PROPOSAL WHITE PAPER BAA 03-012

Project title: **Development of Multi-probes for Optical Near-field Imaging of Dynamics Processes in Nanomaterials**

Principal Investigator:

Dr. Andres La Rosa, Assistant Professor,
Department of Physics
P.O. Box 751
Portland State University
Portland, Oregon 97207-0751

Telephone (503) 725-8397

Fax: (503) 725-9525

E-mail: andres@pdx.edu

Team members:

North Carolina State University (NCSU)
Silicon Wafer Engineering and Defect Science Center (SiWEDS)

Dr. George Rozgonyi, Director
Dr. A. Karoui, Research Associate

Arizona State University (ASU)
Applied Nanobioscience Center (ANBC)

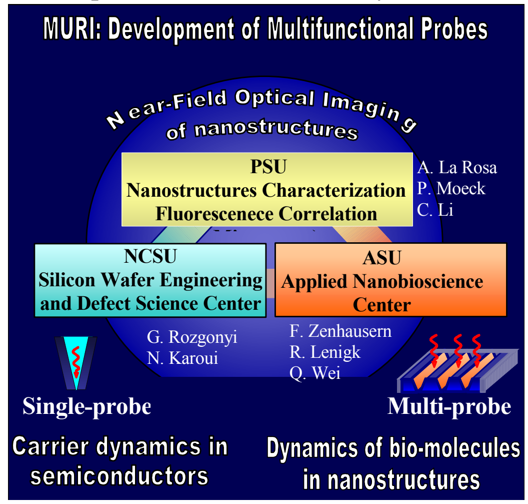
Dr. Frederic Zenhausern, Director
Dr. R. Lenigk, Research Associate
Dr. Q. Wei, Research Associate

Portland State University (PSU)

Dr. Peter Moeck, Assistant Professor
Physics Department,
Dr. Chunfei Li,
Center for Electron Microscopy

I. Identification of the research: Studies of dynamic processes in semiconductor and biological nanomaterials

Nanotechnology is expected to revolutionize science and global economy in the 21st century. An important aspect contributing to the advancement of nanotechnology will be the ability to fully characterize nanomaterial constituents. (For instance, particle-size dramatically affects the physical properties of quantum dots). In particular, it is also important to understand how the physical properties of nanomaterial constituents affect their dynamic response under external excitations. Based on these ideas, and on our expertise, our team is focusing on the development of **multifunctional probes** to characterize **dynamic processes** in nanostructures.



We plan to make possible two areas of study by exploiting the sub-wavelength resolution of Near-Field Optics (NFO). The first uses **single-probes** to study **carrier dynamics** in bulk and nano-crystal **semiconductors** (including carrier lifetime, defect localization, exciton dynamics). The second area involves studies of the **dynamics of biomolecules in nanostructures** (including driving selected bio-molecules through a nanofluidic device, and monitoring their different dynamics using **near-field slit arrays**). These applications will employ nanostructures with tailored characteristics (a critical aspect in the development of nanotechnologies) provided by our NCSU and ASU collaborators. In both applications, we plan to introduce Fluorescence Correlation Spectroscopy (FCS), a very sensitive method that can measure the dynamics of molecular processes from observations of random microscopic fluctuations (i.e. without perturbing the system) in molecular position or number density.

II. Proposed technical approaches

II.1 Studies of carrier dynamics in semiconductors using single probes

We are in the process of developing a frequency-resolved method for imaging transient phenomena in bulk semiconductors and propose to extend the method to analyzing nanoparticles. The technique involves scanning a single probe across the sample, maintaining its aperture at z=10 nm above the surface, and performing near-field measurements at every (x,y) pixel position in the following steps:

a) A flux of ~ 10^{11} photons/s exits the aperture (a ~ 100 nm) and generates a steady state population of excess carriers, N, in the sample region just beneath the probe (for a sample of 1 ms lifetime, N is of the order of ~ 10^{16} carriers/cm^3 while the pump-beam is ON). When the pump-beam is switched OFF, the excess carrier population decreases with time due to recombination processes (of lifetime τ).

