9} A at a 1 V reverse bias. From $C-V$ measurements, the free carrier density, $N_D - N_A$, was found to vary, from sample to sample, between $(4.6–5.6)\times 10^{16}\,\mathrm{cm}^{-3}$ in the first 0.2 μm below the SBD, i.e., the region being probed by DLTS.

After this characterization, the SBDs were bombarded at room temperature with 1.8 MeV protons in a Van de Graaff accelerator along the [000−1] direction as well as 7° off this direction. During bombardment, the dose rate was 1.4×10^{11} protons $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ and the dose was incremented in steps of $1.4\times 10^{14}\,\mathrm{cm}^{-2}$ up to a dose of $7.0\times 10^{14}\,\mathrm{cm}^{-2}$. During irradiation, the temperature did not rise by more than a

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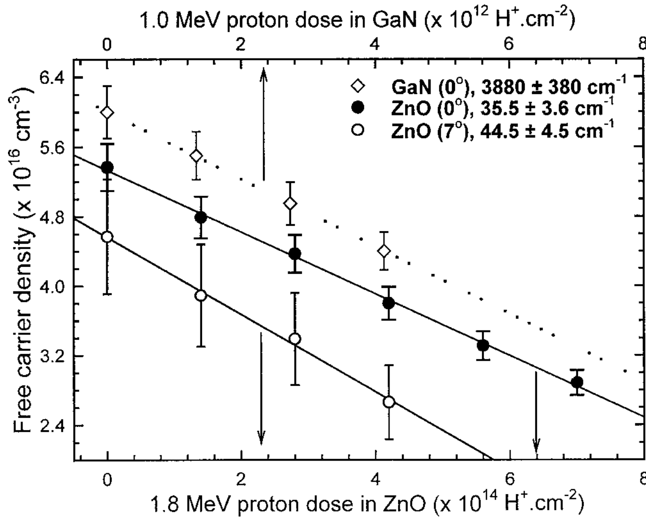

FIG. 1. Free carrier density, $N_D - N_A$, (at 0.2 μm below the interface) determined from $C-V$ measurements as function of 1.8 MeV proton dose in ZnO (solid lines) and GaN (dotted line).

few °C. TRIM calculations indicated that the range of 1.8 MeV protons is about 19.5 μm and therefore only intrinsic defects, but no hydrogen, are introduced in the region probed by DLTS. After each irradiation step, the SBDs and the ZnO were characterized by $I-V$, $C-V$, and DLTS. The diodes used for $I-V$ and $C-V$ measurements were not used for DLTS to ensure that their quality did not degrade due to the DLTS cooling and heating cycles.

$I-V$ measurements showed that proton bombardment degrades the diode quality. For example, the reverse current at a bias of 1 V, (I_R), increased from 1×10^{-9} A for an unirradiated diode to 1×10^{-6} A after bombarding it with a dose of $4.2\times10^{14}\,\mathrm{cm}^{-2}$. Both the forward and reverse $I-V$ characteristics appeared to have a generation–recombination nature after bombardment. This indicates that proton irradiation introduces deep defect levels in the band gap of ZnO.

The most surprising results obtained here were from $C-V$ measurements. In Fig. 1, we depict the free carrier concentration, $N_D - N_A$, as function of proton dose. From the data in Fig. 1, we see that a dose, D, of $7.0\times10^{14}\,\mathrm{cm}^{-2}$ reduces $N_D - N_A$ by $2.49\times10^{16}\,\mathrm{cm}^{-3}$. From this data, the free carrier removal rate:

$$\zeta = \frac{\Delta(N_D - N_A)}{D}, \tag{1}$$

was calculated as $35\pm3.6\,\mathrm{cm}^{-1}$ for irradiation along the [000−1] direction. For bombardment 7° off the [000−1] direction, the value of ζ increased to $45\pm4.5\,\mathrm{cm}^{-1}$. The value of ζ calculated here is about 100 times lower than that of GaN bombarded by 1.0 MeV protons. At this point, it should be noted that Look *et al.* also observed a very small change in the free carrier density of ZnO after high-energy electron irradiation.[3] Possible reasons for this low carrier removal rate will be discussed after presenting the DLTS results.

