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Ultrafast electron dynamics study of GaN

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Ultrafast electron dynamics in *n*-doped GaN was investigated using multiple-wavelength pump-probe techniques. A fast electron cooling with a time constant of 500 fs was observed, indicating the electron as the dominant carrier type in cooling processes. Electrons in band-tail states were found to relax at the same rate as conduction electrons, indicating fast (<500 fs) carrier capture into shallow band-tail states and fast scattering between shallow band-tail electrons and conduction band electrons. Our results agree well with the band-tailing model of Chakraborty and Biswas. Impurity screening potential was thus obtained. With a variation of pump photon energy, conduction band intervalley scattering of GaN was also studied. With a proper selection of pump wavelength, the electron cooling behavior was found to be delayed by intervalley returned electrons with a time constant on the order of 1 ps. By examining the fraction of the delayed cooling component, our data suggested an intervalley scattering threshold energy of 1.34 eV, which is the separation energy between the bottom of the *U* valley and Γ valley conduction band minimum in wurzite GaN. [S0163-1829(99)05221-2]

Femtosecond spectroscopy is a powerful tool for dynamic investigation of nonequilibrium carriers in semiconductors. Ultrafast relaxation processes on the time scales of femtoseconds to picoseconds can be directly measured using femtosecond generation and probing techniques,[1–3] taking advantage of the temporal resolution of femtosecond optical pulses. Understanding these ultrafast dynamics is important for applications of high-speed electronics and optical devices. GaN-based semiconductors have recently attracted a lot of attention for their applications as light emitters in the blue to UV wavelength range.[4] In our previous study,[5] we investigated ultrafast carrier dynamics in $In_{0.16}Ga_{0.84}N$ using femtosecond single-wavelength transient transmission measurements. Carrier cooling with a time constant on the order of 500 fs and a hot phonon effect were observed. Due to the nature of single-wavelength experiments, electron and hole dynamics were not separated in our previous study. In this paper, we report multiple-wavelength femtosecond investigations of the intraband electron dynamics in bulk *n*-type GaN. Electron gas cooling behavior was not only observed in time domain, but was also confirmed by the thermomodulation spectrum. Information on conduction band intervalley scattering and band-tail states was obtained.

In this current study of *n*-type GaN, a below-band-gap IR femtosecond optical pulse (referred to as ''pump'') was used to excite the conduction band electron distribution out of equilibrium, without disturbing the valence band population. The internal thermalization of the electron gas and the subsequent equilibration between the electronic and lattice temperatures (external thermalization) were monitored in the time domain using a femtosecond UV probe pulse by probing the interband absorption changes. The UV probe wavelengths were in the vicinity of the valence-to-conduction band-gap transition, which was close to the peak of the absorption change.[6] By tuning the probe wavelength, the electron population changes and the influence of different relaxation mechanisms at different conduction band positions can thus be obtained. The use of widely separated pump and probe wavelengths was essential to avoid any influence of the valence band carriers on the measured response. In addition, the measurements were performed in the low-perturbative regime, where the system response was linear and the measured changes in transmission can be directly related to the electron distribution variation.

The GaN:Si film was grown by metal organic chemical vapor deposition (MOCVD) on *c*-plane sapphire in an atmospheric pressure reactor.[7] After annealing the substrate at 1050 °C, a 525-Å-thick nucleation layer was deposited at 600 °C. The temperature was then raised to 1080 °C to grow an unintentionally doped GaN layer of 1070 Å followed by a Si-doped GaN layer of 1000 nm thickness. The resulted *n*-type doping concentration was on the order of $2\times10^{18}\ cm^{-3}$. The sample was finished with a 6-nm-thick undoped GaN cap layer. The crystal structure was wurzite.[7]

