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Electron irradiation induced deep centers in hydrothermally grown ZnO

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An *n*-type hydrothermally grown ZnO sample becomes semi-insulating ($\rho \sim 10^8 \Omega \text{ cm}$) after 1-MeV electron-irradiation. Deep traps produced by the irradiation were studied by thermally stimulated current spectroscopy. The dominant trap in the as-grown sample has an activation energy of 0.24 eV and is possibly related to Li_{Zn} acceptors. However, the electron irradiation introduces a new trap with an activation energy of 0.15 eV, and other traps of energy 0.30 and 0.80 eV, respectively. From a comparison of these results with positron annihilation experiments and density functional theory, we conclude that the 0.15-eV trap may be related to V_{Zn} . © 2007 American Institute of Physics.
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Large ZnO crystals can presently be grown from the vapor phase (VP),¹ melt (MLT),² or water solution [hydrothermal (HYD)].³ Unintentionally doped VP and MLT ZnO samples nearly always have low resistivities ($\sim 1 \Omega \text{ cm}$), due to high concentrations (10^{16} – 10^{17} cm^{-3}) of uncompensated shallow donors. In contrast, HYD samples typically have much higher resistivities (~ 200 – $1000 \Omega \text{ cm}$), because the shallow donors are fully compensated by acceptors (e.g., Li) present in the mineralizer,³ and the electrical properties are thus controlled by deep donors. The deep centers in VP and MLT ZnO samples have been previously studied by deep level transient spectroscopy (DLTS).^{4,5} Both materials contained two prominent defects: *E1* at E_C –0.12 eV and *E3* at E_C –0.29 eV. In VP ZnO, *E1* is the primary defect, while in MLT ZnO, *E3* dominates. An electron trap at E_C –0.3 eV was also found in early HYD ZnO single crystals (with net donor density in the range 2 – $8 \times 10^{14} \text{ cm}^{-3}$) by DLTS studies.⁶ The 0.3-eV defect is evidently a native donor and has been attributed to oxygen vacancies (V_O).^{4,6} High-energy (1.8 MeV) proton irradiation can induce point defects in VP ZnO samples, albeit with very low production rates, and in that case DLTS finds two defects, *Ep1* at E_C –0.54 eV and *Ep2* at E_C –0.78 eV.⁷ High-energy (>1.6 MeV) electron irradiation can also create point-defect related acceptors and donors in VP ZnO, with more damage if the beam is directed toward the Zn face than the O face.⁸ However, unlike the case in VP or MLT ZnO, we have found that 1-MeV electron irradiation in HYD ZnO can easily produce semi-insulating (SI) material, with resistivity $>10^8 \Omega \text{ cm}$.⁹ Because such high-resistivity samples cannot be studied by DLTS, we have instead applied thermally stimulated current (TSC) spectroscopy, which has earlier been successfully used to study various other SI wide-band gap materials, such as carbon-doped GaN (Ref. 10) and high-purity 4H-SiC.¹¹

The HYD ZnO sample used in this study was a 5 mm $\times$ 5 mm $\times$ 0.5 mm *c*-axis-oriented plate cut from a larger 10 mm $\times$ 10 mm plate supplied by Tokyo Denpa.¹² Hall-effect measurements were performed at room temperature, with Ohmic contacts prepared by soldering indium dots onto the corners of the sample. The electrical properties included: resistivity of $210 \Omega \text{ cm}$, carrier concentration of $1.6 \times 10^{14} \text{ cm}^{-3}$, and electron mobility of $185 \text{ cm}^2/\text{V s}$. Fitting of the temperature-dependent mobility and carrier concentration was accomplished with the following parameters: donor energies $E_{D1}=48 \text{ meV}$, $E_{D2}=300 \text{ meV}$; donor concentrations $N_{D1}=1.5 \times 10^{16} \text{ cm}^{-3}$, $N_{D2}=1.0 \times 10^{15} \text{ cm}^{-3}$; and acceptor concentration $N_A=1.49 \times 10^{16} \text{ cm}^{-3}$. Note that the donors are rather closely compensated by the acceptors.

Electron irradiation (EI) was carried out at room temperature using 1-MeV electrons produced by a Van de Graaff accelerator. An electron fluence of $2 \times 10^{16} \text{ cm}^{-2}$ was used in two consecutive irradiations giving a total dose of $4 \times 10^{16} \text{ cm}^{-2}$. Recent molecular dynamics simulations have determined 300-K displacement threshold energies of 44 and 34 eV for O and Zn, respectively.¹³ We can then use the McKinley–Feshbach formula to calculate O and Zn Frenkel-pair production rates of 0.37 and 0.61 cm^{-1} , respectively, resulting from bombardment by 1-MeV electrons. For a total electron fluence of $4 \times 10^{16} \text{ cm}^{-2}$, the expected concentrations of O vacancies and Zn vacancies would thus be $1.5 \times 10^{16} \text{ cm}^{-3}$ and $2.4 \times 10^{16} \text{ cm}^{-3}$, respectively. Even though the actual concentrations would likely be smaller, because of defect annihilation processes, still it is known that some Zn vacancies still survive (Ref. 15) and are stable to about 300 °C (Ref. 8). Even if only 10% were to survive, that would still produce an additional acceptor concentration of about $2 \times 10^{15} \text{ cm}^{-3}$, which would be enough to complete the compensation of both the 48- and 300-meV donors and produce highly resistive material.

