# Femtosecond time-resolved study in $In_xGa_{1-x}N$ (0001) ultrathin epilayers: Effects of high indium mole fraction and thickness of the films

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In view of promising full-solar-spectrum photovoltaic systems based on $In_xGa_{1-x}N$ ternary alloys, femtosecond time-resolved study in ultrathin epilayers was employed in order to extract the fundamental properties of material. Two different thicknesses of epilayers were employed with relative high indium mole fractions. State filling effect at various probing energy states has been observed for both epilayers. Saturation of state filling as well as enhanced photoinduced absorption occurred at higher probing wavelengths. Furthermore, coherent acoustic phonon oscillations were also observed for both ultrathin epilayers with a thickness dependent oscillation frequency. Finally, absorption band edge of these alloys has been determined. © *2006 American Institute of Physics*.
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Nitride semiconductors have attracted a great deal of attention due to their potential applications as blue light optoelectronic devices[1] and multijunction solar cells.[2] The energy gap of wurtzite InN has been found to be about 0.7 eV.[3] This fact has extended the range of the energy gaps of group III-nitride alloys from the deep ultraviolet to the practically very important near infrared spectral region. It has been shown that the band gap of $In_xGa_{1-x}N$ alloys can be varied continuously from 0.7 to 3.44 eV,[4] providing almost perfect fit to the solar spectrum. This unique opportunity to design multijunction solar cells is based on the interesting properties of this single ternary alloy system. In view of these promising full-solar-spectrum photovoltaic systems, carrier dynamics plays a crucial role in understanding fundamental properties of these materials. These optical properties provide applicable information to manufacture third-generation solar cells and systems. Recently, ultrafast carrier dynamics in these alloys have been investigated[5] following strong fluence excitations which are well above stimulated emission threshold. This work has revealed dynamic information of $In_xGa_{1-x}N$ epilayers for In mole fraction up to $x=0.33$ from degenerated pump-probe measurements. Increasing the In mole fraction of these alloys the energy gap shrinkages modify the electronic band structure. Here, we report on nondegenerated photoinduced absorption measurements in ultrathin films of 50 and 100 nm with very high In mole fractions $x>0.85$. Furthermore, we investigate the dynamic behavior dependence on the thickness of these epilayers near the quantum confinement limit. The utilized experimental technique is a noncollinear supercontinuum pump-probe configuration in conjunction with a regenerative Ti:sapphire amplifier system with 100 fs pulses at 800 nm. This system amplifies the pulses to approximately 1 mJ at a repetition rate of 1 kHz. The temporal variation in the optical absorption was monitored as a change in the reflectivity and transmission, which was a direct measure of the photoexcited carrier dynamics within the probing region. In this work, optical pumping at a fluence of 2.0 $mJ/cm^2$ has been used to excite the high In mole fraction ultrathin epilayers and determine its temporal behavior.

The high indium mole fraction samples used in these experiments are 50 nm $In_{0.89}Ga_{0.11}N$ and 100 nm $In_{0.85}Ga_{0.15}N$ epilayers, grown by nitrogen radio-frequency plasma source molecular-beam epitaxy on Ga-face $GaN/Al_2O_3$ (0001) substrates at a deposition temperature of 435 °C.[6] The GaN layer on the sapphire substrate was 4 $\mu$m thick and it was grown by metal-organic chemical vapor deposition. The compositions of the films were confirmed by x-ray diffraction measurements. From reciprocal space maps of the symmetric (002) and the asymmetric (105) Bragg reflections, we have found that the lattice constants $\alpha$ and $c$ were 3.507 and 5.599 Å for $x=0.85$ (thickness, 100 nm) as well as 3.527 and 5.611 Å for $x=0.89$ (thickness, 50 nm), respectively. As seen from these results, both ultrathin films can be considered as relaxed.

In order to realize the morphology of these films as well as the surface roughness, we have implemented atomic force microscopic (AFM) measurements at a scanning area of $2 \times 2$ $\mu m^2$. The results are shown in Fig. 1, presenting an intense grainy behavior for both epilayers. Furthermore, the rms surface roughness of these ultrathin films is small, 0.9 and 0.81 nm for $In_{0.85}Ga_{0.15}N$ and $In_{0.89}Ga_{0.11}N$, respectively.

