FINAL PROGRESS REPORT

for

STUDY OF CARRIER DYNAMICS WITHIN QUANTUM CONFINED ENERGY LEVELS IN SELF-ASSEMBLED NANOSCALE QUANTUM DOTS

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in the area of Material Sciences and Engineering

to

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by

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Proposal Abstract

Statement of Objectives: The objective of this project is to study the ultrafast carrier dynamics of in two types of semiconductor quantum dots: self-assembled quantum dots (SAQDs) and patterned quantum dots (PQDs) and to correlate these dynamics with the shape, size and material composition of the dots, thereby obtaining a fundamental scientific understanding of these nanoscale systems.

Expected Significance of the Proposed Effort: In the past few years, SAQDs and PQDs have emerged as a very unique system for understanding the important physics of nanoscale zero-dimensional systems. While SAQDs are technologically superior since they have been incorporated in electronic and optoelectronic devices, the PQDs enable us to decouple the nucleation from the ripening thereby leading to a better understanding of the dot formation process. However, the fundamental physics and scattering mechanisms in both these dot systems are far from understood. In the literature, there is neither a consensus on the scattering processes responsible for carrier relaxation and recombination in QDs nor is their agreement on the measured relaxation times in the dots. Scientific opinions are divided on the existence of the "phonon-bottleneck", a phenomenon that refers to the suppression of relaxation rates in nanoscale dots when the intersubband energy spacing is greater than the longitudinal-optical (LO) phonon energy. Researchers have proposed mechanisms such as multiphonon relaxation, Auger-scattering, electron-hole scattering and have measured intersubband relaxation times ranging from hundreds of picoseconds to a few ps. We believe that the carrier dynamics in QDs are very intricately related to the strain-driven formation process of QDs during epitaxy. These processes determine the shape and size of the dots, which determine the energy spacings and spectral position of discrete energy levels, which in turn determine their carrier dynamics, i.e. radiative recombination and non-radiative thermalization and scattering, within the energy levels. Hence different dots could have different carrier dynamics depending on (a) the shape, size, areal density and composition of the dots (b) the number of electron-hole pairs created per dot by the external excitation and (c) the operating temperature. *Our goal is to undertake a comprehensive study of the structural, electronic and dynamic aspects of these nano-assembled dots and to correlate their electronic properties and scattering mechanisms with their structural characteristics.*

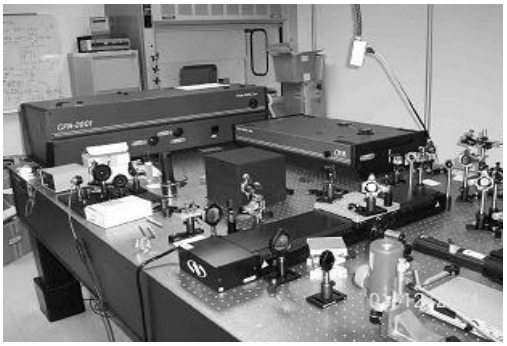
Results from Prior Work: In the past three years, we were primarily looking at SAQDs but as the project evolved we have found elegant ways to form PQDs and investigate the differences between PQDs and SAQDs. The QDs were grown by using epitaxial systems at the Center for High Technology Materials (CHTM). The various growth mechanisms and crystal facets were identified. A Scanning Tunneling Microscopy (STM) was set up in Dr. Huffaker's laboratory to define PQDs. A comprehensive theoretical model was developed to obtain the band structure of the SAQDs. The PI, his post-doctoral researcher and a student spent a week (July 2003) with Dr. Larry Carr at National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory to measure the carrier dynamics in the dots. However due to the long duration of the pulses (~300ps), the ultrafast dynamics of the dot could not be measured. Consequently, the PI has set up an active collaboration with Dr. Toni Taylor's group at Los Alamos National Laboratory (LANL) to measure the ultrafast dynamics in the quantum dots. Concurrently, the PI also built a femtosecond spectroscopy characterization facility in his lab to undertake picosecond excitation correlation (PEC) measurements on SAQDs. These experiments have been very successful and have yielded measurements of the carrier lifetimes in QDs. These results are discussed in detail in Section D. Support from this work has resulted in eleven conference presentations and seven journal publications.

