Efficient Auger Charge-Transfer Processes in ZnO

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Photoluminescence and magneto-optical measurements are performed on a line peaking at 3.354 eV (labeled as NBX) in electron-irradiated ZnO. Even though the energy position of the NBX line is close to that for bound excitons in ZnO, it has distinctively different magneto-optical properties. Photoelectron paramagnetic resonance measurements reveal a connection and a charge-transfer process involving NBX and Fe and Al centers. The experimental results are explained within a model which assumes that the NBX is a neutral donor bound exciton at a defect center located near a Fe impurity and an Auger-type charge-transfer process occurs between NBX and Fe^{3+} . While the NBX dissociates, its hole is captured by an excited state of Fe^{3+} and the released energy is transferred to the NBX electron, which is excited to the conduction band and subsequently trapped by a substitutional Al_{Zn} shallow donor.

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I. INTRODUCTION

Carrier recombination processes are among the most important ones in semiconductor physics as well as of technological relevance, as they largely determine the performance of minority-carrier devices such as light-emitting diodes and solar cells. Of particular significance are trapping and recombination involving defect levels, since they can affect electrical and optical properties of a material in a fundamental way. Defect-mediated recombination processes can be described by the Shockley-Read-Hall (SRH) model [1,2], which states that free electrons and holes can be captured by a defect state within the band gap and subsequently recombine. Here, various physical mechanisms for carrier capture by defects are considered including optical, multiphonon, and cascade processes, etc. [3] Carrier recombination processes can also be mediated by an excitonic Auger process via a defect [4–7]. In this case, the energy released due to the nonradiative Auger capture and recombination of a free electron-hole pair is transferred to a third particle (electron or hole) which is then excited to a higher-energy state. The involved Auger particle can be either free or bound to the defect center involved in the nonradiative recombination [4,5,8–10]. Beyond the aforementioned carrier recombination processes mediated by one defect, intercenter charge transfer involving more than one defect center has also been shown to be important and sometimes even dominant in carrier trapping and

recombination [8–11]. For instance, an efficient intercenter electron transfer, facilitated by the extended electron wave functions, could occur from a shallow donor [8] or a pseudodonor [11] to a deep-level defect in silicon and play a dominant role in carrier recombination.

Understanding defect-related recombination processes is particularly important for the technologically relevant material ZnO. ZnO has a wide and direct band gap of 3.3 eV and a large exciton binding energy. It is also nontoxic, sustainable, and cheap and can be readily synthesized with high quality as bulk crystals and thin films and in various nanostructured morphologies [12–17]. All these attributes make ZnO a very promising material for a wide range of applications including light-emitting diodes and lasers [18,19], gas sensors [20], solar cells [21], and photodetectors [22] and as transparent conductive oxide in displays [23,24]. In addition to that, ZnO is much more resistant to radiation damage than other common semiconductor materials, such as Si, GaAs, CdS, and even GaN. Therefore, it is currently considered among the key electronic materials for space applications [25]. However, all of the aforementioned applications require a good understanding and precise control of the optical and electrical properties of ZnO, which are known to be strongly affected by intrinsic defects and impurities. A very effective tool to create intrinsic defects and associated complex defects in semiconductor materials in a controlled manner is electron irradiation. It is successfully used to study and identify defects in Si, GaAs, and ZnO, to name just a few but very important material systems [26–28]. It becomes indispensable when considering space applications of semiconductor devices, as the created defects may also interact with residual impurities further modifying electronic properties of the active material. In this work, by studying

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electron-irradiated ZnO, we demonstrate that intercenter charge transfer can be surprisingly efficient despite much smaller Bohr radii of free carriers and free excitons than those in silicon, using comprehensive photoluminescence (PL), magneto-optical, and electron paramagnetic resonance (EPR) measurements. We further identify the dominant physical mechanism for the observed charge-transfer process as the Auger capture of a hole from a bound exciton of one defect center by another deep-level defect. This represents unambiguous proof of such an efficient bound-excitonic Auger capture process between two defect centers in a semiconductor.

