Femtosecond dynamics of exciton bleaching in bulk GaN at room temperature

Yin-Chieh Huang, Gia-Wei Chern, Kung-Hsuan Lin, Jian-Chin Liang, and Chi-Kuang Sun[a)]
Department of Electrical Engineering and Graduate Institute of Electro-Optical Engineering, National Taiwan University, Taipei, Taiwan, 10617 Republic of China

Chia-Chen Hsu
Department of Physics, National Chung Cheng University, Chia-Yi, Taiwan, Republic of China

Stacia Keller and Steven P. DenBaars
Department of Electrical and Computer Engineering, University of California, Santa Barbara, California 93106

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Femtosecond transient transmission pump–probe technique was used to investigate exciton dynamics in a nominally undoped GaN thin film at room temperature. An exciton ionization time of 100–250 femtoseconds was observed by the time-resolved pump–probe measurement. A comparison experiment with pre-excited free carriers also confirmed the observation of the exciton ionization process in bulk GaN. © *2002 American Institute of Physics.*
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GaN-based semiconductors have received an ever-increasing interest for optoelectronic applications in the blue and ultraviolet spectral region.[1] It is well known that the near band-edge low-temperature optical properties in III–V semiconductors are dominated by the many-body Coulomb electron–hole correlations, or the dynamics of excitons.[2] With increasing temperature, the exciton linewidth broadens due to scattering processes with longitudinal optical (LO) phonons and the excitons become thermally ionized.[3] Knox *et al.*[4] had observed an ionization time of ~300 fs for resonantly excited excitons in GaAs quantum wells at room temperature. Wegener *et al.*[5] used a simple rate-equation model for exciton ionization to fit the measured pump–probe transmission trace for InGaAs quantum wells. An exciton ionization time of ~200 fs was measured.[5] A similar procedure was adopted by Becker *et al.*[6] in the measurement of CdZnTe quantum wells, and a fast ionization time of ~110 fs was obtained. GaN with a hexagonal crystal structure has a direct band gap of 3.42 eV at room temperature. Free excitons in GaN are composed of three bands labeled as E_{XA}, E_{XB}, and E_{XC}.[7] The binding energy (E_{ex}) and the effective Bohr radius (a_B) of the *A* exciton have been reported to be ~21 meV and ~29 Å.[7] Because wide-gap semiconductors have a large E_{ex} value on the order of the thermal energy k_BT at room temperature, excitonic resonances can not be easily ionized. However, exciton ionization has been convincingly observed up to room temperature through optical absorption measurement in high-quality GaN epilayers recently.[8,9] By using transmission-type pump–probe measurement[10,11] around the excitonic transition energy, here we report the direct measurement of exciton ionization process in bulk wurzite GaN.

The 2.5 μm-thick GaN film used in our study was grown by metalorganic chemical vapor deposition on *c*-plane sapphire.[7] The crystal structure is wurtzite. In Fig. 1, the solid circles shows the measured low-intensity absorption spectrum of the nominally undoped GaN sample at room temperature. The *A*-exciton peak (3.41 eV, 363 nm) and the Coulomb enhancement of the continuum absorption can still be clearly observed.

The time-resolved experiments were performed with a mode-locked Ti:Sapphire laser. The output laser pulses were frequency doubled in a beta barium borate crystal to reach the exciton energy. The frequency-doubled pulses had a pulsewidth of ~150 fs at a wavelength around the *A*-exciton resonant peak. The full width half maximum of the output spectral bandwidth was 2.5 nm. One tenth of the UV beam was reflected by a beam splitter to be used as the probe beam while the rest passed through the beam splitter was used as the pump beam. We rotated the polarization of the pump

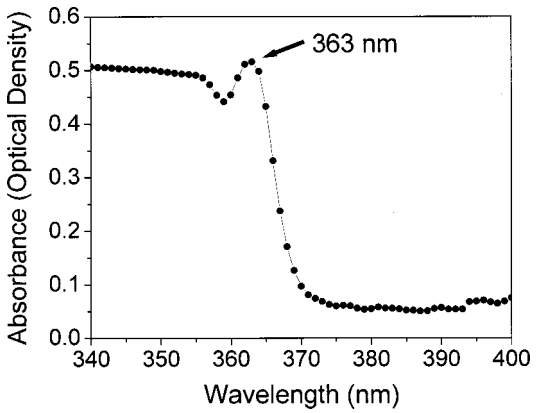

FIG. 1. Absorption spectrum for an unintentionally doped 2.5 μm GaN thin film. A strong exciton resonance around 363 nm can be observed.

