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Production and annealing of electron irradiation damage in ZnO

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High-energy ($>$1.6 MeV) electrons create acceptors and donors in single-crystal ZnO. Greater damage is observed for irradiation in the [0001] direction (Zn face) than in the [000$\bar{1}$] direction (O face). The major annealing stage occurs at about 300–325 °C, and is much sharper for defects produced by Zn-face irradiation, than for those resulting from O-face irradiation. The defects appear to have a chain character, rather than being simple, near-neighbor vacancy/interstitial Frenkel pairs. These experiments suggest that ZnO is significantly more ''radiation hard'' than Si, GaAs, or GaN, and should be useful for applications in high-irradiation environments, such as electronics in space satellites. © *1999 American Institute of Physics.* [S0003-6951(99)04232-1]

Wurtzitic ZnO is a high-band gap (3.437 eV at 2 K) semiconductor which has many applications, such as piezoelectric transducers, varistors,[1] phosphors, and transparent conducting films. Most of these applications require only polycrystalline material; however, recent successes in producing large-area single crystals[2] have opened up the possibility of producing blue and UV light emitters,[3] and high-temperature, high-power transistors. The main advantages of ZnO as a light emitter are its large exciton binding energy (60 meV), and the existence of well-developed bulk and epitaxial growth processes; for electronic applications, its attractiveness lies in having high breakdown strength and high saturation velocity. Optical UV lasing, at both low and high temperatures, has already been demonstrated,[3,4] although efficient electrical lasing must await the further development of good, *p*-type material.[5]

For space-based applications, especially those in near-earth orbit, it is important to have radiation-resistant materials. In particular, the Van Allen belt contains high fluxes of electrons (0–10 MeV), and protons ($>$10 MeV). In the present study, we have used a Van de Graaff accelerator to obtain high-energy electrons, and have measured the changes in the electrical and optical properties as a function of bombardment energy (1–2 MeV) and annealing temperature (250–800 °C). The conclusion is that ZnO may be much more resistant to radiation damage than are other common semiconductor materials, such as Si, GaAs, CdS, and GaN. This fact, coupled with the excellent optical and electrical properties mentioned earlier, would seem to suggest that ZnO devices should be pursued for space applications.

The ZnO samples used here were 6 mm×6 mm×0.5 mm pieces cut from 2 in. wafers, which themselves were sliced from boules grown by a seeded vapor transport technique. The wafer surfaces were oriented perpendicular to the crystalline *c* axis; thus, the bombarding electrons could be directed onto the (0001) Zn face, or the (000$\bar{1}$) O face. Con-

sider the (0001) plane, in which a layer of Zn atoms is on top. An electron impinging on this face, and displacing a Zn atom, knocks it into an interstitial region, forming a simple Frenkel pair; however, an electron hitting the opposite face has a more difficult time displacing the Zn atom, because, in this direction, each Zn atom has a short-bonded O atom immediately beneath it.[6] The reverse conclusions hold for O-atom displacement; thus, the ''easy'' direction for Zn-atom displacement is [0001] and the easy direction for O-atom displacement is [000$\bar{1}$]. From these considerations, we might expect different defects to be created for different irradiation directions, and that indeed is the case. However, defect annihilations, primarily due to Coulombic attractions, must also be taken into account.

The ZnO crystals, grown by Eagle–Picher, Inc., were of very high quality, with 300 K and peak Hall mobilities of about 225 and 2000 cm^2/V s, respectively, and photoluminescence (PL) donor-bound-exciton linewidths of $<$0.3 meV.[7] Electrical properties, determined from temperature-dependent Hall effect (TDH) analysis, were similar to those reported previously:[2] two donors, with approximate energies 30 and 60 meV, respectively, and concentrations of 1×10^{16} and 1×10^{17} cm^{-3}, respectively, and an acceptor of concentration 2×10^{15} cm^{-3}. The irradiations were performed under vacuum, with the sample mounted on a water-cooled stage; the energies were 1.0–2.0 MeV and the current densities were typically 2–6 μA/cm^2. The fluence at each energy was kept constant at 4×10^{16} cm^{-2}. After the sequence of irradiations was complete, the samples were subjected to annealing steps at temperatures of 250–800 °C. Each anneal was carried out for 10 min., in flowing N$_2$. Sample EP97027 was irradiated on the Zn face, and sample EP97036, on the O face. Although the two samples came from different boules, their initial electrical and optical properties were nearly identical.

