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Thickness effect on ultrafast thermalization of carriers in above-band-gap states in ZnO epitaxial films

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Abstract
Energy-dependent free-carrier dynamics was investigated in 70 nm (thin) and 1 μm (thick) ZnO epifilms using the optical pump–probe technique. The far-above-band-gap dynamics in the thin epifilm reveals the prolonged relaxation and the slow recovery of renormalized band gap. The band-gap renormalization (BGR) effect is affected by the inefficient carrier–phonon scattering. In addition, the loss of excited carrier density via surface trapping results in an energy-dependent BGR buildup time. However, the far-above-band-gap dynamics in the thick epifilm reveals fast relaxation followed by BGR recovery, which is independent of the photon energy. The near-band-gap dynamics shows an ultrafast carrier thermalization both in the thin and the thick epifilms.

1. Introduction

Due to its wide band gap of 3.37 eV [1], ZnO has been a candidate material for ultraviolet light emitters. With the large exciton binding energy of 60 meV [2], which is larger than other II–IV compound semiconductors and GaN, free excitons are stable even at room temperature (RT). Strong RT ultraviolet spontaneous and stimulated emissions make ZnO a promising material for exciton-related photonic devices [3].

The third-order optical nonlinearity, including nonlinear refraction and two-photon-absorption (TPA), in a ZnO thin film near two photon exciton resonance had been investigated by the Z-scan method with femtoscond pulses near-IR range [4]. In addition, using the same method with frequency doubling Ti : sapphire laser, the ZnO thin film has revealed enormous TPA coefficient and appearance of free carrier absorption (FCA) near exciton resonance in the UV range [5]. Recently, there were some studies to investigate carrier dynamics in ZnO thin films and nanostructures using transient absorption and PL spectroscopy [6–11]. From the time-resolved PL studies under high excitation of 70 μJ cm^{-2} in a 233 nm thick ZnO epifilm, Takeda *et al* [10] reported the buildup of electron–hole plasma (EHP) followed by band-gap renormalization (BGR), a shrinkage of the band gap due to the screening of Coulomb interaction by the free carriers. They also showed the recovery of BGR through EHP emission by using the optical Kerr gate method. It can be seen from the transient absorption spectroscopy that the Burstein–Moss effect reduces absorption, whereas the BGR effect normally induces absorption with photo-excitation above the band-gap states [9, 11]. In addition, the steady-state PL spectrum also reported the Burstein–Moss and BGR effects with dependence

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of carrier concentration in GaN and ZnO [12–14]. Therefore, it is imperative to understand the thickness effect on free-carrier thermalization in ZnO epifilms since they play important roles in stimulated emission and the gain process in real photonic device structures. By exciting the free carriers to the above-band-gap states of two extreme thicknesses of epifilms, we observed and compared the intra-band relaxation via carrier–phonon scattering against the interaction between the free carriers and the sample surface.

In this study, we compare free-carrier dynamics in thin (70 nm) and thick (1 μm) ZnO epitaxial films by using the femtosecond pump–probe technique with photon excitation energy above the band gap, and under low excitation fluence of 10 μJ cm^{-2} at RT. In the thick ZnO epifilm, the free-carrier relaxation time is on the order of 1 ps and the BGR recovery time is similar to the previous reports. The obtained time constants are independent of the excitation energy above the band-gap states. However, in the thin ZnO epifilm, the transient differential transmission reveals prolonged relaxation time of tens of picoseconds (ps) for far-above-band-gap states, while it shows an ultrafast relaxation time less than 1 ps as we decrease the excitation energy close to the band gap. We also conclude that the loss of excited carrier density due to the surface trapping contributes to a decrease in the BGR effect for the far-above-band-gap states.

2. Experiment

Our c-axis-oriented ZnO thin films with thickness of 70 nm and 1 μm were grown on the c-plane sapphire substrates by pulsed laser deposition with a base vacuum of 2.1×10^{-8} Torr and working pressure of 1.1×10^{-7} Torr using a KrF excimer laser for different deposition times [15]. Hall measurements yielded a background electron concentration of 1.68×10^{18} cm^{-3} for the 70 nm epifilm and 1.87×10^{17} cm^{-3} for the 1 μm epifilm, respectively.