b) An incident IR beam, exiting the same aperture probe, interacts with the time-dependent excess of the carrier population, causing the IR-transmission signal to change accordingly. For silicon, the free carrier absorption coefficient is given by $\alpha_{FC}=KN\lambda_{IR}^2$ with K=3.5x10^{-18} cm^2/μm^2. For N=10^{16}

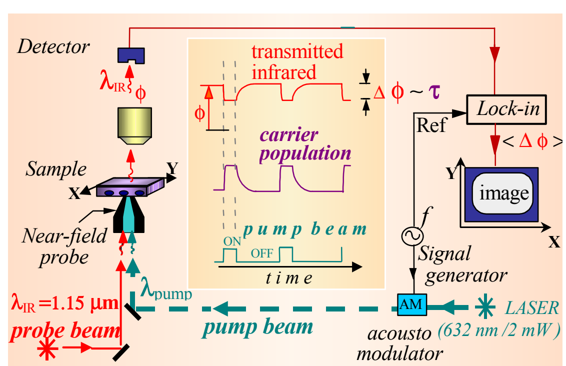


Fig.1 Experimental arrangement for time-resolved studies, with a timing diagram of the measurement process (inset at the center).

carriers/cm^3, α_{FC} ~ 0.1 cm^{-1} and the expected change $\Delta\phi$ in infrared transmission intensity (between the ON and OFF states of the pump beam) is on the order of $\Delta\phi/\phi \sim \alpha_{FC} \times \Delta z = 10^{-5}$.

c) A synchronous detection scheme allows to determine $\Delta\phi$. The pump modulation frequency is kept fixed during scanning, and an image is recorded for each frequency *f*. In a given image, areas in which recombination is slow (or fast), compared to *1/f*, provide low (or high) contrast $\Delta\phi$. Studies on the dynamic response of carriers to optical excitation can be obtained by probing the sample at different modulation frequencies. A preliminary result is shown in Fig. 2.

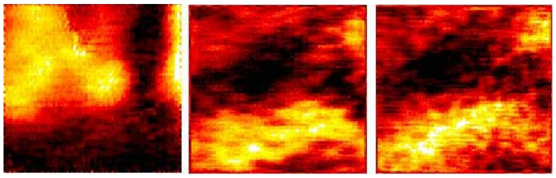


Figure 2. $\Delta\phi$ vs lateral position: Mapping carrier lifetime in silicon. The images capture, pixel by pixel, the dynamic response of carriers (measured in terms of the changes $\Delta\phi$ experienced by the infrared probe beam) while the excitation source (pump beam) is modulated. **Left**: 100 Hz; **center**: 1 kHz; **right**: 20 kHz. Images correspond to the same 7.5 x 7.5 μm^2 region.

We envision that the additional studies (proposed here) on a variety of bulk semiconductor materials will place this time-resolved technique on more solid ground. Test situations include: characterizing the high carrier mobility in the 15-80 nm thick device zone in SiGe heterostructures and the ultra thin 3 nm thick layer in silicon on insulator devices. The participation of the SiWEDS Center in providing tailored samples is crucial to corroborating the near-field measurements with control measurements obtained using standard techniques. The SiWEDS Materials Characterization group at NCSU has a long-standing reputation in correlating the electrical, structural, and chemical properties of semiconductors.

We will extend our near-field technique to the study of nano-crystals. This study takes advantage of the fact that excited e-h pairs are prevented from diffusing out of the excitation region, thus increasing the S/N ratio of the detection system by 3 orders of magnitude, which makes studies of e-h pairs in the *weakly confined regime* (particles of radius > 5 nm) possible. For the more demanding case of the *strongly confined regime* (particles of radius < 5 nm) cross correlation detection schemes (see next section) will be explored in this proposal. Adding Fluorescence Correlation Spectroscopy analysis to study charge carrier dynamics in nanoparticles would be unique.

Completion of the above activities will provide the ground for a future development that considers increasing the functionality of the probe by using the same metal-coated aperture as one electrode of a resonant capacitive circuit resonance frequency; making the sample itself part of the resonant circuit will allow simultaneous optical and electrical characterization at sub-wavelength resolution. It is not included here yet because it could overtax the resources of this MURI program, but it is mentioned to provide a sense of the direction of our future research activities

II.2 Monitoring the Dynamics of Bio-molecules with Multiple probes and Fluorescence Correlation Spectroscopy (FCS).

