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Charge transfer dynamics in Cu-doped ZnO nanowires

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Time resolved photoluminescence (TRPL) and transient absorption (TA) spectroscopy reveal an ultrafast charge transfer (CT) process, with an electron localization time constant 39 ± 9 ps, between the ZnO host and the Cu dopants in Cu-doped ZnO nanowires. This CT process effectively competes with the ZnO band edge emission, resulting in the quenching of the ZnO UV emission. TRPL measurements show that the UV decay dynamics coincides with the buildup of the Cu-related green emission. TA measurements probing the state-filling of the band edge and defect states provide further support to the CT model where the bleaching dynamics concur with the TRPL lifetimes. © 2011 American Institute of Physics. [doi:10.1063/1.3558912]

Significant advances in nanofabrication techniques have afforded excellent controls over the growth of dislocation free, highly faceted, single crystal ZnO nanowires (NWs).¹ These NWs exhibit remarkable optical and electrical properties that are highly attractive for potential applications, such as nanoscale optoelectronic devices, transistors, sensors energy conversion devices, etc.^{1–3} Doping transition metal (TM) ions in ZnO can significantly alter the host's physical, electrical, chemical, and optical properties, e.g., observations of room-temperature ferromagnetism in Cu-doped ZnO (CuZnO).⁴ Both theoretical and experimental investigations have also shown that Cu can be used as a *p*-type dopant into the naturally *n*-type ZnO.^{5,6}

TM doping in semiconductors usually results in the quenching of the host's band edge emission and the activation of the dopant's luminescent transitions.⁷ These processes are typically associated with an energy or charge transfer (CT) process from the host to the dopant as well as the opening up of additional nonradiative (NR) defect related relaxation channels.^{8,9} In the case of CuZnO, the substitution of Cu at the Zn sites (i.e., Cu_{Zn} acceptor) gives rise to a green luminescence (GL) band (peaking at ~ 2.48 eV) with a characteristic phonon-related fine structure and the zero phonon line (ZPL) at 2.86 eV at low temperature.¹⁰ A recent review by Reshchikov *et al.*¹¹ aptly summarizes the extensive efforts to date about the Cu-related GL band in ZnO. While there are general consensus that the Cu_{Zn} transitions are of the CT type where the hole is transferred from a highly shielded *d* shell of the Cu atom to a level highly perturbed by the surrounding oxygen atoms,¹⁰ direct experimental evidence of the CT process and the CT rate between the ZnO host and the Cu subsystem has not been reported. Based on Dahan's model of intermediately bound excitons for Cu-doped ZnO, we hypothesized that following above band gap photoexcitation in samples with the Fermi level below the ground state of Cu_{Zn}, electron capture by the neutral Cu_{Zn} acceptor [i.e., Cu²⁺(*d*⁹)] occurs and the hole is captured by the potential created by this tenth electron to form the [Cu⁺(*d*⁹+*e*),*h*] state; which eventually returns back to the Cu²⁺(*d*⁹) state upon GL emission.^{7,11,12} Investigating the dynamics of this

CT mechanism is the main objective of this paper. Through femtosecond time-resolved spectroscopy [i.e. time-resolved photoluminescence (TRPL) and transient absorption (TA)], we found clear evidence of the CT between the ZnO host and the Cu dopants in CuZnO NWs with an electron localization time constant of 39 ± 9 ps.

Samples of well-aligned undoped ZnO and CuZnO NWs were synthesized using a chemical vapor transport method on a double-side polished sapphire substrate. The experimental setup was described in previous reports.^{13,14} Homogenous Cu doping was achieved and the doping concentration determined through x-ray photoelectron spectroscopy (XPS) was ~ 1 at. % for the low-doping (L-CuZnO) and ~ 2 at. % high-doping (H-CuZnO) samples, respectively. From XPS, the Cu_{Zn} dopants were also found to exist in the Cu²⁺(*d*⁹) configuration. Figure 1(a) shows a representative scanning electron microscopy (SEM) image of the NWs (i.e., ~ 50 – 100 nm in diameter and 1 – 2 μm in length). Figure 1(c) shows the high resolution transmission electron microscopy image of a single NW grown along the [001] direction. The corresponding selected area electron diffraction (SAED) pattern confirmed the wurtzite ZnO phase of the NW samples with no detectable secondary phases, consistent with our high resolution x-ray diffraction data (see Ref. 15).