In the following, we will describe transient absorption measurements for each ultrathin epilayer obtained at a fluence of 2.0 $mJ/cm^2$. In these measurements we have used excitation wavelength of 400 nm (3.1 eV), which is well above the energy gap of epilayers. Figure 2 shows the transient absorption changes of the 50 nm $In_{0.89}Ga_{0.11}N$ epilayer measured for different probing wavelengths ranging from 450 to 900 nm. For the probing wavelengths ranging between 450 and 750 nm, the measurements appear to have a sharp pulse-width limited drop, followed by a wavelength dependent recovery to small positive values. At the larger probing wavelength of 850 nm, the absorption measurements appear to have a positive pulse-width limited rise followed

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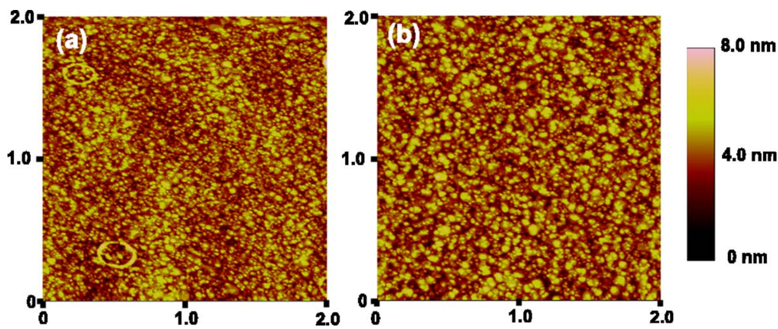


FIG. 1. (Color online) AFM measurements in $2 \times 2\ \mu m^2$ total scanning area for both InGaN epilayers. (a) $x=0.89$ and 50 nm thicknesses and (b) $x=0.85$ and 100 nm thicknesses, respectively. The $z$-axis full scale is 8 nm in both (a) and (b).

by a fast decay bringing the signal below the zero level at 2.5 ps. Then the signal is recovered to the equilibrium value with a slower decay time (20 ps). Furthermore, we note a decrease for both contributions (negative and positive) with increasing probing wavelength at 900 nm. We should point out that for all probing wavelengths under investigation in this work we observe pronounced oscillations after the first 20 ps (upper inset in Fig. 2). The amplitude of these oscillations decreases with increasing probing wavelength.

Figure 3 shows the transient absorption changes of the 100 nm $In_{0.85}Ga_{0.15}N$ epilayer measured for different probing wavelengths ranging from 450 to 900 nm. For the probing wavelengths ranging between 450 and 850 nm, the signal depicts again a sharp pulse-width limited drop followed by a wavelength dependent recovery to small positive values. The only noticeable difference appeared at the 900 nm probing wavelength, where the signal depicts a positive sharp rise (pulse width limited) followed by a fast decay (2.5 ps) below the zero level and then the signal is recovered toward equilibrium (within 20 ps).

Following above band gap excitation of the 50 nm $In_{0.89}Ga_{0.11}N$ epilayer, the generated carriers induce a decrease in the absorption (up to 750 nm probing wavelength) due to state filling effect.[7] This behavior was verified from measurements performed at different excitation fluences ranging between 0.5 and 5 mJ/cm$^2$, where linearity of the absorption peaks as a function of the carrier density appeared. The temporal behavior of these curves is wavelength dependent. With increasing wavelength, we are probing closer to the band edge where the electron "sea" resides, providing longer delay for the absorption recovery to equilibrium values. The recombination of the carriers is within the first few picoseconds and reflects the temporal dynamic of the particular probing energy states. The small positive component of the absorption changes for large delay times is attributed to the lattice temperature changes via optical phonon emission.