The second application addresses the challenging aspect, still elusive to NFO, of imaging moving species. The single probe imaging modality does not work here simply because of the relatively slow response in the electronic feedback circuit (which typically has ~1 kHz bandwidth) and therefore unable to follow moving objects. The alternative to be explored in this MURI proposal consists in driving moving bio-molecules through microchannels and monitor their dynamics using **near-field slit arrays.** This application benefits from the already ongoing activities on the fabrication of microfluidic devices at the Applied Nanobioscience Center–ASU; the integration of these devices with near-field optics is at the hart of our collaboration.

For this MURI project, we propose to incorporate FCS to monitor the dynamics of single molecules in microfluidic channels. The underlying principle of FCS is that both (*i*) the time correlation of random fluctuations of a system when undisturbed at equilibrium, and (*ii*) the rates of relaxation to equilibrium after a small perturbation, are governed by the same parameters. Thus, monitoring the intensity of the fluorescent emission from individual molecules would provide information on the lifetime of the excited state.(This scheme, therefore, can also be applied in the study of the charge dynamics in quantum-dots).

Using FCS and an integrated opto/microfluidic device, we propose to study the time course of biomolecules in microfluidics. Figure 3 shows the integrated nanofluidic channel and near-field slit array fabricated by the team at ASU. Currently, the detection principle within those devices is as follows: at a given driving field, whether electrical or hydrodynamic, the molecules will move along the channel at different velocities due to their difference in mass, charge, conformation, etc. When these fluorescently-labeled molecules move across the near-field slit

Fig. 3 Left: Schematic of an integrated near-field nanofluidic channel device for near-field screening of bio-molecules, fabricated by the ASU team. By guiding bio-molecules through nano-fluidic devices the screening speed increases (relative to a scanning process when using near-field single probes) while the near-field slit array slits (aperture<λ) allow monitoring their motion with high lateral resolution. **Right:** Foreseen apparatus arrangement for Fluorescence Correlation Spectroscopy analysis of bio-molecules (to be implemented in this MURI project)

array, each will be lit up by the near-field excitation emanating from each of the slits in the array. The molecules are detected as periodic signals in time-domain by a photodetector. At such device dimensions and sample volumes, the proposed system will allow us to study the kinetics of antibody-antigen reactions occurring in typically less than 20 ms.

III. Potential impact on DOD capabilities

Our goal is to develop single and multiple nanoprobes for investigating dynamic processes in nanostructures. Areas of potential military applications include: detecting toxic molecules, elucidating the optimal design of hybrid bio-mechanical systems, and nanoelectronics. The durability and stability of semiconductor systems, as well as the phase transformations that hybrid semiconductor/biological systems may undergo under severe environmental conditions, constitute several key issues in military applications which can be addressed by our diagnostic tools. It is noteworthy the incorporation of Fluorescence Correlation Spectroscopy (FCS) in our measurements to extract information about the parameters that govern the dynamics of molecular processes from observations of spontaneous microscopic fluctuations, i.e. without perturbing the system. We believe our research project can favorable impact the AFOSR interest in the area of "*develop nanoprobes, nanoantennas and molecule detectors*".

IV. Deliverables

- A unique diagnostic tool for the optical and electrical characterization of semiconductor and biological materials with nanoscale lateral resolution.
- Construction of a hybrid optical/microfluidic device for ultrasensitive detection of the kinetics of bio-molecular reactions.

V. Management plan

Drs. Zenhausern, Rozgonyi, and La Rosa constitute the Executive Committee, and will meet on an as-needed basis in addition to holding a conference call at least every three months to monitor the progress of the project. Dr. La Rosa will assume the duty of supervising all the detailed aspects to ensure a successful completion of the project and will inform the Executive Committee. At each site, Deputy Directors (Dr. Karoui at NCSU, Dr. R. Lenigk at ASU and Dr. La Rosa at PSU) will be responsible for the implementation, direction and supervision of the day-to-day activities.