Intended Effort and Proposed Timeline: The renewed project is intended for three years. In the first phase of the project , we have made excellent progress in determining the various crystal facets and growth mechanisms of the SAQDs and the PQDs along with the determination of their band structure. In addition, we have developed expertise to measure the carrier lifetime in the QDs. In the next phase, we hope to put these two pieces of information together to obtain a correlation between the shape, size and growth conditions of these dots with the possible scattering mechanisms. We are teaming up with Dr. Stuart Trugman, of the condensed matter theory group, at LANL to develop a model to determine the scattering mechanisms from the measured carrier lifetime. At the end of the project, we hope to have a comprehensive theoretical and experimental model, which will enable us

to determine the dominant scattering mechanisms in the different QD ensembles and obtain a scientific understanding of the nanoscale scattering mechanisms. A detailed plan of action is described in section IV(E).

Progress Report

In this project, we are investigating the structural properties such as shape, size and composition of the dot/barrier material system the PQDs and the SAQDs and then correlating this information with their electronic and optical properties. The size and shape of the uncovered and covered dots have been determined using the plan view and cross-sectional scanning tunneling microscope (STM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) in Prof. Huffaker's laboratory. Patterned QDs have been developed to decouple QD nucleation from QD ripening to better control size and shape. The theoretical modeling of the bandstructure along with the experimental determination of the absorption spectra has been undertaken using the Fourier transform infrared (FTIR) spectrometer in Prof. Krishna's laboratory. Moreover, we have also measured carrier lifetimes in the QDs using the femtosecond set up in Prof. Krishna's laboratory and the long wavelength femtosecond spectroscopy set up in Dr. Toni Taylor's group at LANL. In the second phase of this project (next three years), we wish to correlate the data obtained from the previous measurements to develop a comprehensive theoretical and experimental model to understand the scattering mechanisms in these nanoscale systems. We will be collaborating with Dr. Stuart Trugman, of the theoretical condensed matter group at LANL. *We believe that the carrier relaxation process in QDs depends critically on three factors: (i) the size, shape and areal density of the dots, (ii) the number of electron-hole pairs created by the incident excitation and (iii) the temperature of the sample*.



The femtosecond spectroscopy characterization facility that was set up in the PI's laboratory to undertake carrier lifetime measurements using picosecond excitation correlation (PEC). Complimentary pump-probe measurements will be performed in collaboration with Dr. Toni Taylor at LANL..

In the first phase of this project, we have made the following progress.

- ***Patterned QD Formation***

We have demonstrated optical and electrical properties of PQDs grown on GaAs substrate. We are able to reduce RTPL spectral FWHM from PQDs by about 33 % when compared to self assembled (SA) QDs grown under same growth conditions. Because the PQDs are laterally decoupled, they have unique and apparently more atomic-like optical properties compared to SAQDs. PQDs have a peak EL efficiency of 9.2% at 120 K that is similar to that of SAQDs indicates that carrier capture and recombination process is efficient and comparable to self assembled QDs. Low leakage current (20 nA) and low resistance (6.5 Ω) indicate that regrowth and mask removal process does minimal damage to the device. Calculated activation energy from temperature dependent photoluminescence and electroluminescence is about 50 meV for PQDs and 35 meV for SA QDs, indicating that PQDs have better exciton localization when compared to SA QDs.

• ***In-situ Mask formation and removal using MOCVD***

We have demonstrated an in-situ mask removal technique for use in selective area epitaxy (SAE) by MOCVD. The mask material is native aluminum oxide (Al_xO_y) formed by wet thermal oxidation of a thin AlGaAs layer. The Al_xO_y layer is patterned using standard photolithography and wet chemistry outside of the chamber. The Al_xO_y layer forms a high-quality, pin-hole free SAE mask that can be removed within the MOCVD chamber using an in-situ HCl etch process. After in-situ mask removal, subsequent growth processes produce an atomically smooth and uniform surface. Scanning electron microscopy and atomic force microscopy are used to characterize surface features and measure RMS roughness after each processing step. Using this processing scheme, we form a buried InGaAs quantum well stripe that emits room-temperature photoluminescence. The in-situ mask removal may have significant applications in nanopatterned growth processes where protection of the growth surface from atmospheric exposure reduces surface contamination to improve electrical and radiative interface characteristics.

