# Ultrafast Optical Characterization of Wide Bandgap Semiconductors and Polyatomic Molecules

**Title:** Ultrafast Optical Characterization of Wide Bandgap Semiconductors and Polyatomic Molecules

**Authors:** Henry O. Everitt

**Performing Organization:** Duke University
325 North Building, Research Drive
Durham, NC 27708

**Sponsoring Agency:** U. S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

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**Abstract:**

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**Subject Terms:**

- Ultrafast
- Wide Bandgap
- Semiconductor
- Nanostructures
- Plasmons
ULTRAFAST OPTICAL CHARACTERIZATION OF WIDE BANDGAP SEMICONDUCTORS AND POLYATOMIC MOLECULES

FINAL PROGRESS REPORT

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Duke University

4(4) Statement of the problem studied

The focus of this effort was to measure the carrier dynamics in wide bandgap III-nitride materials. Measurements of carrier capture and recombination in InGaN and AlGaN/GaN MQWs revealed a similar carrier capture time for both materials but a recombination time in the AlGaN/GaN system at least a factor of ten faster. Studies of surface plasmon-enhanced recombination rates in GaN QWs indicated an acceleration of recombination rates by a factor of 100 simply by placing a silver coating <10 nm from the QW. GaN quantum dot optical properties were studied using both ultrafast and continuous wave techniques. The interplay of carrier confinement and piezoelectric field was ascertained in the manner in which it affected the luminescence wavelength and lifetimes. Generally speaking, the larger QDs demonstrated superior optical performance, while smaller QDs behaved much like quantum wells of the same thickness.

In addition, and at no cost to the grant, a graduate student studied the excitation and relaxation of rare earth-doped GaN, especially Eu- and Er-doped GaN, as a function of temperature to map out the radiative and nonradiative relaxation pathways. A visiting researcher studied the spectra and ultrafast relaxation dynamics of ZnO thin films. Likewise, undergraduate researchers studied 1) variable stars in globular clusters, 2) the application of rotational shear interferometry to astronomical imaging, and 3) used a prism coupling technique was used to measure the indices of refraction of ZnSiN films for the first time.

4(5) Summary of most important results

Ultrafast Characterization Facility

In 1998, we began to build a new facility to characterize wide bandgap III-nitride materials. This collaborative project involved researchers in the Duke EE and Physics Departments. Samples were provided from Steve DenBaars of UCSB through a DARPA contract with Craig Casey of Duke EE, and from unpaid collaborators Hadis Morkoc of VCU and John Muth and Saleh Bedair of NCSU. Our long-term goal is to develop the capability to do photoluminescence, photoluminescence excitation spectroscopy, degenerative and non-degenerative differential transmission, and time-resolved photoluminescence in the challenging blue-UV spectral region. A successful DURIP proposal by collaborator Stephen Teitsworth of Duke to AFOSR allowed us to purchase a commercial regenerative amplifier, tunable optical parametric amplifier, and nonlinear crystals for pump wavelengths spanning 200 nm to 12 microns. These systems were operational throughout 2002.
A new collaborator, Prof. April Brown, joined Duke in 2002 as chair of the ECE Dept. Prof. Brown co-mentors one of Dr. Everitt’s graduate students (Soojeong Choi) and wrote a DURIP proposal to purchase a streak camera for use in time-resolved photoluminescence measurements. It is anticipated that an increasing number of samples for study in Dr. Everitt’s lab will come from the MBE machines of Prof. Brown.

**Carrier relaxation pathways in InGaN and AlGaN/GaN MQWs**

We completed measurements of carrier relaxation processes in GaN-based multiple quantum well laser structures. Photoluminescence and photoluminescence excitation spectroscopy were performed on each sample to identify the peak emission and absorption wavelengths. We previously reported measurements of the electron capture times at the 0.5 ps level. In 2002, time resolved, wavelength non-degenerate differential measurements were used for the first time to characterize the relaxation pathways fully. The pump was the pulsed, frequency tunable output of the optical parametric amplifier, frequency converted to the UV using a series of nonlinear crystals. A pulsed white light continuum centered at 400 nm was generated by frequency doubling half the output of the regenerative amplifier and passing it through a D2O water cell as the probe in these measurements.