VI. Potential Team

Dr. G. Rozgonyi	Director Silicon Wafer Engineering and Defect Science Center (SiWEDS), North Carolina State University	Expert in defect diagnostic tools. Recognized scientist and currently the Director of the SiWEDS Center, a consortium of seven universities and seven silicon wafer manufacturers. He will supervise the MURI activities in the semiconductor area, and provide access to a variety of state-of-the-art integrated circuit and photovoltaic samples with tailored characteristics
Dr. F. Zenhausern	Director Applied Nanobioscience Center, Arizona State University	Expert in Optics and in the manufacture of microfluidic devices, and the inventor of the Apertureless Near-field Optical Microscope. He will supervise the MURI activities in the biology applications area and provide his insights on the integration of hybrid devices for Life Science application.
Dr. A. Karoui	Research Associate, SiWEDS Center, North Carolina State University	Expert in the characterization of SiGe and SOI materials. He will be instrumental in the implementation of near-field optics at the NCSU site, and responsible for the NCSU facility on a daily basis.
Dr. R. Lenigk and Dr. Q. Wei	Research Associates, ANBC, Arizona State University	Hands-on expertise in fabricating fluidic interfaces connecting macro- to nano-channels. Through constant interaction with the PI, they will be instrumental in finding efficient ways to integrate optics into microfluidic systems and in developing on-chip bioassays.
Dr. P. Moeck	Assistant Professor, Department of Physics, Portland State University	Expert in Electron Microscopy and Crystallography. Dr. Moeck will provide quantum dot samples and help the PI to characterize this project's samples fully.
Dr. C. Li	Center for Electron Microscopy, Portland State University (PSU)	Scientist in charge of the operation and administration of the PSU Electron Microscopy Center. He personally will be involved in taking electron images of the quantum dots and opto/microfluidic devices used in this project.

VII. Summary of estimated costs

Direct costs

	NCSU Sample Prep	NCSU Post doc	ASU Fab & Test	PSU Equipm. & Test	PSU Post-doc	PSU Summe r salary	**Total**
FY-04	15k	50k	50k	70k	50k	12k	247k
FY-05	20k	50k	70k	80k	50k	12k	282k
FY-06	25k	50k	90k	50k	50k	12k	277k
Total	60k	150k	210k	200k	150k	36k	**$806k**

Indirect cost (applicable to salaries, at 42% rate): **$141k**

TOTAL (direct + indirect) **$947k**

LA ROSA, ANDRES H.

PROFESSIONAL EDUCATION

• Ph. D. in Physics	North Carolina State University	Raleigh, North Carolina	1990-96
• Master of Science in Physics	Southern Illinois University	Carbondale, Illinois	1988-90

APPOINTMENTS

• Assistant Professor Physics Department	Portland State University	Portland, Oregon	1999 –
• Consultant Scientist	University of Delaware Center for Nanomachined Surfaces	Newark, Delaware	1999
• Research Scientist	Firmenich Inc.	Princeton, New Jersey	1997-99
• Research Associate	North Carolina State University	Raleigh, North Carolina	1996-97

PUBLICATIONS

H. P. Chiang, A. H. La Rosa, P. T. Leung, K. P. Li, and W. S. Tse; "Optical spectroscopy for single-molecules near a microstructure at varying substrate temperatures;" *Optics. Commun.* **205**, 343-350 (2002).

B. Biehler and A. H. La Rosa, "High frequency-bandwidth optical technique to measure thermal elongation time responses of near-field scanning optical microscopy (NSOM) probes," *Rev. Sci. Instrum*. **73**, 3837 (2002).

A. H. La Rosa and H. Hallen, "A compact method for optical induction of proximal probe heating and elongation", *Appl. Optics* **41**, 2015-9 (2002).

H. D. Hallen and A. H. La Rosa, "Near-Field Scanning Optical Microscopy as an Imaging Tool for Silicon Carrier Processes," Proc. of International Conference on Silicon Dielectric Interfaces, Research Triangle Park, NC 25-27, (February 2000)**.**

A. H. La Rosa, B. I. Yakobson and H. D. Hallen, "Optical imaging of carrier dynamics with sub-wavelength resolution," *Appl. Phys. Lett*. **70**, 1656-8 (1997).

A. H. La Rosa, C. L. Jahncke, H. D. Hallen, "Time as a contrast mechanism in near-field imaging," Ultramicroscopy **57**, 303-8 (1995).

