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Femtosecond optical spectroscopy studies of high-pressure-grown (Al,Ga)N single crystals

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Abstract. We present our time-resolved studies of the carrier dynamics in high quality Al0.86Ga0.14N single crystals, grown using a solution technique in a high nitrogen gas pressure autoclave. Our optical measurements were performed using a femtosecond, pump-probe spectroscopy, by invoking the two-photon-absorption-type process and scanning the normalized transient differential transmissivity signal ($\Delta T/T$) of the probe beam. Our time-resolved $\Delta T/T$ photoresponse consisted of a Gaussian-shape correlation signal with the pulse width of ~300 fs, which in two-color experiments was followed by a bi-exponential hot-electron relaxation transient. By plotting the autocorrelation signal amplitude versus the total energy of the absorbed pump and probe photons, we were able to very accurately determine the optical bandgap of Al0.86Ga0.14N, as equal to 5.81±0.01 eV.

1. Introduction
The III-V nitrides, such as GaN, AlN and most recently the (Al,Ga)N system, have been widely investigated due to their excellent optical and electrical properties and potential applications in novel devices, such as ultraviolet (UV) and blue laser sources, and acoustic wave generators [1-3]. (Al,Ga)N compounds are also very promising in high-frequency, high-temperature, and high-power applications, as they exhibit very large bandgap $E_g$, low microwave losses, and high thermal conductivity. Recently, nonlinear optical properties of III-V semiconductors in the transparent region of their absorption spectrum have attracted widespread attention due to their ultrafast response and relatively low dependence on the light frequency [4, 5]. The optical nonlinearity of semiconductors is described by the third-order optical susceptibility $\chi^{(3)}$, which is a complex quantity. The most often studied is the two-photon-absorption (TPA) process, which corresponds to the imaginary part of $\chi^{(3)}$ and is widely applied to pulsewidth measurements and optical spectroscopic studies. In this communication, we report our femtosecond optical study of the TPA process in high-pressure grown (Al, Ga)N crystals.

2. Growth of (Al, Ga)N single crystals
The Al$_{0.37}$Ga$_{0.63}$N crystals with the Al content 0.37 < x < 0.9 have been synthesized from a solution in Ga melt in a high-pressure nitrogen gas system consisting of a 40-mm-diameter pressure chamber with three-zone internal furnace, compressor, and the electronic system for stabilizing and programming both pressure and temperature. A set of three thermocouples was used to monitor and control the temperature and temperature gradient in the furnace. First, nitrogen gas was pumped up to 3 kbar.
Next, the pressure was transmitted into the growth chamber and increased up to the required value by a pressure intensifier. The furnace inside the pressure chamber was outfitted with BN isolation and a W/Re heater, so the maximum temperature of about 1750-1800 °C could be obtained. At such high temperature, the diffusion of N into Ga melt is increased, facilitating the Al$_{1-x}$Ga$_x$N crystal growth [6]. We used polycrystalline (Al,Ga)N pellets as precursors and placed them in the Ga melt in the upper part of the graphite crucible inside the growth apparatus. The synthesis process of the actual Al$_{0.86}$Ga$_{0.14}$N samples studied in this work was conducted under a thermal gradient of about 20 K/cm during 6-7 days. The crystals grew in the colder part of the graphite crucible. In order to prevent the growth of pure GaN crystals, the applied combinations of pressure and temperature during the synthesis were always out of the stable region for the GaN phase. After processing, the crystals were etched from the remaining untreated Ga/Al melt using hydrochloric acid and aqua regia. They were colorless platelets up to 0.5 mm size and exhibited the hexagonal form and wurtzite structure [6].

3. Femtosecond spectroscopy and two-photon-absorption process

Figure 1 presents our femtosecond optical spectroscopy pump-probe setup, consisting of a commercial mode-locked Ti:sapphire laser (repetition rate 76 MHz) and two homemade second-harmonic generators. The UV pulses with the width of ~150 fs and photon energies ranging from 2.93 to 3.44 eV were used as the pump and focused on the Al$_{0.86}$Ga$_{0.14}$N crystal surface with a spot diameter of ~100 µm and the incident angle of ~30°. The probe pulses were also ~150-fs wide and were either near-infrared (NIR) light, directly generated by the Ti:sapphire laser, or UV light after passing through the second-harmonic generator. The probe beam was aimed perpendicularly to the sample surface and its average power was on the same order as the pump. In both above configurations, pump and probe beams had always the photon energy much smaller than the optical bandgap of (Al,Ga)N. Both the one-color (UV) and two-color (UV-NIR) pump-probe spectroscopy experiments were performed in a transmission mode, by measuring the normalized differential transient transmissivity ($\Delta T / T$) signal of probe light as a function of the delay time between the pump and probe pulses. Two-photon-absorption typically denotes the process of simultaneous absorption of two photons of identical or different energies in order to excite a system under test from one energy level (usually the ground state) to the second, higher one (excited state). According to the study of Sheik-Bahae et al. [7], the TPA coefficient $\beta$ for a direct-$E_g$ semiconductor at a photon energy $\hbar \omega$ can be written as:

![Fig. 1 Femtosecond optical spectroscopy pump-probe setup.](image-url)
\[
\beta(\omega) = K \sqrt{\frac{E_p}{n_0^2 E_g}} F_2 \left( \frac{\hbar \omega}{E_g} \right), \quad \text{where} \quad F_2 = \left( \frac{2x-1}{2x} \right)^{3/2},
\]

where \( K \) is a material independent constant, \( E_p \) is the matrix element related to the inter-band momentum and is \(-21 \) eV for most semiconductors, and \( n_0 \) is the refractive index.

In the regime of low attenuation of the incident pump and probe beams, the experimental \( \Delta T/T \) transient measured in the Fig. 1 setup follows the TPA process and can be expressed as:

\[
\Delta T/T = -\beta dP_{\text{eff}},
\]

where \( d \) is sample thickness and \( P_{\text{eff}} \) is the effective, absorbed pump beam power per pulse.

4. Experimental results and discussion

Figure 2 presents a typical time-resolved \( \Delta T/T \) signal, measured in the one-color experiment by exciting our Al\(_{0.86}\)Ga\(_{0.14}\)N crystal with 400-nm pump and probe light. The experimental \( \Delta T/T \) waveform can be very accurately fitted as Gaussian-shape pulse with the full-width-at-half-maximum (FWHM) of 300 fs. Thus, a large transmission decrease observed around the zero delay represents the TPA autocorrelation process of simultaneous absorption of the pump and probe photons.

![Fig. 2 TPA autocorrelation response of a Al\(_{0.86}\)Ga\(_{0.14}\)N single crystal. The \( \Delta T/T \) signal was measured using 400-nm-wavelength probe and pump pulses.](image)

The two-color experimental arrangement, due to an ultra low absorption of the NIR probe light, allowed us to observe not only the sub-picosecond correlation signal at the zero delay time, but also a subsequent transient electron-phonon relaxation of optically excited carriers as is shown in figure 3(a). The inset in figure 3(a), which presents the \( \Delta T/T \) signal on a much longer time scale, demonstrates that the carrier relaxation is a bi-exponential decay process (solid red line), consisting of an initial 12-ps electron-phonon time constant, followed by a slow, \(~130\)-ps-long relaxation. Figure 3(b) shows the initial correlation signal by numerically subtracting from the waveform plotted in figure 3(a) the carrier bi-exponential relaxation component. We note that, as in the case of one-color experiments, the transient has a Gaussian shape with FWHM of 310 fs. Since the TPA correlation signal can only be observed when the simultaneously absorbed pump and probe photons have their total energy at least equal to the Al\(_{0.86}\)Ga\(_{0.14}\)N bandgap, we must conclude that in the two-color case, the correlation effect actually involves three photons: one pump photon and two probe photons, as any other combination would give the total photon energy either way too large or too low.

The two-color measurements were repeatedly performed by varying the pump and probe wavelengths. This way we could observe the optical transition edge of our (Al,Ga)N samples in detail. We noted that at the 428-nm-pump wavelength (the corresponding probe had the wavelength of 856 nm) the
correlation $\Delta T/T$ signal disappeared. By calculating the total energy of corresponding pump and probe photons, we could conclude that the $E_g$ of our Al$_{0.86}$Ga$_{0.14}$N crystal was equal to 5.81±0.01 eV.

Fig. 3. (a) Time-resolved $\Delta T/T$ signal of a Al$_{0.86}$Ga$_{0.14}$N crystal, measured using 380-nm-pump and 760-nm-probe beams. The inset shows the same waveform (grey dots), but in a much wider time window with the slow carrier relaxation fitted (solid line) as a bi-exponential decay. (b) Correlation transient extracted from the signal shown in (a) by subtracting the bi-exponential tail.

5. Conclusion
We have performed both one- and two-color time-resolved femtosecond pump-probe spectroscopy on Al$_{0.86}$Ga$_{0.14}$N single crystals, synthesized using a high-pressure solution grown method. Since photon energies of our pump and probe beams were always much lower than the (Al,Ga)N $E_g$, the measured, ~300-fs-wide $\Delta T/T$ correlation signal was a result of a coherent (simultaneous) absorption of the pump and probe photons. In the two-color scheme, we also observed picosecond relaxation of photo-excited carriers that followed the initial ultrafast correlation signal. By varying the energies of the pump and probe photons coherently absorbed by our Al$_{0.86}$Ga$_{0.14}$N crystal, we also determined its bandgap $E_g = 5.81±0.01$ eV.

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References