Reduced subpicosecond electron relaxation in GaN_xAs_{1-x}

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We report on time resolved femtosecond carrier dynamics in molecular beam epitaxy grown GaN_xAs_{1-x} with a nitrogen fraction of 1.3%. The intraband carrier relaxation time in GaN_xAs_{1-x} is found to be significantly larger than in GaAs. We compare the experimental results with carrier-polar optical phonon scattering rates calculated within the band anticrossing model. From the results we conclude that the slowing down of the carrier relaxation is a result of the strongly modified band structure in GaN_xAs_{1-x}. © *2005 American Institute of Physics*.
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Due to their unique electronic properties, the III-N_x-V_{1-x} semiconductor compounds have attracted steadily growing interest over the past few years. This interest is motivated by the wide range of possible optoelectronic applications of this material system[1–4] as well as by the intriguing physical properties. Well-known features are the large band gap bowing observed in many III-N-V semiconductors,[5] an increase of the electron effective mass,[6] a reduced temperature dependence of the band gap energy,[7] and the possibility of an enhanced free electron concentration.[8] However, to the authors' knowledge, no information is available about the carrier dynamics on a femtosecond time scale. The nitrogen related modification of the conduction band structure[9,10] is expected to strongly affect the carrier relaxation. This relaxation dynamics of optically excited carriers is of importance for device design and can give fundamental insight into the electronic properties of this material system.

In this letter the intraband carrier relaxation is investigated by pump-probe transmission measurements with excitation energies between 1.42 and 1.72 eV (excitation wavelengths between 870 and 720 nm, respectively). The observed differences between GaN_xAs_{1-x} and GaAs are interpreted in terms of the band anticrossing model[10] (BAC). This model describes the conduction band of GaN_xAs_{1-x} as being split into a lower-energy (E^-) and a higher-energy (E^+) band, resulting from the interaction with an electronic N level. The valence band remains unaffected. The dominant carrier relaxation mechanism in GaN_xAs_{1-x} is found to be, as for GaAs, the LO phonon emission via the Fröhlich interaction. This scattering channel is strongly modified due to the altered electronic band dispersion.

A 250-nm-thick GaN_xAs_{1-x} film with a nitrogen fraction of 1.3% was grown by molecular beam epitaxy at 450 °C on top of a 1 μm $Al_{0.6}Ga_{0.4}As$ etch stop layer on (001) oriented GaAs and subsequently annealed at 800 °C for 60 s.[11] The room temperature band gap energy of the GaN_xAs_{1-x} was determined by photomodulated reflectivity to 1.21 eV (1025 nm, i.e., a reduction of 210 meV compared to GaAs), the nitrogen fraction was calculated from the band gap energy via the relationship between nitrogen fraction and band gap energy as given by the BAC model.[10] After mounting the sample upside down on a (0001) oriented sapphire plate, the substrate and the etch stop were removed by etching in 30:1 H_2O_2:NH_4OH and 10% HF, respectively. In the degenerate pump-probe setup a Ti:sapphire laser with the central wavelength tunable between 1.42 and 1.72 eV (870 and 720 nm, respectively) was used. The full width at half maximum of the laser spectrum was about 10 nm, the time resolution was about 100 fs. The spot diameter of pump and probe beams at the sample surface was 80 μm, the beams enclosed an angle of 6° (with pump normal incident), and the pump/probe intensity ratio was maintained at 10:1. In order to minimize coherent contributions to the transmission change during the presence of the pump pulse, and to allow effective blocking of pump light in front of the detector, the polarizations of pump and probe were chosen orthogonal. The carrier excitation density was kept constant throughout all measurements at approx. 3×10^{17} cm^{-3}. We checked that the relaxation times determined did not change for lower excitation densities down to 8×10^{16} cm^{-3}. All measurements were carried out at room temperature.