The total sequence of irradiations and anneals, for each sample, is designated as follows: (1) as-grown; (2) 1.0 MeV; (3) 1.3 MeV; (4) 1.6 MeV; (5) 2.0 MeV; (6) 2.0 MeV; (7) 2.0 MeV; (8) 2.0 MeV; (9) 250 °C; (10) 300 °C; (11) 350 °C;

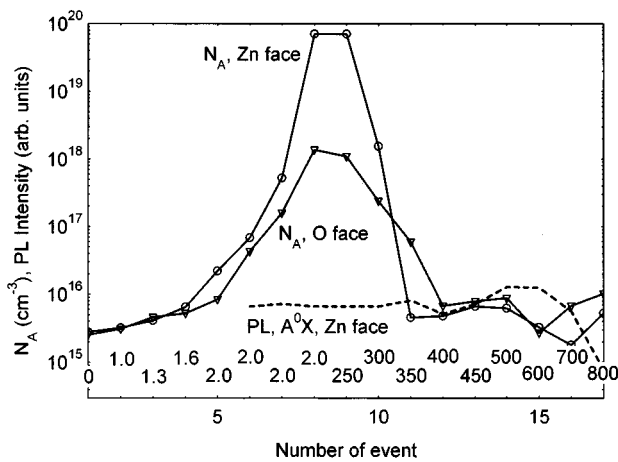[a]Electronic mail: david.look@sn.wpafb.af.mil

FIG. 1. Acceptor concentration measured after electron irradiation events (Nos. 1–8; energies in eV), and annealing events (Nos. 9–17; temperatures in °C). Also shown is the intensity of the A^0X photoluminescence spectrum, normalized by the D^0X spectrum in order to eliminate nonradiative effects. The solid and dashed lines are simply meant to guide the eye.

(12) 400 °C; (13) 450 °C; (14) 500 °C; (15) 600 °C; (16) 700 °C; (17) 800 °C. In Fig. 1, we present Hall effect and PL data as a function of event number. The acceptor concentration N_A is chosen as the Hall effect parameter of interest, because N_A is well fitted from temperature-dependent mobility data, whereas the fits of N_D depend, of course, on how many donors are assumed to be present. (See Refs. 2 and 8 for a description of the methodology used to fit the TDH data.) For a comparison of N_A with PL data, the integrated acceptor-bound-exciton (A^0X) spectrum was chosen, since acceptors are involved in each case. Actually, the A^0X data are normalized by using the D^0X data as a divisor, since then the effects of nonradiative centers are largely removed.

We first note, from Fig. 1, that very little increase in N_A takes place for electron-bombardment energies up to 1.6 MeV. The same holds true for the PL intensities (not shown), which have decreased less than a factor-two after the 1.6 MeV irradiation. (It is also important to note that each irradiation in the sequence involves a rather large dose, $4 \times 10^{16} \, \text{cm}^{-2}$.) This fact shows that c-axis-irradiated ZnO experiences much less damage from high-energy electrons than does its counterparts, Si, GaAs, CdS, or even GaN. As argued in a previous paper,[8] such a high ($>$1.6 MeV) damage threshold cannot be explained by simple, nearest-neighbor Frenkel-pair production, because such a process would require unrealistically high atomic displacement energies (133 eV for Zn, 484 eV for O). Instead, multiple displacements must be required to produce stable defects. In fact, by using Van Vechten's theoretical displacement energies (18.5 eV for Zn, 41.4 eV for O),[9] along with a formula derived in Ref. 8, a three-displacement chain (Zn–O–Zn) would require 1.55 MeV, in good agreement with experiment. The final defect in this case might be a $V_{Zn}-Zn_O-O_{Zn}-Zn_I$ complex, with the Zn_I perhaps being knocked away from the rest of the complex. The idea here is that the positively charged Zn_I must be more than a nearest-neighbor distance away from the negatively charged V_{Zn} to avoid immediate recombination, so that the simple $V_{Zn}-Zn_I$ Frenkel pair would be unstable. If the chain defect suggested