A. H. La Rosa, C. Jahncke, H. Hallen, "Time-resolved contrast in near-field scanning optical microscopy of semiconductors," SPIE **2384**,101-8 (1995).

A. H. La Rosa, B. I. Yakobson and H. D. Hallen, "Origins and effects of thermal processes on near-field optical probes," *Appl. Phys. Lett*. **67**, 2597-9 (1995).

H. D. Hallen, A. H. La Rosa, C. L. Jahncke, "Near-Field Scanning Optical Microscopy and Spectroscopy for Semiconductor Characterization," Physica Status Solidi (A) **152**, 257-268 (1995).

HONORS

Honorary degree **DOCTOR HONORIS CAUSA** from the University Jose Faustino Sanchez Carrion, Huacho-Peru (1996).

Elected member of "Sigma Pi Sigma", National Physics Honor Society; received into the Chapter at North Carolina State University (1991).

PATENT

H. D. Hallen, A. La Rosa, C. L. Jahncke; "Signal Detection for an Alignment-free Atomic Force Microscope;" North Carolina State University, NCSU No. 95-61 (1995).

RESEARCH SUPPORT

- Department of Defense, Army Research Office, DURIP Program. “Instrumentation development to integrate Optics, scanning probe microscopy and micromechanics”, $50,000, Grant DAAD19-01-1-0424 (2001).
- PSU-Office of Graduate Studies and Research, “Design and construction of opto-mechanical micro-devices for fast screening of macromolecules using Micro-Electro Mechanical Systems (MEMS) Technology,” $5,000, Faculty Enhancement Grant (2003).

COLLABORATORS

- Dr. George Rozgonyi, Director
  Silicon Wafer Engineering and Defect Science Center (SiWEDS)
  North Carolina State University
- Dr. Frederic Zenhausern, Director
  Applied Nanobioscience Center (ANBC)
  Arizona State University

SYNERGISTIC ACTIVITIES

- Annual presentations on Optical Technologies at local high schools:

  At Skyview High School, 1300 N.W. 139th Street, Vancouver WA, 98685; in coordination with Ms. Carol Ramsey, Physics Teacher. May-2000.

  At the "Science Day" event, attended by several local high school institutions, at Oaks Park, Portland, Oregon. May 2000.

  At Wilsonville High School, 6800 S.W. Wilsonville Road; Wilsonville, OR 97070; in coordination with Mr. Robert Derry, Science Teacher. May 2001.

  At Molalla High School, Molalla, OR 97038; in coordination with Ms. Emmely Briley, Physics Teacher. April 2003.
- “Scholarship of Teaching and Community Engagement Resource Team (STRT)” award. Center for Academic Excellence, Portland State University (2002-2003).
- Member of the Physics department team that was awarded the “Departmental Engagement” Minigrant, Center for Academic Excellence, Portland State University (2003).
- Provost’s PSU Foundation Faculty Development Award, “Fomenting University-High School Institutional Relationship” (2003).

Brief background

Dr. La Rosa has hands-on experience in designing, constructing and implementing near-field scanning optical microscopes. From 1993 to 1996, he was a graduate student member of the Precision Engineering Center at North Carolina State University (NCSU), which was one of the very first research institutions involved in near-field scanning optical microscopy (NSOM) development. At NCSU he built every component involved in the functioning of an NSOM microscope, which included probe fabrication, optical set-up with visible and near-infrared laser sources, modification of feedback circuitry of commercial electronic systems, and construction of sensitive electronic preamplifiers. He also participated in the development of a far-infrared NSOM microscope.

After receiving his Ph. D. degree, Dr. La Rosa worked as Research Scientist at Firmenich Inc., a chemical company located in Princeton, New Jersey. The use of scanning probe monitoring techniques in support of the development of chemical sensory components in an artificial olfactory system ("electronic nose") was part of his duties there. He was involved also in developing an apertureless NSOM system. More recently, in 1999, Dr. La Rosa worked as a Consultant Scientist at the Center for Nanomachining Surfaces (CNS) at the University of Delaware. At the CNS he operated commercial scanning probe microscopes (from ThermoMicroscopes Inc., now a Veeco company), including the Aurora NSOM system. Dr. La Rosa came to Portland State University in 1999 and took a tenure track faculty position in the Physics Department.