TSC spectroscopy involves filling electron and hole traps by illumination at low temperature and then warming

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FIG. 1. Arrhenius plots of DC for the ZnO sample before and after irradiation. The curves were obtained while cooling the sample at a rate $\beta=0.3$ K/s under a bias $V_b=1$ V.

the sample in the dark while recording the current due to the thermal emission of carriers from the traps. To keep the initial conditions the same, the sample was always cooled from 400 to 83 K in the dark. During cooling, the dark current (DC) was measured as a function of temperature. The traps were filled at 83 K by illumination with 400-nm (near-band gap) light, produced by a 15-W halogen lamp and a bandpass filter. The photocurrent (PC) response was recorded at 83 K during a 5-min illumination period and the decay of persistent photocurrent was then recorded for 30 s after switching the light off. After that, the TSC spectrum was measured during warming at a heating rate of $\beta=0.3$ K/s under a bias of 0.1 or 1 V, depending on the resistivity of the sample. From the TSC peak temperature T_m for a given trap, the approximate activation energy can be determined from the relation¹⁴

$$E_T = kT_m \ln(T_m^4/\beta). \quad (1)$$

Note that TSC characterization by itself cannot tell whether a peak is due to an electron trap or a hole trap. However, based on a comparison of the measured activation energies with those determined in earlier samples by DLTS or other means, we can speculate on the origins of the TSC traps observed in our as-grown and irradiated HYD ZnO samples.

An Arrhenius plot of DC measured upon cooling at $V_b=1$ V for the HYD ZnO sample before and after the first and second EIs is presented in Fig. 1. Before the EI (top curve), the sample shows mid-resistive behavior, with the conductivity controlled by relatively shallow donors. After the first EI (middle curve), the resistivity greatly increases and has a conductivity activation energy of about 0.3 eV, and after the second EI (bottom curve), the sample becomes semi-insulating. In total, the DC at 400 K is reduced by nearly four orders of magnitude. Positron annihilation spectroscopy has been used previously to study point defects introduced in VP ZnO by 2-MeV EI. The results show that Zn-vacancy acceptors are important in the electrical compensation.¹⁵ Thus, it is reasonable to conclude that the significant reduc-

FIG. 2. Net TSC spectrum (i.e., TSC-DC) for the as-grown sample following 400-nm illumination at 83 K. The bias and heating rate were $V_b=0.1$ V and $\beta=0.3$ K/s, respectively. The inset displays the time dependence of the PC at 83 K.

tion in conductivity of HYD ZnO after electron irradiation is due to the introduction of zinc vacancies.

The net TSC spectrum (i.e., TSC-DC) for the as-grown sample (before EI) is shown in Fig. 2. The PC response measured at 83 K is shown in the inset of the figure. The response consists of: (i) an initial transient, related to trap-filling processes; (ii) a saturation region, with equal rates of carrier emission and capture; and (iii) a decay or persistent photocurrent, related to the thermal emission of carriers from shallow traps at 83 K. The TSC spectrum is dominated by a broad peak centered at 135 K, but also includes a shoulder at 160 K and a small peak at 215 K. Using Eq. (1), the activation energies are estimated to be 0.24 eV for the 135-K peak and 0.30 eV for the 160-K shoulder. Recently, a Li-related acceptor state with a thermal activation energy of approximately 0.26 eV in a similar Tokyo Denpa ZnO sample was determined to play a key role in electron trapping phenomena.¹⁶ Thus, we tentatively assign the 0.24-eV center to Li_{Zn} acceptors. Also, the weak 0.30-eV center in the as-grown sample could possibly be related to oxygen vacancies, as reported in earlier DLTS studies on VP and HYD ZnO samples.^{4,6}

It is difficult to directly compare the magnitudes of the TSC spectra of the as-grown and irradiated samples, because the TSC signal is proportional to the dominant carrier lifetime in each case and the carrier lifetimes are unknown. However, the PC is also proportional to carrier lifetime, and thus a rough normalization can be effected by dividing the TSC signal by the PC signal at 83 K. Such a normalization should be reasonably accurate for at least the low temperature traps. In Fig. 3 is displayed the net, normalized TSC curves [i.e., $[\text{TSC-DC}]/[\text{PC}(83\text{ K})]$] for the as-grown and irradiated samples. The traps in the as-grown sample have been discussed above. After the first EI, traps at 94 and 375 K are clearly observed and the use of Eq. (1) gives energies of 0.16 and 0.80 eV, respectively, for these centers. A more accurate Arrhenius analysis (not shown) of the 94-K trap gives an energy of 0.15 eV, in agreement with the more approximate value mentioned earlier. In an optical-DLTS study on VP ZnO, a hole trap located at 0.16 eV above the

FIG. 3. Net and normalized TSC spectra [i.e., $[TSC-DC]/[PC(83\text{ K})]$] for the as-grown and irradiated samples following 400-nm illumination at 83 K. The bias and heating rate were $V_b=1\text{ V}$ and $\beta=0.3\text{ K/s}$, respectively.

valence band edge was found to be introduced by 100-keV proton implantation.¹⁷ Thus, we believe that the 0.15-eV center, introduced by electron irradiation in HYD ZnO, may also be a hole trap. Since electron irradiation is known to produce stable Zn vacancies,¹⁵ and since the V_{Zn} (0/-) transition energy has been determined from density functional theory to be about 0.11 eV,¹⁸ it is possible that this trap is V_{Zn} related.