By varying the pump wavelength and monitoring the corresponding changes in the relaxation pathways, a clearer picture of the relaxation mechanisms emerged. First, relaxation in GaN and InGaN epilayers was investigated to set the baseline performance. Next, ultrafast carrier relaxation was studied in both the InGaN MQWs provided by the S. DenBaars group of UCSB and the AlGaN/GaN MQWs provided by the H. Morkoc group of VCU. Data was collected as a function of pump wavelength and intensity. Carrier capture was observed to occur within 0.5 ps of excitation in both types of samples, independent of excitation wavelength. For high intensity excitation, stimulated emission was observed to operate in a “sand from the hourglass” manner in which carriers removed in the MQW confined states are replaced from stockpiled carriers in the barrier levels. After stimulated emission quenched, carrier recombination was observed to operate in 50-100 ps for the AlGaN/GaN MQWs while lasting at least 600 ps in the InGaN MQWs.

![Figure 1](image.png)

*Figure 1. Time-resolved, wavelength nondegenerate differential transmission measurements of carrier relaxation in InGaN MQWs as a function of pump wavelength.*
Surface Plasmon-enhanced Recombination

We began a new course of investigations in collaboration with Prof. Eli Yablonovitch of UCLA. His group provided us with a single InGaN quantum well with a thin cap layer (8 nm) over which was grown an even thinner layer of silver. Spontaneous emission into free space from an unsilvered quantum well occurs at a rate determined by Fermi’s golden rule to be a function of the dipole matrix element and the photon density of states. Because the photon density of states of a surface plasmon can be dramatically larger than the free space value, the expectation was that the recombination rate could be dramatically accelerated. This can only occur if the emission from the quantum well is coincident with the asymptotic resonance frequency of the surface plasmon. Preliminary continuous wave photoluminescence data from UCLA had indicated that this may indeed be the case.

In 2001 and 2002, we undertook time-resolved photoluminescence measurements to confirm such accelerations directly. In collaboration with colleagues in Japan, we measured the luminescence decay times for the sample from the silvered and unsilvered sides as a function of excitation and emission wavelengths. We found as much as a factor of 100 acceleration in recombination times. A phenomenological model was developed to characterize this behavior and predicted a strong sensitivity to the separation between quantum well and silver coating. A factor of 10,000 enhancement is predicted for a similar, optimized structure. Further work is underway to demonstrate the validity of the phenomenological model and to extend the work into quantum dots.

![Figure 2. Time-resolved photoluminescence from the silvered and unsilvered portions of an InGaN quantum well, demonstrating the accelerated rate of surface-plasmon mediated recombination.](image)

Emission Efficiency of GaN QDs

GaN quantum dots grown by the Hadis Morkoc group of VCU were studied using continuous wave and time-resolved photoluminescence techniques in collaboration with
researchers in Japan. The quantum dot samples were typically grown stacks of 20 or 40 layers in order to improve the emission intensity. Time-resolved photoluminescence of the quantum dots was performed using a frequency-tripled Ti:Sapphire laser and a streak camera during a visit by NRC post doc Arup Neogi to Japan, then analyzed here at Duke. It was observed that single layer QD emission was weaker and faster than multiple layer QDs, probably because of cooperative relaxation through vertically coupled QDs in the multilayer systems. It was further observed that the smaller QDs were dominated in the optical properties by carrier confinement, with emission energies blue-shifted above the GaN bandgap. Fairly short emission lifetimes were observed, and a shift in emission energy with time revealed a quenching of the smallest dots as recombination and nonradiative relaxation depopulated them in favor of the largest dots. Conversely, the largest dots were dominated by the effects of the piezoelectric field which red-shifts the emission below the GaN bandgap. Fairly long emission lifetimes were observed, and efficient emission with little nonradiative loss was observed even at room temperature. The surprising conclusion reached was that the larger QDs behaved more like quantum dots while the smaller ones behaved more like quantum wells.

Figure 3. Time-resolved photoluminescence from GaN quantum dots (single layer QDs) as a function of temperature and excitation energy.

Eu-doped GaN
Rare earth-doped GaN, particularly Eu-GaN and Er-GaN, have received attention recently because of their potential as atomic-like narrow linewidth (1-10 nm), long radiative lifetime (0.1-1 ms) emission in the visible wavelength region. The Duke USSL has employed the streak camera to perform time-resolved photoluminescence measurements in order to characterize the energy transfer pathways of these compelling emitters. In the earliest work, it was found that 300nm pulsed excitation of the GaN host created a rapid (0.4 µs) rise in the TRPL signal for the 4f-4f transitions $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_3$, followed by a biexponential decay. The slower of the two decay features (~200 µs), normally associated with radiative decay of the $^5D_0$ state, was found to include nonradiative decay to an impurity/trap state as well. The faster of the two decay features (< 50 µs) was almost unobservable below 180K but grew dramatically in amplitude above 180K. This too was attributed to interaction with an impurity/trap state whose energy defect with $^5D_0$ was estimated to be 16 meV. A rate equation model was developed to reveal the roles of various contributing energy transfer mechanisms and to extract their individual decay constants. The final model clearly revealed the important role played by the impurity/trap state and the inappropriateness of ascribing the slower decaying feature as solely the radiative decay process.