FIG. 1. (Color online) (a) SEM image showing the cross-sectional view of vertically grown H-CuZnO NWs on a sapphire (110) substrate. (b) Low- and (c) high-magnification TEM images of an individual H-CuZnO NW. Inset of (b) shows the corresponding SAED pattern.

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FIG. 2. (Color online) (a) TIPL spectra of undoped ZnO, L-CuZnO, and H-CuZnO NWs samples at 10 K under 325 nm excitation. (b) Band edge PL decay dynamics of ZnO, L-CuZnO, and H-CuZnO NWs at 10 K. (c) PL decay of the band edge and Cu-related SGL emission from the H-ZnCuO sample at 10 K. Solid lines are fits to the data. Dashed line shows the system temporal response. Temperature dependent plot of the band edge (UV) decay time and the rise time of the SGL band. TA decay profiles of the undoped ZnO and H-ZnCuO sample with 325 nm pump/500 nm probe pulses at 10 K. Solid lines are fits to the data.

Femtosecond laser pulses (~ 150 fs) generated from an optical parametric amplifier (OPA) pumped by a 1 kHz regenerative amplifier was used as the excitation source. The fluence was kept to a minimal of $\sim 80 \pm 10$ nJ/cm² per pulse to avoid any multiphoton effects and photodamage to the NW samples. Low temperature time integrated photoluminescence (TIPL) and TRPL measurements were performed in a conventional backscattering geometry. The PL signals were time-resolved using a streak camera system. For TA experiments, UV pump pulses from an OPA were focused onto a 200 μ m spot and overlapped with white-light continuum probe pulses where the pump-induced changes were detected using a lock-in amplifier.^{15,16}

Figure 2(a) shows the low temperature (10 K) TIPL spectra of the undoped ZnO, L-CuZnO, and H-CuZnO NW samples following 325 nm excitation. In the undoped ZnO NWs, the excitonic band edge emission (i.e., from free/bound excitons) dominates. The undoped ZnO NWs also exhibit a weak GL band. The origins of this GL band in undoped ZnO has been the subject of a long standing controversy, where it has been attributed to originate from trace Cu impurities¹⁰ and/or from donor-acceptor pair recombination (i.e., involving Cu⁺ ions or oxygen/zinc vacancies).^{17,18} In the Cu-doped samples, the structured green luminescence (SGL) band was clearly visible and the fine structure can be ascribed to the LO phonon replicas with an energy spacing of ~ 72 meV.¹¹ This SGL band originates from a radiative transition from the excited state to the ground state of Cu_{Zn}, i.e., $[\text{Cu}^+(d^9 + e), h] \rightarrow [\text{Cu}^{2+}(d^9)] + h\nu$, where the excited state of Cu_{Zn} is visualized as hole bound to a d^{10} shell or as an intermediately bound exciton to a neutral d^9 configuration.¹² The delocalization of the wave function of the tenth electron in Cu_{Zn} arises from the hybridization of

the Cu d states with the Zn $4s$ states at bottom of the conduction band. The hole is localized by the potential formed by this electron.¹² TRPL measurements of the GL band (at the peak ~ 2.48 eV) at 10 K allow us to distinguish the origins of the GL band where undoped ZnO NWs sample has a lifetime $\tau_{\text{defect}} = 0.50 \pm 0.02$ ns while that of the H-CuZnO is $\tau_{\text{Cu}} = 0.35 \pm 0.01$ μ s (see Ref. 15). The GL band from the undoped ZnO NWs is likely to be dominated by contributions from the defect states (e.g., oxygen and zinc vacancies).¹⁸

