DEFECTS IN ZINC OXIDE NANOWIRES: A STUDY OF
THE CHARGE TRAPPING DYNAMICS AND
MECHANISMS

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Defects in Zinc Oxide Nanowires: A Study of the Charge Trapping Dynamics and Mechanisms

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The key to the design and optimization of novel nanoscale semiconductor devices for optoelectronic applications is through a deep understanding of how to control or tailor the charge carrier dynamics. Such control could be achieved by means of hybrid nanostructures fabrication, doping, and even through defects engineering. Hence, investigations into the role of defects on the charge carrier dynamics (i.e., relaxation, trapping, recombination, and separation) occurring in the femtoseconds to picoseconds timescale in semiconductors has attracted considerable attention in the recent years.

In this thesis, ultrafast spectroscopy techniques, such as time resolved photoluminescence (TRPL), transient absorption spectroscopy (TAS), z-scan technique were performed on unintentionally-doped (un-doped) as-grown and post-fabrication thermally annealed ZnO nanowires (NWs) as well as the intentionally Cu-doped ZnO NWs. These NW samples were synthesized by the vapor transport method. The origin of the green emission (GE), recombination mechanism, and the charge-trapping dynamics to the GE-centers, Cu ions, as well as various chemisorbed species were investigated.

Our results revealed that the GE in un-doped ZnO NWs involves the transitions of the electrons in the conduction band and/or shallow (delocalized) donor levels with holes trapped at the GE-centers (i.e. \(V_{ZnO}\) di-vacancies) that are located at 0.88 eV above the valence band maximum. Importantly, an ultrafast excitonic Auger-type hole-trapping process to the GE-centers occurring in a sub-ps timescale was also uncovered by TAS – shedding new light on the mechanism behind the fast and efficient charge trapping of photoexcited carriers.
In addition, it was found that mechanisms of charge trapping and the PL transients from the GE band in the un-doped and Cu-doped ZnO NWs are significantly different even though the spectral shape and positions are nearly identical. In the former, ultrafast hole trapping in the sub-ps timescale occurs in the un-doped ZnO while the charge trapping time from the ZnO host to the Cu dopant in the latter occurs within 38 ps.

Lastly, it was uncovered that the surface hole or electron traps have strong influence on the charge carrier dynamics in ZnO NWs. It was found that photoexcited holes were captured by surface chemisorbed \( \text{O}_2^- \) within a few hundred ps in the air-annealed samples; and photoexcited holes are trapped by \( V_{\text{O}}^{2+} \) occurring within tens of ps in the H\(_2\)-annealed ZnO NWs. These fast carrier trapping processes introduced by annealing effectively compete with the ZnO band-edge emission (BE) dynamics and provide efficient photo-excited charge separations in ZnO NWs.

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Journal publications:


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CHAPTER 1

Introduction

1.1 Background

Over the past few decades, there has been tremendous progress in the research field of ultrafast carrier dynamics in semiconductors. The driving force behind this is the endless need for faster response and efficient processing of information. The knowledge of how to control the charge carrier dynamics that include the charge carrier trapping, separation, and recombination occurring in the femtosecond to picosecond and even the nanosecond timescales, is essential for designing, tailoring and optimizing the novel semiconductor devices.\(^1\)

Particularly, one-dimensional (1-D) systems (such as nanowires (NWs), nanorods) have received considerable attention in recent years due to their unique thermal, chemical, electric, mechanical and/or optical properties.\(^2,3\) They are regarded as promising “building blocks” for the novel functional devices on a nanometer scale, such as nanoscale transistors, sensors and optoelectronic devices. Potential applications based on optoelectronic properties of 1-D semiconductor nanomaterials include the areas of optoelectronics, photovoltaics, photocatalysis, photonics, and photodetectors, etc.\(^2,3\) Among many factors, the photoexcited carrier dynamic processes in the sub-picosecond to nanosecond timescales play a critical role in the performance of the above applications.\(^1,4\) However, even though these sophisticated devices have already been produced, the charge
carrier dynamics have not been fully established and many fundamental questions remain open to a large extent.

1.2 Defects in Semiconductors

In 1-D semiconductors, the intrinsic or exintrinsic defects could be easily formed in the bulk or on the surfaces during the material growth.\(^2,3\) In general, the types of defects in semiconductor include: vacancy (\textit{i.e.}, a vacancy after missing an atom A as denoted by \(V_A\)), interstitial (\textit{i.e.}, interstitial site is occupied by an atom A as denoted by \(I_A\)), antisite (\textit{i.e.}, a host atom B is replaced by another host atom A), Frenkel pair (\textit{i.e.}, a \(V_A-I_A\) complex), Schottky pair (\textit{i.e.}, a complex of a cation vacancy plus an anion vacancy), and extrinsic defects (\textit{i.e.}, defects involving foreign atoms). The type and concentrations of defects in semiconductor are highly dependent on the growth conditions and post-fabrication treatments. Except for the abovementioned defects in the material, due to the large surface-to-volume ratio of 1-D semiconductors, there are also large amount of chemisorptions on the surfaces.\(^5\) For example, on the surfaces of semiconductor nanostructures, oxidizing adsorbates such as molecular oxygen in the ambient usually captures the electrons by forming negative ions (\textit{e.g.}, \(O_2^-\)), which can result in a depletion layer near surface. In contrast, on the surface of p-type semiconductor, extra electrons could be accommodated by capturing the electron from the reducing adsorbates such as \(H_2\) leaving behind the positive ions (\textit{e.g.}, \(H^+\)), that result in an accumulation layer near the surface.

The optoelectronic properties of semiconductor nanostructures are extremely sensitive to these abovementioned defects. For the influence of defects on the charge
carrier dynamics, the intrinsic defects, and extrinsic defects, as well as the surface adsorbed species, offering alternative relaxation pathways for the de-excitation of photo-excited carriers, will affect the optical properties and also play an important role in the carrier dynamics of the 1-D nanostructures. It is therefore imperative that we gain a clear understanding of their origins, their effect on the carrier dynamics and their relaxation mechanisms. The knowledge gained would allow us to devise appropriate fabrication and processing methods to engineer the defects for practical optoelectronic applications.

1.3 Motivation for Research

Zinc oxide (ZnO), a wide-bandgap semiconductor ($E_g = 3.37$ eV at 298 K), is one of the most important functional materials today due to its diverse morphology, physio-chemical properties, and wide applications. Potential applications for ZnO nanomaterials (e.g., thin films, NWs, nanorods) include areas of optoelectronics, photovoltaics, photocatalysis, photonics, and photodetectors etc.

Compared to thin films, 1-D ZnO nanostructures (i.e., NWs, nanords) have a larger surface area to volume ratio. In particular, the surfaces of nanomaterials play a critical role in the performance of nanodevices where chemical reactions, carrier separation etc occur at the dielectric/inorganic semiconductor interface. For example recent studies have shown the superiority of nanorods/nanowires-based devices over thin films in the application of photodetection and photovoltaics, photocatalyst and the surface defects in semiconductor nanostructures play a crucial role in enhancing the performance of nanoscale devices. For instance, both the photocatalysis efficiencies and the solar energy conversion efficiency in photovoltaic performance depend strongly on the fast
charge separation/migration and suppression of recombination of photogenerated electrons and holes at surface or interface.\textsuperscript{17-19} Furthermore, enhanced photocatalytic activity was reported in ZnO NWs with high green emission (GE) intensities though its exact enhancement mechanism remains unclear.\textsuperscript{20-22} Moreover, the charge carrier trapping process by surface states, such as the negatively charged adsorbed oxygen ions served as hole-acceptors after photoexcitation, significantly affects the transport, photoconduction properties and photoresponse of ZnO NW based UV photodetectors.\textsuperscript{23} The dynamics and the mechanism of carrier-trapping to the intrinsic and extrinsic defects in ZnO NWs have rarely been investigated in depth. It was also reported that that hybrid ZnO NW arrays/GaN thin film based LEDs exhibit higher efficiencies compared to ZnO thin film based devices due to the possibility of waveguided emission that improved the extraction efficiency.\textsuperscript{24}

In view of the above research findings, ZnO NWs are selected as the research objects instead of other ZnO nanostructures in this thesis and it is clear that a deeper understanding of the origins of the defects, their influence on the material’s optoelectronic properties and carrier dynamics in the material is key to optimizing the device properties to realize fast response, high sensitivity UV detectors, high efficiency solar cells, photocatalysts and hybrid LEDs. Detailed insights into many fundamental questions such as the carrier recombination, trapping/separation are urgently needed.

### 1.4 Objectives of the Work

Ultrafast optical spectroscopy (UOS) techniques are powerful techniques for studying the carrier dynamics in semiconductors.\textsuperscript{1, 17} In recent years, UOS using the
femtosecond laser pulses with a temporal resolution of hundreds of femtoseconds or better is one of the main techniques to investigate charge carrier dynamics in nanomaterials. Time-resolved photoluminescence (TRPL) spectroscopy and transient absorption spectroscopy (TAS) have now been most widely used to investigate the charge carrier dynamics in semiconductor nanostructures.

The main objective of the work is to elucidate the dynamics and the mechanisms of the ultrafast charge trapping in ZnO NWs using various UOS techniques. Specifically, the work explores the following three areas:

1. To investigate the origin(s) of GE and the GE-centers related carrier dynamics in ZnO NWs through a systematic study involving un-doped, air-annealed and H$_2$-annealed ZnO NWs.
2. To investigate the charge transfer dynamics to Cu dopant from the ZnO host in Cu-doped ZnO NWs and establish the mechanisms of GE in un-doped and Cu-doped ZnO NWs.
3. To investigate the effects of other intrinsic defects and chemisorbed species on the charge carrier dynamics in ZnO NWs through a systematic study involving post annealing samples in oxidizing or reducing atmosphere, and laser illumination in vacuum.

1.5 Organization of the Thesis

In this thesis, the investigation of the role of defects on the charge carrier dynamics in 1-D semiconductors, including as-grown, air-annealed, H$_2$-annealed ZnO nanowires, Cu-doped ZnO nanowires are carried out. Various ultrafast optical
spectroscopy techniques have been performed on samples, such as TRPL, z-scan, TAS techniques.

The thesis is organized as follows. The first chapter describes the background, motivation, and objectives of this thesis. In addition, the type of defects, the role of defects on the performance of functional semiconductor nanostructures is briefly introduced.

Chapter 2 introduces the general optical properties of ZnO nanostructures, and the proposed origins and recombination models for the commonly observed green mission. The basic ultrafast carrier dynamic processes from generation till returning to the equilibrium state in semiconductor were also presented.

Chapter 3 presents a detailed description of the ultrafast laser system in our lab, how to generate the femtosecond pulse, the fundamental principles and experimental setups of ultrafast optical spectroscopy techniques and other characterization techniques used in this study.

In chapter 4, comprehensive UOS studies on the origin of the GE and the charge-trapping dynamics in as-grown, air-annealed and H2-annealed un-doped ZnO NWs fabricated by the vapor-phase transport method are presented. The results of time integrated photoluminescence (TIPL), TRPL at room temperate and low temperate, z-scan measurements, probe wavelength dependence and pump power dependence of transient transmissions of three nanowires are discussed. The results of this chapter are mainly adapted from my published paper in Physical Review B.25

Chapter 5 provides the investigation of the difference in GE-related charge carrier dynamics in intentionally Cu-doped and un-doped ZnO NWs. By using temperature
dependent TRPL, the carrier trapping processes and GE recombination mechanisms in these two kinds of samples are presented.

In chapter 6, the effects of surface hole/electron traps on the charge carrier dynamics in ZnO NWs are investigated. From the TRPL and X-ray photoelectron spectroscopy (XPS) results of as-grown, air-annealed and H₂-annealed un-doped ZnO NWs, the charge carrier trapping time from ZnO host to surface adsorbates or intrinsic defects in different samples are derived. The main content of this chapter is from my published paper in Physical Chemistry Chemical Physics.²⁶

Finally, a summary of the main conclusions and recommendations for the further research are described in Chapter 7.
CHAPTER 2

Properties of ZnO and Review of Charge Carrier Dynamics in Semiconductors

2.1 Background of ZnO

Zinc oxide (ZnO), a wide-bandgap semiconductor ($E_g = 3.37$ eV at 298 K), is one of the most important functional materials today due to its diverse morphology, physical/chemical properties. Recent studies have shown that the defects in ZnO play a crucial role in enhancing the performance of photovoltaic and photocatalytic devices. For example, enhanced photocatalytic activity was reported in ZnO nanostructures with high green emission (GE) intensities though its exact enhancement mechanism remains unclear. Hence, a deep understanding of the origin of the defects related emission and the role of defects on the charge carrier trapping/separation (following photo-excitation) is key to optimizing the performance of ZnO-based nanoscale devices.

2.1.1 Optical properties of ZnO nanostructures

Typically, ZnO nanostructures exhibit a bandedge emission (BE) in the near-UV and a defect-related emission occurring in the visible region due to the different kinds of defects in the materials. The wide range of visible emissions in ZnO nanostructures is due to the different kinds of defects depending on the fabrication method/conditions. According the theoretical calculations in the previous literatures, these defects give rise to
various energy levels located within the bandgap of ZnO as summarized in Fig. 2.1 below. Hence, ZnO can exhibit different emission bands in the visible range due to the presence of these intrinsic defects.

![Figure 2.1](image)

**Figure 2.1** A schematic of the calculated energy levels (eV) corresponding to conduction band of different intrinsic defects in ZnO from the results of different literatures. The candidate of the green emission proposed in this thesis is V\textsubscript{ZnO} divacancy as marked with green color.

According to the previous reports, ZnO nanostructures prepared by low-temperature wet-chemical methods typically yield a green to yellow emission (peaking from 520 – 650 nm) – attributed to the deep sub-surface defects (e.g., oxygen vacancy, Li doping or zinc interstitial),\textsuperscript{28-31} since there is no obvious influence on the defects related emission by the surface coated surfactant as shown in Fig. 2.2(a). On the other hand, a broad GE band centered around 500 – 515 nm (over a narrower range of wavelengths) is commonly observed in ZnO nanostructures prepared by the high-temperature vapor-phase transport (VPT) method\textsuperscript{32-34} [see Fig 2.2 (a) and (b) as an example] – attributed to the on/near surface defects\textsuperscript{34-37} according to the strong reduction of the GE intensity after the surfactant coating as shown in Fig. 2.2(a).
Figure 2.2 Representative previous reports in order to show the defects related emission by different methods. ZnO nanostructures prepared by (a) wet chemical and (b) VPT methods. Figures are adopted from Ref\textsuperscript{28} and Ref\textsuperscript{34}. 
2.1.2 Review of the Proposed Origins of Green Emission

Despite the extensive studies on the GE in ZnO, there is still no consensus on its origin. Proposed origins include: (a) extrinsic Cu impurities and (b) intrinsic defects like oxygen vacancy (V\textsubscript{O}),\cite{39, 40} zinc vacancy (V\textsubscript{Zn}),\cite{41} oxygen antisite (O\textsubscript{Zn}),\cite{42} Zn interstitial (Zn\textsubscript{i})\cite{43, 44} or their complexes.\cite{34, 45} Amongst the abovementioned intrinsic point defects, both V\textsubscript{O} and V\textsubscript{Zn} are commonly believed to be the source of the GE in ZnO. For V\textsubscript{O}, it was proposed that the GE originate from the recombination of electrons in the singly ionized oxygen vacancy (V\textsubscript{O}\textsuperscript{+}) with the photoexcited holes in the VB.\cite{39} Nevertheless, anti-correlations between the occurrence of the GE and the electron paramagnetic resonance (EPR) signals from V\textsubscript{O} in ZnO tetrapods\cite{34} and also that between the occurrence of the GE and the concentration of V\textsubscript{O} from XPS measurements\cite{26} in our H\textsubscript{2}-annealed ZnO NWs suggest otherwise. Recently, it was suggested that V\textsubscript{O}\textsuperscript{+} give rise to the red emission of ~1.89 eV according to EPR measurements.\cite{46} Next, V\textsubscript{Zn} was also proposed as a likely source of the GE given that V\textsubscript{Zn} has a calculated transition level of ~0.9 eV above the valence band maximum (VBM).\cite{41} However, recent EPR and optically detected magnetic resonance (ODMR) revealed that the isolated V\textsubscript{Zn} defect in bulk single crystals had a red emission of ~1.6 eV with a large Stokes shift of ~0.8 eV.\cite{47} Furthermore, it was also reported that isolated V\textsubscript{Zn} from ZnO thin films exhibit a red emission with a lifetime of ~1–4 ns;\cite{48} thereby casting further doubts on V\textsubscript{Zn} as a contender for GE. Apart from point defects, defect-complexes were also proposed as one of the candidates for GE. Recent density functional calculations considered V\textsubscript{O}\textsuperscript{+}V\textsubscript{Zn} di-vacancies (V\textsubscript{ZnO}) (i.e., missing a Zn-O dimer) as a possible origin of the GE.\cite{45} It was calculated that the \( \varepsilon(q/q+1) \) charge transition of V\textsubscript{ZnO} is located at about 2.2–2.5 eV below the conduction
band minimum (CBM) and possesses a small lattice relaxation energy in the range of 70–120 meV. The $V_{\text{ZnO}}$ origin of the GE is further supported by another DFT study, which had also calculated the $\varepsilon(+/0)$ transition level of $V_{\text{ZnO}}$ to be located at ~ 0.6 – 0.8 eV above the valence band maximum (VBM)\textsuperscript{49} – the electron transition from the CB to $V_{\text{ZnO}}$ would result in the GE (~ 2.5 eV). Furthermore, $V_{\text{ZnO}}$ is also predicted to be the predominant defect type on the nonpolar (10\,\overline{1}0) surface of ZnO instead of $V_{\text{O}}$.\textsuperscript{50} As the GE is believed to originate from the surface defects,\textsuperscript{34–36} $V_{\text{ZnO}}$ could therefore be a prime suspect.