Figure 1 shows the transmission transients of GaN_xAs_{1-x} for several excitation wavelengths between 740 and 860 nm. For comparison the transmission change of a GaAs reference sample is shown for 860 nm. The pump pulse is centered at zero time delay (marked by the vertical line). For all wavelengths we find a positive transmission change $\Delta T/T_0$ with a sub-ps decay time. The maximum of $\Delta T/T_0$ near zero time delay is found at positive times with respect to the maximum of the pump intensity for all wavelengths. This clearly indicates that the changes follow the integrated pump pulse intensity and hence are dominated by population of electronic states. A qualitative change of the transients within the first 200 fs is observed around 830 nm, which will be discussed below. The relaxation time constants are determined by fitting a mono-exponential decay to the transients within the time range well after thermalization ($t>200$ fs) extending for typically 1 ps.

Figure 2 summarizes the maximum optical nonlinearities, i.e., the height of the initial peak around zero time delay for both GaN_xAs_{1-x} and GaAs. The inset depicts the conduction band density of states of GaAs and $GaN_{0.013}As_{0.987}$ as

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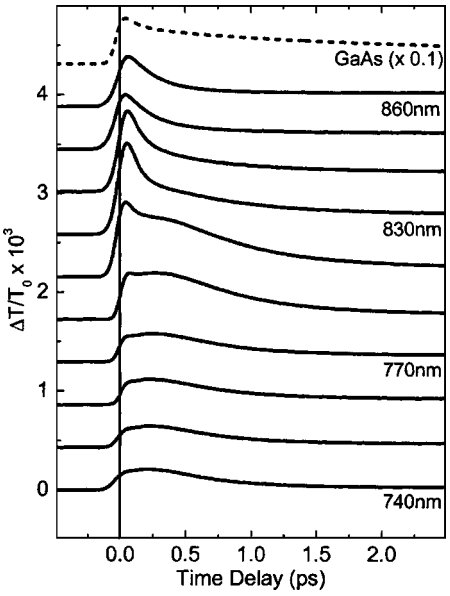

FIG. 1. Time resolved transmission changes of $GaN_{0.013}As_{0.987}$ for different excitation wavelengths (from bottom: 740, 750, 760, 770, 790, 810, 830, 840, 850, and 860 nm, respectively) and of GaAs (dashed line, excitation wavelength 860 nm, scaled by 0.1). The curves are shifted vertically for clarity. The vertical line marks the zero time delay.

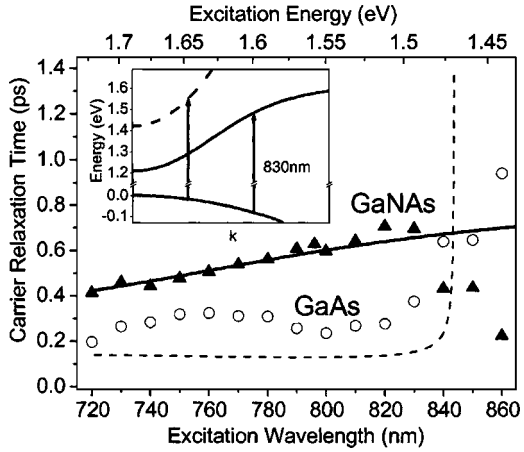

FIG. 3. Relaxation time constants of GaAs (open circles) and $GaN_{0.013}As_{0.987}$ (filled triangles) as function of the excitation wavelength. The solid and dashed lines show the calculated relaxation times for $GaN_{0.013}As_{0.987}$ and GaAs, respectively. The inset shows the heavy-hole valence band (solid, lower branch) and the conduction band of N-free GaAs (dashed) and the E^- band of $GaN_{0.013}As_{0.987}$ (solid, upper branch). (see Ref. 10). The vertical arrows indicate an excitation at the same laser wavelength for both materials.