![Figure 4. Room temperature TRPL data for the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_3$ transitions, and a schematic diagram of the rate equation model that describes the salient energy transfer mechanisms. The inability of most models to reproduce the data eliminated them from consideration as a description of the energy transfer pathways.](image)

Ultrafast studies of ZnO films

Toward the end of this project, former student Umit Ozgur returned to perform a variety of measurements on commercially available ZnO bulk materials and on ZnO thin films sputtered on a sapphire substrate at VCU. Several bound and free exciton transitions along with their first excited states have been observed at VCU at low temperatures, with the main neutral-donor- bound exciton peak at 3.3605 eV with a linewidth of 0.7 meV dominating the PL spectrum at 10 K (Figure 5a). This bound exciton transition remained below 150 K, whereas the A-free exciton transition at 3.3771 eV persisted up to room temperature. A free exciton binding energy of 60 meV is obtained from the position of the
excited states of the free excitons. Additional intrinsic and extrinsic fine structures such as polariton, two-electron satellites, donor-acceptor pair transitions and LO-phonon replicas have also been observed and investigated in detail. Time-resolved PL measurements at room temperature reveal a bi-exponential decay behavior with typical decay constants of ~170 ps and ~864 ps for the as-grown sample (Figure 5b). Thermal treatment is observed to increase the carrier lifetimes when performed in a forming gas environment.

Figure 5. a) Temperature dependent peak positions of A-free exciton, $FX_{\Gamma_5}^{n=1}$ and its 1LO- and 2LO-phonon replicas. Also shown temperature evaluation of the peak position of two major neutral-donor bound exciton transitions at 3.3606 and 3.3650 eV. The $FX_{\Gamma_5}^{n=1}$ data were fit using Varshni equation and LO-phonon replicas were fit with the equation shown on the figure. b) Room temperature time resolved PL data for the FG treated sample at two different excitation densities. The solid lines are from bi-exponential fits to the experimental data. The inset shows the time-integrated PL for the two excitation densities.
Listing of Publications and Presentations

Peer-Reviewed Publications


17. Ü. Özgür and, H. O. Everitt, "Ultrafast carrier relaxation in GaN, In$_{0.05}$Ga$_{0.95}$N and an In$_{0.05}$Ga$_{0.95}$N / In$_{0.15}$Ga$_{0.85}$N Multiple Quantum Well," *Phys. Rev. B*. **67**, 155308 (2003). e-Print Archive cond-mat / 0210214, 9 October 2002. Selected for *Virtual Journal of Ultrafast Science*, May, 2003.


**Contributed Presentations**


4. Ü. Özgür, M. J. Bergmann, H. C. Casey, Jr., H. O. Everitt, and J. F. Muth, "Refractive Indices determined by waveguide measurements for Epitaxial AlxGa1-xN films with x=0.0, 0.04, 0.07, 0.10, 0.20," 6th Annual Wide Bandgap III-Nitride Workshop, Richmond. (March 2000)


1. Ü. Özgür, M. J. Bergmann, H. C. Casey, H. O. Everitt, and J. F. Muth, "Refractive indices obtained by waveguide measurements of epitaxial AlxGa1-xN films with x=0.0, 0.04, 0.08, 0.11, 0.20" Epitaxial Layers," American Physical Society Annual Meeting, Atlanta. (March 1999)

(7) Scientific Personnel Supported
Ümit Özgür (Graduate Student)
Chang-won Lee (Graduate Student)
Soojeong Choi (Graduate Student)
John Foreman (Graduate Student)
Arup Neogi (NRC Post Doctoral Researcher)
Hongying Peng (NRC Post Doctoral Researcher)
Chandra Jacobs (Undergraduate)
Brice Crawford (Undergraduate)
Jay Strader (Undergraduate)
Mark Ammons (Undergraduate)
Ben Cook (Undergraduate)

(8) Inventions
None.