![Figure 2.3](image)

**Figure 2.3** Two proposed recombination models for green emission: (a) photoexcited electrons trapped in the deep donors recombine with the holes in the valence band or shallow acceptors and (b) photoexcited electrons in the conduction band or shallow donors recombine with the holes trapped in the deep acceptors.

Furthermore, the recombination mechanism of the visible emission in ZnO has also been subjected to extensive studies. From the literature, different recombination models for the GE in ZnO have been proposed. For example, one model involved the transitions of the electrons from the deep levels to the valence band or shallow acceptors; while the other involved the transitions of electrons from conduction band and/or shallow donors to the deep levels introduced by deep donors or deep acceptors as shown.
in Fig. 2.3. The detailed investigation of the origin of GE and the recombination models will be presented in Chapter 3.

2.2 Review of the Charge Carrier Dynamics Semiconductors

Before going into the discussion on the charge carrier dynamics in ZnO NWs, I would like to briefly review the basic carrier dynamical processes in semiconductors. When a semiconductor is excited with an ultrashort optical pulse, the electrons and holes can undergo several stages of dynamical processes in the spatial and temporal domains before returning to their equilibrium states. We can broadly categorize these carrier dynamic processes into the following five regimes: (1) carrier generation, (2) thermalization, (3) carrier removal, (4) carrier diffusion and (5) structural effects. Figure 2.4 shows the timescales for various processes in different regimes in the range from femtosecond to microseconds. As we can see, some dynamic processes do not occur sequentially and occurs simultaneously. There is also no clear boundary between regimes. For instance, the carriers are thermalized by carrier-carrier scattering at the same time as the energy is transferred to lattice phonons by carrier-phonon scattering.
2.2.1 Carrier Generation

Figure 2.5 illustrates schematically the charge carriers generation and relaxation processes occurred in a photoexcited direct band-gap semiconductor. The photon energy which is larger than the band-gap energy can excite the electrons in the valence band to the conduction band via the one-photon absorption [see the left of Fig. 2.5(a)]. Thus, under the excitation fluence \( I \) \((i.e., \) energy per unit area\), the maximum free carriers density will be

\[
N = \frac{(1-R)I\alpha}{h\omega}
\]  

(2.1)

where \( \alpha \) is the absorption coefficient, \( R \) is the reflectivity, \( h\omega \) is the photon energy of incident light.

In the case of an indirect band-gap semiconductor, one-photon absorption is occurred through the phonon absorption to conserve momentum. If the value of photon energy is less than the band-gap energy, the charge carriers can also be excited by the
multiphoton absorption [see the right of Fig. 2.5(a)], which is a nonlinear process in contrast with the one-photon absorption process.

After excitation, the phase coherence between the electromagnetic field of the ultrashort optical pulse and the photoexcited carriers is lost because of the scattering mechanisms, such as carrier-carrier scattering and carrier-phonon scattering. The photoexcited carriers are then free after this dephasing. The free carriers can absorb the photon energy and transit to the higher energy levels, however the density of free carriers is not changed. In contrast, if the carriers are excited very high above the bandgap, such energetic charge carriers can lose their energy by creating additional excited carriers, which is called impact ionization [see Fig. 2.5 (c)].

**Figure 2.5** Illustration of some carrier dynamic processes occurred in the regimes of a direct band-gap semiconductor. VB the valence band and CB is the conduction band. **a**, one-photon absorption (left), multiphoton absorption (right). **b**, free-carrier absorption. **c**, Impact ionization. **d**, carrier distribution. **e**, carrier–carrier scattering. **f**, carrier–phonon scattering. **g**, radiative recombination. **h**, defects and surface recombination. **i**, Auger recombination. (Figure adapted from Ref.51)
2.2.2 Thermalization

Carrier-carrier and carrier-phonon scattering cause the redistribution of the charge carriers in the valence and conduction bands. Carrier–carrier scattering [Fig. 2.5(d)] can result in the dephasing in less than 10 femtoseconds via an electrostatic interaction between the two charge carriers. Then after hundreds of femtoseconds, a Fermi–Dirac distribution of carriers is formed, i.e., the carriers can be characterized by a temperature. The term “hot” for carriers refers to the distribution of the electrons or holes with higher temperatures than the one of the lattice. The “hot carriers” can reach the bottom of the band within several picoseconds via carrier-phonon scattering during which the excess energies of the carriers are transferred to the crystal lattice by emitting phonons through carrier-phonon scattering process [see Fig. 2.5(e) and (f)]. Due to the small energy of emitted phonon, many scattering processes are needed before carriers and lattice return to thermal equilibrium.

2.2.3 Carrier Recombination

Compared to the thermal equilibrium in a non-photoexcited semiconductor, there are still excess free carriers after thermalization, which can be removed through radiative or non-radiative recombination, or diffusion of carriers out of the excitation region. In a semiconductor, since the different recombination processes can occur independently, the total (or effective) recombination rate can be simply presented as a sum of the individual recombination rate. The total (or effective) carrier lifetime can then be given by the inverse sum of the reciprocal individual recombination lifetime $\tau_i$ as:
Chapter 2 Properties of ZnO and review of charge carrier dynamics in semiconductors

\[
\frac{1}{\tau_{\text{eff}}} = \sum_i \frac{1}{\tau_i} \quad (2.2)
\]

During the interband radiative recombination, free electrons in the conduction band recombine radiatively with free holes in the valence band by emitting photons. Since, the band-band radiative recombination rate is determined by the free electrons concentrations \(n\) and free holes concentrations \(p\), the net recombination rate \(U_{\text{rad}}\) can be give as:\(^{53}\)

\[
U_{\text{rad}} = B(np - n_i^2) \quad (2.3)
\]

where \(n_i\) is the intrinsic carrier concentration, the coefficient \(B\) represents the quantum-mechanical probability of a radiative transition.

In some semiconductors, the photoexcited charge carriers can be trapped by ionized donors and holes are captured by ionized acceptors, then electrons trapped in the neutral donors will recombine radiatively with the holes trapped in the neutral acceptors, which is known as donor–acceptor pair (DAP) transition. The emitted photon energy in a DAP transition is given by:

\[
h\omega = E_g - E_A - E_D + \frac{e^2}{4\pi\varepsilon_0 R} \quad (2.4)
\]

where \(E_g\) is the band-gap energy, \(E_A\) and \(E_D\) are the acceptor and donor binding energies, respectively, and \(R\) is the distance between the donor and acceptor.\(^{54}\)

The free carriers can also recombine non-radiatively via the band-to-band Auger recombination process, as illustrated in Fig. 2.5. In this model, an electron in the conduction recombines with a hole in the valence band, and the excess energy is transferred to a third free carrier, which can be further excited higher in the conduction band or deeper into the valence band [see Fig. 2.5(i)]. The Auger recombination rate is
either proportional to $np^2$ or to $n^2p$, which is dependent on the third carrier being either a hole in valence band or an electron in conduction band. Therefore, the net Auger recombination rate can be represented as:

$$U_{\text{Auger}} = C_n(n^2p - n_0^2p_0) + C_p(np^2 - n_0p_0^2)$$  \hspace{1cm} (2.5)

where $n$ and $p$ are free electron and hole concentrations, $C_n$ and $C_p$ are the Auger coefficients for the $eeh$ and the $ehh$ processes, respectively. Therefore, Auger recombination is efficient at high carrier densities. Furthermore, the Auger recombination rate increases exponentially as the band-gap is decreased.

The structural defects in the semiconductor (i.e., intrinsic or extrinsic point defects or their complex, stacking faults, dislocations, etc.) or the surface states can generate the defect levels within the forbidden gap, which act as either recombination centers or nonradiative traps. For instance, the free electrons can recombine radiatively or non-radiatively with the holes trapped on the deep levels, which is known as free-to-bound transitions as show in Fig. 2.5 (h). For the radiative capture process, the photon emission via recombination gives rise to characteristic lines in the photoluminescence spectrum which correspond to the different depth of the defects levels. In the non-radiative trapping processes, if the energy levels of defects are close to the conduction (or valence) band, the free carriers can be trapped at shallow levels quickly and they can also return back to the conduction band or valence band due to thermal excitation. For the deep defects levels, the carriers can be captured via multiphonon emission, phonon-assisted cascade capture process or band-trap Auger-like capture process. In the multiphonon emission capturing process, the lattice vibrations cause the vibronic coupling between the free carriers states and the defect energy levels, thus enable the capture of carriers via
dissipating their excess energy in the form of localized phonons. In the cascade capture process as introduced by M. Lax, the free carriers in the band are first trapped by shallow excited states of defect center, and then diffuse down during losing their energies through a series of closely spaced levels by emitting one phonon each step.

Similar to the band-to-band Auger recombination as discussed above, in the band-trap Auger recombination model as discussed by P. T. Landsberg or Haug, when two independent carriers meet at the defect site, one of the carriers is captured into the deeply bound state due to the electron-electron interaction, while the excess energy is transferred to a third carrier which is excited into higher energy level.

### 2.2.4 Carrier diffusion

In contrast to the carrier recombination, the total number of the photoexcited carriers would not be changed by carrier diffusion which only removes carriers from the originally photoexcited region to the other parts of the material on the time scale of picoseconds-to-nanoseconds. The carrier diffusion is affected by the band structure as well as the carrier temperature. For example, carrier confinement due to the bandgap renormalization in a highly excited semiconductor can slow down the diffusion time. The diffusion time can also be shortened when the carrier temperature is increased.

### 2.2.5 Structural effects

After photoexcited carriers and the lattice reach to an equilibrium, the material can be regarded as if it had been heated by the laser beam via the traditional ways. However, this heating effect is achieved on a short time scale of tens to hundred of picoseconds. The
vaporization of material can occur when the lattice temperature is greater than the melting point. The laser pulse only heats a region that is controlled by the absorption depth and the spot size. The surrounding regions of the material remain at room temperature. If the phase of crystal is not changed, the temperature will return back to the ambient value due to thermal diffusion.

2.3 Summary

This chapter reviewed the optical properties of the ZnO and discussed the origins and the proposed models for the green emission which is commonly observed in the ZnO nanostructures. The carrier dynamical processes in semiconductor following photoexcitation are also reviewed. The photoexcited carriers mainly undergo the thermalization via carrier-carrier, carrier-phonon scatterings, and carrier-removal via radiative and nonradiative recombinations. The knowledge of these fundamental carrier dynamic processes in semiconductor will facilitate the following analysis of the carrier dynamics occurred in the ZnO NWs.
3.1 Introduction

In this thesis, carrier dynamics in semiconductors are investigated by several kinds of ultrafast optical spectroscopy (UOS) techniques, such as time-resolved photoluminescence spectroscopy (TRPL), transient absorption (also called pump-probe) measurement, nonlinear transmission (also called z-scan) measurement. In addition, other supplementary experimental measurements, such as scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) will also be performed on samples in order to provide the information of structure, size and chemical states of semiconductors. In this chapter, the femtosecond laser system will be briefly discussed first. Then in the later part, the above-mentioned UOS techniques and the home-built spectroscopy setups for data acquisition will be introduced.

3.2 Synthesis of ZnO Nanowires

3.2.1 Un-intentionally doped ZnO NWs

Vertically aligned ZnO NWs were grown on double side polished c-plane sapphire substrate by the vapor transport method (VPT) as shown schematically in Fig. 3.1. Briefly, a mixture of ZnO powder (99.999%, Aldrich) and graphite powder (99.999%, Aldrich)
with a weight ratio of 1:1 was used as the source. After coating a thin layer (1–2 nm) of Au on the substrate as a catalyst, the substrate was placed in a quartz tube. The temperature was slowly raised and kept at about 850 °C for 15 mins for NW growth. High-purity argon mixed with 5% oxygen with a constant flow rate of 50 sccm was used as the carrying gas. The as-grown sample was then divided into three pieces: one piece was kept without any further treatment – \textit{as-grown}; one piece was annealed in air (at atmospheric pressure) at 600 °C for 30 mins – \textit{air-annealed} and another piece was annealed in forming gas at (90% Ar + 10% H\textsubscript{2}, H\textsubscript{2} pressure: 25 mbar) at 420 °C for 30 mins – \textit{H\textsubscript{2}-annealed}.\textsuperscript{25}

\textbf{Figure 3.1} Schematic illustration of the experimental set-up for the growth of metal oxide nanostructures by vapor transport method.

### 3.2.2 Cu doped ZnO NWs

For Cu-doped ZnO NWs synthesis, a mixture of ZnO (99.99%, Aldrich) and CuO (99.99%, Aldrich) were ground for 30 min, and calcined in air at 500 °C for 16 h. The powder was pressed and then sintered again at 800 °C for 12 h to achieve homogeneous Cu-doped ZnO powder. The mixture of Cu-doped ZnO powder and the graphite power (99.99%, Aldrich) were ground for 30 min before being put into the middle of a quartz tube. Argon mixed with oxygen was used as the carrying gas. The temperature of the
furnace was ramped to the desired 960 °C and cooled down naturally to room temperature after 5 minutes of growth on sapphire substrate. We wish to emphasize that the growth temperature of these ZnO NWs have a strong influence on their emission properties. These un-doped samples in this study were fabricated at a temperature of ~850 °C while those un-doped ZnO NWs used as a control in the earlier charge transfer study of Cu-doped ZnO NWs were fabricated at a temperature of ~960 °C. The latter un-doped ZnO NWs possess a very weak GE band in comparison to the BE.$^{58}$

3.3 Femtosecond Laser System

Ultrashort pulsed laser is the key of the high resolution ultrafast optical spectroscopies. As mentioned in the chapter 2, the carrier dynamic processes upon over-band-gap photoexcitation happened from hundreds femtoseconds to microseconds. In order to investigate the ultrafast carrier dynamics, an ultrashort pulse with duration shorter than the carrier dynamics process itself should be used to perturb the system. At our Femtosecond Dynamics Laboratory or xC-lab (located at the Division of Physics and Applied Physics PAP 01-14, Nanyang Technological University), the femtosecond laser pulse is generated by the laser system comprising the following main commercial instruments as shown in Fig. 3.2:


3. Coherent Legend F – 1 kHz femtosecond Ti: Sapphire Regenerative Amplifier system.
4. TOPAS-C– a two stage optical parametric amplifier (OPA) of white light continuum.

Figure 3.2 shows the schematic of the femtosecond laser systems in the xC-lab. The detail description of the function of these instruments will be shown in the following sub-sections.

![Figure 3.2 Schematic of the femtosecond laser system at the Femtosecond Dynamics Laboratory in NTU.](image)

**3.3.1 Seed laser for regenerative amplifier**

![Figure 3.3 Vitesse Laser Head Schematic as provided by Coherent.](image)
The Vitesse 800 as shown in Fig. 3.3 is a compact diode-pumped solid-state oscillator that seeds the subsequent Coherent Legend Regenerative Amplifier. It operates at a fixed wavelength of 800 nm with pulse width < 100 fs, repetition rate of 80 MHz, and the average power > 750 mW. In Vitesse, there are two laser heads, one is the Verdi laser head, and another one is the Verdi Pumped UltraFast (VPUF) laser head. In Verdi laser head, Nd:YVO₄ (Neodymium: Yttrium Orthovanadate) is the pump laser gain medium, LBO (Lithium Triborate) is used as the second harmonic generator to generate the green light output at 532 nm. The output green light from the Verdi laser is transmitted to VPUF laser head to pump the Ti:Sapphire crystal. Here, Ti:Sapphire crystal is used as gain medium. The cavity formed by the Negative Dispersion Mirrors (NDM) which provide the negative dispersion compensation that is required for the generation of femtosecond pulses. The modelocking is obtained by means of the Kerr-Lens Modelocking (KLM).
For the optical Kerr effect, it is a process due to the nonlinear response of the refractive index to the electromagnetic field of an optical wave. When the intensity of the electric field associated with the light is sufficiently high, the atoms of the material can be distorted and the refractive is altered. The refractive index of the medium can be described as:

\[ n(r) = n_0 + n_2 I(r) \]  

(2.1)

where \( n_0 \) and \( n_2 \) is the linear and second-order refractive indexes respectively, \( n(r) \) is the overall refractive index. \( I(r) \) is the incident light intensity. Due to the fact that the Gaussian distribution of the power density of the laser beam, according to this equation, the refractive index changes across the beam profile. So, the refractive index is larger in the center than at the edge of the beam. Therefore, the Kerr medium works like a lens for the laser which is called Kerr lens. Such lens is only formed upon the arrival of a modelocked pulse, which narrow the modelocked pulses. The slit in the modelocking device in Vitesse allow only narrow beams to pass. The Kerr lens is formed only when the

\[ n_0(2) = n_0 + n_2 I_0 \]

where \( n_0(2) \) is the overall refractive index.
sufficiently high power is created. Therefore, a starter is used to trigger the initiation of modelocking by introducing the extremely high peak powers via changing the cavity length. The pulse will become narrowed, amplified and dominant pulse, and can pass unattenuated through the slit. The modelocked output is then obtained to serve as the seed for the Legend regenerative amplifier.