For the smaller probing wavelength of 450 nm, the positive absorption change at the larger delay times depicts a pronounced oscillatory behavior (upper inset in Fig. 2). These cosinelike absorption oscillations are attributed to the coherent acoustic phonons of the 50 nm $In_{0.89}Ga_{0.11}N$. The phase component of the cosine argument was close to zero for all probing wavelengths, suggesting that the excitation of the oscillation was displacive and the system was under an equilibrium position due to carrier screening after photoexcitation.[8] We should point out that the time delay until this equilibrium is reached is less than 20 ps for all probing wavelengths up to 750 nm. Performing a fast Fourier transform we are able to estimate that the energy of these vibrations is approximately 0.4 meV. The observed oscillation frequency (0.1 THz) was found to be independent of probing wavelength and excitation fluence. The only factor which is fluence dependent is the amplitude of the oscillations due to the larger number of carriers present.

At large probing wavelengths of 850 and 900 nm, the particular electronic band structure of the material at the specific indium mole fraction of 0.89 generates the conditions for photoinduced absorption (PIA).[9] However, due to the high accumulation of the carriers at these energy states, the state filling effect brings the signal to negative values. At the

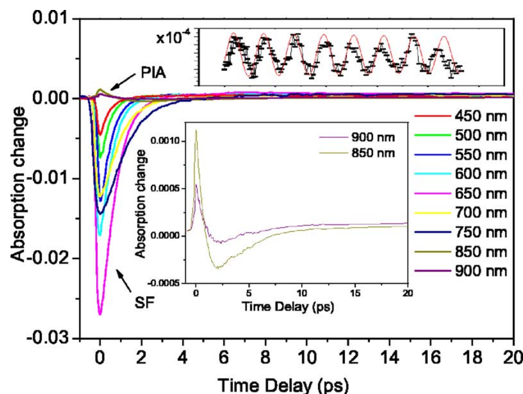


FIG. 2. (Color online) Transient absorption measurements in $In_{0.89}Ga_{0.11}N$ ultrathin epilayer with thickness of 50 nm at a fluence of 2.0 mJ/cm$^2$. The different color curves present the dynamic behavior of the sample at different probing wavelengths well above the energy gap. The lower inset shows the absorption changes at higher probing wavelengths (850 and 900 nm). The upper inset shows the cosinelike absorption oscillations (data points) of coherent acoustic phonons of the material at 450 nm probing wavelength for a delay time of 100 ps. The red solid line represents the cosine fit function of acoustic phonon mode with frequency (0.1 THz) extracted from the fast Fourier transform analysis.

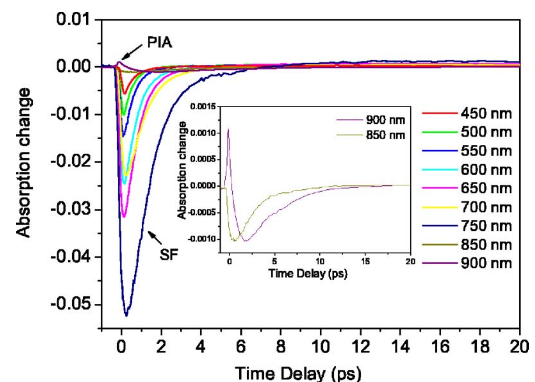


FIG. 3. (Color online) Transient absorption measurements in $In_{0.85}Ga_{0.15}N$ ultrathin epilayer with thickness of 100 nm at a fluence of 2.0 mJ/cm$^2$. The different color curves present the dynamic behavior of the sample at different probing wavelengths well above the energy gap. The inset shows the absorption changes at higher probing wavelengths (850 and 900 nm).

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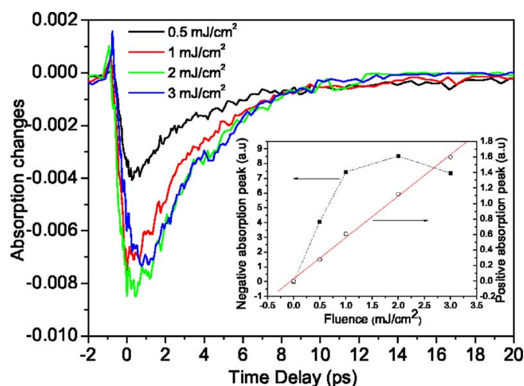


FIG. 4. (Color online) Transient absorption measurements in $In_{0.85}Ga_{0.15}N$ ultrathin epilayer with thickness of 100 nm at fluences ranging from 0.5 to 3.0 $mJ/cm^2$ and 900 nm probing wavelength. The different color curves present the dynamic behavior of the sample at different excitation fluences. The inset shows the linearity of the positive absorption peak (right) as a function of the excitation fluence. The red line represents a linear fit throughout the experimental data points. The negative absorption peak (left) as a function of the excitation fluence initially presents a linear behavior and then saturation effects appear.

same time, the temporal behavior of these states is quite large compared to the above probing wavelengths. We should point out that the positive component of this absorption change for long delay times is very small without any acoustic oscillation mode.