• ***Formation trends of QD ensembles formed using MOCVD***

We have generated and published a growth matrix designed to produce high QD density, defect-free QD ensembles which emit at 1.3 μm using MOCVD. In our study, we balance the nucleation rate and adatom surface migration to achieve high surface densities ($1x10^{11}$ dots/cm^2) and avoid QD coalescence or defects that commonly characterize MOCVD-grown QD ensembles designed for longer wavelength emission. Room-temperature photoluminescence (RT-PL) spectra from corresponding surface QDs depend on QD size and density and show an emission wavelength up to 1600 nm. Ground state PL from capped QDs is measured at 1.38 μm with a 40 meV linewidth. We have demonstrated the first ground-state 1.3 μm electroluminescence (EL) from a QD light emitting diode structure (LED) grown on n-type GaAs by MOCVD.

• ***Stacked SAQD active regions grown using MOCVD***

We have introduced tensile layers embedded in a GaAs matrix to compensate compressive strain in stacked 1.3 μm InAs quantum dot (QD) active regions. The effects of the strain compensation were systematically investigated in 5-stack and 10-stack QD structures where we have inserted $In_xGa_{1-x}P$ (x=0.30 or 0.36) layers. High-resolution x-ray diffraction spectra quantify the overall strain in each sample and indicate > 35% strain reduction can be accomplished. Both atomic force and transmission electron microscope images confirm that strain compensation improves material crystallinity and QD uniformity. With aggressive strain compensation, room temperature QD photoluminescence intensity was increased by an order of magnitude demonstrating a reduced defect density.

• ***Theoretical modeling of the bandstructure of the self assembled quantum dots:***

Theoretical modeling and experimental characterization of InGaAs/GaAs QDs intersubband heterostructures, grown by molecular beam epitaxy (MBE) were undertaken. In this heterostructure, the self-assembled dots are confined to the top half of a 110 Å InGaAs well which in turn is placed in a GaAs matrix. Using transmission electron microscopy (TEM), the quantum dots are found to be pyramidal in shape with a base dimension of 110 Å and height of 65 Å. The band structure for the above mentioned DWELL heterostructure was theoretically modeled using a Bessel function expansion of the wavefunction. The energy levels of the three lowest states of the conduction band of the quantum dot are calculated as a function of the electric field (Fig. 2). Intersubband n-i-n detectors were fabricated using a 10 layer DWELL heterostructure. The spectral response of the detector is measured

at a temperature between 30-50K and compared with the prediction of our theoretical model.