With increased Cu doping, the SGL band is enhanced while the excitonic band edge emission is quenched in the CuZnO samples. Indeed, TRPL of the ZnO band edge emission at 10 K shown in Fig. 2(b) confirms that the PL lifetimes shorten (from a mean lifetime of $\tau_{\text{PL}} = 175 \pm 8$ ps in the undoped samples) with increasing Cu doping: consistent with a picture of increased CT between the ZnO host and the Cu dopants. In the L-CuZnO samples, two decay lifetimes were obtained from the fits [i.e., $\tau_1 = 45 \pm 5$ (amplitude $A_1 \sim 77\%$); $\tau_2 = 176 \pm 8$ ps ($A_2 \sim 23\%$)], with the shorter τ_1 originating from the recombination of the e-h pairs from the hybridized s - d states (i.e., from the mixing of the Cu d states with the Zn s states of the ZnO conduction band) and the longer τ_2 from the usual free/bound excitons. In the H-CuZnO samples, the longer τ_2 has been quenched and this is attributed to the opening of additional NR (defect-related) relaxation pathways associated with the higher Cu doping; while only $\tau_1 = 38 \pm 5$ ps remains. Figure 2(c) shows the TRPL dynamics for the ZnO band edge emission (~ 3.35 eV) and the SGL peak (~ 2.48 eV) that were obtained within the same streak camera image for the H-CuZnO NWs. The decay of the band edge emission is followed consecutively by the buildup of the SGL emission. Fits to the decay and the growth dynamics with the system response deconvolved, yield a decay lifetime $\tau_{\text{decay}} = 38 \pm 5$ ps and a rise time $\tau_{\text{rise}} = 38 \pm 4$ ps, respectively. Figure 2(d) shows the band edge decay lifetime and the SGL rise time as a function of temperature. These lifetimes were found to correspond well with one another (at specific temperatures); indicating that this CT pathway between the ZnO and the Cu dopants exhibits weak temperature dependence.

As a further test of the CT model, TA measurements were conducted at 10 K to investigate the carrier dynamics in the undoped ZnO and CuZnO samples. Probing at a wavelength of 500 nm (at the peak of the GL band and below the ZPL of 2.86 eV) will allow us to interrogate the carrier populations at the conduction band edge (i.e., electrons) and the defect states (e.g., zinc vacancies—i.e., holes). The phonon replica in CuZnO does not constitute a real state unlike the defect states and hence should not contribute to the transient dynamics. Depopulation of the band edge electrons will manifest as a recovery (i.e., decay) of the photobleaching (PB) signals to the equilibrium while the hole occupancy of the long-lived traps (or defect states) will result in a prolonged PB lifetime in the differential transmittance (DT) signals. Depopulation of the band edge carriers could arise from a few possibilities: radiative or NR recombination; multiphonon emission; or the opening of additional NR pathways (e.g., the fast trapping of the carriers at the defect/surface states or CT from the host to the dopants).

Figure 2(e) shows the TA measurements (i.e., 325 nm pump/500 nm probe for the undoped ZnO NWs and the

FIG. 3. (Color online) A schematic of the phenomenological model and the relaxation pathways in undoped ZnO (a) and CuZnO (b) samples.

H-CuZnO samples. The undoped ZnO NWs exhibit a rapid increase in transmittance (i.e., PB) where the band edge states are rapidly filled as the photoexcited electrons relax to the conduction band edge (i.e., <1 ps). Subsequently, as the carriers at the band edge are trapped at the defects/surface states or undergo radiative recombination, there is reduced transmittance (or an increase in absorption) in the DT signals with an average lifetime $\tau_{\text{bleach}} = 190 \pm 8$ ps. For the H-CuZnO samples, there is a lifetime shortening to $\tau'_{\text{bleach}} = 32 \pm 4$ ps. The prolonged PB lifetime in undoped ZnO, which is absent in H-CuZnO indicates that the CT process competes with the carrier (i.e., electron/hole) trapping. Similar DT dynamics were also obtained from the L-CuZnO samples, which lends further support to the CT picture. Details of the TA studies of ZnO NWs will be discussed in another publication.