The 100 nm $In_{0.85}Ga_{0.15}N$ epilayer presents similar behavior with the thinner $In_{0.89}Ga_{0.11}N$ epilayer. Although the structure of these ultrathin samples is almost the same (Fig. 1), the small deviation of indium mole fraction $\Delta x = 0.04$ as well as the different thicknesses of the samples modify the energy band structure and consequently the carrier dynamics. The modification of electronic band structure was verified from spectroscopic ellipsometry measurements in our samples. With 100 nm thickness and $x = 0.85$ the absorption change depicts state filling effect up to 850 nm probing wavelength. The decay time of this alloy gradually increases due to the high accumulation of carriers at larger probing wavelengths. The recombination for both samples is attributed to the In-rich regions, which act as nonradiative recombination centers,[10] as well as to the fact that these ultrathin epilayers are quite relaxed. The large lattice mismatching of these samples as well as the small surface roughness provide additional recombination mechanisms (induced traps and surface recombination) for both alloys.

For the higher probing wavelength of 900 nm, the sample 100 nm $In_{0.85}Ga_{0.15}N$ depicts PIA followed by state filling effect. This behavior is also confirmed from experimental measurements at different excitation fluences (Fig. 4). The positive change in absorption increases linearly with increasing carrier density within the probing region (inset of Fig. 4). This linear increase of absorption peak is attributed to the high accumulation of photogenerated carriers and the secondary reexcitation of carriers due to the probing wavelengths. At the same time, the negative absorption peak initially exhibits a nearly linear dependence at low fluences indicating state filling followed by saturation above a threshold of 1 $mJ/cm^2$. This behavior may be attributed to the saturation of state filling.

Finally, we should point out that the oscillation behavior of the 100 nm $In_{0.85}Ga_{0.15}N$ epilayer for small probing wavelengths is weak with smaller oscillation frequency ($\sim$0.05 THz). We believe that the coherent phonon excitation for both alloys is probably due to photoexcited carrier-induced stress in the epilayer, and the detection is based on the refractive index changes caused by acoustic deformation potential-exciton coupling.[8] Furthermore, during the relaxation processes of electrons and holes, due to the periodic distribution of the photoexcited carrier population, carriers are easily coupled to the selective acoustic phonon mode with wave vector corresponding to the inverse period width (thickness of the epilayers).

We should point out that the observed PIA at both epilayers is evidence of the absorption band edge of particular samples. Comparing with photoluminescence measurements at room temperature this absorption edge is far above the fundamental gap due to the Moss-Burstein shift.[3] From our observations the absorption band edge of these alloys is between 750 and 850 nm for the 50 nm $In_{0.89}Ga_{0.11}N$ and between 850 and 900 nm for the 100 nm $In_{0.85}Ga_{0.15}N$. This difference is attributed to the small indium composition deviation as well as the thickness of epilayers. These absorption band edges are also experimentally confirmed from spectroscopic ellipsometry measurements at the same samples.

In conclusion, we have investigated carrier dynamics in relaxed ultrathin $In_xGa_{1-x}N$ ternary alloys of high In content using ultrafast laser pulses at various fluences. Probing with different wavelengths the temporal behavior of the energy states was resolved with 100 fs resolution. State filling effect has been found to play a crucial role in the carrier dynamics of these ultrathin epilayers. At higher probing wavelengths used in this work, PIA occurred followed by state filling. Furthermore, saturation of states appeared at a threshold of 1 $mJ/cm^2$, providing information of the particular density of states for both alloys. Even small differences in the In mole fraction and the thickness of the epilayers are able to modify the energy band structure of material causing changes on the efficiency of coupling between valence and conduction bands. Finally, the absorption band edges of these alloys could be determined from our femtosecond time-resolved measurements.

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