Defects produced in ZnO by 2.5-MeV electron irradiation at 4.2 K: Study by optical detection of electron paramagnetic resonance

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The effect of 2.5 MeV electron irradiation *in situ* at 4.2 K on the properties of single crystalline ZnO is studied by photoluminescence (PL) and optically detected electron paramagnetic resonance (ODEPR). A new PL band is produced by the irradiation, and several annealing stages are observed upon annealing to room temperature, the first starting at ~110 K. Three new ODEPR signals are observed in the PL whose emergence and disappearance correlate with the PL changes. The annealing stages are taken as evidence of host interstitial atom migration beginning at the 110 K anneal. No hyperfine structure is observed for the ODEPR signals, so the defects involved cannot be identified at this stage.

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I. INTRODUCTION

Essential to the successful application of any semiconductor is the understanding of its intrinsic defects, i.e., vacancies and interstitials, because they provide the various diffusion mechanisms involved in processing and device degradation, as well as often controlling, directly or indirectly, background doping, compensation, minority carrier lifetime, and luminescence efficiency. There is currently growing interest in zinc oxide (ZnO) as a wide band-gap semiconductor for possible electronic and optical applications. Readily grown as large single crystals, with a band gap of 3.4 eV, it potentially offers many complementary and/or competitive advantages in these applications to the similar band-gap material GaN, to which it provides, in addition, a close lattice match.[1] The only direct and unambiguous method for introducing vacancies and interstitials for experimental studies is by high-energy electron irradiation, where host atoms can be displaced from their lattice sites by recoil from an electron-nucleus Rutherford scattering event. In addition, the most successful experimental technique for identifying and studying the defects has proven to be electron paramagnetic resonance, detected either directly (EPR) or optically (ODEPR). In the case of ZnO, early EPR studies in the 1970s have already identified vacancies produced by electron irradiation on each of the two sublattices—V_{Zn}^{-} and V_{Zn}^{0} on the Zn sublattice,[2–4] and V_{O}^{+} on the O sublattice.[5,6] They were found to be stable at room temperature, but their stability at elevated temperatures was not explored. No experimental information concerning interstitials has been obtained, however. Recently, theoretical studies of the intrinsic defects have also been initiated.[7]

In the present study, we explore by photoluminescence (PL) and ODEPR the defects produced in ZnO after 2.5 MeV electron irradiation *in situ* at 4.2 K. In this way we can expect to freeze in the intrinsic defects produced and explore their stability as the samples are annealed in stages up to room temperature. Since the vacancies have been established to be stable, if annealing is found to occur, it can be assumed to reflect the migration of interstitials. We might reasonably expect easier migration of the interstitials because it has been found to be the case in each of the few semiconductors so far, for which the identity of host atom interstitials has been established (ZnSe,[8–10] diamond,[11–13] GaN,[14–16] Si[17]).

In the present study, we find that annealing does indeed occur at several stages as the ZnO samples are warmed to room temperature, as revealed both in the PL and in the ODEPR. Because both Zn and O have only very low abundance nuclei with magnetic moments (^{17}O, $I=5/2$, 0.04%, and ^{67}Zn, $I=5/2$, 4.1%), we observe no hyperfine structure in the ODEPR spectra. Identification of the defects is therefore not possible at this stage, but we will tentatively conclude that the PL changes and the accompanying emergence and disappearance of the ODEPR signals reflects the motion of one or the other of the host interstitials.

II. EXPERIMENTAL DETAILS

Most of the samples studied were cut from a $10\times6\times0.5$ mm undoped single crystal wafer grown using a seeded chemical vapor transport technique by Eagle-Picher, Inc., with *c* axis along the narrow dimension, which we label EP1. Also briefly studied was a sample cut from a similar wafer, labeled CE1, but grown using a melt process by Cermet, Inc.