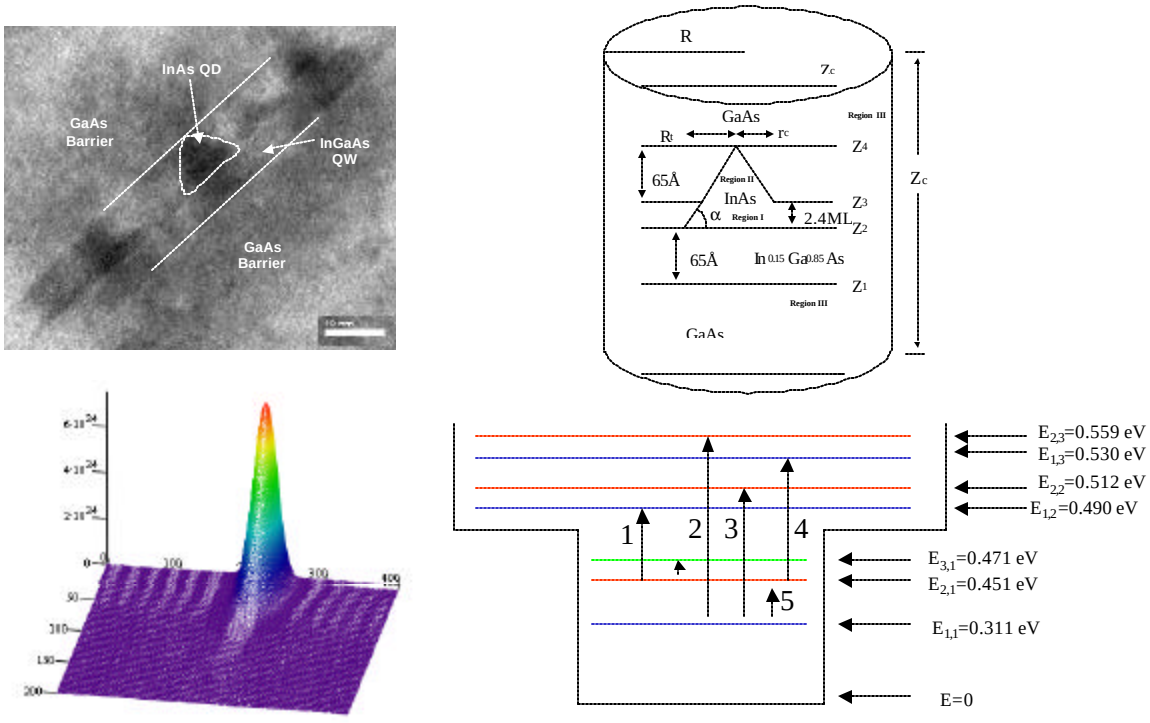


Figure 2: Theoretical modeling of the QD bandstructure using finite element analysis. The top two figures denote the TEM image and the definition of the model based on the TEM image. The bottom figure shows the ground state wavefunction and the calculate bandstructure of the QDs.

We have also undertaken an alternative method to investigate the bandstructure of the quantum dots. In this approach, the potential as obtained from the TEM image is divided into different regions as shown in Fig. 3(a). These regions are then mapped on to complex planes and Neumann conditions are used on the inner contours and Dirichlet conditions are used on the outer contours. Using the Jacobi-Tau polymonial expansion, the wavefunctions are evaluated. Fig. 3(b) shows the grid used for the Jacobi-Tau expansion and Fig16(c) shows the results of the wavefunctions obtained for the ground state and the first excited state.