calculated within the BAC model.[10] Excitation of heavy holes only is taken into account since the effective mass and hence the density of states (DOS) of heavy holes is larger than the mass of light holes. The maximum optical nonlinearity is related to the density of final states, since a small DOS enhances the bleaching of the transmission at a given excitation density, thus leading to a comparably larger change of the transmission. Thereby a small DOS is correlated with a large maximum optical nonlinearity and vice versa. Additionally, for energies approaching the gap energy the screening of the Coulomb interaction between excited carriers and holes (Coulomb enhancement)[12] has to be taken into consideration. The GaAs sample exhibits an increase of the peak height with increasing wavelength towards the band gap ($\lambda_{gap}=873$ nm at room temperature), which is related to the conduction band DOS in GaAs (see inset of Fig. 2) and an increased Coulomb enhancement. Excitonic effects play a less significant role in GaN_xAs_{1-x} since carriers are excited with excess energies of 100 meV and above with respect of the conduction band minimum. In comparison, the nitrogen containing material shows two significant differences: (a) the maximum optical nonlinearity of GaN_xAs_{1-x} is smaller than that of GaAs for all investigated wavelengths, and (b) a local maximum appears at 830 nm which is absent in GaAs. The height of the peaks (a) indicates that the DOS in GaN_xAs_{1-x} is larger than in GaAs, as is predicted by the BAC model (see inset of Fig. 2). The local maximum (b) is also associated with the band structure of GaN_xAs_{1-x}. For a nitrogen fraction of 1.3% an excitation at 830 nm generates carriers near the inflection point of the band structure (see inset of Fig. 3). The inflection point corresponds to a comparably steep band and hence a comparably smaller DOS.

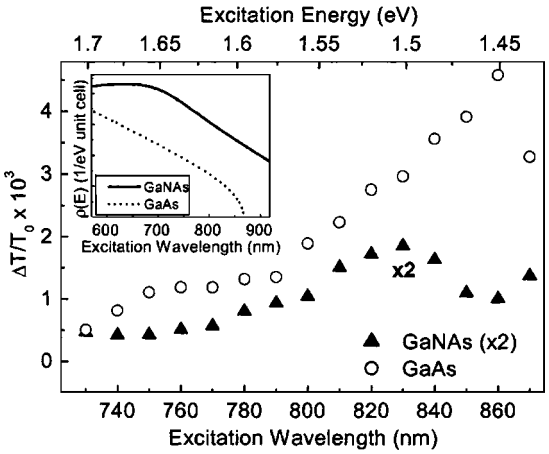

FIG. 2. Maximum of $\Delta T/T_0$ around zero time delay of GaAs (open circles) and GaN_xAs_{1-x} (filled triangles, scaled by a factor of 2) as function of the excitation wavelength. The inset shows the conduction band density of states of GaAs (dotted line) of $GaN_{0.013}As_{0.987}$ (solid line).

Figure 3 summarizes the carrier relaxation times in the conduction band of GaAs and of GaN_xAs_{1-x}. The main energy relaxation mechanism in III-V semiconductors is the longitudinal optical (LO) phonon emission via Fröhlich interaction. The LO phonon energy is 36 meV (292 cm^{-1}) in both material systems, GaAs and GaN_xAs_{1-x}. Excited carriers relax by emitting phonons with this energy and a **q** vector as given by the band dispersion satisfying both energy and momentum conservation. In GaAs we find carrier relaxation times of around 300 fs over a wide wavelength range. The increase approaching the band gap ($\lambda_{gap}=873$ nm at room temperature) is related to bandfilling and, for energies less than one LO phonon energy above the band edge (excitation wavelengths above 844 nm), to relaxation mechanisms with smaller interaction strengths (e.g., emission of acoustic phonons). The carrier relaxation times in GaN_xAs_{1-x} are larger than in GaAs for wavelengths smaller than 840 nm. This is in strong contrast to N implanted GaAs, where the carrier relaxation is found to be dominated by capture into implantation related defects on a 100 fs time scale.[13]

In order to examine the influence of the Coulomb interaction (see, e.g., Ref. 12) on relaxation dynamics we spectrally resolved the probe pulse. At the excitation densities

used, no significant dependence of relaxation times on probe energy was found.