II. EXPERIMENTAL DETAILS

The samples used are nominally undoped melt-grown and monocrystalline ZnO wafers from Cermet Inc. with an electron concentration of $1 \times 10^{17} \text{ cm}^{-3}$ at room temperature (RT). They are subjected to electron irradiation at RT with an energy of 1.2 MeV and a fluence $\Phi = (4-5) \times 10^{17} \text{ cm}^{-2}$ [29]. The dominant residual impurities determined by secondary ion mass spectrometry (SIMS) measurements are found to be Al, Fe, and Si with atomic concentrations of approximately 3.5×10^{16} , 5.3×10^{16} , and $(2-3) \times 10^{17} \text{ cm}^{-3}$, respectively. No other impurities are found within the SIMS detection limit of $5 \times 10^{15} \text{ cm}^{-3}$ with the possible exception of H, which could be present with a concentration below its detection limit of $5 \times 10^{17} \text{ cm}^{-3}$. The PL and magneto-PL measurements are performed at 4 K in a split-coil superconducting magneto-optical system allowing variations of both temperature (2–300 K) and an applied magnetic field (0–10 T). Continuous-wave PL is excited by a solid-state laser with a frequency-doubled output at 266 nm and detected by a photomultiplier tube combined with a 0.8 m double-grating monochromator. The magneto-PL measurements are performed in the Faraday configuration (with an applied magnetic field $\mathbf{B}$ parallel to the c axis of the crystal and also parallel to the wave vector $\mathbf{k}$ of the detected light) and in the Voigt configuration ($\mathbf{B} \perp c$ and $\mathbf{k} \parallel c$). Additionally, the angles between $\mathbf{B}$ and the c axis are varied from 0 to 90° within the (11-20) plane at the fixed magnetic field of 8 T. EPR measurements are carried out within the temperature range of 4.2–77 K at a microwave frequency of 9.4 GHz. For photo-EPR studies, several diode lasers and a wavelength-tunable pulsed Ti:sapphire laser with a repetition rate of 76 MHz are used to provide illumination at specific wavelengths. The light intensity is kept constant over the whole wavelength range. To ensure the same initial conditions, the samples are each time cooled down in the dark from RT prior to 5-min light illumination.

III. RESULTS AND DISCUSSION

Typical 4 K PL spectra of the as-grown reference (the dashed line) and electron-irradiated (the solid line) ZnO

FIG. 1. PL spectra of the as-grown (the dashed line) and electron-irradiated (the solid line) ZnO samples measured at 4 K.

are shown in Fig. 1. As commonly seen in high-quality single-crystalline ZnO, the low-temperature PL emission is governed by excitonic transitions within the near-band-edge spectral range. The dominant transitions in the as-grown reference sample, labeled as the I_9 , I_7 , I_6 , I^* , I_4 , and I_{6B} lines following the notations from Meyer *et al.* [30] and Chen, Chen, and Buyanova [31], arise from neutral donor bound excitons (D^0X) (the I_6 – I_9 lines) and excitons bound to an isoelectronic center (the I^* line). Upon electron irradiation, the overall PL intensity in the excitonic spectral range is quenched. This quenching is most severe for the I_4 line, which was previously assigned to hydrogen substituting for oxygen, H_O [30]. This indicates that the H atoms are removed from the oxygen lattice site and out-diffuse from the crystal, which is not surprising as the used irradiation energy exceeds the threshold to affect the oxygen sublattice ($E_{\text{irr}} > 0.6 \text{ MeV}$). In addition, a new line labeled as NBX peaking at 3.354 eV emerges on the low-energy side of the spectrum.

Properties of the NBX transition are evaluated using magneto-optical measurements. The energy positions of the corresponding Zeeman components, determined from magneto-PL measurements, are plotted as a fan diagram in Fig. 2. To compensate for a diamagnetic shift of the NBX transition, the data are depicted with respect to the energy corresponding to the center of gravity of the Zeeman-split components. The NBX center is most likely a neutral donor bound exciton, judging from detailed information on the analysis of the magneto-PL data described in Supplemental Material [32]. An analysis of the Zeeman splittings is performed using the following spin-Hamiltonian relevant to a neutral donor exciton:

$$\mathcal{H} = \mu_B \mathbf{B} g_h \mathbf{S}_h - \mu_B \mathbf{B} g_e \mathbf{S}_e. \quad (1)$$

Here, S_e and S_h are the effective spins of the electron and hole, respectively, forming the NBX, which are equal to $1/2$ in the present case, i.e., $S_e = 1/2$ and $S_h = 1/2$. The electron and hole g tensors are given by $\mathbf{g}_e$ and $\mathbf{g}_h$, respectively.