[a)]Author to whom correspondence should be addressed; electronic mail: sun@cc.ee.ntu.edu.tw

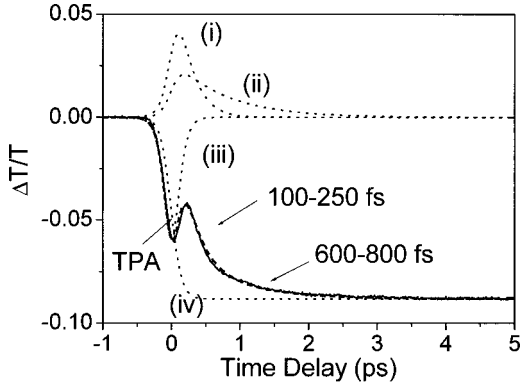

FIG. 2. Measured transient response of the unintentional doped GaN thin film with a central wavelength of 362.1 nm. The solid line is the measured probe transmission change. The dashed line is a convolution fitting result with four fitting components: (i) fast exponential decay with time constant 100–250 fs, (ii) slow exponential decay with time constant 600–800 fs, (iii) TPA, and (iv) negative step function.

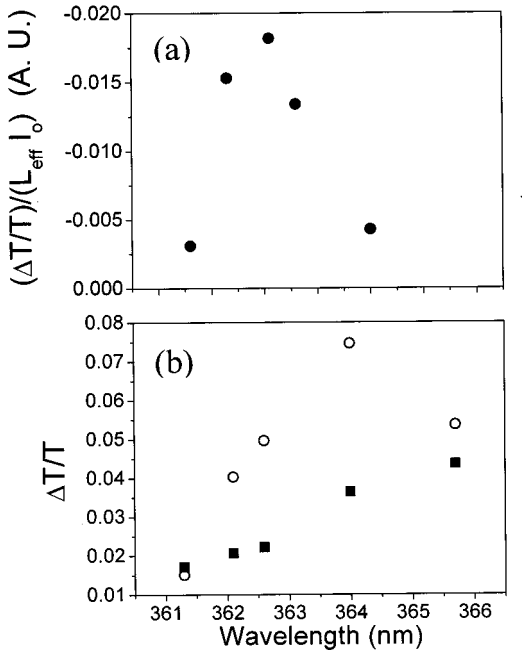

FIG. 3. Magnitude of (a) the TPA coefficient, (b) fast time constant component (open circle) and slow time constant component (solid square) vs laser excitation wavelength. Time constants of 200 fs and 750 fs were chosen for the fast and slow components in the fitting. The excited average carrier density was kept fixed for different wavelength experiments.

beam by using a half-wave plate so that the polarizations of the pump (*s*) and the probe (*p*) beams were orthogonal to each other. The pump and probe beams were focused onto the bulk GaN sample by a focusing objective. After the sample, we measured the transmitted and reflected probe intensity by using a photodetector. A polarizer (*p* polarized) was placed in front of the photodetector to remove any possible pump scattering light. We chopped the pump beam while the intensity of the reflected and transmitted probe beams were recorded as a function of the temporal delay between the pump and probe beams through a lock-in amplifier.

Figure 2 shows a typically measured probe transmission change $\Delta T/T$ of the nominally undoped GaN thin film as a function of probe delay. The pump/probe photon energy was 3.42 eV (362.1 nm) corresponding to the exciton resonance. By measuring the incident pump power (6.9 mW, before the sample), reflected and transmitted pump powers, and the focused pump/probe beam diameter (14 μm), an effective absorption coefficient of 1.9×10^4 cm^{-1} was obtained. The corresponding average carrier density is 3.5×10^{17} cm^{-3} with a maximum carrier density of 1.8×10^{18} cm^{-3} at the incident surface. The probe transmission changes consisted of four components corresponding to two-photon absorption (TPA), exciton dynamics, and carrier dynamics (described next). We have continuously varied our incident pump power from 6.9 down to 0.4 mW with the maximum surface carrier density ranged from 1.8×10^{18} down to 1×10^{17} cm^{-3} (corresponding average carrier density 2.4×10^{16} cm^{-3}). For the whole experimental range, the TPA and exciton-dynamics components showed a linear behavior while the slow components showed a slight magnitude saturation under high excitation. We have also performed time-resolved reflection measurements to investigate the contribution of carrier-induced reflection changes to the measured transient transmission signals. It was found that at wavelengths shorter than 371 nm, the measured transmission changes are dominated by the carrier-induced absorption changes rather than reflection modulations. In order to analyze the measured transmission curve quantitatively, various phenomenological response functions were used in a convolution fitting procedure to extract the corresponding contributions and the measured time constants. The solid line in Fig. 2 is the probe transmission change obtained directly from our experiment. The dashed line is a convolution-fitting result consisting of four contributions of the corresponding carrier dynamics. A 240 fs hyperbolic-secant-squared profile was used as input pulse autocorrelation in the fitting. At zero-time delay, a negative transmission change with a width of the pump–probe autocorrelation was observed, which is usually ascribed to the so-called "TPA peak."[12] The TPA peak magnitude was linearly proportional to the pump intensity within our experimental range. Assuming the nonlinear absorption is small ($\beta I_0 \ll \alpha$, which is our case), where β is the TPA coefficient,[13] I_0 is the incident light intensity at the input end, and α is the linear absorption coefficient. β can then be calculated from the extracted transmission change. We found that the recovered TPA term exhibits a resonant feature around 362 nm corresponding to the *A*-exciton position, which can be attributed to the excitonic (Coulomb) enhancement of the TPA process [shown in Fig. 3(a)].[14] This resonant TPA feature also confirms the existence of the hydrogenlike exciton line in the pure GaN film.