Experiments were performed using a Kerr-Lens-Modelocked Ti:sapphire laser which generates 120 fs pulses with a repetition rate of 80 MHz. The laser output wavelength was tuned between 720 and 740 nm with an average output power of 300 mW. Measurements were performed using a standard pump-probe geometry. One portion of the infrared beam, with half of the available power, passed through a variable delay stage and was used as the pump beam. The other half of the infrared beam was focused into a 500-μm-thick beta barium borate (BBO) crystal to produce frequency-doubled probe pulses tunable between 360 and 370 nm (3.44–3.35 eV), corresponding to the vicinity of conduction-valence band-gap transition (3.39 eV at room temperature). After the BBO crystal, the infrared pulses were removed using a color glass filter. The average power of the doubled UV beam was 3 mW, and its duration was 140 fs measured at the position of the sample by cross correlation with the pump beam in a second BBO crystal. The pump and probe were focused into the sample using a lens with a focal length of 5 cm. The focal spot diameter for the IR and UV beams was 45 and 39 μm, respectively. The transmitted IR pump was rejected using an iris and a color glass filter so that only the UV probe signal was detected. The pump beam was chopped and the detected probe signal was measured as a function of the temporal delay between the pump and probe using a lock-in amplifier. Experiments using a probe wavelength shorter than 358 nm were prohibited by the strong absorption in the 1-μm-thick GaN films, while a good quality thinner GaN:Si film was not available. No transmission changes were induced for experiments using probe wavelengths longer than 372 nm due to the fact that the probe wavelength will be below the fundamental band gap of GaN.

Within our experimental tuning range, IR-pump-induced free carrier absorption could be assumed to be frequency independent and the difference in electron temperature changes generated by different pump photon energy (with the same pump fluence) should thus be negligible. Therefore, the experimental results can be interpreted as probing the evolution of the same population distribution changes under fixed temperature variation by wavelength tunable pulses.[6] Inside the conduction band, since the electron internal thermalization is much faster than the cooling processes, due to extremely frequent electron-electron scattering, the heated electron population should cool down to the lattice temperature with the same time constant. The measured cooling time for different probe wavelengths, corresponding to different electron positions, should thus be the same. However, if the pump IR photon energy is higher than the intervalley scattering threshold, the electron cooling behavior will then be strongly modified by an extra contribution from intervalley scattered electrons and an additional delayed cooling behavior should thus be observed.[8]

Figure 1 shows the measured probe transmission changes $\Delta T/T$ for the GaN:Si film as a function of probe delay for different pump/probe wavelengths, with a fixed pump fluence of 70 μJ/cm^2. The electron dynamics at pump/probe wavelengths of 720/360 nm (top trace), 725/362.5 nm, 730/365 nm, 735/367.5 nm, and 740/70 nm (bottom trace) were vertically displaced for clarity. The signal gradually vanished when the probe wavelength was tuned below bandgap. At zero time delay, a positive transmission peak with a width of pump-probe cross correlation was observed. Even though Dougherty *et al.*[8] attributed a similar signal to spectral artifact, we believe that the positive transmission peak in our experiments should have contributions from ionization of midgap states which are responsible for the observed yellow luminescence from our sample. The ionization of midgap states was evidenced by the positive residue signal at long delays. Figure 2 shows an enlargement of the 730/365 nm trace. After zero time delay, a negative transmission change was observed for all traces with a $\Delta T/T$ signal size on the order of 2×10^{-4}. This negative transmission change was attributed to carrier heating by pump-induced free carrier absorption. This negative transmission change relaxed with a time constant on the order of 500 fs, corresponding to the fast electron cooling process. This 500 fs electron cooling time agrees well with the carrier cooling time observed in our previous experiments in bulk InGaN (Ref. 5) and bulk GaN (Ref. 9), indicating electron cooling as the dominant carrier cooling processes. It is interesting to notice that this behavior with the same 500 fs time constant was also observed in below-band-gap probe measurements with probe wavelengths of 367.5 nm (3.37 eV) and 370 nm (3.35 eV). This is attributed to extremely fast electron capturing and scattering processes for Si-dopant-induced shallow band-tail states, with a time constant much shorter than 500 fs, so that the electron population in band-tail states could cool with the whole conduction electron gas at the same time. This below-band-gap signal was not contributed from refractive index