Figure 3.6 Kerr-lens modelocking principle [Adapted from Wikipedia60].

3.3.2 Pump laser for regenerative amplifier

The Evolution-15 is used as the pump of the Legend regenerative amplifier. Nd:YLF (neodymium-doped yttrium lithium fluoride) is used as the gain medium. LBO is used as the second harmonic generator to generate the green light output at 527 nm. The specifications of output of the Evolution laser in our lab are 1 kHz repetition rate, the average power of 12.0W, the energy per pulse of 12.0 mJ, the wavelength of 527 nm, 300 ns pulse width.
3.3.3 Legend Ti:Sapphire regenerative amplifier

The peak energy of the femtosecond laser from the Vitesse is insufficient for use in the most of the measurement of ultrafast spectroscopies. Thus the ultrashort laser pulse is amplified in the Coherent Legend Ti:Sapphire regenerative amplifier system by the technique of chirped pulse amplification (CPA). In the CPA technique, the modelocked ultrashort laser pulse from the seed laser undergoes stretching in the pulse stretcher, then followed by the recompression to obtain the initial pulse duration after the pulse compressor as shown in the schematic Fig. 3.6. During the process of amplification, the stretcher introduces large dispersion to produce a long, chirp optical pulse, whereas the compressor operates on the same principle but with opposite in sign in the dispersion. The purpose of stretching the pulse is to reduce the intensity of the ultrashort pulse in order to make sure the energy is lower than the damage threshold of the Ti:Sapphire crystal. A relatively large (~$10^5$) stretching ratios can be achieved based on diffraction grating.

![Figure 3.6 Schematic of chirped pulse amplification](image-url)
Finally, a pulse-train at a wavelength of 800 nm with the pulse duration of ~150fs, the pulse energy of ~1mJ, and a tunable repetition rate up to 1 kHz is obtained from Legend regenerative amplifier.\textsuperscript{62} The part of the output is used as input for TOPAS-C, and other part is used as probe light in the pump-probe measurement.

### 3.3.4 TOPAS-C optical parametric amplifier

TOPAS-C optical parametric amplifier is used to tune the wavelength (or photon energy) of the femtosecond laser emitted from the Legend. The beam at 800 nm wavelength from Legend is used as the input for TOPAS-C, which is split into three parts. One small fraction of beam (about 1-3 $\mu$J) is focused into a sapphire plate to produce a white-light continuum (WLC). This WLC and the other small fraction of beam are collimated into a non-linear crystal for the pre-amplification where parametric amplification takes place. The amplified signal beam will be easily separated due to the non-collinear overlap geometry. This amplified signal is amplified again in a second amplification stage where the last larger fraction of the initial input pump beam and signal beams are collimated collinearly in the second nonlinear crystal. At last, the signal and idler output will be used as input for the mixers of TOPAS-C to tune the wavelength of output laser beam. TOPAS-C optical parametric amplifier can therefore provide a wide range of wavelength of short pulses ranged from 236 - 2600 nm.\textsuperscript{63} It should also be noted that the average power of output of TOPAS-C was wavelength and pump-power dependent. The pulse width of output beam is almost same as the input beam and the repetition rate is the same as the pump laser (1 kHz).
3.4 Time-Resolved Photoluminescence Spectroscopy

Figure 3.7 A schematic of the operating principle of the streak camera.

The recombination dynamics of photoexcited carriers in a sample can be probed by monitoring the time evolution of its photoluminescence. The repetition rate of pulse laser used to excite sample from TOPAS is 1 kHz with a time interval between two pulses of 1 ms. Therefore, it should be noted that the longest lifetime that can be measured at this 1kHz repetition rate is 1 ms. If the emission lifetime is longer than 1 ms, the photoexcited carriers will not fully relaxed between consecutive pulses. For samples with emission lifetimes longer than 1 ms (e.g. phosphorescent samples), it is possible to reduce the repetition rate of the regenerative amplifier with the SDGII signal delay generator (e.g. to 250 Hz or even 100 Hz). The PL signals from samples are collected in a conventional backscattering geometry and detected by a charge-coupled device array (Princeton Instruments, Pixis 400B) coupled to a monochromator (Acton, Spectra Pro 2500i). The temporal evolution of PL was resolved by an Optronis Optoscope streak camera system triggered at 1 kHz. The ultimate temporal resolution of streak camera is around ~10 ps when operated at the shortest time window of 330 ps. Figure 3.7 shows the schematic operating principle of the streak camera. The incident light in the streak camera is formed into a slit image on the photocathode. Then the electrons converted from the incident light
on photocathode pass through a pair of the accelerating electrodes. A high voltage is applied to the sweep electrodes. Electrons arrived at different times will enter the MCP (micro-channel plate) at different positions. After passing through the MCP, the multiplied electrons will impact against the phosphor screen and are converted into photons which can be detected by CCD. The intensity, and the time and space of the incident light can be read from the brightness and position of the phosphor screen respectively. A typical setup for the measurement of time-resolved photoluminescence spectroscopy (TRPL) is shown in the Fig. 3.8.

![Figure 3.8 Schematic of TRPL setup in the XC-lab.](image-url)
3.5 Transient Absorption Spectroscopy

Pump-probe spectroscopy is one of the most common types of UOS techniques. Various pump-probe techniques have been developed. Here, I briefly introduce the experiment of transient absorption spectroscopy (TAS) used in our lab. Transient absorption or more commonly known as optical pump-optical probe spectroscopy is sensitive to the sum of electron and hole occupation of specific regions in the energy bands and can therefore be used to probe the charge carrier populations involved in both the radiative and non-radiative transitions occurred in the femtosecond timescale.

3.5.1 Principle of the pump-probe method

![Figure 3.9](image)

**Figure 3.9** (a) Schematic of the pump-probe technique; (b) A schematic energy level diagram to show the PB, PIA and SE processes.

In this technique, an ultrashort laser pulse is split into two portions; a relatively strong pump beam is used for sample excitation to generating a non-equilibrium state, as shown in Fig. 3.9 (a). A relatively weaker probe pulse which is delayed through a delay line subsequently measures the pump-induced changes in the optical constants of the sample. Measuring the transient changes in the transmission or reflectivity as a function of
time delay between the pump and probe pulses will yield the relaxation dynamics of carriers in the sample. By changing the wavelength of pump or probe light, the carrier population dynamics in different energy levels of interest in the sample can be monitored. Generally, there are three kinds of processes to contribute to the pump-probe signals: pump-induced absorption (PIA), photo-bleaching (PB), and stimulated emission (SE) as shown in Fig. 3.9 (b). Photo-bleaching is the phenomena of the decrease of the absorption of transmitted probe light which induce the positive differential transmission signal. One of the reasons to induce the PB is the state-filling of the excited state due to the occupation by the photo-excited carriers. On the other hand, the depletion of the carriers in the ground state can also result in the PB of the probe light. SE can also contribute the positive differential transmission signal which is due to the increase of the intensity of transmitted probe light. PIA occurs when the probe light is capable of further exciting the photo-excited carriers to the higher energy states, it contributes the negative signal in the transient transmission spectra due to the increased absorption (i.e., the decreased transmission) of probe light. Therefore it is necessary to distinguish the PB, PIA, SE during the data interpretation to ascertain the origin of the pump-probe signal.

3.5.2 Generation of the white light continuum

The white-light continuum (WLC) probe is generated by focusing a small fraction of the Legend output (800 nm, 1 kHz) on the thin sapphire plate. The WLC is the result of the self-focusing in the media. The repletion rate and polarization of WLC is identical with the input pulse. It should be noted that the intensity of the input pulse should not be very high. Above the threshold (~ 0.5 μJ) for the generation of WLC, there will be
multiple unstable emissions peaks with broad spatial and frequency fluctuations in the WLC as shown in Fig. 3.10 (b). Besides, the transversal mode of the input laser pulse, spot size and position of the sapphire at the focal point will also affect the generation of the stable WLC.

![Figure 3.10](image)

**Figure 3.10** (a) White light continuum spectrum shown from CCD array for the stable and unstable continuum. (b) Variation of the beam spot with increasing input power (top to bottom).

### 3.5.3 Pump-probe setup

In our pump-probe measurement, differential transmission \((\Delta T/T)\) spectra of samples is performed in a non-degenerate pump-probe configuration with chirp-correction, where \(\Delta T/T = (T - T_0)/T_0\) (where \(T_0\) is the transmission of probe beam without pump excitation of the sample, \(T\) is transmission of probe beam with pump excitation of the sample). The pump pulses were focused onto a 200 µm spot and overlapped with white-light continuum probe pulses generated with a thin sapphire plate (that was focused by a
parabolic mirror to a spot of ~20 μm diameter). The direction of the probe pulse is perpendicular to the substrate. Pump-induced changes were monitored using a monochromator/PMT configuration coupled to a lock-in amplifier. The pump beam was chopped at 83 Hz and used as the reference frequency for the lock-in. The system response was determined by the two-photon absorption cross correlation between pump and probe pulses in ZnO for 500 nm. Figure 3.11 shows a schematic and photograph of the white-light pump-probe setup in our xC-lab.
**Figure 3.11** Schematic (top) and photograph (bottom) (the blue line represents the pump beam, the red line stands for the 800 nm probe light, white line is the generated white light) of optical pump-white light probe setup.

### 3.6 Z-scan Technique

“Z-scan” technique was developed by Sheik Bahae et al.\textsuperscript{65,66} in 1990’s to measure the nonlinear optical parameters in materials, such as the refractive index, absorption coefficient. Generally, two types of z-scan techniques have been widely used, one is the “open-aperture” z-scan, and another one is the “close-aperture” z-scan.

From the “open-aperture” z-scan, we can determine the absorption cross-sections of ground state or excited states, which will be used to interpret the observed differential transmission signal (stage filling or pump induced absorption) from pump-probe measurements in this thesis. In the this experiment, the sample is mounted on a linear stage and traversed along a direction parallel to the beam propagation direction (i.e., the z-axis) over the focal length of a lens, where all the transmittance through the sample is collected by a detector by using a focusing lens without any aperture placed in front of it. In our case, an input Gaussian laser beam with pump intensity of 0.2 GW/cm\textsuperscript{2} was focused perpendicularly onto the sample by a convex lens with 30 cm focal length. The beam waist at the focal point was 37 ± 3 µm and this was confirmed using a standard two-photon absorption experiment performed on a 0.5 mm thick ZnSe bulk crystal. As the sample was moved over the focal length along the beam propagation axis, the transmittance of the laser beam through the sample with respect to the focal point (i.e., \(z_0\)) at different z positions were recorded.

The “close aperture” Z-scan is used to obtain the nonlinear refraction of materials, which is not adopted in our experiment. In this technique, an aperture is placed in front of
the detector to make sure only the central region of the laser beam to reach the detector. Figure 3.14 shows the schematics of the “close aperture” and “open aperture” z-scan techniques.

![Figure 3.14 Schematics of (a) “close aperture” z-scan and (b) “open aperture” z-scan techniques.](image)

### 3.7 Other Characterization Techniques

**Scanning Electron Microscope (SEM)**

SEM is a type of electron microscope that takes images of a sample by scanning the surfaces of the sample with a focused electron beam using a raster scanner. The interaction of the accelerated electron beam with the sample generates a variety of signals (e.g., secondary electrons and backscattered electrons) which contain the information of the sample’s morphology and composition. The resolution of SEM can reach to 1 nm. In my experiment, the topographies of the vertically aligned ZnO NWs are imaged by a field emission SEM (JOEL JSM-6700F FESEM) operated at 10 kV.
Transmission Electron Microscope (TEM)

TEM is a microscope where an accelerated and focused electron beam interacts with the electrons in the sample when it passes through an ultra thin sample. The changes of the transmitted electrons after the interaction has relation with density, thickness of the specimen, and therefore an image with dark and bright regions can be generated. The magnified image is then focused onto an imaging device, such as a fluoroscope, or to be detected by a sensor such as a CCD camera. The resolution of TEM can be 0.1~0.2 nm. In my experiment, the surface morphologies of the ZnO NWs were examined using a TEM (JEOL 2100 TEM) operated at 200 kV.

X-ray photoelectron spectroscopy (XPS)

XPS is a surface sensitive technique that measures the chemical state and elemental composition that exist within a few uppermost layers of the material. XPS spectra are obtained by irradiating a material with X-ray beams where the kinetic energy and number of electrons that escape from the material are simultaneously measured. In my experiment, XPS measurements on as-grown, H2-annealed, and air-annealed ZnO NWs were performed using a VG ESCALAB 220i-XL system with a monochromatic Al Ka (1486.6 eV) X-ray source.

3.8 Summary

In this chapter, the operation of the femtosecond laser system, the methodologies and instrumentations of the different types of UOS techniques as well as the morphology,
chemical composition characterization techniques employed in the samples have been briefly introduced. These various UOS techniques which are complementary with each other are performed on samples in order to yield a complete and detailed picture of the charge carrier dynamics in the ZnO NW system.
CHAPTER 4

Origin of Green Emission and Charge Carrier Dynamics in ZnO Nanowires

4.1 Introduction

As discussed in section 2.1.2 in Chapter 2, the origins of the commonly observed green emission (GE) from ZnO nanostructures remain highly controversial despite extensive studies over the past few decades. Furthermore, the dynamics and the mechanism of carrier-trapping to the intrinsic defects have rarely been investigated in depth. Elucidating the origin of the GE in un-intentionally-doped (un-doped) ZnO nanowires (NWs) prepared by the VPT method and its charge trapping dynamics using UOS techniques are the main foci of this chapter. This was performed in a comparative study involving as-grown, air-annealed, and H₂-annealed ZnO samples.

Ultrafast optical spectroscopy (UOS) techniques like femtosecond transient absorption spectroscopy (TAS) and time-resolved photoluminescence (TRPL) are powerful probes of carrier dynamics in semiconductor nanostructures. In the chapter, TAS revealed an ultrafast sub-picoseconds (sub-ps) Auger-type hole-trapping to the GE-centers that permits the fast and efficient charge trapping/separation in these NWs. This could account for the enhanced photocatalytic activity reported in ZnO nanostructures. Our findings therefore have important implications for the development of high efficiency ZnO-based photovoltaic and photocatalytic devices.
4.2 Results and Discussions

4.2.1 SEM & TEM of ZnO NWs

Figure 4.1 (a) SEM image of the as-grown ZnO NWs. Inset shows the top view of the NWs. TEM images and selected-area electron diffraction (SAED) patterns of the (b) as-grown, (c) air-annealed and (d) H$_2$-annealed ZnO NWs.

Figure 4.1 (a) shows a representative scanning electron microscope (SEM) image of the uniformly distributed, vertically aligned as-grown ZnO NWs with diameters ranging from 80–100 nm and lengths of ~1 μm were grown on a sapphire substrate by the
VPT method. The NWs are grown along the [0001] direction and are enclosed by (10\(\overline{1}0\)) facets with a wurtzite structure – consistent with the previous results of ZnO NWs prepared by the same method.\textsuperscript{22, 35} Post-fabrication thermal annealing of the as-grown samples under oxidizing/reducing ambient was used to modulate the concentration of GE-centers. The structural form of the NWs were not severely altered after the post-fabrication annealing [Fig. 4.1 (c) and (d)] though the H\(_2\)-annealed samples were found to have a roughened polycrystalline surface with small ZnO particulates (~2.5 nm in diameter) and some NWs are bundled together after air-annealing. For the H\(_2\)-annealed sample, it is necessary to demonstrate that the crystalline structure inside the NW is largely not affected by the H\(_2\)-annealing. From the enlarged high resolution TEM (HRTEM) image of Fig 4.1(d) as shown below in Fig. 4.2, we can see clearly the single-crystalline structure. The spacing between neighboring layers is 0.52 nm, which is the distance between (00 01) layers of ZnO. So, the SAED figure shows the single-crystal pattern.
Figure 4.2  The enlarged high resolution TEM (HRTEM) image of Fig 4.1(d) for H₂-annealed sample.

4.2.2  Mechanism of GE in un-doped ZnO NWs
Figure 4.3 RT time-integrated PL spectra plotted on a semi-log scale for the as-grown (black), air-annealed (blue), and H$_2$-annealed (green) ZnO NWs with 325 nm laser pulses at the excitation fluence of 50 µJ/cm$^2$.