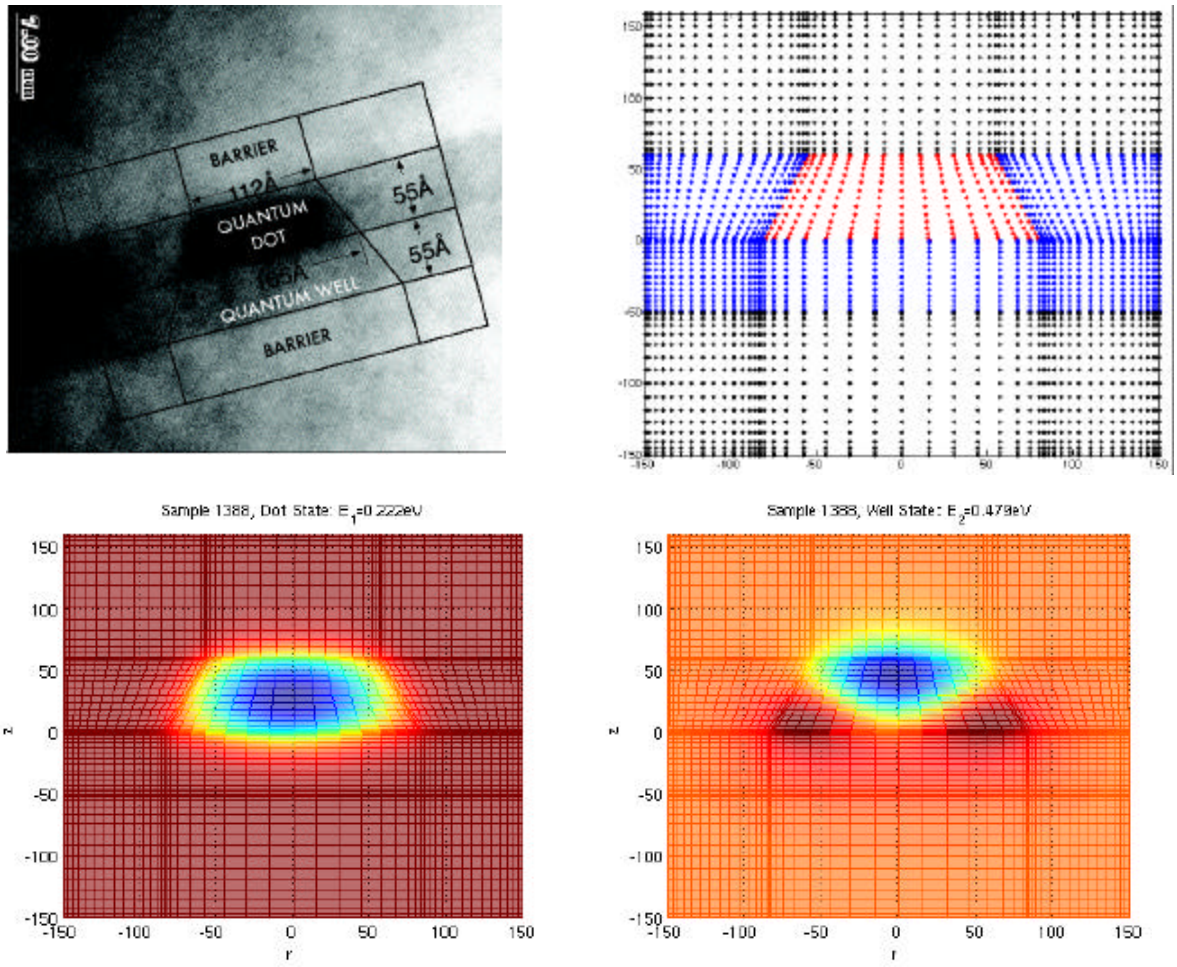
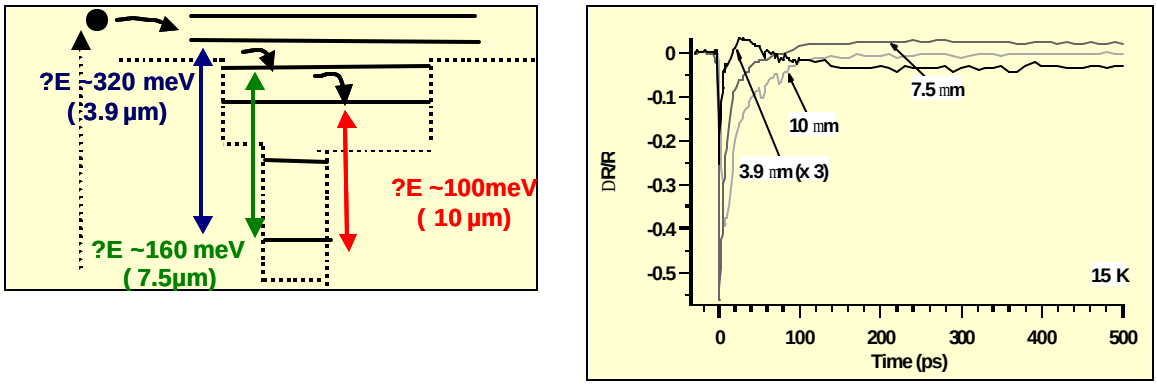


Figure 3: Theoretical modeling of the QD bandstructure using spectral based Jacobi Tau method. The top two figures denote the TEM image and the definition of the grid for the potential. The bottom figure shows the wavefunction for the ground state and the first excited state.