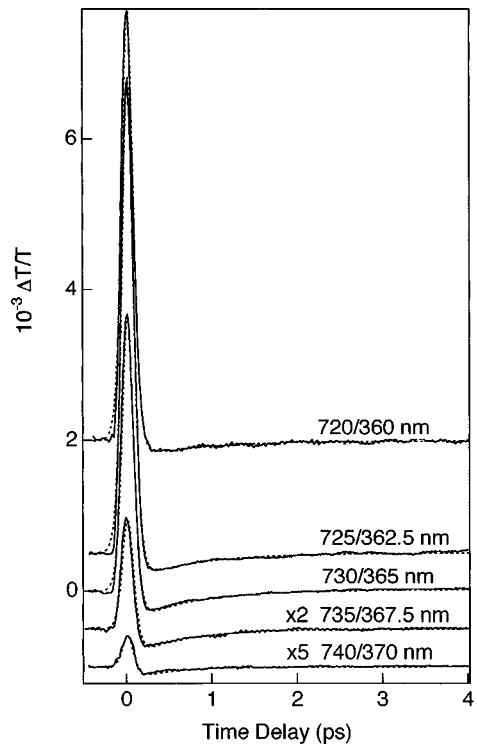

FIG. 1. Measured transient transmission changes (solid lines) for pump/probe wavelengths of 720/360, 725/362.5, 730/365, 735/367.5, and 740/370 nm (from top to bottom). The experimental results are vertically displaced for clarity. Dotted lines on top of the results are the generated convolution fits.

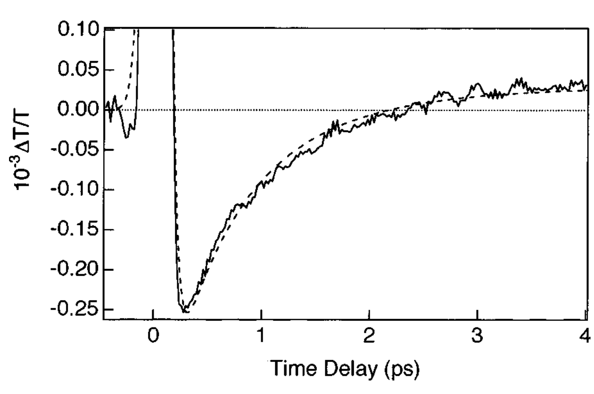

FIG. 2. Measured transient transmission changes (solid lines) for a probe wavelength of 365 nm and a pump wavelength of 730 nm. The negative component is enlarged for clarity. The dotted line on top of the result is a convolution fit.

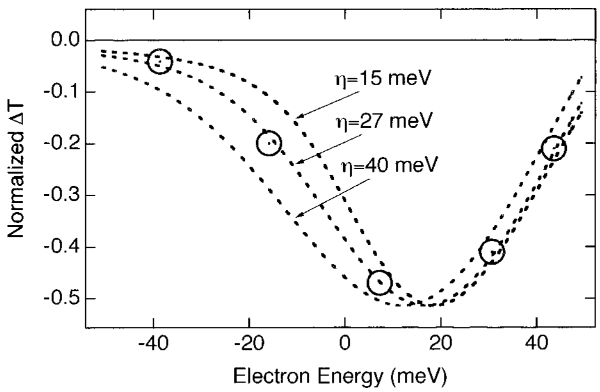

FIG. 3. Amplitude of the fast negative transient (open circles) vs probed electron energy with respect to the conduction band minimum. The dashed lines are calculated transmission changes for perturbative temperature variation with different impurity screening potentials.

change induced by above-band-gap electrons. To verify this, we have repeated our experiments using a lightly doped GaN sample with pump-probe wavelengths of 740/370 and 370/370 combinations. No signals were found even with much higher pump fluence.