After the TPA peak, a fast exponential decay component (positive) with time constant of 100–250 fs followed by a slower one (positive) of ~600–800 fs time constant can be observed and extracted from the pump–probe trace by using fitting processes. We choose 200 fs for a fast component in the specific fitting shown in Fig. 2. We have also included a negative step function in our convolution fitting to represent the band gap-renormalization response. As demonstrated in previously reported results in bulk InGaN,[10,11] the slower time constant is attributed to the thermalization process of the photoexcited electron–hole pairs into lattice temperature. It is thus plausible to ascribe the fast decay time constant to the ionization of the resonantly created excitons into

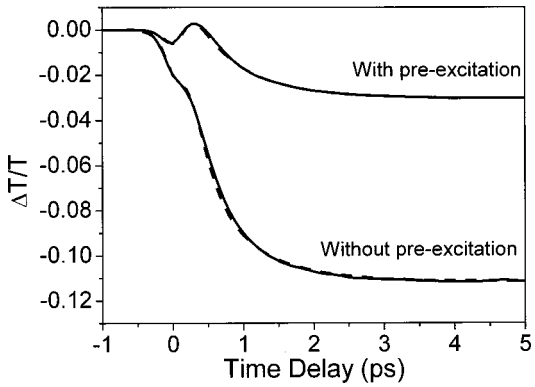

FIG. 4. Measured transient transmission response of the unintentionally doped GaN thin film with and without pre-excited carriers. The laser excitation wavelength was 364.8 nm. The solid lines are the measured probe transmission changes. The dotted lines are convolution fittings with four fitting components accounted for fast exponential decay of time constant 200 fs, slow exponential decay of time constant 750 fs, TPA peak, and negative step function. The corresponding retrieved transmission changes are listed in Table I.

electron–hole pairs by the interaction with LO phonons. The prolonged thermalization time constant of free carriers, compared to above band gap excitation, also confirms the ionization process. It is interesting to notice that we can observe this exciton ionization process even under our high excitation condition, as shown in Fig. 2, with a maximum surface photocarrier density close to the Mott-transition density.[15] This is probably due to the fact that the measured signals are not just contributed from the near surface response, but from the whole sample. However, in a recent low-temperature (10 K) experiment, a remarkable persistence of the excitonic resonances in GaN at carrier densities well above the Mott density at early time delays has already been observed.[16]

Experiments on the nominally undoped GaN by tuning the laser wavelength around excitonic absorption peak from 361.3 to 365.7 nm (center wavelength) were also performed. Incident pump powers were varied from low (0.4 mW) to high (6.9 mW) excitation levels for all experimental wavelengths. The resonance of the ionization component to the excitonic peak wavelength is shown in Fig. 3(b) (open circle), where we plot the magnitude of fast time constant component (fitting with 200 fs) versus the laser wavelength with a fixed photoexcited carrier density. However, the following slower time constant component does not possess the resonant feature around the exciton peak as shown in Fig. 3(b) (solid square). This is because the thermalization of electrons and holes is mainly due to intraband carrier scattering and is not related to exciton dynamics.

We also performed a comparison experiment to study the dependence of the fast decay time constant on background carrier density. An additional pump beam was used to produce a large amount of background carriers in the GaN sample before the transmission pump–probe measurement. These pre-excited background carriers (lead time 5 ps) will influence the following exciton dynamics due to the screening effect. The corresponding probe transmission changes as a function of time delay were shown in Fig. 4. The laser central wavelength was tuned to 364.8 nm around the exciton absorption peak. The retrieved transmission changes are listed in Table I. With a pre-excited carrier density of 1.1×10^{18} cm^{-3}, the strength of the fast ionization component (200 fs) decreases significantly with respect to other terms. Since the carrier density is close to Mott transition, excitons are unstable against the background electron–hole pairs. As a result, the initial formation of excitons is inhibited. This explains the decreased strength of the fast time constant.

TABLE I. Retrieved relative probe transmission changes with and without a pre-excited background free carriers.

$\Delta T/T$	Without pre-excitation	With pre-excitation
TPA	−0.034	−0.018
200 fs	0.049	0.009
750 fs	0.043	0.030

In conclusion, the exciton dynamics in bulk GaN thin film were investigated by UV femtosecond pump–probe measurement. We found that in addition to the thermalization process of free carriers, another fast relaxation process dominates the initial bleaching dynamics in bulk GaN. The corresponding strength of this fast time constant has a resonance around the excitonic absorption, and is attributed to the ionization of excitons into electron–hole pairs. Another comparison experiment with pre-excited background carriers also confirms this interpretation.

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