The absorption spectrum was measured using a spectral photometer (Jasco V-670) with a resolution of 0.5 nm. RT time-resolved experiments were performed using a femtosecond optical pump–probe technique which employed a frequency-doubled mode-locked Ti : sapphire laser with 82 MHz repetition rate (Tsunami, Spectral Physics Inc.) equipped with a frequency doubler (Model 3980, Spectral Physics Inc.). This system provided ultraviolet excitation wavelengths ranging from 358 to 363 nm. The laser pulses, with a width of around 150 fs, were split into the pump and probe beams with a contrast ratio of 20 : 1. The pump beam was chopped and the detected probe signal was measured as a function of time delay between the pump and the probe beams by a lock-in amplifier (SR830). In order to reduce the coherent artefact, resulting from two beams' interference if they possess the same polarization as well as distinguishability in detection, we kept the polarization of pump and probe beams orthogonal to each other.

Because our c-axis-oriented ZnO epitaxial films were grown on the c-plane sapphire substrate, its crystal axis is normal to the surface. The probe beam incident normally to the sample surface has polarization orthogonal to the c-axis.

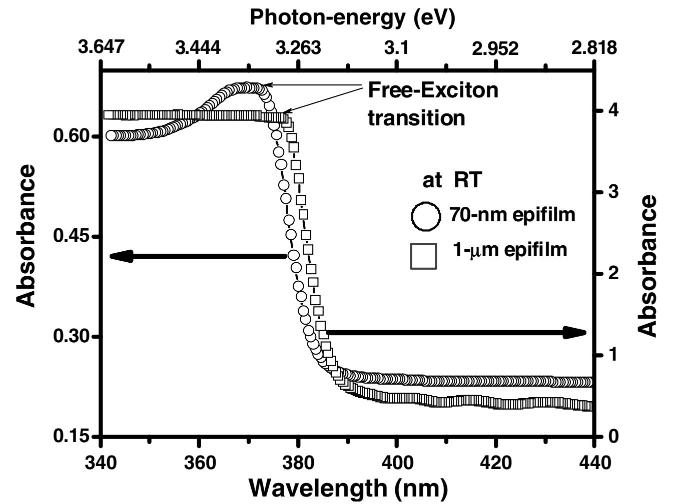

Figure 1. Room-temperature absorption spectrum from 70 nm and 1 μm ZnO thin films.

Although there is a small angle (~8°) made between the pump beam and the surface normal, the pump beam with TE polarization is also orthogonal to the c-axis. The time-resolved setup in this work is independent of polarization.

3. Results and discussion

Figure 1 shows the measured absorption spectrum of the 70 nm and the 1 μm ZnO epifilms at RT in which the reflectance from the surface was taken into account. It reveals that the absorption edge for the 70 nm epifilm is around 3.333 eV (372 nm), but for the 1 μm epifilm is around 3.293 eV (376.5 nm). The absorption edge is corresponding to the free exciton transition and the spectral shape of the absorption edge is dominated by band-tail states. The apparent red shift correlated with increased film thickness is attributed to the background electron concentration or the compressive strain for the c-axis-grown films [16, 17]. Using the exciton binding energy of 60 meV in ZnO at RT, we estimate the band-gap energy to be 3.393 eV (365.5 nm) and 3.353 eV (369.8 nm) for thin and thick epifilms, respectively. To study the photo-excited carrier dynamics, we then measured the transient above-band-gap differential transmission of these two epitaxial films under low optical excitation fluence on the order of 10 μJ cm^{-2} at RT.