Figure 4.3 shows the room-temperature (RT) PL spectra for the as-grown, air-annealed, and H$_2$-annealed ZnO samples. All the three samples exhibit a strong BE peak at around 378 nm (3.28 eV) and a broad GE band peaking at 505 nm (2.46 eV). Apart from the GE intensity variation, similarities in the GE spectral shape amongst the three samples indicate that the GE originates from a common origin. The BE becomes quenched while the GE band becomes enhanced after air-annealing – consistent with the previous reports for oxygen-annealed, VPT-grown ZnO NWs.$^{69, 70}$ The decrease of BE should be due to the increased defects which act as trapping centers for the photoexcited carriers. The increase in the GE intensity after air-annealing can be tentatively attributed to the increased concentration of $V_{ZnO}$, this assumption is supported by the findings that
\( V_{ZnO} \) has lower formation energy on the nonpolar (10\( \overline{1} \)0) surfaces and is preferentially formed during the air annealing and the subsequent cooling to RT.\(^{50}\) The decrease in the GE intensity following hydrogenation is also commonly observed in ZnO nanostructures prepared by the same method\(^{71}\) and this is attributed to the passivation of the acceptor-like defects by the formation of hydrogen-related defects complex (\( e.g., \) \( V_{Zn-H_2} \)).\(^{72}\)
Figure 4.4 Comparisons of the normalized pump fluence dependent TIPL spectra of the GE band of the (a) as-grown, (b) air-annealed and (c) H$_2$-annealed ZnO NWs with increasing pump fluence at 10 K. The dashed red line at the peak of the GE band is a guide to the eye; Comparisons of the TIPL spectrum (solid line) of the GE with the temporal evolution of the GE band at various times following photoexcitation of the (b)
The structured peaks separated by the energy of longitudinal optical phonon in GE (peaking at ~2.43 eV) at low temperatures (LT), commonly seen in VPT-grown ZnO nanostructures, is observed in the un-doped ZnO NWs [Fig. 4.4 (a) and (b)]. This structured GE was previously suggested to originate from the Cu dopant at the Zn site (i.e., CuZn). However, subsequent EPR studies showed a null signal for Cu ions in un-doped ZnO tetrapods (prepared by vapor transport method) despite exhibiting a structured GE band at LT. It was also found that the intensity and/or the position of the GE were dependent on the fabrication gas and the annealing conditions, indicating that the GE-centers were more likely intrinsic defects. Furthermore, similar fine structures were also observed in the deep-level emissions at LT in many un-doped wide-bandgap semiconductors, such as the blue and yellow emission band in GaN, yellow emission in ZnO thin film, and green emission in In$_2$O$_3$ NWs. In view of these reports, observation of a structured GE band in un-doped ZnO at LT may not be a key indication of the GE originating from Cu impurities. This argument is strongly supported by the distinct PL transients exhibited by the un-doped ZnO NWs and (intentionally) Cu-doped ZnO NWs from our detailed TRPL studies (see the results and discussions in Chapter 5). Hence, we believe that this structured GE in un-doped ZnO NWs arises from the transitions between shallow donors and a deep acceptor level – described in a vibronic model. Lastly, we also wish to emphasize that the growth temperature of these ZnO NWs also have a strong influence on their emission properties. These un-doped samples in this study were fabricated at a temperature of ~850 °C while those un-doped ZnO NWs...
used as a control in the earlier charge transfer study of Cu-doped ZnO NWs were fabricated at a temperature of ~960 °C (experimental details for the growth of Cu-doped ZnO NWs can be found in Ref. 45). The latter un-doped ZnO NWs possess a very weak GE band in relation to its BE.\textsuperscript{58}

Next, we shall examine the recombination mechanism at the GE-centers. The GE lifetime is relatively long (~μs) as evident from the TRPL decay transients shown in Fig. 4.4 (b). Therefore, we expect that carrier trapping to these centers will be fast, otherwise, carrier-recombination via the BE (with sub-ns lifetimes) will be favored and the GE will be greatly suppressed. Fig. 4.4 (a) shows the normalized pump fluence dependent GE spectra from the representative air-annealed sample at 10 K. The GE band (peaking at ~2.43 eV) remains relatively invariant with negligible spectra shift as the pump fluence increases – which is consistent for all the other samples as well. Similar behavior is also observed for measurements at RT. Fig. 4.4 (b) shows the temporal evolution of the GE band from the same air-annealed sample obtained at different times. There is no noticeable spectral/energy shift of the GE band at various times compared to the time-integrated photoluminescence (TIPL) spectrum within an experimental accuracy of <10 meV. Similar results had also been reported for the yellow emission in GaN.\textsuperscript{79} The absence of an energy shift of the GE with increasing pump excitation or increasing temporal delay rules out the possibility of donor-acceptor pair (DAP) recombination between the localized donors and acceptors. Since the photon energy of DAP recombination has the relation: \( \hbar \omega_{\text{DAP}} = E_g - E_A - E_D + e^2 / (4 \pi \varepsilon \varepsilon_0 R_{DA}) \), where \( E_g \) is the bandgap energy, \( R_{DA} \) is the distance of the donor and acceptor, and \( E_D \) and \( E_A \) are the donor and acceptor binding energies, respectively. Therefore, such recombination would
result in key spectral and temporal signatures of: (i) blue shift of the emission spectra with increased pump excitation as the closer DAPs become excited; and (ii) red shift of the emission peaks as the closer pairs recombine faster since the recombination rate is dependent on the distance between the donor and acceptor. However, DAP involving shallow (delocalized) donors or acceptors would induce very small shifts (of a few meV).\textsuperscript{80, 81} It was reported that shallow acceptors arising from the stacking effect yields a PL band at around 3.31 eV in ZnO at LT.\textsuperscript{82} However, the absence of such peak near 3.31 eV in the LT PL spectrum rules out the possibility of these shallow acceptors in our samples (see Fig. 4.5). Thus, the GE involves the transitions of the free electrons in the CB and/or those electrons trapped at shallow (delocalized) donor levels with holes trapped at the deep levels (\textit{i.e.}, GE-centers) as proposed in Fig. 4.6(b).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.5}
\caption{Low Temperature PL spectra of as-grown ZnO NWs measured by 325 nm He-Cd cw laser with a pump fluence of 50 µJ/cm\textsuperscript{2}.}
\end{figure}

\subsection*{4.2.3 State-filling of the GE-centers}
To validate the hypothesis of fast carrier trapping to the GE-centers, TAS is used to probe the carrier-trapping dynamics. Femtosecond TAS with UV-pump/sub-bandgap probe differential transmission (DT or $\Delta T/T$, where $\Delta T/T = (T - T_0)/T_0$, $T_0$ is the transmission of probe beam without pump excitation of the sample, $T$ is transmission of probe beam with pump excitation of the sample) measurements (with the pump/probe beams aligned nearly parallel to the vertically aligned NWs) were performed.

Figure 4.6 (a) Linear absorption spectra (solid) and the GE band (dashed) of the air-annealed ZnO NWs; (b) DT spectra taken at 2 ps after excitation ($T = 300$ K) for the different samples. Inset shows a schematic of the energy levels excited and probed in the pump-probe measurement where CB: conduction band; VB: valence band; GE-C: GE-Centers.
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Figure 4.6 (a) shows the linear absorption spectra and the GE band in the representative air-annealed sample. However, due to the strong light scattering by the NW ensemble, transitions involving the defect states in the bandgap could not be resolved in the linear absorption spectrum. Figure 4.6 (b) shows the DT spectra at a time delay of 2 ps following 350 nm photo-excitation. The photo-bleaching (PB) band (i.e., positive $\Delta T/T$ signals) centered at about 470 nm (or 2.64 eV) is present in all three samples. Previously, an increase of pump-induced absorption of visible light was observed in ZnO nanoparticles (prepared by wet chemical methods) – attributed to the absorption of probe beam by the photoexcited electrons trapped at the NP surfaces. Similar to our observations, the bleaching of the sub-bandgap light induced by above-bandgap excitation was also recently observed in other wide-bandgap semiconductor NWs (i.e., GaN, In$_2$O$_3$, SnO$_2$ NWs – prepared by thermal evaporation methods, which was attributed to the state-filling effect of the sub-bandgap defect states. We believe that the contrasting results are due to the different absorption cross-sections and location of the defect energy levels in ZnO nanostructures prepared by different methods. Complementary z-scan measurements were therefore also conducted to verify the observed $\Delta T/T$ results as shown below.

**Z-scan Measurements:** Open aperture z-scan measurements at 470 nm were performed to verify the observed $\Delta T/T$ results. This wavelength is the same as the peak wavelength of the photo-bleaching (PB) band in the $\Delta T/T$ spectra. In many aspects, the results from a non-degenerate pump-probe measurement are analogous to that from a z-scan measurement. One involves pump and probe pulses that are mechanically delayed with respect to each other, while other involves sequential pulses that are “delayed” at the
same repetition rate of the laser. However, one advantage of the latter technique is that the magnitude of the transmittance through the sample will unambiguously tell one the relative magnitudes of the absorption cross-section of a particular state/energy level. For example, observations of increased transmittance in a z-scan spectra (i.e., saturable absorption) can be interpreted as the ground state absorption cross-section being larger than the excited state absorption cross-section and vice versa for decreased transmittance (i.e., reverse saturable absorption).
**Figure 4.7** (a) Open-aperture z-scans at 470 nm for as-grown, air-annealed, and H$_2$-annealed ZnO NWs and (b) single-crystal bulk ZnO (dark yellow).

Figure 4.7 shows that the ZnO NWs exhibit a saturable absorption in contrast to the reverse saturable absorption for a piece of hydrothermally grown single-crystal bulk ZnO at 470 nm. In the former, the nonlinear absorption at 470 nm arises from a competition between the defect states saturable absorption and the two-photon absorption across the ZnO bandgap. Observations of saturable absorption were reported for ZnO thin films with large amount of defects.$^2$ Hence it is clear that in our samples, the absorption cross section of the defect ground state is much larger than that of the defect excited states. Following photo-excitation, the defect ground state is depleted of electrons, while the excited state becomes filled with electrons. There is less absorption from the subsequent pulses and hence results in an increased transmittance of these pulses through the sample (i.e., PB). In this regard, the observed positive $\Delta T / T$ arises because of the larger absorption cross section of the defect states in the bandgap. In contrast, reverse saturable absorption was observed for the bulk ZnO sample [see Fig. 4.7(b)], due to the dominance of the two-photon absorption across the ZnO bandgap over this wavelength and the reduced contribution from defect state absorption (because of the presence of fewer defect states). Therefore, the z-scan results attest that the observed positive $\Delta T / T$ of sub-bandgap light is due to the state-filling-induced absorption bleaching of the visible probe light rather than stimulated emission.

Next, we continue to analyse the $\Delta T / T$ results. In the limit of a small change in transmittance with $\Delta T / T << 1$, the state-filling-induced transmission changes can be expressed as.$^{88}$
Chapter 4 Origin of green emission and charge carrier dynamics in ZnO NWs

\[
\Delta T / T \approx -\Delta \alpha (h\omega) d = \sum_i (n_i^e + n_i^h) \alpha_{0,i} (h\omega) d ,
\]

(4.1)

where \( \alpha_{0,i} (h\omega) \) is the contribution of transition \( h\omega_i \) to the ground-state absorption at the probe wavelength, \( n_i^e \) (\( n_i^h \)) are occupation numbers of the electron (hole) states involved in the transition, and \( d \) is the thickness of the sample. State-filling of either the hole or electron states results in a decrease in absorption or an increase in transmission. Therefore, under the conditions of the same excitation fluence and equivalent sample thicknesses, the relative magnitude of the state-filling-induced absorption bleaching (at a specific probe wavelength) from the DT spectra is reflexive of the magnitude of the ground state absorption \( \alpha_0 \) of the defects states in the bandgap. Its magnitude is also a measure of the relative population (or concentration) of the GE-centers – with the air-annealed sample possessing the largest concentration of GE-centers. This is nonetheless consistent with the relative GE intensities from the different samples in Fig. 4.3. Hence, the occupancy of the photoexcited electrons in the CB (\( n^e \)) and holes trapped in the GE-related deep levels (\( n^h \)) are monitored, as illustrated by a schematic in the inset of Fig. 4.6(b).

The GE peak exhibits an energy redshift of \( \sim 180 \) meV relative to the PB peak (at \( \sim 2.64 \) eV or \( \sim 470 \) nm) as shown in Fig. 4.6. We attribute this redshift to the energy difference between the level interrogated by the probe beam and the CB bandedge and/or shallow donor level (\( i.e. \), whose electrons are involved in the GE) – see Fig. 4.8 (b). The probe is sensitive to the hot electrons relaxing down to the CBM/ shallow donor level and the holes in the GE-centers; and therefore the PB arises due to the state filling of the electrons/holes at these energy levels. The broad PB peak spanning from 450 to 600 nm is likely due to the broad distribution of the energy levels of the GE-centers monitored by
the probe. From the PB peak, the energy level of the GE-centers is located at \( \sim 0.88 \text{ eV} = (E_g + 0.18 - 2.64 \text{ eV}) \) above the VBM, which agrees well with the calculated \( \varepsilon(+/0) \) transition level of \( V_{ZnO} \) (\( i.e., \sim 0.6 - 0.8 \text{ eV} \) above the VBM) published in a recent density functional study.\(^49\) Previously, positron annihilation spectroscopy (PAS) of pressurized melt grown single-crystal ZnO and theoretical calculations revealed that \( V_{ZnO} \) exists in a neutral state and is present in high concentrations (\( \sim 10^{17} \text{cm}^{-3} \)).\(^89\) Therefore, the neutral \( V_{ZnO} \) (or \( V_{ZnO}^0 \)) can be one of the more likely candidates of the source of GE.

### 4.2.4 Excitonic Auger-type ultrafast hole-trapping to the GE-centers

Next we turn our attention to examine the hole-trapping dynamics to these GE-centers. From the build-up time of the PB peak at the 470 nm probe wavelength, the nature of this hole-trapping process could be validated in a pump-fluence dependent study. Given that the probe is resonant with the state-filling of the GE-centers and the CBM, the build-up time from the DT spectra is in fact a convolution of the signals from the interband trapping of the holes from the VB to the GE-centers and those from the electrons undergoing fast intraband relaxation to the CBM from higher levels in the CB. The intraband relaxation rate of the photoexcited electrons in the CB is dependent on the amount of excess energy above the CBM and the carrier densities, which should be almost comparable in these samples under the same excitation conditions. This intraband electron relaxation is expected to be extremely fast [\( e.g., \) occurring at sub-30 fs for electron energies greater than 0.1 eV above the CBM at the ZnO (10\( \overline{10} \)) surface\(^90\)]. Hence, the
build-up dynamics measured here is clearly dominated by the interband hole-trapping process from the ZnO host to the GE-centers.

Figure 4.8 (a) Normalized $\Delta T/T$ transients of the photo-bleaching (PB) build-up for the as-grown, air-annealed and H$_2$-annealed ZnO NWs at 470 nm probe wavelength. The pump wavelength used was 350 nm and the pump fluence was 50 $\mu$J/cm$^2$. The solid line is the system response and the dashed lines are the fitting curves with the system response deconvolved; (b) A schematic of the proposed excitonic Auger-type ultrafast hole-trapping at the GE-centers. GC: GE-centers.
Figure 4.8 (a) shows the normalized DT transients of the PB build-up for the as-grown, air-annealed and H$_2$-annealed ZnO NWs at 470 nm probe wavelength, where the best-fit rise times $\tau_{rise}$ are $\sim$370 ± 20 fs, 180 ± 10 fs and 450 ± 20 fs, respectively. Interestingly, the rise time is the slowest for the H$_2$-annealed sample, while it is the fastest for the air-annealed sample. As the build-up time is dominated by the hole-trapping process to the GE-centers, the variation in $\tau_{rise}$ is therefore attributed to the different concentrations of the GE-centers present in these three samples. Since the hole-trapping rate is determined by the expression $\tau_{h}^{-1} = c_p N_{GE}$, where $c_p$ (cm$^3$/s) is the hole-capture coefficient; the higher the concentration of the GE-centers, the faster is the hole-trapping time ($\tau_{h}$). The capture cross section of the photoexcited holes can be calculated: $\sigma_h = (\tau_{h}v_{th}N_{GE})^{-1}$, where $v_{th}$ is the hole thermal velocity $\sim$10$^7$ cm/s, $N_{GE}$ is the concentration of GE-centers. Due to the fast hole-trapping times, $\sigma_h$ would be quite large. Though we could not directly measure $N_{GE}$ in our samples, suppose $N_{GE}$ is in the order of $\sim$10$^{17}$ cm$^{-3}$, i.e., typical for as-grown ZnO bulk, $\sigma_h$ will be as large as $\sim$10$^{-12}$ cm$^2$. This value is comparable to the hole capture cross-section of deep hole-traps in ZnO thin films.