- ***Measurement of Carrier Lifetime in Quantum Dots using Pump Probe Spectroscopy:***

In this work, we probe carrier relaxation in QDs using an optical pump, mid-IR probe system. By tuning the probe wavelength and pumping above the GaAs band edge, we can time-resolve carrier relaxation in the QDs. The output of a 1 kHz regenerative amplifier producing 2 mJ, 60 fs pulses at 800 nm was split into two beams to excite the sample and pump an optical parametric amplifier (TOPAS, Light Conversion Systems). The signal and idler beams from the TOPAS were mixed in a nonlinear crystal to generate the tunable 3-20 μm mid-IR probe. The device structure and allowed energy levels are shown in Figure 17(a). The sample was pumped at 800 nm with a fluence of 1.83 mJ/cm^2, exciting a carrier density of ~8x10^{19} cm^{-3} in the 0.2 μm n$^+$ GaAs cap layer. Wavelengths of 3.9, 7.5, and 10 μm were chosen to probe (in reflection) the continuum states and the high and low energy bound QW states, respectively. Figure 4 (b) depicts measurement schematic of the QD structure at 15 K. The

dynamics at very early times (<1 ps), including the positive peak for the 10 µm curve at 295 K, are due to the GaAs matrix at all wavelengths and temperatures; this was verified by measuring a reference GaAs substrate and comparing to the DWELL sample. However, it can be seen from Figure 4(b) that the 3.9 µm curve recovers quickly towards zero, corresponding to carriers excited above the GaAs band edge relaxing to the bottom of the band. This saturates the continuum states at 3.9 µm, causing a positive bleaching signal. Carriers then begin to relax into the QW, evidenced by the subsequent rise in ΔR/R of the 7.5 and 10 µm traces and the corresponding decay of the positive ΔR/R feature in the 3.9 µm trace. Within the QW, the carriers slowly relax from the higher energy state to the lower energy state, as shown by the delayed rise time of the 10 µm curve compared to the 7.5 µm curve. Similar dynamics are observed at 295 K, with the differences that the 7.5 and 10 µm curves never return to zero. This can be explained by thermal emission; a fraction of the carriers captured into the QW are thermally excited back into the continuum states. Temperature-dependent measurements at each probe wavelength (not shown) indicate that this is an important factor for temperatures above 100 K, agreeing



with spectral response measurements.

Figure 4: (a) Schematic of the bandstructure and the probe wavelengths. (b) Time-resolved dynamics at wavelengths 3.9, 7.5, and 10 µm at 15 K. The 3.9 µm trace is multiplied to clearly identify the positive ΔR/R signal. Note that the 3.9 µm probe recovers the fastest whereas the 10 µm probe recovers the slowest. The difference between their recovery is a measure of the intersubband relaxation time.

- ***Carrier Lifetime in Quantum Dots using Pico Second Excitation Correlation***

We have used Pico-second Excitation Correlation (PEC) experiment with sub-picoseconds laser pulses to study the carrier dynamics in InAs/InGaAs quantum dots in a well detector. The set up for the PEC measurement is shown in Fig. 18..Two peaks located at 1030 and 1160nm are found in the PEC signal at room temperature as shown in Fig. 18. The peak at 1160 nm is associated with the quantum dot whereas the other peak is attributed to the wetting layer. An analytical model is proposed for the PEC technique using the carrier rate equation and an analytical expression was derived for the PEC signal.

$$S(d) = \frac{n_0^2}{(1+Bn_0 t_{nr})^2} \frac{t_{nr}}{c(e^{-d/t_{nr}}-1)} \left[\frac{\ln(1-c)}{c} - \frac{\ln(1-ce^{-d/t_{nr}})}{ce^{-d/t_{nr}}} \right] \qquad (Eq.6)$$

This model was used to fit the experimentally obtained PEC signal and is shown in Fig.
The measured interband time of 0.8-0.9 ns is in very good agreement with lifetimes measured by other

groups using other techniques.