The experimental setup used to obtain the data described in this paper is identical to that of earlier ODEPR work on ZnSe, which should be referred to for further details.[18] Briefly, the experiments were performed at 20 GHz in an EPR spectrometer capable of irradiation *in situ* at 4.2 K with 2.5 MeV electrons from a Van de Graaff accelerator. Subsequent PL and ODEPR experiments were accomplished by inserting into the TE_{011} microwave cavity a fused quartz capillary tube, which served as a light pipe to extract the PL, and within which was threaded an optical fiber which allowed for the sample (located a few millimeters below the lightpipe) to be photoexcited with ultraviolet light. To monitor the PL and the ODEPR signals, the luminescence was detected with either a silicon (EG&G 250UV) or cooled germanium (North Coast EO-817S) diode detector, and, for most of the experiments, excitation ($\leqslant$20 mW) was supplied by the 351 nm (3.53 eV) line of an argon ion laser. (No distinguishable difference in either the PL or ODEPR was observed for excita-

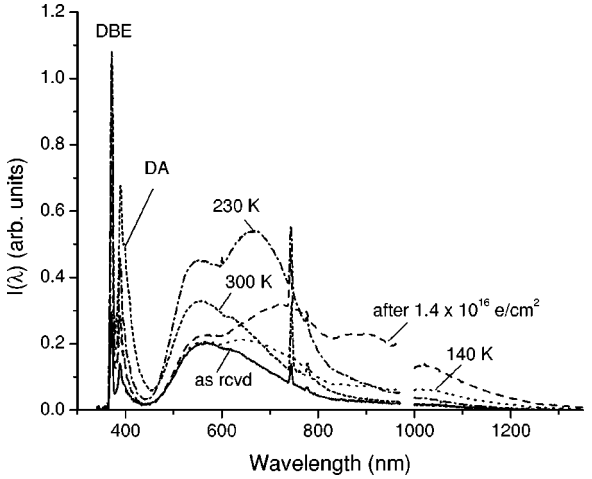

FIG. 1. PL spectra, corrected for monochromator and detector response, for sample EP1k at 1.7 K. Shown are the spectra before and after 2.5 MeV electron irradiation *in situ* at 4.2 K, and after selected 30 min annealing stages.

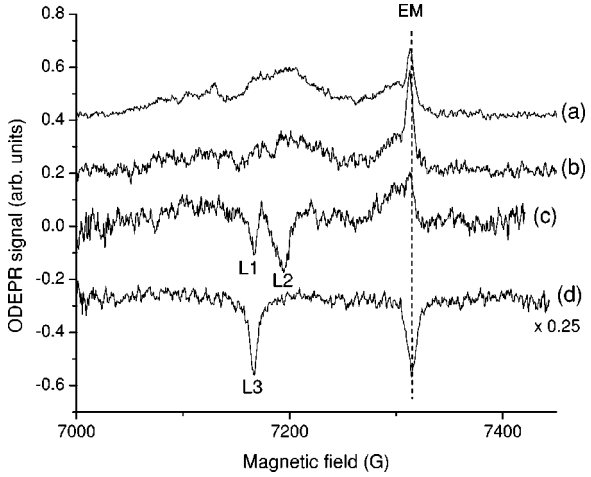

FIG. 2. ODEPR spectra (**B**⊥**c**) detected in the PL of sample EP1k at 1.7 K. (a) as received, (b) after 2.5 MeV electron irradiation to a fluence of 1.4×10^{16} e/cm^2 *in situ* at 4.2 K, (c) after 30 min anneal at 165 K, (d) after 30 min anneal at 230 K.

tion by the 351 nm or the 364 nm argon laser line.) For the measurements, the samples were immersed in pumped liquid helium ($\sim$1.7 K). For the ODEPR experiments, microwave power from a 300-mW Gunn diode was on-off modulated at $\sim$700 Hz, and synchronous changes in the luminescence were detected via lock-in detection. The (0001) Zn-surface of the sample was either indium-soldered, or glued using GE varnish, onto a brass post, cut at 45° in order to provide equal O-surface area for the horizontal electron irradiation and subsequent vertical photoexcitation. (The magnetic field could be rotated in the horizontal plane and therefore only directions between **B**⊥c axis and 45° to the c axis were accessible.)

