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Persistent photoconductivity and thermally stimulated current related to electron-irradiation induced defects in single crystal ZnO bulk

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ABSTRACT

Persistent photoconductivity (PPC) in 30 MeV-electron-irradiated ZnO single-crystals is studied by excitation using light emitting diodes (LEDs) with various wavelengths above and below the band gap. The PPC with extremely long time constants of a few tens of days is observed for the illumination with ultraviolet and blue LEDs at 90 K. An electron paramagnetic resonance signal with a *g*-value of 1.996 appears after illumination at 77 K, suggesting the presence of an oxygen vacancy related defect. These results support a mechanism of PPC proposed by Van de Walle, suggesting a transfer from the electron-irradiation induced 2+ charge state of the oxygen vacancy to the metastable + charge state due to the illumination. Two thermally stimulated current peaks with ionization energies of 545 and 664 meV appear after electron irradiation. These traps are tentatively assigned to the zinc vacancy and interstitial oxygen.

ZnO, with a 3.36 eV direct band gap and a large excitation binding energy of 60 meV, has been widely used for many applications such as piezoelectric transducers, varistors, and gas and ultra-violet light sensors. Recently, large single crystals grown by the hydrothermal method [1] are expected to offer many complementary and competitive advantages to GaN, which has a similar band gap and lattice constant with ZnO. However, as-grown ZnO is synthesized nearly always as an n-type material, and residual impurities and native defects in as-grown samples are different between the vapor phase and hydrothermal methods [2,3]. The difference may be attributed to alkali metals introduced from LiOH and KOH used as the solvent [1], although Li has been expected as a p-type dopant [4,5]. In such cases, these alkali metals behave as compensation centers of native donor defects such as an oxygen vacancy, changing ZnO into a highly resistive material. In order to confirm the theoretical calculations [6,7] of the native defects, several experiments using single crystal ZnO have been performed using deep-level-transient spectroscopy (DLTS) [2,3,8–11], admittance spectroscopy [12], and thermally stimulated current (TSC) studies [13,14]. Furthermore, theoretical studies [6,7] pointed out the importance of the oxygen vacancy (V_o) in ZnO for the persistent photoconductivity (PPC). In many cases, PPC is attributed to the existence of defects which are metastable between a shallow and a deep energy state. One such defect is the deep unknown (DX) center, which is formed when shallow donors convert into deep donors after a large lattice relaxation. In the case of ZnO, PPC can be caused by the variation of the charge states of V_o as suggested by calculations, in contrast with those of polycrystalline [15] and porous [16] ZnO.

In the present study, PPC related to irradiation-induced defects in 30 MeV electron-irradiated bulk ZnO single crystals is studied for excitation above and below the band gap. Two TSC peaks, appeared after electron-irradiation, are also reported. Possible candidates of these traps are discussed.

The ZnO single crystals [1] used in the present study were grown at Tokyo Denpa Co., Ltd. using the hydrothermal method. The dimensions of the c face cut-samples used here was $5 \times 5 \times 0.5$ mm^3, which showed a resistivity of 10^3–10^4 Ω cm. A 30 MeV electron irradiation was performed at room temperature with a beam current 18 μA/cm^2 using an electron linear accelerator facility at Kyoto University Research Institute. The irradiation dose was 7.8×10^{17} e$^-$/cm^2. The relativistic mass of an electron with an energy of 30 MeV is ∼20 times larger than that with 1 MeV. Furthermore, for the sample with 30 MeV irradiation, the maximum energy transferred to the target atoms is estimated

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to be ∼450 times larger than that for 1 MeV irradiation [17]. The resistivity after irradiation showed an order of 10^5 Ω cm. In photoluminescence (PL) taken at 20 K using a He–Cd laser, the intensity of green emission from electron-irradiated ZnO wafers was three times larger than those of unirradiated samples, suggesting the artificial introduction of V_o as an origin of the green emission [6]. Al and Au alloy electrodes for PPC and TSC measurements were fabricated on the four corners of samples 5 × 5 mm^2 in area. The bias voltage for PPC measurements was 5 V except for that (10 V) at room temperature. In the TSC measurements using a Van der Pauw technique, a bias voltage of 20 V was also applied to the electrodes, the same in the cases of ZnO [13] and GaN [18]. For the PPC measurements, samples were cooled down to the desired temperature and illuminated for 20 min with an ultra-violet-emitting diode (a peak wavelength of λ = 365 nm with a full width at half maximum (FWHM) of 10 nm at 300 K) for the excitation above the energy band gap. The measurements for excitation below the band gap were also performed in comparison with the illumination above the energy gap, using blue (λ = 475 nm, FWHM = 25 nm), green (520 nm, 35 nm), and red (645 nm, 18 nm) light emitting diodes. For TSC measurements, samples were cooled down to 85 K and initialized by illumination for 20 min with a blue light emitting diode (LED).

