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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 [0001] 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 piezo-electric transducers, varistors, phosphors, and transparent conducting films. Most of these applications require only polycrystalline material; however, recent successes in producing large-area single crystals have opened up the possibility of producing blue and UV light emitters, and high-temperature, high-power transistors. The main advantages of ZnO as a light emitter are its large exciton binding energy, the saturation velocity. Optical UV lasing, at both low and high temperatures, has already been demonstrated, although efficient electrical lasing must await the further development of good, p-type material.

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 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 (0001) O face. Consider 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. 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 [0001]. 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 cm²/V s, respectively, and photoluminescence (PL) donor-bound-exciton linewidths of <0.3 meV. Electrical properties, determined from temperature-dependent Hall effect (TDH) analysis, were similar to those reported previously: two donors, with approximate energies 30 and 60 meV, respectively, and concentrations of 1 × 10¹⁶ and 1 × 10¹⁷ cm⁻³, respectively, and an acceptor of concentration 2 × 10¹⁵ 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/cm². The fluence at each energy was kept constant at 4 × 10¹⁶ 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 N₂. 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;
above is accurate, then the acceptor might be $V_{Zn} - ZnO - O_{Zn}$ and the donor, $Zn$. 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 $O - Zn - O - Zn - O$. 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 $O - Zn - O - Zn$; 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 $V_{Zn} - ZnO - O_{Zn} - Zn$. 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,\textsuperscript{10} we can calculate Zn displacement rates of 1.7 and 1.9 cm\textsuperscript{-1} at these energies; however, the O displacement rate, at say 1.6 MeV, is only about 0.23 cm\textsuperscript{-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:\textsuperscript{11}

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

where the subscript $i = 0, 1, 2, \ldots$ denotes the annealing step [$T_0 = 298.2$ K (25 °C), $T_1 = 523.2$ K (250 °C), etc.], $\tau = 600$ s is the annealing time, $\nu$ is a frequency factor ($\nu = 10^{13}$ s\textsuperscript{-1}, as commonly assumed), and $E_A = E_{A0} + \alpha(T_i - T_0)$ is the activation energy. The parameter $\alpha$ allows for a change in $E_A$ as

\[ N_{i+1} = N_s + (N_i - N_s)\exp[-\nu \tau \exp(-E_A/kT_i)], \quad (1) \]
Thus, we believe that the ZnO crystals produced in recent times, and also in the past, is close to that found in most high-quality environments. 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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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 $E_A = E + aT$.

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 (≥1.6 MeV), and fluences (≥ 1 × 1013 cm$^{-2}$). Thus, these preliminary experiments indicate that ZnO devices should be useful in high-irradiation environments.