III. RESULTS

In Fig. 1, we show PL results for sample EP1k after 2.5 MeV electron irradiation to a fluence of 1.4×10^{16} e/cm^2 *in situ* at 4.2 K. The irradiation has produced a prominent new double-humped band, centered at $\sim$750 and 900 nm, which trails into the near infrared. It begins to disappear at $\sim$110 K, being substantially reduced by the anneal at 140 K, which is shown in the figure. (Several annealing steps were performed on the sample but only those which demonstrate the major changes are shown in the figure for clarity.) A new band centered at $\sim$680 nm begins to grow in at $\sim$180 K, reaching a broad maximum at $\sim$230 K as also shown in the figure. It, in turn, disappears upon annealing at 280 K with a time constant of $\sim$36 min. This general pattern of emergence and disappearance of the particular PL bands shown in the figure is characteristic of all of the samples studied. (However, in a sample taken from the Cermet wafer, CE1a, the 680 nm band appeared more stable, annealing at 295 K only after $\sim$8–10 h.) In the particular sample shown in Fig. 1, EP1k, the donor bound exciton (DBE) and donor-acceptor (DA) PL bands are observed to have increased substantially in intensity both as a result of the 2.5 MeV irradiation and the subsequent anneals. This may be evidence of donors having been produced by the two processes, but we cannot rule out simple improvements in the surface region of the crystal (partial healing of near-surface absorptive or recombination processes) as the cause. This was observed in many of the samples studied, but not all. In particular, it was not observed in sample CE1a.

In a pair of separate samples from the EP1 wafer, the dependence of the irradiation-produced broad double-humped PL vs 2.5 MeV electron fluence was explored. The intensity of the PL band was observed to increase linearly up to $\sim5\times10^{15}$ e/cm^2, but with little further growth up to $\sim5\times10^{16}$ e/cm^2. Most of the studies were therefore performed with fluences of ~1–1.5×10^{16} e/cm^2.

In Fig. 2, we show the ODEPR signals seen in EP1k before and after the irradiation and at two distinct stages in the subsequent anneal. Before the irradiation, Fig. 2(a), the shallow effective-mass (EM) donor resonance[19–23] is observed along with several broad, structureless, weak signals to lower field. These broad signals show evidence of anisotropy, changing character somewhat vs magnetic-field orientation, but no attempt has been made to try to extract the components and analyze them. After the irradiation, Fig. 2(b), there is little change with the possible exception of an increase in the EM signal. In Fig. 2(c), the first new spectra, labeled L1 and L2, are observed to emerge upon anneal at $\sim$140 K. They are shown in the figure after a 165 K anneal which tends to optimize them. Their g values are given in Table I. Although they are weak, they were seen in most of

TABLE I. g Values for the ODEPR spectra.

Spectrum	$\mathbf{g}_\parallel$	$\mathbf{g}_\perp$
EM	1.9570(3)	1.9551(2)
L1	1.9959(4)	1.9959(3)
L2	1.9868(4)	1.9902(3)
L3	1.9952(3)	1.9959(2)

the samples studied, particularly those with only modest irradiation fluences, but the relative strengths of L1 and L2 seem to vary, suggesting that they arise from separate spin-dependent processes. The spectral dependence of the signals, determined by monitoring with selective optical filters reveals that they arise throughout the total PL band, as seen in Fig. 1 after the 140 K anneal. They are negative signals indicating that they arise from defects involved in spin-dependent recombination processes that *compete* with the PL.