Fig. 1 shows the PPC taken at 90 K for the illumination with various LEDs. The photocurrent for the excitation above the energy band gap using an ultra-violet LED increases more in comparison with those below the band gap, showing the effective excitation from the valence band to the conduction band. Furthermore, for the excitation below the band gap the photocurrent using the blue LED is larger than those using other LEDs. This suggests the presence of photo-responsible defects for the blue band region located at around 2.5 eV from the valence band. To clarify the artificially introduced defects, we concentrate on the PPC phenomena using the blue LED. Fig. 2 shows the PPC spectra for the excitation with blue LED taken at various temperatures. The decay kinetics of PPC seen here follow stretched exponential functions as described in previous works [19],

$$I_{PPC}(t) = I_{PPC}(0)\exp[-(t/\tau)^{\gamma}], \quad (\gamma < 1), \tag{1}$$

where $I_{PPC}(0)$ is the factor defined as the PPC buildup level at the moment of light excitation being removed, τ is the PPC decay time constant, and γ is the decay exponent. The solid curves in Fig. 2 are the least squares fit of data with Eq. (1). τ and γ values are 2.0×10^6 s and 0.125 at 90 K and 8.70×10^3 s and 0.37 at 300 K. The temperature dependence of τ for PPC in the higher temperature region can be described by [19],

$$\tau \propto \exp(E_t/kT) \tag{2}$$

where E_t is the potential barrier between the metastable and the stable states of the electron-induced defects. The data in the higher temperature region give a value of ∼165 meV for the capture barrier (E_t) as shown in an inset in Fig. 2.

To confirm the origin of the PPC phenomena observed here, we measured the electron paramagnetic resonance (EPR) after illumination with the blue LED for 10 min at 77 K. Results are shown in Fig. 3. EPR signals with $g_{\|} = 1.996$ for $\mathbf{B} \parallel c$ axis and $g_{\perp} = 1.998$ for $\mathbf{B} \perp c$ axis are observed in electron irradiated samples as reported by many researchers [20–22]. These signals have been assigned to the oxygen vacancy of + charge state (V_o^+). The $g_{\|} = 1.996$ signal observed after the blue light illumination disappears after successive illumination with a red LED and appears again with the blue light illumination. These results suggest that the 2+ charge state (V_o^{2+}) is artificially produced by the electron-irradiation, and transfers to the metastable V_o^+ with its unpaired electron with the blue light illumination, as proposed by Van de Walle [22,23]. The red light illumination to the V_o^+ state causes electron transitions

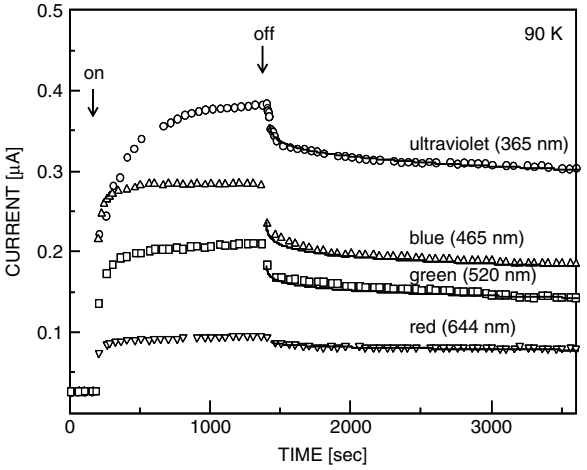

Fig. 1. Persistent photoconductivity (PPC) taken using LEDs with various wavelengths in an electron irradiated single crystal ZnO.

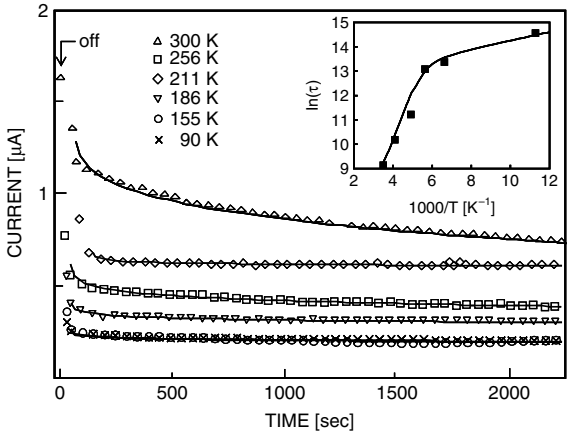

Fig. 2. PPC decay obtained at five representative temperatures in an electron irradiated single crystal ZnO. The solid curves are the least squares fit of data by the stretched-exponential function of Eq. (1). The inset shows the Arrhenius plot of the PPC decay time constant τ ($\ln\tau$ vs. $1/T$).

either from the valence band to the V_o^+ state, namely a transition to the 0 charge state (V_o^0) due to electron capture, or from the V_o^+ state to the conduction band, namely a transition to the 2+ charge state (V_o^{2+}) due to electron removal. On the other hand, an EPR signal with $g_{\|}$-value = 2.005 ± 0.003 for $\mathbf{B} \parallel c$ axis appears after illumination with the blue LED as reported previously [24] and disappears for the $\mathbf{B} \perp c$ axis. This g-value is close to an unknown defect with $g_{\|} = 2.003$ observed by optical detection of electron paramagnetic resonance (ODEPR) experiments [25]. One possible origin of $g_{\|} = 2.003$ was attributed to the defect, which may exist only near the sample surface [25].

According to their calculations [7,23], the oxygen vacancy is a "negative-U" center, implying that $\varepsilon(2+/+)$ for the V_o^{2+} state lies above $\varepsilon(+/0)$ for the V_o^+ state in the band gap. Once generated, V_o^+ does not immediately decay into the 2+ or 0 charge state because of energetic barriers. Also the 0 charge state, $\varepsilon(2+/0)$, lies at about 2.7 eV above the valence band, namely 500–600 meV above the + charge state. Therefore, the oxygen vacancy must be considered as the origin of the PPC observed here. In other word, once the electron is trapped in the V_o^{2+}, the oxygen vacancy is in the + charge state and will still repel electrons by analogy with the PPC in GaN [26], causing the PPC. The capture barrier of ∼165 meV estimated in the present study may be associated with the thermal activation from the + charge state to the 0 charge state rather than that to the 2+ charge state, because according