Generally, free carriers can be trapped by deep centers in semiconductors via one of the following mechanisms: multiphonon emission, phonon-assisted cascade capture process, or Auger recombination processes (classical vs excitonic). However, the extremely fast $\tau_h$ uncovered by TAS strongly suggests that the energy loss is dominated by a non-phonon mechanism. Given the large energy separation between the GE-center and the VBM ($\sim$1 eV) and the ultrafast hole trapping lifetimes ($\tau_h$ ~ hundreds of fs), the
calculated energy-loss rate of 1.6-2.7 eV/ps is many orders of magnitude greater than the relaxation rate expected for the multi-phonon emission and the cascade capture process.\textsuperscript{96,97} The classical Auger recombination requires two independent free carriers to be located at the impurity site and hence is expected to be inefficient. On the other hand, the excitonic Auger capture mechanism as proposed by Hangleiter is more likely.\textsuperscript{98,95} It is because the large extension of the exciton wave function in $\kappa$ space can lead to an increase in the excitonic Auger transition probability $W$ ($W \sim \alpha_0^{-3}$,\textsuperscript{98} where $\alpha_0$ is the exciton Bohr radius and in ZnO, the free exciton Bohr radius of ZnO is very small (~1.8 nm)). Following above bandgap photoexcitation, free excitons are formed in ZnO. When a free exciton meets the GE-center, its hole can be captured by the GE-center while its electron is excited to higher energy levels in the CB, taking with it the excess energy – see Fig. 4.8(b). These electrons in the higher energy levels subsequently relax back to the CBM via phonon emission.

Probe wavelength and pump-fluence dependent DT were also performed on the as-grown, air-annealed and H$_2$-annealed samples to further investigate the hole-trapping dynamics. Figure 4.9(a)-(c) shows the build-up dynamics at probe wavelengths from 440 to 600 nm. Figure 4.8 (d) shows the fitted rise times which vary from 180 $\pm$ 20 fs to 1200 $\pm$ 50 fs, where $\tau_h$ is fastest at the peak of the PB band (~470 nm). The broad PB peak spanning from 450 to 600 nm is likely due to the broad distribution of the energy levels of the GE-centers monitored by the probe. The longer wavelengths correspond to the higher energy levels of the GE-centers with respect to the VBM as shown in Fig. 4.8(b). Therefore the different rise times for the different probe wavelengths reflects the various hole-trapping times to the different energy levels of the GE-centers. Consistent with our
above results where a sample with a higher concentration of GE-centers exhibits a faster hole-trapping rate \( \tau_{h}^{-1} = c_p N_{GE} \), it is interpreted that \( \tau_{h} \) is dependent on the density of states (DOS) distribution of GE-centers where the energy levels with a shorter \( \tau_{h} \) possess a higher DOS. Therefore, away from the DOS maximal (i.e., near the PB peak position), the PB signal decreases as shown in Fig. 4.6 (b) and \( \tau_{h} \) becomes slower.

![Figure 4.9](image)

**Figure 4.9** Normalized \( \Delta T/T \) transients of the (a) as-grown, (b) H\(_2\)-annealed and (c) air-annealed ZnO NWs as a function of probe wavelengths; (d) The fitted rise time as a function of probe wavelength; The solid line in (a)-(c) is the system response and the dashed lines are the fitting curves with the system response deconvolved. The pump wavelength used was 350 nm.
Lastly, Fig. 4.10 shows the build-up dynamics as a function of increasing pump fluence. Figure 4.10 (b) shows the fitted rise times which shortens from $350 \pm 20$ fs to $250 \pm 10$ fs with increasing pump fluence. This behavior is consistent with the excitonic Auger-type mechanism where increasing free exciton concentrations results in an increase in the hole capture coefficients – hence the shortening of the hole-trapping lifetimes. The excitonic Auger-like mechanism could therefore account for the ultrafast sub-ps hole-trapping times to the GE-center, thus validating our earlier hypothesis.

Based on the above results, we propose that $V_{\text{ZnO}}^0$ di-vacancies on/near the ZnO (10 10) surface can be one of the most likely candidates of the GE-centers in our VPT-prepared ZnO NWs. The photoexcited holes in the VB are subsequently trapped at $V_{\text{ZnO}}^0$ by an excitonic Auger-like process on an ultrafast (hundreds of femtoseconds) timescale ($i.e., V_{\text{ZnO}}^0 + h^+ \rightarrow V_{\text{ZnO}}^+$). The resultant $\varepsilon(+ / 0)$ charge transition from CB to $V_{\text{ZnO}}^+$ then
give rise to the GE (i.e., $V_{ZnO}^0 + e \rightarrow V_{ZnO}^0 + h_{GE}$). Charge separation of the photo-generated electron-hole pairs by this ultrafast hole-trapping mechanism will suppress the BE emission at low pump fluence. This is indeed observed for a low pump fluence of ~0.5 µJ/cm² (see Fig. 4.11) – consistent with the reports of VPT-grown ZnO NWs. These trapped holes on the ZnO NW surfaces with long (µs) recombination lifetimes are highly beneficial for the oxidative processes in a photocatalytic reaction. Our findings could therefore account for the enhanced photocatalytic activities in oxidative reactions at the ZnO (10 10) surface, and in the VPT-fabricated ZnO nanostructures with strong GE intensities. On the other hand, using the application of ZnO-based ultraviolet light LED and lasers as an example, high crystal quality ZnO must be fabricated with the GE from the defects suppressed. According to our results, the GE-centers in VPT-fabricated ZnO nanostructures are mainly located at the surfaces of ZnO and originate from $V_{ZnO}^{0}$ di-vacancies. Therefore, the following strategies can be employed to suppress the GE: (i) utilizing surface plasmons of Au nanoparticles, (ii) surfactant coating, and annealing to change the $V_{ZnO}^{0}$ di-vacancies to other point defects.
Figure 4.11 PL spectrum of as-grown ZnO NWs excited at 325 nm fs laser pulses with low fluence at room temperature. Note that the extremely weak BE peak compared to the strong GE, indicating that the GE-centers had trapped most of the photo-excited holes.

### 4.2.5 Comparison of $\Delta T/T$ with TRPL

Figure 4.12 (a) shows the temporal behaviors of the $\Delta T/T$ dynamics monitored at the center wavelength of the bleaching band for differently-treated samples. Each of the $\Delta T/T$ trace exhibits a fast increase in the transmittance and is followed by non-exponential decays. Since, the magnitude of $\Delta T/T$ is determined by the sum of the occupation numbers of electron ($n^-$) and holes ($n^+$) involved in the transitions as stated above. Therefore, the recovery of $\Delta T/T$ signal is attributed to be the de-population of the photoexcited electrons in the conduction band and holes trapped in the GE-centers.

Transient $\Delta T/T$ can be repented as:

$$\frac{\Delta T(t)}{T} \sim \frac{n^-}{\tau_{BE}} + \frac{n^+}{\tau_{GE}},$$  

(4.2)
Figure 4.12 (a) Comparison of the Normalized $\Delta T/T$ at 470 nm (2.64 eV). The solid lines are triple-exponential decay fitting curves with deconvolution. (b) Normalized BE PL decay transients of the three samples. The symbols are data points. The solid lines are triple-exponential fits in (a) and bi-exponential fits in (b) fits to the data with the system temporal response deconvolved. The fitted time constants and the respective weighting factors (in %) are compiled in Table 1.

In this case, the decay times of $\Delta T/T$ signal should be comprised of lifetimes of BE ($\tau_{BE}$) and GE ($\tau_{GE}$). The $\Delta T/T$ decay curves are fitted by the sum of a single exponential rise and triple-exponential decay function with the system response deconvolved. Since the GE lifetime is much longer than the maximum of pump-probe
delay time, it is necessary to fix the slowest decay time (\(\tau'_3\)) as \(\tau_1\) (because at RT the GE is mainly composed of the recombination between the conduction electrons and holes trapped at deep defect levels with lifetime of \(\tau_1\)) during the fitting procedure, and then allow the other parameters to be fit for variation. The best-fit values of the decay time constants and the weighting factors (in %) are listed in Table 4.1.

### Table 4.1 Summery of best-fit values of the decay time constants and the weighting factors (in %) for \(\Delta T/T\) monitored at 470 nm and TRPL of BE. (\(\tau'_3\) is fixed as GE lifetime \(\tau_1\)).

<table>
<thead>
<tr>
<th>sample</th>
<th>(\triangle T/T) decay life time</th>
<th>BE lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\tau'_1) (ps)</td>
<td>(\tau'_2) (ps)</td>
</tr>
<tr>
<td>As-grown</td>
<td>40 (38%)</td>
<td>266 (50%)</td>
</tr>
<tr>
<td>Air-annealed</td>
<td>28 (49%)</td>
<td>185 (34%)</td>
</tr>
<tr>
<td>H₂-annealed</td>
<td>20 (53%)</td>
<td>123 (36%)</td>
</tr>
</tbody>
</table>

Figure 4.12 (b) shows the BE TRPL decay curves for three samples that are fitted with bi-exponential decay function. According to our previous work, the shortening of the BE lifetimes was attributable to the introduction of nonradiative centers (i.e., chemisorbed O₂ molecules in air-annealed, and V₀ in H₂-annealed samples, respectively). Comparing with the BE lifetime as shown in Table 1, it is encouraging to find that the \(\Delta T/T\) decay time constants \(\tau'_1\) and \(\tau'_2\) match fairly well with the values of \(\tau_f\) and \(\tau_s\) for all three samples. In addition, if the \(\tau'_3\) was not considered as the GE lifetime, then the fitted \(\tau'_1\) and \(\tau'_2\) of \(\Delta T/T\) by triple-exponential decay function would be incomparable to the BE
dynamics. Moreover, the decay of $\Delta T / T$ cannot be well-fitted with the bi-exponential decay function. These results further confirm our hypothesis that we are indeed probing the electrons decaying from conduction band to valance band and to GE-related deep defects levels simultaneously. Since the bleaching band is located at 470 nm ($\sim 2.64$ eV), which therefore corresponds to the positions of the transitions levels of GE below the conduction band.

4.3 Summary

In summary, a comprehensive ultrafast optical spectroscopy study on the origin of GE and charge-trapping dynamics was performed on un-doped as-grown, air-annealed and H$_2$-annealed ZnO NWs fabricated by the VPT method. A sub-bandgap absorption bleaching band was observed in TAS upon above bandgap photoexcitation, which is due to the state-filling of the electrons in the conduction band/shallow donor level and the holes trapped at the GE-centers. The GE involves the transitions of the electrons in the CB and/or shallow (delocalized) donor levels with holes trapped at the GE-centers that are located at 0.88 eV above the VBM. Importantly, an ultrafast excitonic Auger-type hole-trapping process to the GE-centers occurring in a sub-ps timescale was uncovered by TAS, which is strongly dependent on the concentration of GE-centers, the DOS of energy levels of the GE-centers, and also the free exciton densities. Our findings shed new light on the ultrafast charge trapping mechanism in ZnO NWs, which has strong implications for the development of ZnO-based photocatalytic and optoelectronic devices.
5.1 Introduction

ZnO with wurtzite structure, due to its wide bandgap (3.37 ev) and large exciton binding energy (60 meV) at room temperatures is considered as a promising material for optoelectronics. In the fabrication of ZnO based optoelectronic devices, metal dopants like Al, Ga ions are usually used as donors to form n-type ZnO and Sb, In, Cu were used as the acceptors to realize the p-type ZnO. These metal dopants in ZnO can significantly alter the host’s physical, optical, electrical, and chemical properties. The metal ions usually results in the quenching of the host’s near bandedge emission (NBE) and luminescence associated with the dopant. Therefore, it is critical to investigate the dynamics of charge transfer to metal ions in metal ions doped in ZnO systems. Furthermore, among the various kinds of metal dopants, some metal ions, such as Cu ions, can also give the strong luminescence in the visible range. Cu-doped ZnO nanostructures can be promising materials for the application of ZnO visible light LED. The Cu dopant which substitute at the Zn sites can give rise to the structured GE via a charge transfer process between the ZnO host and the Cu dopants following above band-gap photoexcitation. In Dahan’s model, photoexcited electron was captured by the neutral
Cu\textsubscript{Zn} acceptor (i.e. Cu\textsuperscript{2+}(d\textsuperscript{9})) and the photoexcited hole was then trapped to form the \([\text{Cu}^+ (d\textsuperscript{9} + e), h] \) state which returns back to the Cu\textsuperscript{2+}(d\textsuperscript{9}) state upon GL emission.\textsuperscript{95}

Normally, the luminescence of un-intentionally doped (un-doped) ZnO nanostructures consists of a near-band-edge (UV) emission and a broad defect-related (visible) emission. A green emission (GE) centered around 500 – 510 nm is commonly observed in ZnO nanostructures prepared by the high-temperature vapor-phase transport (VPT) method.\textsuperscript{32-34} Previously, this GE in un-doped ZnO was attributed to arise from unintentionally doped extrinsic Cu impurities.\textsuperscript{38} However, presently, it is still unclear if the GE in un-doped ZnO arises from the un-intentionally-doped Cu ions given that the optical properties of the GE (especially that of the time-resolved optical properties) from un-doped and Cu-doped ZnO are still not well-studied.

In this chapter, through a detailed comparative study using steady-state PL, temperature-dependent TRPL, from un-doped and Cu-doped ZnO nanowires (NWs), distinct transient PL signatures from the temperature dependence of the GE lifetime for the un-doped ZnO NWs and the (intentionally) Cu-doped ZnO NWs were uncovered, despite the fact that the GE exhibited similar spectral shapes and peak positions in the steady state. This significant finding could help the community to gain a clearer understanding of the origin of GE in un-doped ZnO and permit a straightforward method to distinguish the presence or absence of Cu dopants in ZnO.

5.2 Results and Discussions

5.2.1 SEM, TEM and XPS of Cu-doped ZnO NWs
Figure 5.1(a) shows SEM image of the Cu-ZnO NWs. NWs are vertically aligned with diameter of ~100 nm and length of ~1 μm, and growth along [001] direction as shown in TEM in Fig. 5.1(b). The SAED pattern confirmed the wurtzite structure of C-ZnO NWs with no detectable secondary phases. The SEM and TEM images of un-doped ZnO NWs were shown in Chapter 4. Comparing Fig. 4.1 in Chapter 4 with Fig. 5.1, it is shown that un-doped and Cu-doped ZnO NWs have similar morphologies.

Figure 5.1 (a) SEM image of vertically-aligned Cu-doped ZnO NWs grown on a sapphire substrate. (b) Low- and (c) high-magnification transmission electron micrographs of an individual Cu-ZnO nanowire. Inset of (b) shows the corresponding SAED pattern.
The concentration and the valence state of Cu dopant in the ZnO matrix are determined by X-ray photoelectron spectroscopy (XPS). The calculated surface atomic composition percentages from XPS survey scan are 62.4, 2.2, and 35.4 for Zn, Cu, and O, respectively. Therefore, the Cu concentration in Cu-ZnO NWs is \(~2\) at\%. The Cu 2p\(_{3/2}\) and 2p\(_{1/2}\) core-levels shown in Fig. 5.2(b) are located at 933.38 and 953.17 eV, respectively, indicating the divalent states of Cu ions.\(^ {103, 104}\)

To measure the time integrated PL and time resolved PL, the samples were excited using 1 kHz 325 nm UV excitation pulses (with pulse duration of \(< 150\) fs) from a regenerative Ti: Sapphire amplifier. TIPL spectra were collected in a conventional backscattering geometry and detected by a charge-coupled device array coupled to a monochromator. TRPL was recorded by a streak camera system, which has an ultimate system resolution of 10 ps when operated in the shortest time window of 330 ps.
5.2.2 Similarities of the GE bands

Figure 5.3 (a) Low temperature (10 K) PL spectra of un-doped and Cu-doped ZnO NWs. (b) Room temperature (300 K) PL spectra of un-doped and Cu-doped ZnO NWs. Samples are excited with 325 nm at the fluence of 50 µJ/cm².

Figure 5.3(a) shows the low temperature PL spectra measured at the peak of the GE band for the as-grown ZnO and Cu-doped ZnO NWs. The peak positions of the GE in our un-doped and Cu-doped ZnO NWs are slightly different at room-temperature (RT) and low temperature: the maximum of GE in un-doped one is located at 505 nm (2.45 eV) at RT, and at 510 nm (2.43 eV) at 10k, whereas, the peak of GE in Cu-doped ZnO NW is invariant at both temperatures at 500 nm (2.48 eV). These GE peak positions are in good agreement with that of GE in the un-doped single-crystal ZnO bulk prepared by the VPT method and with that of GE in Cu-doped hydrothermally grown single-crystal ZnO. In addition, the fine structure of GE observed in un-doped ZnO at low temperatures in previous report was suggested to be the feature of Cu²⁺ ions. However, there was no evidence of the EPR signal of Cu²⁺ in un-doped ZnO tetrapods prepared by VPT method which exhibited structured GE (at ~ 510 nm) at a low temperature. And in fact, the fine structure of the defects emission was also observed in many un-doped wide band-gap semiconductors, such as the yellow emission in ZnO thin film, blue and yellow emission...
band in GaN,\textsuperscript{73-75} and green emission in In\textsubscript{2}O\textsubscript{3} NWs.\textsuperscript{77} In view of these reports, the observation of GE with fine structure in the low temperature as proof of the existence of Cu ions in ZnO is inappropriate. Other experiments are warranted to distinguish the GE in un-doped and Cu-doped ZnO.