The normalized transient differential transmissions ($\Delta T/T$) as a function of time delay for excited photon energies of 3.464 eV (358 nm) and 3.444 eV (360 nm), having excess energy of 71 and 51 meV above the conduction band edge (CBE), in a 70 nm film with $E_g = 3.393$ eV are shown in figure 2. Here, the difference in transmission, $\Delta T = T$ (with pump) − T(without pump), represents the change of transmission through the sample with and without optical pumping. It shows a negative dip resulting from TPA coinciding with the pump pulse. The transient response instantaneously increases to become positive after the pump pulse then gradually decreases to negative again. Finally, the negative transient response returns to the

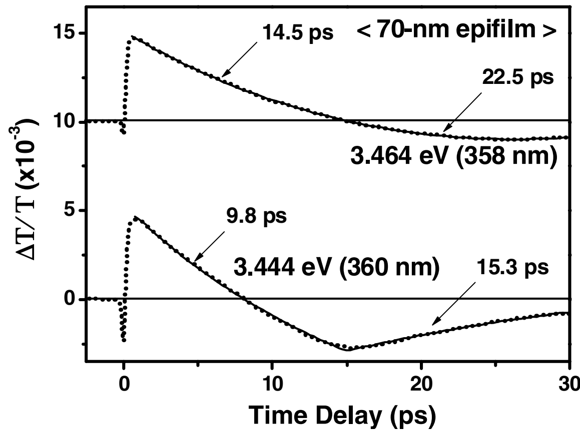

Figure 2. Measurement of normalized transient differential transmission (dotted lines) as a function of time delay for excitation photon energy at 3.464 and 3.444 eV in the 70 nm ZnO epifilm. Solid lines are fitting curves. Traces are vertically displaced for clarity.

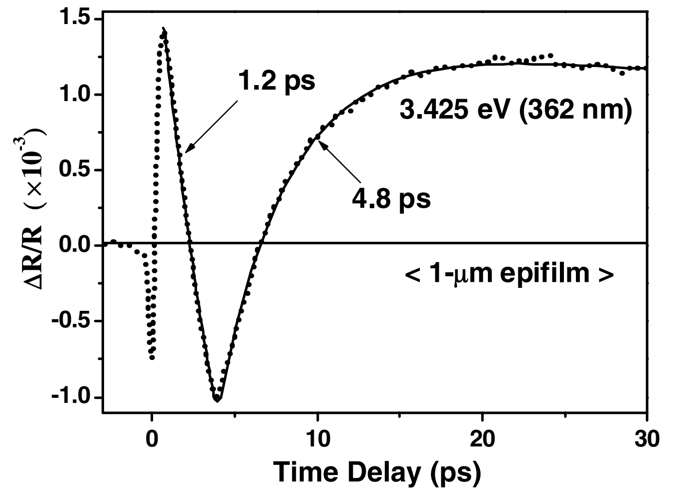

Figure 3. Measurement of normalized transient differential reflectance (dotted line) as a function of time delay with excitation photon energy at 3.425 eV in the 1 μm ZnO epifilm. Solid line is a fitting curve.

original level at long time delay. In general, the excited free carriers will result in both the Burstein–Moss effect, also called the band-filling effect, and the BGR effect in semiconductors [18]. Here, the measured transient differential transmission, varying from positive (induced transmission) to negative (induced absorption), reflects that the Burstein–Moss effect is diminished by the BGR effect with the excited carriers quickly relaxing to the CBE. The transient differential transmission at 3.444 eV is similar to that at 3.464 eV, except that it decays slightly faster to result in earlier transition to negative differential transmission.

In order to extract the free-carrier relaxation times in the 70 nm ZnO film, we use the response function of $A_1\ \exp(-t/\tau_1) - A_2\ \exp(-t/\tau_2)$ to fit traces in figure 2, where A_1 term is a fast exponential decay component due to the Burstein–Moss effect and A_2 term is a slow exponential decay component corresponding to the BGR recovery. A relaxation time (τ_1) of 14.5 and 9.8 ps is found for photon energy of 3.464 and 3.444 eV, respectively. The prolonged relaxation process is mainly due to the carrier–phonon scattering with their excess kinetic energy. Both times are longer than 1 ps observed in ZnO films using time-resolved PL techniques [10]. The recovery time for BGR (τ_2) of 22.5 and 15.3 ps corresponding to photon energy at 3.464 and 3.444 eV, respectively, is close to the non-radiative recombination time on the order of 10 ps reported in ZnO nanorods [11].