above is accurate, then the acceptor might be $V_{Zn}-Zn_O-O_{Zn}$ and the donor, Zn_I. To be more complete in these arguments, we must consider other possible chain defects. For Zn-face irradiation, we can calculate the following threshold energies: 0.38 MeV for O–Zn; 0.40 MeV for Zn alone; 0.94 MeV for O–Zn–O–Zn; 1.55 MeV for Zn–O–Zn; and 1.81 MeV for O–Zn–O–Zn–O–Zn. For O face irradiation, we get: 0.24 MeV for O alone; 0.74 MeV for O–Zn–O; 1.17 MeV for Zn–O; 1.50 MeV for O–Zn–O–Zn–O; and 2.53 MeV for Zn–O–Zn–O. Other, longer chains could be formed for energies above 3 MeV. Suppose we postulate that each atom displaced simply replaces the atom below it, if it has enough kinetic energy to knock out that particular atom; then, as discussed above, the Zn–O–Zn sequence would produce the defect $V_{Zn}-Zn_O-O_{Zn}-Zn_I$. Now it is likely that V_{Zn} has acceptor states close to the valence band, as is true for most of the cation vacancies in the II–VI and III–V compounds; thus, although we do not know the donor/acceptor nature of some of the other possible defects, it is quite reasonable to assume that the acceptor defect observed in Fig. 1 is related to V_{Zn}. If we also postulate that a chain of at least three displacements is necessary to avoid Coulombic annihilation, then the lowest-threshold surviving defects should be Zn–O–Zn, for Zn-face irradiation, and Zn–O–Zn–O, for O-face irradiation. This model would predict a threshold energy of 1.55 MeV in the former case, and 2.53 MeV, in the latter. Indeed, the 1.55-MeV threshold is observed in Fig. 1 for Zn-face irradiation, and a higher threshold, about 2 MeV, is found for O-face irradiation. From standard theory,[10] we can calculate Zn displacement rates of 1.7 and 1.9 cm^{-1} at these energies; however, the O displacement rate, at say 1.6 MeV, is only about 0.23 cm^{-1}, nearly an order-of-magnitude lower. This is another reason to believe that the acceptor-defect production begins with a Zn, rather than an O, displacement.

Another observation is that the N_A determined from the Hall-effect measurements does not correlate well with the A^0X PL spectrum over the region of high N_A production (i.e., for electron energies $>$1.6 MeV). This fact suggests that the excitons are still binding to preexisting "shallow" ($\sim$200 meV) acceptors, rather than to the irradiation-induced acceptors, which are probably much deeper. There appears to be some correlation between PL and Hall data in the 400–600 °C anneal region, but, by then, most of the irradiation-induced acceptors have annealed out.

Finally, we consider the dominant N_A annealing stage at about 325 °C. Clearly, the annealing after Zn-face irradiation is much sharper than that after O-face irradiation. If each defect anneals (annihilates) independently, then the isochronal annealing process for a defect of concentration N can be described as follows:[11]

$$N_{i+1} = N_\infty + (N_i - N_\infty) \exp[-\nu\tau \exp(-E_A/kT_i)], \quad (1)$$

where the subscript $i = 0, 1, 2.....$ denotes the annealing step [$T_0 = 298.2 \, \text{K} \, (25 \, °\text{C})$, $T_1 = 523.2 \, \text{K} \, (250 \, °\text{C})$, etc.], $\tau = 600 \, \text{s}$ is the annealing time, ν is a frequency factor ($\nu = 10^{13} \, \text{s}^{-1}$, as commonly assumed), and $E_A = E_{A_0} + \alpha(T_i - T_1)$ is the activation energy. The parameter α allows for a change in E_A as