**Figure 5.4** Temperature dependent PL spectra of (a) as grown un-doped and (c) Cu-doped ZnO NWs. Integrated GE intensity as function of reciprocal temperature in the (b) as-grown un-doped and (d) Cu-doped ZnO NWs. The lines are the fitting curves by using Eqn. 5.1. The solid lines represent the fitting curves by using Eqn. (1). Activation energies for each temperature range are also indicated. Samples are excited with 325 nm at the fluence of 50 µJ/cm\textsuperscript{2}.

In order to acquire more information about the GE, the temperature-dependent PL spectra is performed on un-doped and Cu-doped ZnO NWs. Fig. 5.4 shows the
temperature-dependent PL spectra for as-grown un-doped and Cu-doped ZnO NWs. For the both two samples, the integrated intensity of the GE have similar trend with temperature. In the first range of 10–150 K, the GE intensity decreases. In the second range, 150–250 K, the GE intensity increase with increasing temperature, such a feature is usually known as negative thermal quenching (NTQ). The intensity then decreases again with increasing temperature. The temperature-dependent integrated GE intensity can be fitted with a model developed by Shibata as

$$ I(T) = I(0) \frac{1 + \sum_{q=1}^{m} D_q \exp(-E'_q / K_B T)}{1 + \sum_{j=1}^{m} C_j \exp(-E_j / K_B T)} $$

(5.1)

where $D_q$ and $C_j$ are constant, $K_B$ is the Boltzmann constant, $E$ is the thermal activation energy for processes that PL intensity increases ($E'_q$) and decreases ($E_j$) with increasing temperature, respectively. The fitted activation energies are indicated in the Fig. 5.4(c) and (d). The thermal activation energies $E_{1/1}$, 14 meV and 16 meV for the un-doped and Cu-doped samples respectively, may correlate with thermal activation of shallow donors which are involved in the GE recombination. And $E_{1/2}$, 97 meV and 220 meV for the undoped and Cu-doped samples respectively, may arise from the thermal activation of holes trapped in GE-centers.

According to Shibata’s model, $E'_q$ in Eq. 5.1 describes the energy separation between the excited state and an intermediate level. NTQ behavior of GE that the PL intensity increases with increasing temperature has also been observed in un-doped and Cu-doped ZnO nanorods prepared by chemical bath deposition, hydrothermal and vapor transport methods in different groups recently. It was observed that the NTQ
behavior of GE was disappeared after coating of a Al₂O₃ thin film on the surface of the ZnO nanorod. Therefore, NTQ behavior of GE is related with surface states. The holes trapped by the surface states formed by such as chemisorbed O₂ molecular can be thermal excited to the excited states of GE-centers in the ZnO at elevated temperatures, which thus brings about the increase of the GE (e.g., NTQ). Therefore, $E'_q$ can be assigned to the energy level difference between the surface states and GE-centers. The surface chemisorption in ZnO NWs will be discussed in next chapter.

5.2.3 Differences in the charge trapping dynamics

TRPL spectra of the un-doped and Cu-doped ZnO NWs as shown in Fig. 5.5 provide clear validation that origins of GE in two samples are indeed from different sources. For comparison, the TRPL spectra of the un-doped and Cu-doped ZnO NWs were recorded with the streak-camera at the same sweep-speed (of 10 ps). The onset of the GE, which represents the carrier-trapping by GE-centers, is obviously different in the two samples. For the Cu-doped one, the decay of the NBE is followed consecutively by the build-up of the GE. The fitted decay time in Fig. 5.5(c) of NBE and rise time of GE in Cu-doped one are: $\tau_{\text{decay}} = 38 \pm 5$ ps and a rise time $\tau_{\text{rise}} = 38 \pm 4$ ps respectively. Figure 5.6 summarizes the NBE lifetime and the GE rise time as a function of temperature for the Cu-doped ZnO sample. It is clear that the decay time and rise time correspond well with each other in different temperatures, indicating that the weak temperature dependence of the charge transfer pathway between the ZnO host and the Cu dopants. The charge transfer time maybe affect by other factors such as the concentration of the Cu dopants or the other intrinsic defects, not the temperature.
Figure 5.5 (a) TRPL images of as-grown un-doped (upper panel) and Cu-doped (lower panel) ZnO NWs recorded by streak camera at room temperature. (b) The normalized BE and GE TRPL signals in as-grown un-doped (upper panel) and Cu-doped (lower panel) ZnO NWs. They were extracted at the peak of the emission band from the TRPL images in figure 2(a), respectively. Samples are excited with 325 nm laser at the fluence of 50 µJ/cm².

On the other hand, for the un-doped ZnO NWs, GE and BE appears simultaneously, indicating the fast carrier-trapping to the GE-centers. Due to the limitations of the system response of the streak camera, such fast carrier trapping time by the GE centers could not be elucidated from the TRPL studies. Complementary transient absorption spectroscopy presented in the earlier section 4.2.4 in Chapter 4 revealed a hole trapping time to GE-centers of several hundreds of fs in un-doped ZnO NWs. Consequently, it is highly unlikely that the Cu ions are the source of GE in our un-doped ZnO NW.
Figure 5.6 Summary of the fitted decay time of NBE and rise time of green emission band in Cu-ZnO NWs as a function of temperature.

5.2.4 Differences in GE recombination dynamics

In addition to investigating the differences in trapping time of the carriers to GE-centers in the un-doped and Cu-doped ZnO NWs, we turn our attention to examine the recombination processes in the two samples. Temperature-dependent TRPL was carried out on samples. As shown in Fig. 5.7, the decay of GE became faster and the calculated average lifetime decreases gradually with increasing temperature. The lifetime shortening is similar to temperature-dependent TRPL in Cu-doped ZnS particles in the previous report, where increased contribution from nonradiative recombination processes at higher temperatures was explained as a cause for the shortened lifetime of GE of Cu$^{2+}$.\textsuperscript{109}
Figure 5.7 (a) Normalized TRPL of GE as a function of temperature from Cu-doped ZnO NWs. The inset is the temperature-dependent average lifetime of GE decay.

Figure 5.8 (a) shows the RT TRPL decay transients extracted at the peak of the GE band for the three samples: as-grown, air-annealed and H2-annealed. These PL transients showed triple-exponential decay which can be fitted by the relation:

\[ I(t) = \sum_{i=1,2,3} A_i \exp(-t/\tau_i) \]

where \( \tau_i \) and \( A_i \) are the lifetime and amplitude, respectively. The fitted lifetimes correspond with those reported in the literature with two fast decay components of hundreds of nanoseconds (\( \tau_1 \) and \( \tau_2 \)) and a slower decay in microseconds (\( \tau_3 \)).\(^ {110, 111} \) The fitted lifetimes and their weighting factors are shown in Table 4.1. These relatively long lifetimes precludes any possibility of recombination between the electrons in the CB and/or electrons trapped at shallow donors with the holes in the VB (i.e., occurring on a sub-ns timescale).\(^ {112, 113} \)
Figure 5.8 (a) Normalized GE decay transients for the as-grown (black), air-annealed (blue), H₂-annealed (green) ZnO NWs at RT. (b) Normalized temperature dependent TRPL of GE from as-grown sample. Samples are excited with 325 nm at the fluence of 50 µJ/cm². Solid lines are fitting curves by the triple-exponential decay function.

Temperature dependent GE decay transients from the representative as-grown sample are shown in Fig. 5.8(b). There is no obvious trend in the temperature dependence of the lifetimes, in contrast with an obvious trend of decreasing Cu-related GE lifetimes.
with decreasing temperatures. All the decay curves from 10 K to RT can be well-fitted by the triple-exponential decay function discussed previously. The fitted lifetimes and their corresponding amplitudes (weighting factors) are presented in Fig. 5.9 (a) and (b). The three lifetimes correspond to three different transitions, while the amplitude of the lifetime corresponds to the relative significance of that particular lifetime to the overall recombination dynamics (which reflects the dominance of one transition over another). Figure 5.10 shows a schematic of the proposed model of the GE recombination processes.

### Table 5.1 Summary of the best-fit values of the GE decay transients for three samples at RT. (The pre-exponential factors or amplitudes in percentage are given in parenthesis).

<table>
<thead>
<tr>
<th>Sample</th>
<th>RT GE decay lifetimes</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_1$ ($\mu$s)</td>
<td>$\tau_2$ ($\mu$s)</td>
<td>$\tau_3$ ($\mu$s)</td>
<td></td>
</tr>
<tr>
<td>As-grown</td>
<td>0.13 (75%)</td>
<td>1.01 (7%)</td>
<td>6.92 (18%)</td>
<td></td>
</tr>
<tr>
<td>Air-annealed</td>
<td>0.14 (71%)</td>
<td>0.76 (18%)</td>
<td>5.12 (11%)</td>
<td></td>
</tr>
<tr>
<td>H$_2$-annealed</td>
<td>0.06 (80%)</td>
<td>0.54 (16%)</td>
<td>11.54 (4%)</td>
<td></td>
</tr>
</tbody>
</table>

As the temperature increases, $A_1$ increases, whereas $A_2$ and $A_3$ gradually decrease as shown in Fig. 5.9 (b). At RT, the transitions via process 1 (i.e., with lifetime $\tau_1$) dominate, while those via processes 2 and 3 (i.e., with lifetimes $\tau_2$ and $\tau_3$, respectively) contribute less to the GE. In Chapter 4, the GE-center was suggested to be neutral $V_{ZnO}^0$ before photoexcitation. Therefore, process 1 is assigned to originate from the recombination between the electrons in the CB with the holes trapped at $V_{ZnO}^+$, as shown in Fig. 5.10. With increasing temperature, thermalization of the shallowly trapped electrons to the CB occurs. Hence $A_1$ increases as more electrons are available for transition via process 1. Next, we attribute process 2 to originate from the recombination
between the electrons in the shallow donors (e.g., H\textsubscript{i} and Zn\textsubscript{i}) with the holes trapped at V\textsuperscript{+}\textsubscript{ZnO}. Both $\tau_1$ and $\tau_2$ decreases with increasing temperatures up to ~150 K – consistent with the increased non-radiative trapping of the electrons in the CB and shallow donors to other defects (e.g., V\textsubscript{O}). From 150K to RT, thermalization of the holes trapped at the V\textsuperscript{+}\textsubscript{ZnO} to the VB (albeit at lower probabilities) could result in a subsequent increase in the lifetimes of $\tau_1$ and $\tau_2$. The interplay between these two dynamical processes complicates the trends in the lifetimes. Nevertheless, our assignment of the relaxation pathways for $\tau_1$ and $\tau_2$ can be further validated from the RT GE decay transients of the three samples as shown in Fig. 5.8(a). In the H\textsubscript{2}-annealed sample, the short lifetime components (i.e., $\tau_1$ and $\tau_2$) become even faster and dominate the GE decay dynamics. This is consistent with a higher concentration of electron trapping centers (i.e., V\textsubscript{O}) present in the sample that depopulates the bandedge electron population via an electron transfer process within tens of ps.\textsuperscript{26}
Figure 5.9 (a) Fitted lifetimes of the GE decay with triple-exponential decay function. (b) The amplitude of the fitted lifetimes.

Lastly, we turn our attention to $\tau_3$, which has the smallest contribution to the GE dynamics ($A_3$ is smallest compared to $A_1$ or $A_2$). As seen in Fig. 5.8(a) and Table 4.1, $\tau_3$ is longest in the H$_2$-annealed sample (compared to the as-grown and air-annealed samples) at RT despite possessing the highest concentration of non-radiative electron trapping centers (i.e., VO). This suggests that process 3 is not strongly influenced by the presence of VO and so it alone cannot be the source of $\tau_3$. Furthermore, Figure 5.9(a) clearly shows that $\tau_3$, which occurs in the long microsecond timescale, increases with increasing temperature, indicating that it does not originate from a transition from the CBM. Such behavior hints at an internal transition origin (i.e., from the excited state to ground state) for process 3. Previously, such phenomena was reported for single crystal ZnO$^{114}$ (prepared by chemical vapor transport method) which has a PL decay lifetime of $\sim$1.7
μs$^{105}$ (i.e., comparable to $\tau_3 \sim 1.1$ μs measured at 10K in our air-annealed sample). This long-lived emission arises from a spin–flip process as validated by ODMR measurements.$^{114}$ We therefore attribute process 3 to arise from the relaxation from an excited state (located near the shallow donor level below the CBM) back to the ground state of $V_{ZnO}^0$ as shown in Fig. 5.10. The increase of $\tau_3$ with increasing temperature can be attributed to the escape of electrons from the shallow excited states to the CBM at higher temperatures. This is consistent with the gradual decrease of amplitude $A_3$ with increasing temperatures in Fig. 5.9(b). The longer $\tau_3$ in the $H_2$-annealed sample compared to the other two samples is attributed to the lower concentration of GE-centers present; consistent with the lowest GE intensity.

**Figure 5.10** Proposed model of the three possible recombination processes present in the GE with respective lifetimes $\tau_1$, $\tau_2$ and $\tau_3$. CB: conduction band; VB: valence band; ES: excited state of GE-centers in a triplet configuration (i.e., $V_{ZnO}^+ + e^\uparrow$); SD: shallow donors.
5.3 Summary

To sum up, in this chapter, it is found that even though the emission shape and wavelength of GE between the un-doped and Cu-doped ZnO NWs is similar in the steady state, the carrier trapping processes to the GE-centers upon photoexcitation and the subsequent recombination dynamics are in fact quite different from each other. TRPL reveals the presence of a charge transfer process of ~38 ps between the ZnO host and the Cu dopants following above-bandgap photoexcitation. However, the GE-centers in un-doped ZnO NWs have a limited trapping range in contrast to the Cu dopants. Besides, there is no obvious trend in the temperature dependence of the lifetimes in un-doped ones, in contrast obviously with a trend of decreasing Cu-related GE lifetimes with decreasing temperatures. A clear understanding of these charge carrier dynamics is essential for the design and development of practical high-speed nanowire-based optoelectronic devices, transistors, sensors and energy conversion devices.
CHAPTER 6

Effect of Surface Hole/Electron Traps on the Charge

Carrier Dynamics in ZnO Nanowires

6.1 Introduction

One-dimensional (1-D) systems and quasi 1-D systems such as nanowires and nanorods have received much attention in the recent years due to their potential as building blocks for nanoscale transistors, sensors and optoelectronic devices. In particular, ZnO nanowires (NWs) have received considerable attention due to their unique properties. Potential applications for ZnO NWs include areas of optoelectronics, photovoltaics, photocatalysis, photonics and photodetectors etc. To optimize device properties such as power consumption, fast response, high sensitivity UV detectors, high efficiency of solar cells and photocatalyst, a detailed understanding of photoinduced carrier dynamics in light of the various competing radiative and non-radiative pathways is essential.

With a high surface to volume ratio in NWs, surface defects, near surface traps and surface adsorbed species, offering alternative relaxation pathways for the de-excitation of photo-excited carriers, will play a significant role in the carrier relaxation dynamics of these 1-D systems. Many of the native point defects [oxygen vacancies ($V_O$), Zn vacancies ($V_{Zn}$), oxygen anti-sites ($O_{Zn}$), Zn interstitials ($Zn_i$), etc] are formed during the NW growth and their concentrations are highly dependent on the growth
conditions and post-fabrication treatments. Post-fabrication thermal annealing of ZnO NWs in an oxidizing/reducing gas ambient is commonly used to tune the intrinsic (or native) defects, modify the surface states and modulate the carrier concentrations; effecting changes to the optical and electrical properties of these NWs that result in enhanced gas sensitivity, field emission properties, photoconductivity, and photocatalytic activity.\textsuperscript{51, 116-120}.

Figure 6.1 A schematic illustrating the band bending in the cases of (a) electron depletion and (b) electron accumulation at the NW surface. (c) and (d) shows the corresponding phenomenological model of the trapping pathways in a two-particle picture.

Typically, in an oxidizing ambient,\textsuperscript{52} adsorbates like O$_2$ molecules undergo chemisorption on the NW’s surface by capturing a free electron from the n-type ZnO [\textit{i.e.},
likely $\text{O}_2(g) + e^- \rightarrow \text{O}_2^-(ad)$, resulting in an upward band bending as shown in Fig. 6.1(a). Conversely, in a reducing ambient, adsorbates like atomic hydrogen (H) or intrinsic electron donors like $V_o$ at the surface, transfers their electrons to the semiconductor (i.e., likely $\text{H}(g) \rightarrow \text{H}^+(ad) + e^-$ or $V_o \rightarrow V_o^{2+} + 2e^-$), giving rise to a positively charged surface; resulting in a downward band bending that moves the conduction band below the Fermi level [see Fig. 6.1(b)]. These contrasting scenarios are commonly known to give rise to electron depletion and electron accumulation respectively at the semiconductor NW surface. Upon illumination with photon energies above the band gap energy, photo-excited holes (electrons) in the former (latter) will migrate to the surface traps along the potential slope produced by the band-bending. Such photo-induced charge transfer (CT) processes that ensue forms the basis of the enhanced field emitting properties, photoconductivity response, photocatalytic and photovoltaic performance of ZnO NWs. A detailed understanding of the influence of the surface traps on the CT processes and the lifetime of photogenerated carriers in ZnO NWs is still lacking. Elucidating these ultrafast CT mechanisms that reflect the dynamic interplay between various trapping sites introduced by post-fabrication thermal annealing in ZnO NWs are the main foci of this paper.