The amplitudes of the 500 fs relaxation components are shown in Fig. 3 as a function of probed electron energy respective to the conduction band minimum. The band-gap energy is taken as 3.39 eV, obtained from an absorption spectrum measurement. The relation between negative transient intensity and probed electron position reveals the thermomodulated transmission spectrum of the conduction band electron gas. When the temperature of the electron gas rises, the electron distribution will move toward higher-energy positions. The population at the bottom of the conduction band will thus decrease. This result is reflected in the negative amplitude distribution of the measured thermomodulated transmission spectrum. The distribution of the below-band-gap spectrum provides information on band-tail states of heavily Si-doped GaN. We have fitted our data by using a model of conduction band tailing in the case of a heavily doped parabolic band semiconductor proposed by Chakraborty and Biswas.[10] The density of states ρ under the band-tailing condition is described by[10]

$$\rho=\frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\gamma^{1/2}\frac{d\gamma}{dE}, \tag{1}$$

where the conduction band electron mass m_e of GaN was taken as $0.2m_0$,[11] and γ is a function of electron energy E and impurity screening potential η. Here $\gamma(E,\eta)$ varies with the doping concentration and is described as[10]

$$\gamma(E,\eta)=\frac{\eta}{2\pi^{1/2}}\exp\left(-\frac{E^2}{\eta^2}\right)+\frac{1}{2}E\left[1+\mathrm{erf}\left(\frac{E}{\eta}\right)\right], \tag{2}$$

where erf(x) is an error function. Dotted lines in Fig. 3 are calculated population changes for η equal to 15, 27, and 40 meV. Excellent agreement is obtained using the model of Chakraborty and Biswas[10] with η equal to 27 meV, with a corresponding Si-doping concentration of $2\times10^{18}\,\mathrm{cm}^{-3}$ in the measured sample.

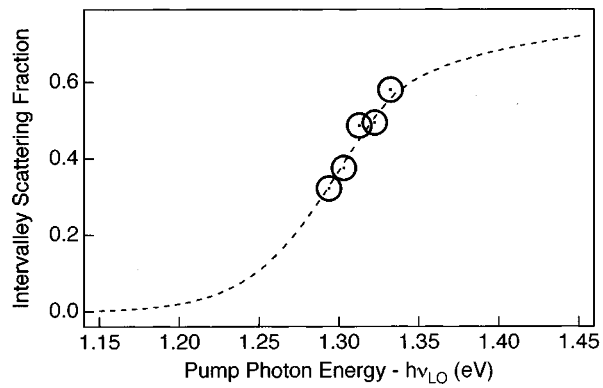

FIG. 4. Intervalley scattering fraction vs pump photon energy minus $h\nu_{\mathrm{LO}}$. The dashed line is a computer-generated fit.

With a close examination of Fig. 2, we can observe a slower decay component following the faster 500 fs relaxation for the 730/365 nm trace. We have fitted the observed negative transients using a two-time-constant response function given by

$$h(t)=\frac{a_1}{\tau_1}\exp\left(\frac{-t}{\tau_1}\right)+\frac{a_2}{\tau_2-\tau_1}\exp\left(\frac{-t}{\tau_2}\right)\times\left\{1-\exp\left[-t\left(\frac{1}{\tau_1}-\frac{1}{\tau_2}\right)\right]\right\}. \tag{3}$$