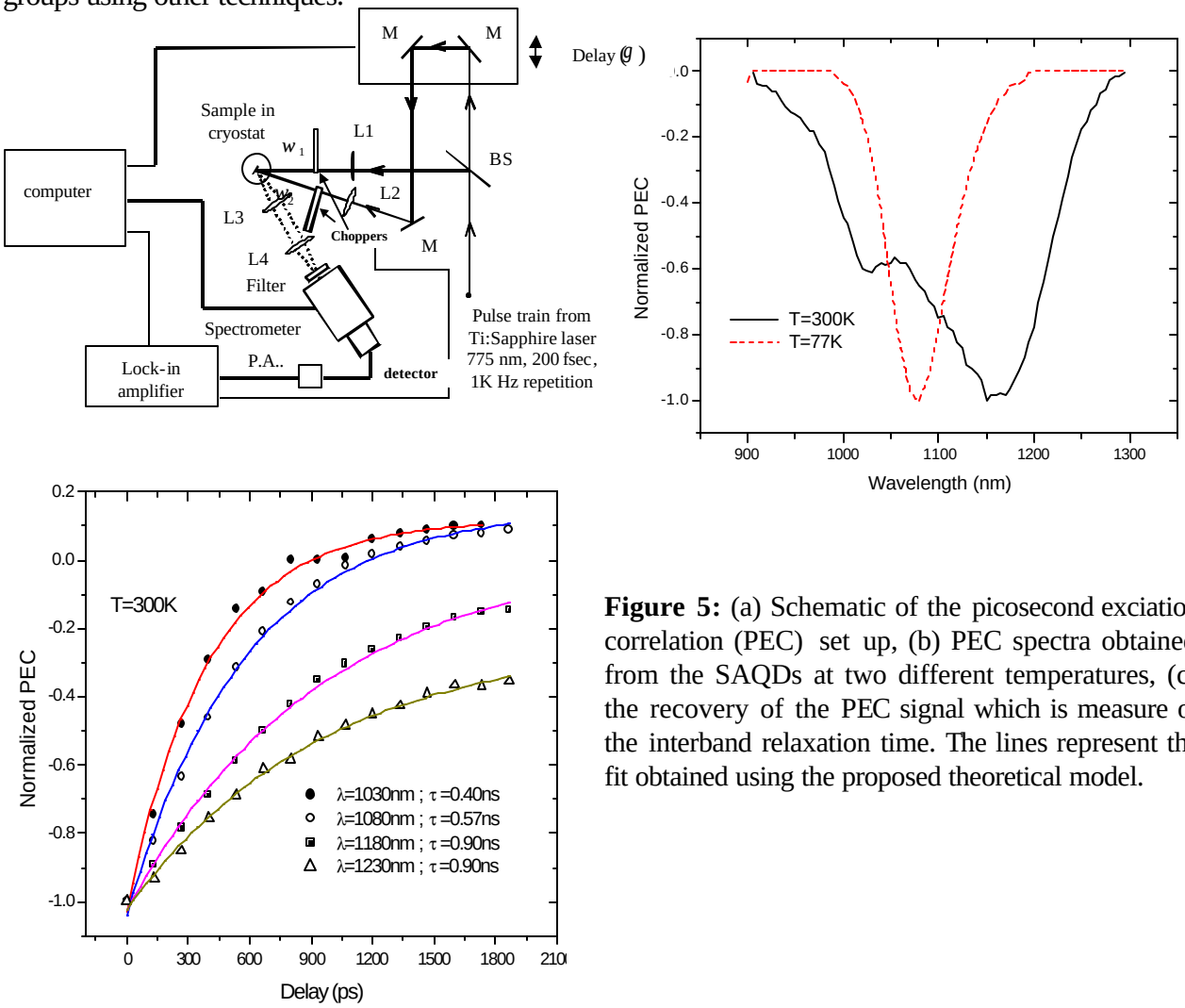


Figure 5: (a) Schematic of the picosecond exciation correlation (PEC) set up, (b) PEC spectra obtained from the SAQDs at two different temperatures, (c) the recovery of the PEC signal which is measure of the interband relaxation time. The lines represent the fit obtained using the proposed theoretical model.

Funding for this project has resulted in the following publications and presentations.