Time resolved photoluminescence (TRPL) spectroscopy is a powerful probe of carrier dynamics and their relaxation pathways in semiconductor NWs. Together with complementary chemical sensitive techniques such as X-ray photoelectron spectroscopy (XPS), an insight into the microscopic origins of the trapping centers and their characteristic trapping timescales can be elucidated. Herein, we report on the ultrafast CT processes in ZnO NWs with post-fabrication thermal annealing in an/a oxidizing/reducing
gas ambient (and with UV-treatment) following above $E_g$ photoexcitation. We found evidences of a hole transfer time constant of $\tau_{ht\text{-}air\text{-}annealed} \approx 400 \pm 80$ ps to the surface adsorbed oxygen species ($O_2^-$) in the air-annealed sample and an electron transfer time constant of $\tau_{et\text{-}H_2\text{-}annealed} \approx 60 \pm 10$ ps to $V_o^{2+}$ in the $H_2$-annealed sample. Furthermore, our studies reveal an ultrafast, localized hole transfer (in the sub-ps-to-ps timescale) to the green emission (GE) related defect states. Unlike the other two CT processes (to $O_2^-$ and $V_o^{2+}$), these hole traps have limited influence over the ZnO band-edge emission (BE) lifetimes. This is contrary to the common perception that the ZnO BE dynamics are strongly influenced by the carrier trapping to the GE-related defects. Importantly, our findings shed new light on the photoinduced CT processes that underpins the novel properties of enhanced photocatalytic activity, photovoltaic performance, and photoconductivity response of ZnO NWs; thereby suggesting a strategy for tailoring the ultrafast carrier dynamics in ZnO NW-based devices.

6.2 UV-illumination Treatment

The preparation processes of the as-grown, air-annealed and $H_2$-annelaed ZnO NWs have already been discussed in Chapter 4. To remove the chemisorbed species, the samples were illuminated with 325nm, 100 $\mu$J/cm$^2$ fluence UV light for 20 mins in a continually evacuated optical cryostat (at a pressure of $10^{-5}$ Pa) at room temperature. Prior to UV-illumination, all the samples were measured at room temperature in air ambient, while the PL measurements of the UV-illuminated samples were performed under vacuum. The fresh $H_2$-annealed sample was kept in a vacuum desiccator to minimize its contact
Chapter 6 Effect of surface hole/electron traps on charge carrier dynamics in ZnO NWs

with air prior to the optical and XPS measurements. XPS measurements were performed using a VG ESCALAB 220i-XL system with a monochromatic Al Kα (1486.6 eV) X-ray source.

6.3 Results and Discussions

6.3.1 TEM & XPS characterization of ZnO NWs

Transmission emission microscopy (TEM) reveals a roughened polycrystalline surface with small ZnO particulates (~2.5 nm in diameter) that was formed in the H2-annealed samples [Fig. 6.2(c)], while there are no observable changes to the surface of the air-annealed samples [Fig. 6.2(b)] compared to the as-grown sample [Fig. 6.2(a)]. The XPS spectra of O1s peak of the as grown, air-annealed and H2-annealed ZnO NWs and their deconvolved peaks are shown in Fig. 6.2(d) – (f); which exhibit distinct differences. The O1 1s peak (530.27 eV) present in all three samples has been attributed to originate from the O2- ions in the ZnO lattice sites. The middle O II 1s peak located at slightly higher binding energy of 531.23 eV, which is present in both the as-grown and the H2-annealed samples, is attributed to O2- ions in the oxygen deficient regions. This binding energy shift arises from a reduced screening of the nearest neighbor O 1s electrons from their nucleus by an electron charge density when a VO is created; thereby raising the effective nuclear charge \( Z_{\text{eff}} \) (i.e., the binding energy) of an O II 1s electron relative to that of an O1 1s electron. Hence, the peak intensity variations of O II 1s peak can be correlated with the surface VO concentration in the sample. The relative increase in the intensity of
this peak in the H$_2$-annealed sample suggests an increased V$_{O}$ concentration on the surface of ZnO NWs after H$_2$-annealing.

Figure 6.2 High resolution TEM images of the sample edges of the (a) as-grown, (b) air-annealed and (c) H$_2$-annealed ZnO NWs. (d) Insets show the region where the close-up TEM images were taken (black scale bar: 100 nm). (d), (e) and (f) show the corresponding
XPS spectra of the respective samples.

The OIII 1s peak, located at ~532.01 – 532.69 eV for the three samples is attributed to the presence of loosely bound oxygen species on the surface of ZnO NWs (e.g., adsorbed O2, -CO3 or H2O). Oxygen chemisorption on the surface of ZnO NW is likely to be more prevalent in the air-annealed samples than in the as-grown and the H2-annealed samples. Previously, it was reported that the rate of O2 chemisorption increases with increasing temperature63, 128 and the chemisorped O2 could diffuse into the bulk during annealing to induce a high density of acceptor-like defects (i.e., VZn, OZn). This would result in the compensation of the donor-like defects (i.e. VO, Zni) and the depletion of the carrier density. Therefore, the substantive increase of the OIII 1s peak relative to the OI peak, as well as the absence of the VO-related OII 1s peak in the air-annealed sample [from Fig. 6.2(e)] are consistent with this interpretation (i.e. a dominant presence of chemisorbed O2 species on the surface of the air-annealed ZnO NWs). Identification of the specific species (e.g., adsorbed O2, -CO3 or H2O) on the surface of the ZnO NWs is beyond the scope of this work and we shall term these loosely bound oxygen species as chemisorbed oxygen species (O2−).

6.3.2 Variation in PL and TRPL properties of ZnO NWs with different treatments

Figure 6.3(a) shows the room-temperature TIPL spectra for the three samples which exhibit a BE peak at ~3.28 eV and a broad defect-related GE band centered at ~2.45 eV of varying intensities. This GE band is typical of ZnO nanostructures prepared
by the vapor transport method; and was believed to have originated from on/near surface defects.\textsuperscript{132-135} Nonetheless, the identity of the defect responsible for the GE remains entwined with controversies.\textsuperscript{34} Previously, it was commonly believed that this defect is VO.\textsuperscript{38} However, recent theoretical works and our experimental results in Chapter 3 have suggested that the neutral V\textsubscript{ZnO}^0 di-vacancy located \(\sim 0.8\) eV above the valence band as a more likely source of the GE.\textsuperscript{136, 137} The XPS and PL experimental data from the air-annealed sample supported this finding about alternative origins of the GE as our results show that there is an inverse relation between a decrease in VO concentration (from XPS) and an increase in GE intensity (from PL) compared to the as-grown sample. Similarly, this inverse relation is also evident from the H\textsubscript{2}-annealed sample where the converse is evident: \textit{i.e.}, an increase in VO concentration (from XPS) and a decrease in GE intensity (from PL). The decrease in GE intensity following H\textsubscript{2} annealing is attributed to the passivation of V\textsubscript{ZnO}^0 through the formation of V\textsubscript{ZnO}-H\textsubscript{2} complexes.\textsuperscript{138}

Next, we shall turn our attention to the dynamical aspects of the BE recombination in relation to the influence from the various defects. Figure 6.3(b) shows the BE PL decay curves for three samples that are fitted with bi-exponential components:

\[
I(t) = A_f \exp\left(-t/\tau_f\right) + A_s \exp\left(-t/\tau_s\right),
\]

where \(A_f\) and \(A_s\) refer to the decay amplitudes (\textit{i.e.}, weighting factors) of the fit and \(\tau_f\) and \(\tau_s\) refer to the decay time constants of the fast and slow components respectively. The former and latter time constants were attributed to arise from the recombination of the excitons near the surface and the bulk respectively,\textsuperscript{139} or more generally, from the defect-rich regions (\textit{i.e.}, dominated by the non-radiative component) and the defect-free regions (\textit{i.e.}, dominated by the radiative component) respectively in \(1/\tau_{PL} = 1/\tau_R + 1/\tau_{NR}\); thereby yielding two different decay time constants
in our ensemble-averaged measurements. Table 6.1 lists the BE decay time constants and their respective weighting factors (in %) for the various samples.

**Figure 6.3** (a) Room-temperature TIPL spectra of the as-grown, air-annealed, and H$_2$-annealed ZnO NWs measured in air ambient. These spectra were overlaid by spectra from the as-grown and air-annealed samples measured in vacuum, following 20 mins of UV illumination in vacuum. All the spectra were obtained in the same experiment geometry. (b) Normalized BE PL decay transients of the corresponding samples in (a). The solid lines are bi-exponential fits to the data with the system temporal response deconvolved. The fitted time constants and the respective weighting factors (in %) are compiled in Table 6.1.
Table 6.1 A summary of the fitting parameters for the as-grown, air-annealed and H$_2$-annealed samples. The average lifetime ($\tau_{\text{avg}}$) is calculated using: $\tau_{\text{avg}} = (A_1\tau_f^2 + A_s\tau_s^2)/(A_1\tau_f + A_s\tau_s)$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\tau_f$ (ps)</th>
<th>$\tau_s$ (ps)</th>
<th>$\tau_{\text{avg}}$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-grown</td>
<td>43 (13%)</td>
<td>286 (87%)</td>
<td>280</td>
</tr>
<tr>
<td>As-grown (After UV)</td>
<td>93 (22%)</td>
<td>440 (78%)</td>
<td>420</td>
</tr>
<tr>
<td>Air-annealed</td>
<td>36 (20%)</td>
<td>190 (80%)</td>
<td>183</td>
</tr>
<tr>
<td>Air-annealed (After UV)</td>
<td>71 (23%)</td>
<td>355 (77%)</td>
<td>338</td>
</tr>
<tr>
<td>H$_2$-annealed</td>
<td>30 (92%)</td>
<td>113 (8%)</td>
<td>50</td>
</tr>
</tbody>
</table>

6.3.3 Hole-trapping time by chemisorbed O$_2^-$ in as-grown and air-annealed ZnO NWs

After air-annealing, the BE becomes quenched while the GE band becomes enhanced as shown in Fig. 6.3(a), typical of oxygen-annealed ZnO materials prepared by physical methods (in thin films$^{140, 141}$ or NWs$^{142}$) reported previously. TRPL measurements [Fig. 6.3(b)] reveal a shortening of the BE lifetimes compared to the as-grown samples. This would arise from a competition amongst various relaxation pathways: hole trapping by GE-centers and by surface chemisorbed oxygen species (O$_2^-$). This latter pathway can be suppressed through ultraviolet (UV) illumination of the samples in vacuum, where neutralization by photo-generated holes will desorb the O$_2$ molecules ($i.e., h^+ + O_2^{(ad)} \rightarrow O_2^{(g)}$). Upon UV illumination at 325 nm under vacuum in an optical cryostat, there is an enhancement of the BE for both the as-grown and air-annealed sample [Fig. 6.3(a)], together with a lengthening of the PL lifetimes [Fig. 6.3(b)] that is attributed
to the suppression of the hole-trapping process. Furthermore, upon exposing the UV illuminated ZnO NWs back to the air ambient, their emission properties prior to UV illumination were recovered, due to the re-adsorption of O$_2$ molecules on the NW surface.

UV illumination has only a marginal effect on the GE band for both the as-grown and air-annealed samples [Fig. 6.3(a)]. The concentration of GE-center is unlikely to be drastically modified by UV illumination. Hence, we would expect that any contributions of GE-center to the BE recombination dynamics to remain largely invariant following UV illumination. From these results, we can obtain the average hole-trapping time constant $\tau_{ht}$ by the chemisorbed O$_2$ in as-grown and air-annealed samples after photo-excitation, using the following relations (See Fig. 6.1c):

\[
\begin{align*}
\text{Before UV:} & \quad \frac{1}{\tau_{PL}} = \frac{1}{\tau_R} + \left( \frac{1}{\tau'_{ht(GE)}} + \frac{1}{\tau_{ht(O_2)}} \right) \\
\text{After UV:} & \quad \frac{1}{\tau'_{PL}} = \frac{1}{\tau_R} + \frac{1}{\tau'_{ht(GE)}}
\end{align*}
\]

(6.1)

where $\tau_R$ is the radiative lifetime of BE, $\tau'_{ht(GE)}$ and $\tau_{ht(O_2)}$ are the characteristic hole trapping time by GE-centers (e.g., $V'_{ZnO}$) and chemisorbed O$_2$ respectively, $\tau_{PL}$ and $\tau'_{PL}$ are the average exciton lifetimes measured before UV illumination in air and after UV illumination in vacuum respectively. From these, we obtain:

$\tau_{ht\text{-as-grown}} = \left[1/\tau_{PL} - 1/\tau'_{PL}\right]^{-1} \approx 900 \pm 200 \text{ ps}$ and $\tau_{ht\text{-air-annealed}} \approx 400 \pm 80 \text{ ps}$. The larger $k_{ht(O_2)}$ of the air-annealed sample (i.e., faster $\tau_{ht\text{-air-annealed}}$) can be attributed to the higher concentration of chemisorbed O$_2$ species present following air-annealing in agreement with our XPS results.
6.3.4 Electron-trapping pathways introduced by H$_2$-annealing

Hydrogen annealing has been previously reported to result in the passivation of the deep centers in ZnO$^{143}$ as well as in the formation of non-radiative defects, such as V$_O$, Zn$_i$ or OH groups through reactions with ZnO. Our results in Fig. 6.3 show that H$_2$-annealing reduces both the BE intensity and the lifetime of BE, in agreement with previous reports.$^{144, 145}$ Through the formation of V$_{Zn}$-H$_2$ complexes, the GE band is also significantly reduced. XPS measurements indicate that there is an increase of V$_O$ concentration after H$_2$-annealing. A likely mechanism for the formation of V$_O$ is:

$$\text{ZnO} + \text{H}_2 \rightarrow \text{Zn} + \text{H}_2\text{O} + \text{V}_O.$$

The removal of an oxygen atom from the ZnO lattice results in the breaking of four Zn-O bonds, which form a symmetric $a_1$ state in the bandgap. For V$_O^0$, the $a_1$ state is occupied by two electrons.$^5$ First principles investigation by Janotti and Van de Walle$^5$ has shown that in ZnO, both the V$_O^0$ and V$_O^{2+}$ charge states are more likely to be formed than V$_O^+$. This is attributed to the unusually large local lattice relaxations [i.e., “negative-$U$” behavior (where $U$ is the on-site Coulomb correlation energy)] that significantly reduces the formation energies of V$_O^0$ and V$_O^{2+}$ relative to V$_O^+$. Recently, based on first principles density functional theory methods, it was also reported that the formation energy of V$_O^{2+}$ is lowest at the surface of the ZnO NWs.$^{41}$

In the V$_O^{2+}$ configuration, the empty $a_1$ state is located close to the CB and could thus function as an electron trap.$^5$ Hence, we attribute the BE suppression to arise from a competition from photo-excited electron trapping by V$_O^{2+}$. UV illumination in vacuum has little or no effect on the freshly treated H$_2$ sample, with the PL spectrum and radiative recombination dynamics remaining invariant to that of the pre-illuminated case. This
shows the deficiency of chemisorped $O_2^-$ after H$_2$-annealing and the non-passivation of the $V_{O}^{2+}$ state (with UV illumination) in vacuum. It is also highly likely that $V_{O}^{2+}$ plays a more dominant role in the formation of the accumulation region than the adsorbed H atoms as any adsorbed H atoms would have been desorbed from the NW surface following UV illumination. With the suppression of the relaxation pathways to both $V_{Zn}$ and chemisorped $O_2^-$ in the H$_2$-annealed NWs, the trapping of the photo-excited electrons to $V_{O}^{2+}$ is therefore the dominant non-radiative process that competes with the BE (see Fig. 6.1d). Before we elucidate the average electron trapping time constant by $V_{O}^{2+}$, we would like to further examine the relative effects of the various non-radiative pathways (i.e., $V_{Zn}$-related defects, chemisorbed $O_2^-$ and $V_{O}^{2+}$) on the BE dynamics of these ZnO NWs.