DLTS in the temperature range 20–330 K revealed the presence of at least three levels in the as-grown (unirradiated) ZnO [curve (a) in Fig. 2], of which the properties and possible origin have been reported[10] and are also summarized in Table I. The most prominent of these defects, $E1$, is located at $E_T = E_C - 0.12$ eV, while the second prominent defect has an energy level at $E_T = E_C - 0.27$ eV. Curve (b) in Fig. 2 shows that proton implantation introduces at least two electron traps with peaks in the temperature region scanned by DLTS. The first of these defects, $Ep1$, has an energy level, E_T, and apparent capture cross section, σ_a, of 0.54 eV and $3\times10^{-13}\,\mathrm{cm}^2$, respectively. This DLTS signature of $Ep1$ is similar, within the experimental error, to that of the $E4$ defect (with unknown origin) detected in low concentrations in unirradiated ZnO. The second defect introduced by proton irradiation, $Ep2$, was not detected in the unirradiated ZnO and has a signature of $E_T = 0.78$ eV and $\sigma_a = 1.5\times10^{-12}\,\mathrm{cm}^2$. It is further instructive to note that $Ep2$ is located deep enough below the conduction band to contribute to generation currents during $I-V$ measurements.

DLTS depth profiling was employed to measure the concentration profiles of the proton irradiation induced defects after each irradiation. The defect concentrations at 0.2 μm below the junction are plotted in the inset of Fig. 2 as function of proton dose. From these data the defect introduction rates, η, for each defect were calculated from

$$\eta = \frac{\Delta N_T}{D}, \tag{2}$$

where ΔN_T is the increase in defect concentration for a dose D. The values of η for $Ep1$ and $Ep2$ thus calculated are 2.4 and 1.9 cm^{-1}, respectively. These introduction rates are more than one order of magnitude lower than those for defects detected in any other semiconductor implanted with protons at room temperature. For example, in GaN with a

TABLE I. Electronic properties of prominent defects detected by DLTS in as-grown and 1.8 MeV proton-bombarded single crystal *n*-type ZnO.

Defect label	E_T (eV)	σ_a (cm^2)	N_T (cm^{-3})	T_{peak}[a] (K)	Similar defects and references
$E1$	0.12 ± 0.02	$2.7\pm1.0\times10^{-13}$	$\approx10^{16}$	70[c]	
$E3$	0.29 ± 0.01	$5.8\pm1.0\times10^{-16}$	10^{14}	184	$L3$?[12]
$E4$	0.57 ± 0.02	$2.0\pm0.5\times10^{-12}$	10^{13}–10^{14}	249	
			η (cm^{-1})		
$Ep1$	0.54 ± 0.02	$3.0\pm1.0\times10^{-13}$	2.4 ± 0.5	251	$E4$[10]
$Ep2$	0.78 ± 0.02	$1.5\pm0.5\times10^{-12}$	1.9 ± 0.4	304[b]	

[a]Peak temperature at a lock-in amplifier frequency of 46 Hz (emission rate of 109 s^{-1}).
[b]Peak temperature at a lock-in amplifier frequency of 2.2 Hz (emission rate of 5.2 s^{-1}).
[c]Peak temperature at a lock-in amplifier frequency of 2200 Hz (emission rate of 5200 s^{-1}).