Neglecting screening, the Hamiltonian of the electron-polar optical phonon interaction can be written as[14]

$$H_{\mathrm{ep}} = iC\sum_{q}\frac{1}{q}[c_q^{+}\exp(i\mathbf{qr} - i\omega_{\mathrm{LO}}t) + c\,.\,c\,.\,] \tag{1}$$

with c_q^{+} the phonon creation operator, C a coupling constant, and $\mathbf{q}$ the wave vector of the involved phonon. Since only emission of phonons contribute to carrier relaxation, the scattering rate can be written as (a detailed derivation is given by Ridley[15]):

$$W(k_i) = C' I(k_i,k_f)^2 \times \int_{q_{\min}}^{q_{\max}} \frac{1}{\frac{\partial}{\partial \cos\theta(k_i,q)}[E(k_f(k_i,q)) - E(k_i) + \hbar\omega_{\mathrm{LO}}]}\,dq \tag{2}$$

with C' a modified coupling constant, $q_{\min} = k_i - k_f$ and $q_{\max} = k_i + k_f$ being the minimum and maximum value of q, respectively; $\mathbf{k_i}$ and $\mathbf{k_f}$ are the initial and final k vector, respectively, satisfying energy and momentum conservation. θ is the angle between $\mathbf{k_i}$ and $\mathbf{q}$ and $E(k)$ is the energy dispersion. $I(k_i,k_f)$ is an overlap integral defined as[15,16]

$$I(k_i,k_f) = \int_{\mathrm{cell}} u_{k_f}^{*}(\mathbf{r})u_{k_i}(\mathbf{r})d\mathbf{r}. \tag{3}$$

The terms $u_{k_f}(\mathbf{r})$ and $u_{k_i}(\mathbf{r})$ are the cell-periodic parts of the final and initial Bloch state, respectively. Assuming a parabolic conduction band for GaAs, one can calculate the inverse scattering rate as shown in Fig. 3. The strong deviation of the calculated relaxation times from the experimental data for wavelengths above 840 nm is related to relaxation mechanisms which are not taken into account in the calculation. Using the BAC model for the conduction band dispersion of GaN_xAs_{1-x}, the only unknown parameter for the calculation of the scattering rates is the overlap integral $I(k_i,k_f)$ which is unity in the case of parabolic bands. Due to the strong nonparabolicity in GaN_xAs_{1-x}, $I(k_i,k_f)$ is expected to be significantly smaller than unity.[15] When assuming for simplicity that this overlap integral is independent of k_i and k_f, the best fit to the GaN_xAs_{1-x} data could be achieved for $I(k_i,k_f) = 0.365$. This constant value fits the relaxation times over a wide wavelength range. A strong deviation towards smaller relaxation times is found for wavelengths larger than 830 nm, where also the qualitative change of the transients within the first 200 fs was observed in Fig. 1. These wavelengths correspond to energy states *below* the inflection point of the band where the dispersion retains the parabola-like character of the unperturbed (GaAs) dispersion. Since $I(k_i,k_f)$ equals unity for parabolic bands,[15] we expect an increase of $I(k_i,k_f)$ approaching the band gap. Indeed a value of 0.6 for $I(k_i,k_f)$ reproduces the carrier relaxation time at 860 nm.

In summary, we have measured the conduction band carrier relaxation times in GaN_xAs_{1-x}. Though governed by LO phonon emission in both material systems, the relaxation times in GaN_xAs_{1-x} are found to be larger than in GaAs over a wide excitation range. Calculation of electron - polar optical phonon scattering rates, taking into account a modified band structure as given by the BAC model, can reproduce the measured relaxation times. Our findings are of relevance for design and modeling of optoelectronic devices utilizing dilute nitride III–V semiconductors.

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