### 6.3.5 Relative effects of GE-centers, chemisorbed $O_2^-$ and $V_{O}^{2+}$ on the BE dynamics of ZnO NWs

In Chapter 4, it is revealed by transient absorption spectroscopy that photoexcited holes are fast captured by GE-centers with in 1 ps. To examine the carrier trapping process to GE-centers, we shall focus on the UV-illuminated as-grown (grey line) and air-annealed (red line) samples (in Fig. 6.3) because where only GE-centers are hole-trapping ways, the other hole-trapping pathway by chemisorbed $O_2^-$ is suppressed by UV-illumination.
The higher (lower) BE intensity of the as-grown sample (air-annealed sample) is commensurate with longer (shorter) BE decay lifetime. We propose that the decrease of BE for the air-annealed sample would arise from the trapping of the photo-excited holes to GE-centers. An earlier study reported the enhancement of the GE and suppression of the BE of ZnO powder following annealing in air at 1000°C. The authors attributed the shortening of the BE lifetimes to exciton trapping by the GE related defects with a calculated exciton trapping lifetime comparable to the intrinsic exciton lifetime (i.e., ~2.0 ns). However, our findings in Chapter 4 revealed an ultrashort sub-ps-to-ps hole trapping process to these GE-centers. In addition, as shown in Fig. 6.3(b), following UV illumination, the BE dynamics of the air-annealed sample recover to approximately that of the UV illuminated as-grown sample. Although air-annealing increases the concentration of GE-centers in ZnO NWs, hole-trapping to the chemisorbed O$_2^-$ plays a more significant non-radiative role in the BE dynamics compared to the hole-trapping process by the GE-centers in these air-annealed samples. The small difference in the BE dynamics between the as-grown and the air-annealed samples after UV illumination could be attributed to the introduction of other types of defects (e.g., O$_{Zn}$) as a consequence of the air-annealing.
Amongst the three main non-radiative relaxation pathways identified: GE-centers, chemisorbed $O_2^{-}$ and $V_0^{2+}$, the first two are dominant in the air-annealed samples while $V_0^{2+}$ is dominant in the H<sub>2</sub>-annealed samples. These contrasting scenarios allow us to further compare the relative effects of these non-radiative relaxation pathways on the BE recombination dynamics through a pump-fluence dependent study. Fig. 6.4 shows a plot of GE intensity as a function of pump fluence and Fig. 6.5 and 6.6 show the TRPL spectra and plots of the best fit parameters for the BE bi-exponential decay as a function of pump fluence for the air-annealed and H<sub>2</sub>-annealed samples, respectively. The weighting factor of the fast decay component, $A_f$ (or the fast decay amplitude) is also plotted together with $\tau_f$, which is associated with the recombination of the excitons from the defect-rich regions. With increasing pump intensities, a saturation of the defect states would be evident from
an initial increase of the decay lifetimes or decrease of the decay amplitude and the eventual leveling of both the decay lifetimes and decay amplitude. Hence, the trend lines (i.e., the saturation or non-saturation behaviour) of $A_r$ and $\tau_r$ as a function of the excitation pump fluence would be indicative of the concentration of the non-radiative centers present in the samples.

**Figure 6.5** Pump fluence dependent TRPL of air-annealed (a) and H$_2$-annealed (b) ZnO NWs. The solid lines are fitting curves by bi-exponential decay function. Black arrows indicate the direction of increasing pump fluence.
With increasing pump fluence, the GE intensity of the air-annealed sample increases linearly, while that of the H$_2$-annealed sample becomes saturated (Fig. 6.4). This clearly shows a saturation of the GE-centers in the latter, while there is an abundance of such states in the former. However, the BE recombination dynamics indicate otherwise: the decay time constants $\tau_f$ and $\tau_s$ (i.e., fast and slow components of the radiative e-h recombination originating from the defect-rich and defect-poor regions respectively) of
the air-annealed sample increases and approaches a plateau while that of the H2-annealed sample merely shows an increasing (non-plateauing) trend. Furthermore, with increasing fluence, the $A_\tau$ values of both samples decreases; but with that of the air-annealed sample exhibiting a sharp decrease that levels off to a plateau. These observations can be explained as follows: (a) for the air-annealed samples, GE-centers are in abundance and are not saturated at these pump intensities. The BE decay lifetimes increase with the removal of the chemisorbed $O_2^-$ by the photo-excited holes and approach a plateau as the desorption and readsorption of $O_2$ reach an equilibrium. (b) For the H2-annealed sample, the saturation of the GE clearly shows that GE-centers have been saturated at these pump intensities. However, the $V_O$ states which are in abundance are not saturated at these pump intensities and this is evident from the increasing (non-plateauing) trend of the BE decay lifetimes and the decreasing (non-plateauing) trend of the decay amplitude $A_\tau$. Hence, from these results and our earlier result that hole trapping to the GE-centers occur on an ultrashort sub-ps-to-ps timescale, we can infer that these GE-centers have a limited effective hole capture radius. Although hole trapping by GE-centers depopulates the bandedge carrier population, the extremely fast trapping exhibited by these states and their localized nature mean that the hole-trapping process to the GE-centers is essentially static in the timescale of the exciton lifetime and would have little influence on the BE dynamics. This is in contrast to the other two non-radiative relaxation pathways (i.e., chemisorbed $O_2^-$ and $V_O^{2+}$), which directly compete with the ZnO BE dynamics.
**6.3.6 Electron-trapping time by V$_{O}^{2+}$ in H$_2$-annealed ZnO NWs**

In view of our findings that H$_2$-annealing depletes the chemisorbed O$_2^-$ on the ZnO NW surface and that V$_{Zn}$ has little influence on the BE dynamics, we can proceed to estimate an upper limit for the average electron trapping time, $\tau_{et}$, by the V$_{O}^{2+}$ defects using the average BE lifetimes in Table 6.1 of the as-grown sample after UV illumination, $\tau'_{PL}$, and that of the H$_2$-annealed sample, $\tau''_{PL}$. Using the following relations:

\[
\frac{1}{\tau'_{PL}} = \frac{1}{\tau_{R}} + \frac{1}{\tau'_{\text{defects}}};
\]

\[
\frac{1}{\tau''_{PL}} = \frac{1}{\tau_{R}} + \left( \frac{1}{\tau''_{\text{defects}}} + \frac{1}{\tau_{et}(V_{O}^{2+})} \right)
\]

(6.2)

where $\tau'_{\text{defects}}$ and $\tau''_{\text{defects}}$ are the characteristic trapping times by the other intrinsic defect states (i.e., O$_i$, Zn$_i$) apart for the dominating non-radiative channel V$_{O}^{2+}$ in the as-grown (UV-illuminated) and the H$_2$-annealed samples, respectively. With $\tau^{-1}_{et(V_{O}^{2+})}$ dominating in the latter equation, we can have the following approximation: $1/\tau''_{PL} = 1/\tau'_{PL} + 1/\tau_{et(V_{O}^{2+})}$, where we estimate $\tau_{et(V_{O}^{2+})} \approx 60 \pm 10$ ps. We further emphasize that this estimate is an upper limit because even though $\tau'_{PL}$ is dominated by the radiative component, there exists a non-radiative contribution (i.e., $\tau^{-1}_{\text{defects}}$) for the as-grown (UV-illuminated) sample. Therefore, the value of $\tau'_{PL}$ is smaller than that of the intrinsic $\tau_{R}$. Hence, $\tau_{et(V_{O}^{2+})}$ would have been even shorter.
6.3.7 Overview of carrier dynamics in air-annealed and H$_2$-annealed samples

![Figure 6.7 Schematic diagram of carrier recombination processes mainly occurred in air-annealed (a) and H$_2$-annealed ZnO NWs following above-bandgap photoexcitation. The distance $d_{hv}$ corresponds schematically to the penetration depth for UV light in ZnO.](image)

Figure 6.7 schematically illustrates the carrier recombination processes mainly occurred in air-annealed (a) and H$_2$-annealed ZnO NWs following above-bandgap
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photoexcitation. UV photons penetrate into ZnO as a mean depth of $d_{ph} \sim 50$ nm, which is calculated by the reciprocal of the absorption coefficient of ZnO at 3.4 photon energy ($\alpha \sim 2 \times 10^5$ cm$^{-1}$). Photoexcited electron-hole pairs diffuse throughout the excitation region near ZnO nanowire surface. They can be trapped by surface chemisorbed species, surface and/or bulk defects, or recombine radiatively by giving NBE. As shown in Fig. 6.7, near each GE-center there is a spatial range in which photoexcited holes in this region will be trapped by GE-center within hundreds of femtoseconds (~180 fs for air-annealed sample, ~450 fs for H$_2$-annealed sample as revealed by transient absorption spectroscopy results presented in Chapter 3). Then, the photoexcited electrons in conduction band and/or shallow donors will recombine with these trapped holes at GE-center, giving rise to the commonly observed GE. Besides, for air-annealed ZnO NWs, a fraction of the photoexcited holes produced out side the range of the GE-center will be trapped by the chemisorbed O$_2^-$ with lifetime of ~ 400 ps, then O$_2$ molecular is photodesorbed. In H$_2$-annealed ZnO NWs, a fraction of the photoexcited electrons will be captured by ionized oxygen vacancies (i.e., $V_0^{2+}$) generated on the surface after H$_2$-annealing with lifetime of ~ 60 ps. The rest of photoexcited electron-hole pairs in air-annealed or H$_2$-annealed ZnO NWs can recombine radiatively, thus giving rise to the NBE.

Finally, we would like to highlight the promising applications of ZnO NWs with more surface hole/electron traps. The present results suggest that post-fabrication thermally annealing in oxidizing/reducing atmosphere can effectively tailor the photoexcited carrier dynamics by introducing the surface hole/electron traps. The fast trapping of photoexcited holes or electrons at surfaces of ZnO NWs, which suppress the rapid recombination, is beneficial to potential applications, such as in the photodetection,
photocatalysis and photovoltaics. For example, after annealing in oxygen ambient, more hole traps like chemisorbed $\text{O}_2^-$ and GE-centers are created. After photoexcitation, parts of the photo-excited holes near the surface GE-centers are first trapped within sub-ps, and some other holes will be trapped by surface chemsorbed $\text{O}_2^-$ within hundreds of ps, all of which lead to the fast increase in conductivity due to the unpaired electrons, i.e., enhanced photoresponse. And also, photo-excited holes fast trapped on the surfaces of air-annealed ZnO NWs can also act as oxidizer in the photocatalytic reaction, for instance, the enhanced photocatalytic activity was reported in ZnO nanostructures with high GE intensities. Furthermore, electrons injected from polymer or dye after visible excitation will rarely be consumed due to the reduced traps (i.e., $\text{V}_0^{2+}$) and will also be pushed into core of nanowire by up-ward band bending, which can result in an increased magnitude and lifetime of the photoconductance in the NW-based solar cells. In H$_2$-annealed ZnO NWs, the photo-excited electrons will be fast trapped in surface $\text{V}_0^{2+}$ within tens of ps, preventing electron-hole recombination, and then they can be transferred easily to an electron traps, such as Pt particles on the surface, to participate in the photocatalytic reactions acting as reducer to generate H$_2$ from water.

### 6.4 Summary

In this chapter, the dynamic interplay between various trapping centers in ZnO NWs following post-fabrication thermal annealing in an/a oxidizing/reducing gas ambient was investigated using TIPL and TRPL spectroscopy and their microscopic origins being correlated using XPS. Our findings reveal the presence of a hole transfer time constant of
$\tau_{\text{hole-air-annealed}} \approx 400 \pm 80$ ps to the surface adsorbed oxygen species ($O_2^-$) in the air-annealed sample and an electron transfer time constant of $\tau_{\text{electron-H_2-annealed}} \approx 60 \pm 10$ ps to the ionized oxygen vacancies (\textit{i.e.}, $V_O^{2+}$) in the H$_2$-annealed sample. Comparatively, a hole transfer time constant of $\tau_{\text{hole-as-grown}} \approx 900 \pm 200$ ps was measured for the untreated as-grown samples. Importantly, our findings shed new light on the dynamic interplay between various trapping centers in ZnO NWs; thereby suggesting a strategy for tailoring the ultrafast carrier dynamics of ZnO NWs. These fast carrier trapping processes introduced by annealing effectively compete with the ZnO band-edge emission (BE) dynamics and provide efficient photo-excited charge separations in ZnO NWs, which is beneficial to the potential applications, such as in the photodetection, photocatalysis and photovoltaics.
CHAPTER 7

Conclusions and Outlook

The main objective of research presented in this thesis is to elucidate the defect origins and the dynamics and mechanisms of the ultrafast charge trapping in ZnO NWs using various UOS techniques. The main results and conclusions presented in the previous chapters will be summarized in this chapter. The future prospects of this work will also be discussed.

7.1 Summary of Results

In this work, the charge dynamics and mechanisms of the charge trapping by intrinsic (i.e., $V_O$ and $V_{ZnO}$) and extrinsic defects (i.e. Cu dopants), and chemisorbed species (i.e., $O_2$ species) in ZnO NWs prepared by the vapor transport method are extensively investigated using UOS techniques in temperature and pump-fluence dependence studies. Varying concentrations and types of GE-centers; and types of surface traps in the ZnO NWs are produced by means of post-fabrication thermal-annealing of NWs in an oxidizing or a reducing ambient, or by the Cu-doping during growth of ZnO NWs.

Through a comprehensive ultrafast optical spectroscopy study, new insights into its origin and the charge trapping dynamics at the GE centers in ZnO nanowires are gained. Transient absorption spectroscopy revealed a sub-band-gap absorption bleaching band arising from the state filling of the electrons in the conduction band and holes trapped in the GE centers. The GE originates from the recombination between the
electrons in the conduction band and/or shallow donor levels and the holes trapped at the
GE centers (which are located at \( \sim 0.88 \) eV above the valence band). Importantly, an
ultrafast excitonic Auger-type hole trapping process to the GE centers occurring in a sub-
ps time scale was also uncovered by TAS. This finding was discussed in Chapter 4.

In addition, from the TRPL results, it was found that carrier trapping processes and
PL transients responding to temperature in un-doped and Cu-doped ZnO NWs were very
different although the shape and energy position of GE bands were similar. For the un-
doped ZnO NWs, the photoexcited electrons are trapped by GE-centers within sub-ps,
while for the Cu-doped ones, electron trapping to the Cu ions occurred within \( \sim 38 \) ps.
Furthermore, the temperature-dependent recombination dynamics of the GE from these
two types of samples are distinct. The unusual temperature dependence of the GE lifetime
in un-doped sample was explained by the emission comprising of three transition
processes. These findings were discussed in Chapter 5.

Through TIPL and TRPL spectroscopy, an ultrafast hole-transfer process to the
surface adsorbed oxygen species occurring within a few hundred picoseconds was
observed in the air-annealed samples; and an ultrafast electron-transfer process to charged
oxygen vacancies occurring within tens of ps was observed in the H\(_2\)-annealed samples.
XPS measurements validated the surface chemical composition from these samples. These
carrier trapping process by the surface chemisorbed species strongly influenced the band
edge emission dynamics, thereby suggesting a strategy for tailoring the ultrafast carrier
dynamics in ZnO NW-based devices. In contrast, the hole trapping by the GE-centers has
less influence on the BE dynamics due to the very fast carrier trapping time. These
findings provide valuable information on the dynamic interplay between various trapping
centers in ZnO NWs and suggest a strategy for tailoring the ultrafast carrier dynamics of ZnO NW-based devices. These findings were discussed in Chapter 6.

7.2 Suggestions for Future Work

Despite our efforts in this work, there are still several open questions that could be addressed in a future work.

(a) Investigating the charge carrier dynamics of ZnO nanostructures prepared by wet chemical methods vs physical deposition methods. Although comprehensive studies have been carried out on as-grown and post-annealed ZnO NWs prepared by the vapor transport method to understand the effect of defects on the charge carrier dynamics, it should be noted that the type of defects in nanostructures prepared by different methods are quite different. Therefore, the influence of defects in the nanostructures prepared by the other method, such as wet chemical method should be investigated in the future. Therefore, as a future work, the comparison of the origins of GE and the GE-center related-carrier dynamics in ZnO nanostructures prepared by the wet-chemical method vs vapor transport method is an interesting topic. In addition, given the wide applications of thin films in the optoelectronic devices, such studies should also include ZnO thin films grown by metal organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) methods.

(b) Investigating the free carrier dynamics in ZnO nanowires by using time-resolved terahertz spectroscopy. Presently, there are few reports about the study of transient
photoconductivity in ZnO NWs. As an extension of our existing work, an investigation on transient photoconductivity in the ZnO NWs by using the optical pump-terahertz probe (OPTP) technique is proposed. This would allow a direct measurement of the free carrier dynamics in the conduction band and valence band, which can be correlated with our findings in Chapter 6 on the effects of surface hole and electrons traps in ZnO NWs. Such an OPTP setup exists at the Institute of Materials Research and Engineering. However, the wavelength of the pump beam is limited to 800 nm or 400 nm wavelengths which limit the possibility of performing single photon excitation of ZnO NWs. This could be achieved through sum frequency generation of wavelengths in the UV (i.e. 300 – 325 nm).

(c) Investigating the carrier dynamics in ZnO nanowire-based devices. As introduced in Chapter 1, the photocatalytic activities, the photoresponse are obviously affected by the surface defects in ZnO nanostructures. A future project could involve the fabrication of functional single ZnO NW sensors where the device performance and effect of surface defects on the charge trapping and separation can be correlated. Such correlated studies would yield deeper insight into the carrier dynamics and recombination mechanisms in a device configuration. Development/Setup of the lab infrastructure for single nanowire studies in TAS and TRPL (i.e. involving confocal microscopy etc) is needed for such studies.

(d) Extending the investigation of charge carrier dynamics to other II-VI semiconductor nanostructures. Furthermore, there are also nanostructures systems, such as the TiO2 nanoparticles used for photocatalyst, dye-sensitized SnO2 thin film solar cells
are worth researching in the future. Preliminary results of carrier dynamics in these systems, such as the different carrier trapping dynamics in TiO$_2$ nanoparticles prepared different situations, and charge transfer time from the dye to SnO$_2$ thin film have been obtained. Detailed ultrafast spectroscopy studies are also urgently needed to gain a clear understanding of the carrier dynamics in these systems.
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