Publications:

1. S. Birudavolu, N. Nuntawong, G. Balakrishnan, Y. C. Xin, S. Huang, S. C. Lee, S. R. J. Brueck, C. P. Hains, and D. L. Huffaker, "Selective area growth of InAs quantum dots formed on a patterned GaAs substrate" Appl. Phys. Lett. Vol. 85, No.12, 2337, 2004
2. N. Nuntawong, S. Birudavolu, C. P. Hains, S. Huang, H. Xu, and D. L. Huffaker, "Effect of strain-compensation in stacked 1.3 µm InAs/GaAs quantum dot active regions grown by metal organic chemical vapor deposition" Appl. Phys. Lett. Vol. 85, No.15, 3050, 2004.
3. A. Amtout, S. Raghavan, P. Rotella , G. von Winckel, A. Stintz and S. Krishna "Theoretical Modeling And Experimental Characterization of InAs/InGaAs Quantum Dots In a Well Detector, *Journal of Applied Physics*, **96**, 3782, October 2004.
4. G. von Winckel, E. A. Coutsias and S. Krishna, "Spectral Element Modeling of Semiconductor Heterostructure', Submitted to Journal of Applied Physics.
5. N. Nuntawong, Y.C Xin, S. Birudavolu, P.S Wong, S. Huang, C. P. Hains and D. L. Huffaker, " Quantum dot lasers based on a stacked and strain-compensated active region grown by metalorganic

chemical vapor deposition " (submitted to Appl. Phys. Lett.)

6. S. Birudavolu, N. Nuntawong, G. Balakrishnan, Y. C. Xin, S. Huang, S. C. Lee, S. R. J. Brueck, C. P. Hains, and D. L. Huffaker, "Emission Characteristics of InAs QDs grown on nano patterned GaAs substrates by mocvd" (submitted for publication in Appl.Phys.Lett.)
7. R. P. Prasankumar, R. D. Averitt, A. J. Taylor (LANL), G. von Winckel, A. Stintz and S. Krishna "Time-resolved mid-infrared dynamics of an InAs/InGaAs quantum-dots-in-a-well heterostructure"(Manuscript in preparation for submission to Physical Review Letters)

Conference Presentations:

1. "Nano-patterned InAs quantum dots formed using MOCVD."S.Birudavolu and D.L.Huffaker, Photonics West 2005, Ca.
2. S. Krishna, S. Raghavan, G. von Winckel, A. Stintz, R. P. Prasankumar, R. D. Averitt, A. J. Taylor (LANL), "Quantum Dots-in-a-Well Detectors: Carrier Dynamics and Performance Characteristics", *American Physical Society meeting*, Montreal, TX, March 2004
3. G.V. Winckel and S. Krishna, "A Theoretical Model for Bias Dependent Shift of Absorption Spectra in Quantum Well Infrared Photodetectors" , IEEE/LEOS Annual Meeting, Glasgow, Scotland, November 2002
4. A. Amtout, S. Raghavan, P. Rotella , G. von Winckel, A. Stintz and S. Krishna "Theoretical Modeling and Experimental Characterization of InAs/InGaAs Quantum Dots In a Well Detector" L*aser and Electro Optic Society Annual Meeting*, October 2003.
5. (INVITED) S. Krishna, "Quantum Dots-in-a-Well Infrared Photodetectors for MWIR, LWIR and VLWIR Applications", *International Symposium on Physics of Semiconductors and Applications*, Gyeongju, Korea, March 2004
6. "Time-resolved mid-infrared dynamics of an InAs/InGaAs quantum-dots-in-a-well detector", R. P. Prasankumar, R. D. Averitt, A. J. Taylor (LANL), G. von Winckel, A. Stintz and S. Krishna (UNM), *Conference on Laser/Electro-optics*, San Francisco May 2004
7. "Investigation of the energy-dependent charge dynamics in InAs SAQD's with Ultrafast Scanning Tunneling Microscopy.", D. Yarotski, A. J. Taylor (LANL), A.L. Gray and S. Krishna (UNM), *Conference on Laser/Electro-optics*, San Francisco May 2004
8. G. von Winckel, E. Coutsias and S. Krishna, "The Helmholtz Eigenproblem in Elliptical Domains using Spectral Tau-Method and Conformal Mapping", International Conference on Spectral and High Order Methods, Providence, RI June 2004.
10. (INVITED) S. Krishna, "Nanostructured Semiconducting Materials for Mid Infrared Applications", Sandia National Laboratory, Albuquerque, October 2004

"Patterned InAs Quantum Dot Formation", S. Birudavolu, S. Q. Luong, C. P. Hains and D. L. Huffaker, University of New Mexico, Albuquerque, NM.