8-1-1999

Production and Annealing of Electron Irradiation Damage in ZnO

David C. Look
Wright State University - Main Campus, david.look@wright.edu

D. C. Reynolds
Joseph W. Hemsky
Wright State University - Main Campus, joseph.hemsky@wright.edu

R. L. Jones
J. R. Sizelove

Follow this and additional works at: https://corescholar.libraries.wright.edu/physics
Part of the Physics Commons

Repository Citation

This Article is brought to you for free and open access by the Physics at CORE Scholar. It has been accepted for inclusion in Physics Faculty Publications by an authorized administrator of CORE Scholar. For more information, please contact corescholar@www.libraries.wright.edu, library-corescholar@wright.edu.
Production and annealing of electron irradiation damage in ZnO

D. C. Look,a) D. C. Reynolds, and J. W. Hemsky
Semiconductor Research Center, Wright State University, Dayton, Ohio 45435

R. L. Jones and J. R. Sizelove
Materials and Manufacturing Directorate, Air Force Research Laboratory,
Wright-Patterson Air Force Base, Ohio 45433

(Received 6 May 1999; accepted for publication 14 June 1999)

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 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 crystals2 have opened up the possibility of producing blue and UV light emitters,3 and high-efficiency 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 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.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 [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.7 Electrical properties, determined from temperature-dependent Hall effect (TDH) analysis, were similar to those reported previously:8 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;

---

a)Electronic mail: david.look@sn.wpafp.af.mil

© 1999 American Institute of Physics

0003-6951/99/75(6)/811/3/$15.00 811
(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),\(^8\) 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 $V_{Zn}^{\prime}–Zn_0–O_{Zn}^{\prime}–Zn_0$ complex, with the $Zn_0$ perhaps being knocked away from the rest of the complex. The idea here is that the positively charged $Zn_0$ must be more than a nearest-neighbor distance away from the negatively charged $V_{Zn}^{\prime}$ to avoid immediate recombination, so that the simple $V_{Zn}^{\prime}–Zn_0$ Frenkel pair would be unstable. If the chain defect suggested above is accurate, then the acceptor might be $V_{Zn}^{\prime}–Zn_0–O_{Zn}^{\prime}$ and the donor, $Zn_0$. 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–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 $V_{Zn}^{\prime}–Zn_0–O_{Zn}^{\prime}–Zn_0$. Now it is likely that $V_{Zn}^{\prime}$ 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 $V_{Zn}^{\prime}$. 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” (∼200 eV) 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:\(^11\)

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

(1)

where the subscript $i=0,1,2,...$ denotes the annealing step $[T_0 = 298.2 \text{ K (25 °C)}, T_1 = 523.2 \text{ K (250 °C)}, etc.]$, $\tau = 600 \text{ s}$ is the annealing time, $\nu$ is a frequency factor ($\nu = 10^{13} \text{ s}^{-1}$, as commonly assumed), and $E_A = E_{A_0} + \alpha(T_i - T_0)$ is the activation energy. The parameter $\alpha$ allows for a change in $E_A$ as
a function of annealing temperature \( T_a \); 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: \( V_{\text{Zn}} - \text{Zn}_0 - \text{O}_0 - \text{Zn}_0 \rightarrow \text{Zn}_{\text{Zn}} - \text{O}_0 - \text{Zn}_{\text{Zn}} \), 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, 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. Thus, we believe that the native shallow donor is a Zn-sublattice defect, probably involving \( \text{Zn}_f \), and is not the O vacancy, as has been commonly assumed by many in the past. Another important aspect, of practical importance, is that electrical and optical damage is minimal even at rather high electron energies (\( \geq 1.6 \) MeV), and fluences (\( \geq 1 \times 10^{15} \) 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.

The authors wish to thank T. A. Cooper, D. Beasley, and L. Callahan for technical assistance, C. W. Litton for helpful discussions, and C. Huang for support and encouragement. D.C.L., D.C.R., and J.W.H. were supported under U.S. Air Force Contract No. F33615-95-C-1619, and some of their work was performed at the Air Force Research Laboratory, Wright-Patterson Air Force Base, OH. Also, partial support was received from the Air Force Office of Scientific Research.

\(^{13}\) F. A. Kröger, The Chemistry of Imperfect Crystals (North-Holland, Amsterdam, 1974).