The dotted lines on top the of experimental data in Figs. 1 and 2 are computer-generated fitting traces. Excellent fits can be obtained with $\tau_1=400-500\,\mathrm{fs}$ and $\tau_2=0.9-1.5\,\mathrm{ps}$. The dotted lines shown in Figs. 1 and 2 were generated with $\tau_1=500\,\mathrm{fs}$ and $\tau_2=1$ ps. The relative amplitude of the slower 1 ps component drastically vanishes with lower pump photon energy. Combined with the 1 ps time constant, this behavior suggests that the 1 ps component should be contributed from the delayed cooling due to intervalley returned carriers[8] in the GaN material system. A similar behavior has previously been observed and was already extensively studied in the ZnSe material system by Dougherty *et al.*[8] Tuning the pump across the intervalley energy threshold accounts for this drastic change. Delayed cooling time due to the intervalley returned electrons of 1 ps is similar to but faster than that of GaAs [3 ps (Refs. 12 and 13)] and ZnSe [1.8 ps (Ref. 8)] material systems. This is probably due to higher density of states and larger longitudinal optical (LO) phonon energy in GaN.

Following the analysis of Dougherty *et al.*, we have plotted the fitting parameter ratio $a_2/(a_1+a_2)$, corresponding to the intervalley scattered fraction, against the pump photon energy minus one LO phonon energy of 90 meV (Ref. 14) in Fig. 4. The fraction of the electron raised to the conduction band valley is estimated[8] with an assumption that the carrier transfer is proportional to the overlap of density of states and free-carrier-absorption-induced carrier distribution. The scattering fraction in our experiments can thus be calculated by comparing the transfer probability to a second conduction band and the transfer probability of staying in the Γ valley. The dotted line in Fig. 4 is the result of a calculated overlap integral assuming a Γ valley electron mass of $0.2m_0$, a second conduction band mass of $0.8m_0$, and an energy separation between valley minima $\Delta E = 1.34$ eV. Excellent agreement between experiments and theory is obtained. While the second conduction band mass strongly depends on the model and parameters we use, the energy separation is not sensitive to model and parameters. According to a local density approximation calculation by Rubio *et al.*[15] and a norm-conserving pseudopotential calculation of wurzite GaN by Palummo *et al.*,[16] the second conduction band minimum should be located at the U point (U_1^c).[17] The energy separation between the nearby conduction band L point ($L_{1,3}^c$) and the conduction/valence band Γ point minimum/maximum (Γ_1^c/Γ_6^v) is 2.1/4.4, 1.78/4.54, or 2.16/5.66 eV according to the calculations of Rubio *et al.*,[15] Palummo *et al.*,[16] and Yeo *et al.*,[18] respectively. According to our experiments, the separation between the U_1^c and Γ_6^v, is thus determined to be 4.73 eV, which is the summation of the band-gap energy ($\Gamma_6^v - \Gamma_1^c$, 3.39 eV) and the measured conduction valley energy difference ($\Gamma_1^c - U_1^c$, 1.34 eV).

In summary, we have studied the ultrafast electron dynamics in n-doped GaN using multiple-wavelength pump-probe techniques. After a quick initial thermalization, we observed pump-wavelength-dependent cooling dynamics. A fast electron cooling with a time constant of 500 fs was observed. By comparing with our previous results, electron cooling could be confirmed as the dominant carrier cooling processes in GaN. Electrons in band-tail states were found to relax at the same rate as conduction electrons, indicating fast (<500 fs) carrier capture into shallow band-tail states and fast scattering between shallow band-tail electrons and conduction band electrons. Our results agree well with a model of conduction band tailing for heavily doped semiconductors proposed by Chakraborty and Biswas. With a Si-doping concentration of $2\times10^{18}\,\mathrm{cm}^{-3}$ in the measured GaN sample, an impurity screening potential on the order of 30 meV was obtained. With variations of pump photon energy, conduction band intervalley scattering of GaN was also studied. With a proper selection of pump wavelength, the electron cooling behavior was found to be delayed by intervalley scattered electrons with a time constant on the order of 1 ps. By examining the fraction of the delayed cooling component, our data suggested an intervalley scattering threshold energy of 1.34 eV, which is the separation energy between the bottom of the U valley and Γ valley conduction band minima in wurzite GaN.

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