From the measurements of far-above-band-gap dynamics, we notice two cases worth discussing. First, the far-above-band-gap dynamics reveals a long-time relaxation as compared with previous reports [10, 11]. Second, an even longer carrier relaxation was observed for excitation to higher lying states when using 3.464 eV than that at 3.444 eV. Because the thickness of the sample used in the study is as thin as 70 nm, the interaction between excited free carriers and the surface of the thin film may play a role in the relaxation process. We therefore estimate the time elapsed for a free carrier to travel a distance of 70 nm by the equation: $t = d/\sqrt{2E_k/m_c^*}$, where d represents the thickness (70 nm) of sample and $m_c^* = 0.28m_0$ is the effective mass of electrons. For the excess energy (E_k) of 71 meV and 51 meV provided, respectively, by the 3.464 eV and 3.444 eV photons, we obtained time constants around 235 and 276 fs. This is close to the reported thermalization time of 200 fs for carrier–carrier or carrier–phonon scattering in ZnO [11]. The physical picture is that an excited free carrier may impinge on the surface of the sample prior to interaction with phonons or other carriers to lose their excess kinetic energy. Thus, we attribute the long intra-band relaxation of the carriers towards the band edge to inefficient thermalization for carrier–phonon scattering after the carriers scattered by the sample surface. Furthermore, some excited free carriers might have been trapped by the surface when they impinge on it. It is known that the BGR effect is concerned about exciting enough free carriers to result in shrinkage of the band gap due to screening of Coulomb interaction [18]. The BGR effect will produce negative differential transmission to the transient response with photo-excitation above the band-gap states [11]. Both the loss of free-carrier density via surface trapping and fast carrier escape from the region of measurement could result in the decrease in the BGR effect e.g. the higher the excess energy, the more probable the loss of carrier density which causes the weaker BGR effect, and thus longer recovery time, for the higher excitation photon energy.

To confirm that the loss of excited free carriers plays an essential role in the onset of the BGR effect, we performed the same carrier dynamics analysis for the 1 μm ZnO epifilm with $E_g = 3.353$ eV under the same optical excitation. The measured normalized transient differential reflectance for photon energy at 3.425 eV, with the excess energy of 72 meV in the conduction band, is shown in figure 3. The temporal behaviour reveals a fast decay followed by the BGR recovery and a slow decay at long times after excitation. As compared with the measurements in figure 2, the dynamics in the 1 μm epifilm reveals an ultrafast relaxation, implying the carrier thermalization due to carrier–phonon scattering in the thick epifilm is more efficient than in the thin epifilm. We also

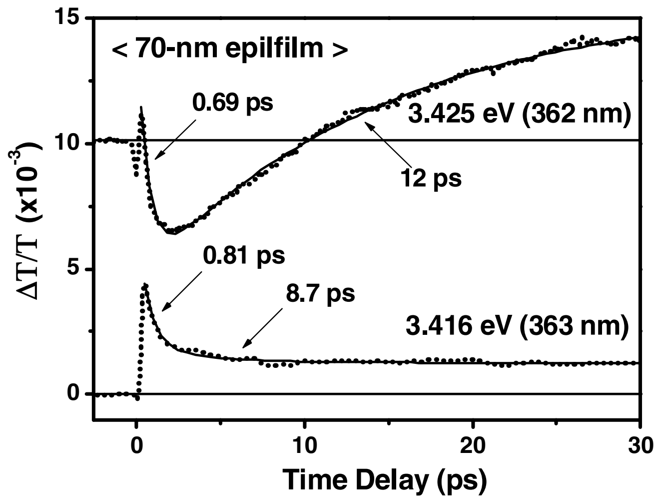

Figure 4. Measurement of normalized transient differential transmission (dotted lines) as a function of time delay with excitation photon energy at 3.425 and 3.416 eV in the 70 nm ZnO epifilm. Solid lines are fitting curves. Traces are vertically displaced for clarity.