FIG. 2. Zeeman splitting of the NBX PL line depicted as a function of the magnetic field in the Faraday (a) and Voigt configurations (c). (b) Angular dependence of the NBX PL line measured at 8 T with the magnetic field rotated from the c axis towards $\mathbf{B} \perp \mathbf{c}$. The energy positions are plotted with respect to the center of gravity of the Zeeman split components. The experimental data are depicted by the open symbols, while the solid lines are fitting curves by the effective spin Hamiltonian given by Eq. (1).

The solid lines in Fig. 2 represent the best fit of the spin Hamiltonian (1) to the experimental data. The electron g tensor is found to be isotropic and, therefore, is reduced to a scalar $g_e = 2.00 \pm 0.04$. The hole g tensor, on the other hand, has an axial symmetry along the crystallographic c axis with the principle hole g values of $g_h^{\parallel} = -1.44 \pm 0.04$ and $|g_h^{\perp}| = 0.74 \pm 0.04$. We note that the deduced hole g factors are significantly different from the values reported for bound exciton transitions in ZnO that involve effective mass holes from the A - or B -valence bands [30,31,33–35]. For all of the above mentioned excitons, $g_h^{\perp}$ is close to zero, in agreement with the $g_h^{\perp}$ values of the A - and B -valence bands of ZnO [30], while in our case $g_h^{\perp}$ is significantly higher (approximately 0.7). Also, the known deeply bound excitons (the so-called Y lines) [36], as well as excitons bound to isoelectronic centers [31,37], show different g values.

In order to further understand the origin of the NBX center, we perform photo-EPR experiments, since this technique was in the past successfully used to complement PL experiments and to unveil the chemical identity of the involved defect species [38]. The effects of the electron irradiation on the EPR spectra are reported elsewhere [23]. Figure 3 displays the EPR overview spectra of the 1.2 MeV electron-irradiated ZnO sample with $B \parallel c$ under optical excitation with different energies. The spectra contain several sets of the EPR signals, and the spin Hamiltonian

$$\mathcal{H} = \mu_B \mathbf{B} g \mathbf{S} + \mathbf{S} \mathbf{A} \mathbf{I} + \mathbf{S} \mathbf{D} \mathbf{S} \quad (2)$$

FIG. 3. EPR spectra of the electron-irradiated ZnO measured at 20 K under different light excitation energies. (a) Overview spectrum. (b) Spectra showing the central magnetic field range in more detail. (c) Simulated spectra of the central Fe^{3+} line.

is employed for their analysis. Here $\mathbf{S}$ is the effective electron spin, $\mathbf{I}$ the nuclear spin, $\mathbf{B}$ an external magnetic field, and μ_B the Bohr magneton. The first term describes the Zeeman interaction with the electron g tensor $\mathbf{g}$. The second term describes the hyperfine interaction with the hyperfine tensor $\mathbf{A}$. The third term is related to the fine structure splitting for $S > 1/2$ with the fine structure tensor $\mathbf{D}$. The obtained spin-Hamiltonian parameters of the monitored EPR signals are summarized in Table I. The first EPR signal consists of six equidistant lines with equal intensity, implying a resolved hyperfine interaction with a nucleus with $I = 5/2$, centered around $g = 2.0016$, that can be attributed to a Mn^{2+} ion substituting for Zn [39]. The second EPR signal consists of five lines with different intensities centered at $g = 2.006$. The central line has the highest intensity and shows, in addition, two satellites, implying a resolved hyperfine interaction with a nucleus with $I = 1/2$. The intensity ratio between the central line and the satellites is given by the isotope ratio (98% with $I = 0$ and 2% with $I = 1/2$). Together with the anisotropy of the signal (not shown here), it can be unambiguously concluded to stem from a Fe^{3+} ion located on a zinc site [40]. The third EPR signal consists also of six equidistant lines and can be assigned to the $(\text{Al}_{\text{Zn}}-\text{V}_{\text{Zn}})^0$ center [23]. The last EPR signal [see Fig. 3(b)] contains only one line with $g \sim 1.957$ and can be attributed to Al_{Zn}^0 [23,41].

Let us now discuss the dependence of the photo-EPR signal intensity on the light excitation energy ($h\nu_{\text{exc}}$) in the range of the excitonic transitions. The Mn^{2+} and the $(\text{Al}_{\text{Zn}}-\text{V}_{\text{Zn}})^0$ signals are found to be independent of the excitation energy ($h\nu_{\text{exc}}$) within this spectral range—see Fig. 3(b). The Fe^{3+} and the Al_{Zn}^0 signal intensities, on the other hand, exhibit a dramatic enhancement when $h\nu_{\text{exc}}$ is tuned in resonance with the NBX energy (3.354 eV). This

TABLE I. Summary of the spin-Hamiltonian parameters of the defects and impurities monitored by EPR in this work. The axial components of the electron $\mathbf{g}$ tensor are denoted as $g_{\perp}$ and $g_{\parallel}$, while the components for the nonaxial centers are given by g_x , g_y , and g_z . For the nonaxial centers, φ is the angle between the z and c axes. The hyperfine interaction tensor $\mathbf{A}$ and the fine structure parameter $\mathbf{D}$ are given in megahertz. The parallel and perpendicular directions are given with respect to the c axis.