In Fig. 2(d) we see two stronger negative ODEPR signals present after the 230 K anneal. They begin to grow in as the L1 and L2 signals disappear at ~180 K, and their intensities follow closely that of the 680 nm band shown in Fig. 1 after the 230 K anneal, disappearing also as the PL band disappears upon anneal at 280 K. Consistent with this is the spectral dependence of the ODEPR signals, which, using various filters reveals their presence only in the spectral region of the 680 nm band. Again, they are negative signals, reflecting spin-dependent processes which compete with the PL. The high-field signal is that of the EM donor signal, but the low-field line, labeled L3, is new, and its g values are included also in Table I. (Although the g values for L3 and L1 are very similar, the anisotropy for L3, which is more accurate than the absolute errors indicated in the table, appears to clearly distinguish it from L1.) Both L3 and the EM signal are correlated with the 680 nm band but their relative intensities can vary from sample to sample. (As an extreme example, the strong negative EM signal is observed to emerge and disappear with the 680 nm band in a similarly irradiated Cermet sample, CE1a, but the L3 spectrum is not observed.) After the 300 K anneal, the remaining ODEPR signals appear closely the same as those before the irradiation, Fig. 2(a).

IV. DISCUSSION

The observation of saturation for the irradiation-produced PL band at the very low electron fluence of only $\sim 5 \times 10^{15}$ e/cm^2, brings up the question as to whether the PL and ODEPR changes being observed could possibly be simply trace impurity atom displacement of some kind caused by the ionization accompanying the electron irradiation, and not host atom displacement damage. To probe this, we therefore excited an unirradiated Eagle-Picher sample for 16 h with 120 mW of multiline Argon laser UV (364 and 351 nm) light at 4.2 K. Assuming that only 0.5% of the absorbed photons produces an electron-hole pair, it is straightforward to show that this should still produce the same total ionization as that produced by the electron irradiation for sample EP1k. No observable production of the broad double-humped PL band shown in Fig. 1 was detected. We can conclude therefore that the PL and ODEPR changes are the result of host atom primary displacement events, i.e., the production of vacancies and host atom interstitials, as originally proposed in the Introduction.

The fact that several annealing stages occur in the PL below room temperature starting at ~110 K, implies that at least one or more of the intrinsic defects produced in the primary damage event must be mobile at these low temperatures. Since it has been established that the vacancies on each of the two sublattices are stable at room temperature,[2–6] the mobile defect must be one of the interstitials (O_i or Zn_i). This important conclusion is the principal one that we can make from our studies at this stage. It fits the general pattern reported in several other semiconductors (Zn_i in ZnSe,[9,10] Zn_i and Te_i in ZnTe,[24] Ga_i in GaN,[14–16] Si_i in silicon,[17] C_i in diamond[11–13]) of the significantly easier diffusion of interstitials compared to vacancies. In some of these other studies, it was concluded that recombination-enhanced motion of the interstitials could also be induced by exciting with near band-gap light at 1.7 K. No evidence of this has been observed in the ZnO samples studied here under prolonged excitation at this temperature.

Three new ODEPR signals have been observed to emerge and disappear in correlation with the PL changes upon annealing the irradiated samples. They are therefore quite likely related to trapped or reconfigured states of the mobile interstitial species. In the case of L3, it is always accompanied with an equally strong negative EM signal, suggesting that, in that case, the spin-dependent recombination competing process involves an electron transfer from the shallow donor to the defect giving rise to L3. (The negative EM signal was also seen at this point in the annealing recovery of the Cermet sample, CE1a, without L3. In that case presumably an electron transfer to a different paramagnetic deep level dominates which is not being observed.) Unfortunately, no resolved hyperfine structure is observed for the observed ODEPR signals, and they are too weak for ENDOR studies. Therefore, their identities must remain unknown at present. But they are clearly important and hopefully in future studies they can provide independent and complementary information to other approaches to help unravel the important defect processes involved.

V. SUMMARY

Recovery occurs at several stages, starting at ~110 K, upon annealing ZnO to room temperature after 2.5 MeV electron irradiation *in situ* at 4.2 K. Observed both in the PL and ODEPR studies, these stages have been attributed to migration by one or the other, or possibly both, of the two host interstitial atoms because it has been established in previous studies that vacancies on the two sublattices are stable in this temperature region. New PL bands are observed to emerge and disappear as a result of the electron irradiation and subsequent anneal, and three new ODEPR signals are observed that appear to correlate with the PL annealing stages. No hyperfine structure is observed for them, so their identities cannot be established at this time.

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