measured the above-band-gap dynamics in the 1 μm ZnO epifilm with variable photon energy from 3.444 to 3.397 eV, which were not shown here, and found the temporal behaviour is similar to the trace obtained for 3.425 eV excitation, except that the peak amplitude is different. It can be found that the free-carrier relaxation time of 1.0–1.2 ps is independent of excitation photon energy in the 1 μm epifilm, while it takes a much longer time (>9 ps) with a dependence upon excitation photon energy in the 70 nm epifilm. These results indicate effective hot carrier thermalization via carrier–carrier or carrier–phonon scattering in the 1 μm epifilm, but inefficient hot carrier thermalization in the 70 nm epifilm. As a result, we found decrease in the BGR effect and the variation of BGR buildup time in the 70 nm epifilm. After the recovery of BGR, the transient differential reflectance will become positive again. Then, it shows a relative slow decay with a time constant on the order of 100 ps due to carrier recombination that cannot be seen within finite time scale in figure 3.

When we decrease the excitation photon energy towards the CBE, the measured normalized transient differential transmissions as a function of time delay for photon energy at 3.425 eV (362 nm) and 3.416 eV (363 nm) in the 70 nm film with E_g = 3.393 eV are shown in figure 4. The data show a negative dip due to TPA around zero time delay, and an obviously quick transition from positive transient response to negative followed by the slow recovery process of negative response. The relaxation observed for 3.425 eV excitation, which provides 32 meV excess energy, is much faster than those observed for 3.464 and 3.444 eV in figure 2, implying the carrier thermalization occurs instantaneously after the pump pulse and the interaction with the sample surface can be ignored. It can be anticipated that both of Burstein–Moss and BGR effects happen almost simultaneously. In addition, the efficient carrier thermalization results in an ultrafast decay and the BGR effect can produce negative differential transmission to the transient response, respectively. Thus, the recovery of BGR via free-carrier recombination causes transferring to the Burstein–Moss effect and the negative transient response returns to positive at longer time delay.

As we further decrease photon energy to near the band gap, the trace obtained for 3.416 eV excitation (23 meV above the CBE), also shown in figure 4, consists of a fast and a slow decay component. There is no negative transient response in this trace. The photo-generated carriers acquire the Fermi–Dirac distribution through carrier–carrier scattering, and then quickly relax to the band edge through carrier–phonon scattering [19]. Under these circumstances, the downshift of band gap by the BGR effect at RT may not be large enough to exceed to the width of thermalized carrier distribution (∼26 meV) limited by the band edge and the Burstein–Moss effect should be always present. Thus, the Burstein–Moss effect still overwhelms the BGR effect when performing the experiment near the band edge. Furthermore, at relatively longer time delay, the carriers will decay through carrier recombination.

By using the same fitting as described above to the trace for 3.425 eV excitation in figure 4, we obtained a fast decay time of 0.69 ps and a recovery time of 12 ps. In addition, we obtained fast and slow decay times of 0.81 and 8.7 ps (with positive sign of A_2) to the trace for 3.416 eV excitation. The fast decay times (0.69 and 0.81 ps) are consistent with the carrier thermalization time on the order less than 1 ps reported in ZnO thin films [9, 10]. Whereas, the BGR recovery time (12 ps) or the slow decay time (8.7 ps) obtained from this work is due to the non-radiative recombination also consistent with previous reports [11].

4. Summary

To sum up, energy dependent free-carrier dynamics in the 70 nm ZnO thin epifilm was investigated by the femtosecond transient absorption and compared with results from similar measurements with the 1 μm thick epifilm. In the thin epifilm, the far-above-band-gap dynamics reveals a prolonged relaxation time and a slow recovery time. The band-gap renormalization effect is affected by inefficient carrier thermalization at the film surface and the loss of excited carrier density via surface trapping to result in an energy-dependent BGR buildup time. However, the far-above-band-gap dynamics in the thick epifilm reveals fast relaxation followed by the BGR recovery, which is independent of the photon energy. The near-band-gap dynamics shows an ultrafast thermalization both in the thin and thick epifilms mainly attributable to the carrier–phonon scattering.

Acknowledgments

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