From the phenomenological model presented in Fig. 3(a), following photoexcitation with 325 nm pulses, free electrons and holes are created high up in the valence and conduction bands, respectively, which rapidly relaxes to the band edge within 1 ps via acoustical phonon emission. The hot carriers subsequently thermalize through electron-phonon scattering. In the undoped ZnO NWs, these carriers could either undergo radiative recombination or be trapped at the defect states with a mean lifetime of $\tau_{\text{PL}} = 175 \pm 8$ ps. The trapped carriers eventually recombine with a radiative lifetime $\tau_{\text{defect}} = 0.50 \pm 0.02$ ns. At 10 K, where phonon emission is suppressed, the band edge PL recombination rate can be expressed as $(1/\tau_{\text{PL}}) = (1/\tau_{\text{R}}) + (1/\tau_{\text{NR}})$ where τ_{R} and τ_{NR} refers to the radiative and NR defect-related components. The timescale of $\tau_{\text{bleach}} = 190 \pm 8$ ps is consistent with the depopulation of the band edge state through radiative recombination.

In the CuZnO samples [Fig. 3(b)], the substitution of Zn atoms with Cu atoms (i.e., Cu_{Zn}) give rise to an additional CT pathway to the Cu as well as increased contributions from the NR pathways (in the form of defects arising from the substitution). The band edge PL rate can be expressed as: $(1/\tau_{\text{PL}}) = (1/\tau_{\text{R}}) + (1/\tau_{\text{NR}}) + (1/\tau_{\text{CT}})$, where $1/\tau_{\text{CT}}$ is the CT rate to the Cu system. With increased contributions from the latter two terms, the band edge emission is quenched. Due to the hybridization of the d states with the s states at the bottom of the conduction band, the neutral Cu_{Zn} acceptor, with an increased electron capture cross-section, takes in an elec-

tron from the conduction band edge (following photoexcitation), and the hole is captured by the potential created by this tenth electron, forming the $[\text{Cu}^+(d^9+e), h]$ excited state.¹² Alternatively, this Cu_{Zn} excited state could also be formed with the capture of an exciton. The fast electron transfer to the $\text{Cu}^{2+}(d^9)$ state is evident from the rapid decay of the DT signals (i.e., $\tau'_{\text{bleach}} = 32 \pm 4$ ps); which is interpreted as a depletion of the band edge electron population due to CT to the Cu dopants. The CT rate can be estimated from the following $(1/\tau'_{\text{bleach}}) = (1/\tau_{\text{bleach}}) + (1/\tau_{\text{CT}})$; where $\tau_{\text{CT}} \approx 39 \pm 9$ ps. This transfer time closely matches the lifetimes of the band edge PL decay (i.e., $\tau_{\text{decay}} = 38 \pm 5$ ps) and the corresponding growth kinetics of the Cu-related emission (i.e., $\tau_{\text{rise}} = 38 \pm 4$ ps); indicating that the electron transfer between the ZnO host and Cu dopants occur within 39 ± 9 ps. In this intermediately bound exciton picture (i.e., $[\text{Cu}^+(d^9+e), h]$) for hexagonal wurzite-type lattices, the excitons eventually undergo radiative relaxation back to the $\text{Cu}^{2+}(d^9)$ state, yielding the SGL band (with $\tau_{\text{Cu}} = 0.35 \pm 0.01$ μs).¹⁰

In conclusion, our findings shed further light on the CT dynamics in the Cu-doped ZnO system.

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