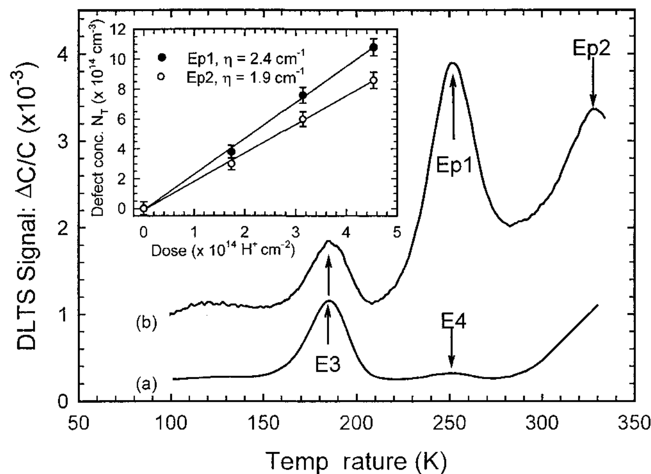

FIG. 2. DLTS (spectra of control Au/ZnO SBDs) [curve (a)] and similar SBDs that were bombarded with 1.8 MeV proton to a dose of 4.2 $\times 10^{14}$ cm^{-2} [curve (b)]. All spectra were recorded using a quiescent reverse bias 2 V, a filling pulse amplitude of 2.2 V, a lock-in amplifier frequency of 46 Hz (i.e., a decay time constant of 9.23 ms) and a filling pulse width of 0.2 ms. The inset depicts the defect concentrations of Ep1 and Ep1 (at 0.2 μm below the interface) as function of 1.8 MeV proton dose.

similar band gap, the major radiation induced defect, with an energy level at $E_T = E_C - 0.20$ eV, is introduced at a rate of about 30 cm^{-1} by MeV protons.

The main question that arises from results presented here is why the defect introduction rate, and together with that, the free carrier removal rate, is so much lower in ZnO than in other semiconductors, some of which have similar crystal structures and atomic densities (for example GaN). There are at least two possibilities that have to be explored. Firstly, the primary defects introduced in ZnO during proton bombardment may be mobile at room temperature (where the irradiation was performed) and, therefore, they may anneal out. In this case, these defects and their effect on the free carrier density, will therefore not be detected by DLTS or $C-V$ measurements. The defects, $Ep1$ and $Ep2$, that we observed may therefore be second generation defects of which the introduction rates are much lower than those of the primary radiation induced defects. A similar situation prevails in Si where vacancies and interstitials anneal out at low temperatures and the second generation defects (divacancies and vacancy-impurity complexes) detected after room temperature irradiation are observed at lower introduction rates.[11] This possibility will have to be investigated by irradiating ZnO at low temperatures and measuring the value of $N_D - N_A$, as well as the DLTS spectrum, as function of increasing temperature.

The second possibility is that the defects detected here, $Ep1$ and $Ep2$, are not the main radiation induced defects in ZnO. The main radiation induced defects may be pairs of shallow donors (too shallow to be detected by DLTS) and deep acceptors (too deep to be detected by DLTS), that are introduced in roughly equal concentrations. Since the number of shallow donors introduced by radiation will balance the number of radiation induced acceptors, we will not observe any drastic change in the free carrier concentration and neither will we detect any major DLTS peaks in the temperature domain investigated. This possibility will have to be verified by performing admittance spectroscopy measurements[12] to facilitate the detection of defect levels too deep to be detected by DLTS, and Hall and photoluminescence measurements to detect the shallow donors (too shallow to be detected by DLTS). At this point, it should be noted that Look *et al.* have reported an increase in concentration of one of the shallow donors in ZnO after electron irradiation.[3]

In summary, by using $C-V$ and DLTS measurements, we have demonstrated that ZnO is extremely resistant to room temperature MeV proton irradiation when compared to other semiconductors, including GaN. The consequence of this is extremely important: ZnO can be used for space applications (where it will be exposed to inherently harsh radiation conditions) for much longer periods of time than any other semiconductor with similar electro-optical properties before becoming useless due to radiation damage. One possible explanation for the extreme radiation hardness of ZnO is that the primary radiation induced defects in it may be unstable at room temperature and that they anneal out before forming harmful compensating centers.

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