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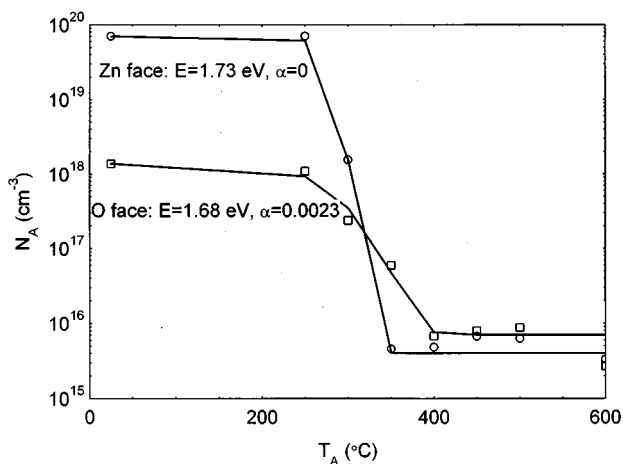
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FIG. 2. Acceptor concentration, as a function of annealing temperature, for samples irradiated on the Zn face, and the O face, respectively. The solid lines are theoretical fits, using first-order kinetics, with activation energy parameterized by $E_A = E + \alpha T$.

a function of annealing temperature T_i; such a change might be expected if more than one type of defect is present.

The annealing data and theoretical fits are shown in Fig. 2. The fit to the Zn-face-irradiated sample is remarkable, because it is accomplished with $\alpha = 0$, strongly suggesting that only one type of defect is created by 2-MeV-electron irradiation on this face, and that the annealing process is simply a collapse of this defect. For the particular defect proposed earlier, the annealing process would be: $V_{Zn}-Zn_O-O_{Zn}-Zn_I \rightarrow Zn_{Zn}-O_O-Zn_{Zn}$, with a fitted activation energy of 1.73 eV. For the O-face irradiation, on the other hand, the best fit gives $\alpha = 0.0023$, which implies the existence of more than one type of defect, with activation energies ranging from 1.68 eV, at the beginning of the anneal, to about 2.03 eV at the end (at about 400 °C). Even if a second-order (uncorrelated) annealing process is assumed for the O-face case, a good fit cannot be obtained for $\alpha = 0$. Thus, we believe that a single type of defect dominates for 2-MeV Zn-face irradiation, and more than one type of defect for O-face irradiation.

As discussed in a previous report,[8] an interesting aspect of the present experiments is that the *electronic* activation energy of the dominant donor produced by the irradiation, about 30 meV, is close to that found in most high-quality ZnO crystals produced in recent times, and also in the past.[2,12] Thus, we believe that the *native* shallow donor is a Zn-sublattice defect, probably involving Zn_I, and is not the

O vacancy, as has been commonly assumed by many in the past.[13] Another important aspect, of practical importance, is that electrical and optical damage is minimal even at rather high electron energies ($\geqslant$1.6 MeV), and fluences ($\geqslant$1 $\times 10^{17}$ cm^{-2}). Thus, these preliminary experiments indicate that ZnO devices should be useful in high-irradiation environments, such as those found in space applications.

In summary, we have presented electrical and optical data on ZnO crystals irradiated with high-energy electrons. Electrical damage is minimal up to energies of 1.6 MeV, and optical damage, to even higher energies. For 2-MeV Zn-face irradiation, a single type of defect is produced, and this defect anneals out at about 300–325 °C, with an activation energy of 1.73 eV. The total defect concentration is lower for O-face irradiation, although more than one type of defect is produced. The high damage-threshold energy (1.6 MeV) suggests that ZnO devices should be useful for radiation environments.

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