The feature at 135 K (0.24 eV), which may be related to the acceptor Li_{Zn} , is dominant in the as-grown sample. On the other hand, the features at 94 K (0.16 eV), 160 K (0.30 eV), and 375 K (0.80 eV), are likely related to point defects. The 160-K feature has the same energy as that of a trap earlier assigned to O vacancies.^{4,6} Finally, the 375-K trap has an energy close to that of $Ep2$ (0.78 eV), introduced in VP ZnO by proton-bombardment.⁷

In summary, thermally stimulated current spectroscopy has been used to investigate the effects of 1-MeV electron irradiation on a ZnO sample grown by the hydrothermal method. A dose of $4 \times 10^{16}\text{ cm}^{-2}$ increases the resistivity from about 10^2 to $10^8\text{ }\Omega\text{ cm}$, likely due to the introduction of zinc vacancies. Before irradiation, a trap at 0.24 eV dominates the TSC spectrum, and it is probably related to Li_{Zn} ,

known to be a major residual impurity in hydrothermal ZnO. Irradiation introduces strong traps at 0.15 and 0.80 eV. The former is possibly related to the Zn vacancy and the latter is reminiscent of $Ep2$, reported in 1.8-MeV proton-bombarded vapor-phase ZnO. An 0.30-eV trap, possibly related to the oxygen vacancy, can be observed in both as-grown and irradiated ZnO.

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- ¹D. C. Look, D. C. Reynolds, J. R. Sizelove, R. L. Jones, C. W. Litton, G. Cantwell, and W. C. Harsch, *Solid State Commun.* **105**, 399 (1998).
- ²J. Nause and B. Nemeth, *Semicond. Sci. Technol.* **20**, S45 (2005).
- ³K. Maeda, M. Sato, I. Niikura, and T. Fukuda, *Semicond. Sci. Technol.* **20**, S49 (2005).
- ⁴F. D. Auret, S. A. Goodman, M. J. Legodi, W. E. Meyer, and D. C. Look, *Appl. Phys. Lett.* **80**, 1340 (2002).
- ⁵H. von Wenckstern, R. Pickenhain, H. Schmidt, M. Brandt, G. Biehne, M. Lorenz, M. Grundmann, and G. Brauer, *Appl. Phys. Lett.* **89**, 092122 (2006).
- ⁶J. C. Simpson and J. F. Cordaro, *J. Appl. Phys.* **63**, 1781 (1988).
- ⁷F. D. Auret, S. A. Goodman, M. Hayes, M. J. Legodi, H. A. van Laarhoven, and D. C. Look, *Appl. Phys. Lett.* **79**, 3074 (2001).
- ⁸D. C. Look, D. C. Reynolds, J. W. Hemsky, R. L. Jones, and J. R. Sizelove, *Appl. Phys. Lett.* **75**, 811 (1999).
- ⁹D. C. Look, Z.-Q. Fang, B. Claflin, and G. C. Farlow (unpublished).
- ¹⁰Z.-Q. Fang, D. C. Look, B. Claflin, S. Haffouz, H. Tang, and J. Webb, *Phys. Status Solidi C* **2**, 2757 (2005).
- ¹¹Z.-Q. Fang, B. Claflin, D. C. Look, L. Polenta, and W. C. Mitchel, *J. Electron. Mater.* **34**, 336 (2005).
- ¹²Tokyo Denpa Co., Ltd., 5-6-11 Chuo, Ohta-ku, Tokyo 143-0024, Japan.
- ¹³D. C. Look, G. C. Farlow, P. Reunchan, S. Limpijumnong, S. B. Zhang, and K. Nordlund, *Phys. Rev. Lett.* **95**, 225502 (2005).
- ¹⁴D. C. Look, *Semicond. Semimetals* **19**, 75 (1983).
- ¹⁵F. Tuomisto, K. Saarinen, and D. C. Look, *Phys. Status Solidi A* **201**, 2219 (2004).
- ¹⁶O. Lopatiuk, L. Chernyak, A. Osinsky, and J. Q. Xie, *Appl. Phys. Lett.* **87**, 214110 (2005).
- ¹⁷A. Y. Polyakov *et al.*, *J. Appl. Phys.* **94**, 2895 (2003).
- ¹⁸A. Janotti and C. G. Van de Walle, *J. Cryst. Growth* **287**, 58 (2006).