Center	S	I	g_x ($g_{\perp}$) g_y	g_z ($g_{\parallel}$)	$ A $	D	φ (deg)
$(\text{Al}_{\text{Zn}}\text{-V}_{\text{Zn}})^0$	1/2	5/2	2.0243 2.0143	2.0045	26.1		22
Fe^{3+}	5/2	1/2	2.0060	2.0060	27	-1780	
Al_{Zn}^0	1/2	5/2	1.9563	1.9577	2.010		
Mn^{2+}	5/2	5/2	2.0016	2.0016	227.8	-650.2	

is more obvious from Fig. 4, which depicts the intensities of the Fe^{3+} and the Al_{Zn}^0 EPR signals as a function of $h\nu_{\text{exc}}$. Such an enhancement is not observed when the excitation energy is resonant with the energies of other bound excitons in ZnO. This behavior clearly indicates that the NBX excitation leads to the recharging of Fe^{3+} and the Al_{Zn}^0 centers. As the NBX energy is well below the band-gap energy of ZnO, the observation cannot be explained by an indirect process via thermal dissociation of the NBX into a free electron and a free hole that are then separately captured by the Al_{Zn}^+ and Fe^{2+} . We also note that the NBX cannot be directly bound to Al_{Zn}^0 , as its associated D^0X (I_6) is well known [30,41]. Neither can it be bound to the same isolated Fe_{Zn} center that gives rise to the Fe^{3+} EPR signal, since the Zeeman pattern of Fe^{3+} and the NBX center are distinctly different [42,43]. Heitz, Hoffmann, and Broser [42] first reported g values of $g_{\parallel} = 1.83$ and $g_{\perp} = 0.27$ for the lowest excited state of Fe^{3+} [$^4T_1(G)$]. Recently, Azamat *et al.* [43] performed detailed experiments on the transitions from the $^4T_1(G)$ state to the $^6A_1(S)$ ground state. It was found that, due to spin-orbit interaction, the $^4T_1(G)$ state splits into four sublevels, and Azamat *et al.* could observe three transitions from the $^4T_1(G)$ excited state to the $^6A_1(S)$ ground state with the effective g values of 1.4, 2, and 1 for the three zero-phonon lines (ZPLs) monitored [43]. Since the NBX line can be observed only after electron irradiation, the NBX must be bound to an irradiation-induced defect. Furthermore, from our studies performed with variable irradiation energies, the defect is formed only when the energy is above a threshold of around 0.8 MeV. This threshold is required to displace a Zn atom [23,44] but will also affect the O sublattice. Thus, the NBX formation involves a defect in either the Zn or O sublattice.

With the above information from the EPR and magneto-optical experiments, we can conclude that the recharging of Fe^{3+} and the Al_{Zn}^0 centers through the NBX excitation must therefore be associated with a charge-transfer process from the NBX to these other defect centers; i.e., the process involves three different defect centers. Since an enhancement of the Al_{Zn}^0 EPR signal can correspond only to a

charge transition of Al_{Zn} from Al_{Zn}^+ to the paramagnetic Al_{Zn}^0 , the electron and hole of the NBX are transferred to Al_{Zn}^+ and the Fe^{2+} , respectively, leading to the Al_{Zn}^0 and the Fe^{3+} detected in EPR. Considering the limited extent of defect wave functions in ZnO, the NBX center should be close to one or both of the Al_{Zn} and the Fe to facilitate such a charge transfer. As the concentrations of the three defects are rather low, it is very unlikely that all three defects are situated in close proximity. In the case of only one of the Al_{Zn} and the Fe located near the NBX center, a charge transfer to the remote third defect could be mediated by the capture of an Auger electron (or hole) that is released to the conduction (or valence) band during the Auger-type capture of the hole (or electron) from the NBX by the nearby defect. We argue that the NBX is bound to a defect in close proximity to Fe, based on the following reasons. First, the electron transfer from the NBX to the Al_{Zn} with a shallow 0/+ charge transition level close to the conduction band is very unlikely, and, even if it occurs, it is not expected to release sufficient energy to excite the remaining hole of the NBX to the valence band. Second, the strongly anisotropic g value of the NBX hole (with a large deviation from 2 and also from the g values for an effective-mass hole) is more consistent with the assumption that the NBX wave function overlaps with the Fe center to such an extent that the strong spin-orbit interaction acting on the Fe^{3+} state also affects the NBX. The recharging of the Fe center from the Fe^{2+} to the Fe^{3+} state upon the NBX excitation, which is accompanied by the recharging of the Al donor to the neutral charge state, can be explained by the intercenter bound-exciton Auger process illustrated in Fig. 4(b). In this model, the NBX hole is captured by the Fe^{3+} center, likely via one of the excited states that subsequently relaxes to its ground state and becomes EPR active:

This leads to the observed increase of the Fe^{3+} EPR signal intensity under light illumination with $h\nu_{\text{exc}}$ resonant with the NBX line. The energy gained during the hole capture is transferred to the NBX electron, which is excited to the conduction band and is subsequently trapped by

FIG. 4. (a) Photo-EPR spectra depicting the normalized intensity of the Al_{Zn}⁰ and the Fe³⁺ EPR signals as a function of the light excitation energy. The experimental data are depicted by the open symbols, while the solid lines act as a guide to the eye. The energy positions of the relevant excitons [NBX, I₉, I₆, I₀, and the free exciton (FX)] are marked by the dashed vertical lines. (b) Illustration of the Auger-type charge-transfer process involving the NBX center, Fe center, and the Al_{Zn} shallow donor.

Al_{Zn}⁺. Ionized shallow donors in semiconductors, such as Al_{Zn}⁺ in ZnO, are well known to have the largest capture cross section among various types of defects in capturing conduction electrons:

This explains the increase of the Al_{Zn}⁰ EPR signal intensity under light excitation with the energy resonant with the NBX.

The observed Auger-type charge transfer is rather efficient, since approximately 15% of all available diamagnetic Fe²⁺ centers (determined by SIMS and quantitative EPR [23]) can be recharged into their paramagnetic Fe³⁺ charge state. This is rather remarkable considering the small Bohr radius even for free holes ($r_h < 1$ nm) in ZnO [30,45,46] given by

$$r_h = \frac{\epsilon/\epsilon_0}{m_h^*/m_0} a_B \quad (5)$$

with the known values of the hydrogen Bohr radius a_B , the effective mass of the hole m_h^* , and the dielectric constant ϵ found in the literature [30]. This implies close proximity between the NBX defect and the Fe center. It also suggests that the hole of the NBX exciton is not very tightly bound to

the potential of a donor where electrons are primary bound particles [47], to assure the efficient energy transfer. The wave function overlap of these two centers can also account for the NBX hole g value, revealed from the performed magneto-optical studies. It is interesting to note that the highly efficient Auger-type charge-transfer processes involving excitons and transition-metal impurities, such as Fe or Cu with unfilled 3d shells, were also reported in ZnS, ZnSe, and GaP [37,48]. This suggests that such intercenter excitonic Auger-type capture and recombination via transition-metal impurities is common in semiconductors, which may be partly responsible for the high efficiency of these impurities in carrier recombination processes in addition to the conventional single-center carrier recombination described by the SRH model. The generation of free electrons (or free holes) during the Auger processes also implies that the same Auger process could also affect the carrier concentration and, thus, the electrical conductivity.

IV. CONCLUSION

In conclusion, we reveal an efficient intercenter charge-transfer process involving impurity and defect centers in electron-irradiated ZnO bulk crystals, based on comprehensive photo-EPR studies complemented by magneto-PL measurements. The photo-EPR experiments unambiguously identify that this process involves an irradiation-induced defect together with the residual Fe impurity and leads to the recharging of the Fe²⁺ center to the Fe³⁺ state. It is suggested that this occurs via the bound-exciton Auger-type charge-transfer process in which the hole of the NBX exciton, which is bound to the irradiation-induced NBX defect, is captured by the Fe²⁺ and the released energy is transferred to the NBX electron. The latter is promoted to the conduction band and may subsequently be trapped efficiently by the Al_{Zn} shallow donor. Considering that Fe and other transition metals are common contaminants in ZnO, intercenter charge-transfer processes of this kind may represent an important shunt path for carrier recombination and even electrical conductivity in this material.

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