4.D IRG1: Complex Nanoscale Materials

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**Focus:** C-SPIN researchers will use their demonstrated expertise in the growth of semiconductors and complex oxides and the fabrication and modeling of nanostructures i.e. quantum wells (QW), wires (QWR), dots (QD), and rings (QR), to:

A. Research the growth of hybrid complex oxide structures (e.g. semiconductor/oxide and oxide/oxide) particularly those in which the interface itself controls the material behavior. We will characterize and model the interface to determine the role of defects, atomic structure, magnetic and electronic states, strain, etc. in defining the optical and electrical interface functionality not attainable in bulk.

B. Explore the behavior of nanostructures formed with discrete domains of different nanomaterials arranged in a controlled fashion such as QD/QW, QD/QWR, QD/QD systems. The understanding of the nature of coupling between nanostructures will then stimulate ways to create “coupled devices”.

**Motivation:** IRG 1 will seize the exciting opportunity to explore and exploit the role of the interface formed between two solid state materials. We will build upon our existing skill set in controlling the chemistry, structure, and growth of semiconductor systems to develop a similar level of control in more hybrid complex oxide materials, e.g. oxide/semiconductor or oxide/oxide systems. Initial work will focus on their extraordinarily rich interfaces, evolving towards reduced dimensionality as our understanding grows. In developing the fundamental science needed for control of strongly correlated electron materials we will not only open a new category of materials, but inspire the continued development of new and more efficient thermoelectric materials, nonlinear optical devices, unusually large magnetism in designed half-metallic systems, artificially layered high Tc superconductors, a 2D electron gas at a polar/non-polar junction, and an emerging class of correlated electronic devices beyond Si based.

Moreover, we will expand our complementary effort in the growth of hybrid nanostructures in order to study interactions between coupled quantum systems, via optical, electronic and magnetic methods. By tuning the nature and degree of coupling (again, often an interface property) we can obtain systems with remarkable properties: geometry dependent excited state lifetimes and fluorescence yield; tailored index of refraction and dispersion; enhanced nonlinear optical coefficients. Such structures appear promising for the development of light-emitting devices, detectors, memory, and applications in nonlinear optics and nanophotonics.

**Proposed Research:** An interdisciplinary team is essential, including experts in growth (Chakhalian, Salamo, Tian, Peng), characterization (Xiao, Murphy, Freeland, Heyes, Johnson, Zou), and modeling, (Fu, Bellaiche, Mullen). Below we describe how the team will explore properties of materials composed of a few atomic layers of (A1) semiconductor/oxide and (A2) complex oxide/oxide composites, with a focus on the interface itself as a nanomaterial. We will also study the behavior of coupled discrete (B1) metal-semiconductor, (B2) semiconductor-semiconductor, and (B3) oxide-semiconductor nanostructures. This will be done by exploiting our ability to grow with monolayer control and our unique ability to control the position and composition of QDs.

**A.1. Semiconductor–oxide composite nanoscale material:** Whereas the inter-atomic interaction that dominates the material properties of semiconductors is short-range covalent bonding, the atom-atom interaction in ferroelectrics is predominantly long-range Coulomb. Combining them into one system can potentially integrate their dissimilar properties to form new material functionalities. For example, it will be exciting to examine how the polarization in the ferroelectric oxide can be used to tune and control the electronic and optical properties of the semiconductor component and, likewise, explore how screening in the semiconductor affects the polarization in the ferroelectric, creating the opportunity for enhanced and perhaps tunable dielectric response, nonlinear optic, optoacoustic coefficients, etc.

Using UHV interconnected MBE chambers Salamo will synthesize semiconductor-complex oxide interface structures. Guided by TEM imaging by Johnson, the collaboration will vary growth conditions, composition, monolayer thickness of composite materials, and map phase diagrams for the nanomaterials. In a complementary theoretical effort, Fu will use first-principles methods to find the atomic structure at
the interface and correlate results with TEM observations by Johnson to understand the properties of the composite nanostructure. This “closed loop” approach will lead to an efficient method to optimize the quality of the interface and its control of material properties.

The team will begin by investigating the growth of GaAs monolayers on strontium barium niobate (SBN). SBN was chosen as the pilot oxide due to its small lattice mismatch with GaAs, its large nonlinear optical and piezoelectric coefficients and Salamo’s extensive experience with this material\textsuperscript{18-22}. The resultant refined interface nanomaterial will be characterized by electronic and optical measurements by Murphy and Xiao. SBN is also unique with 3-fold, 4-fold, and 5-fold open vacancies in its tungsten bronze structure that can accommodate different size dopants to allow flexibility in its optical response, as measured by Xiao. These studies will stimulate on-chip electro-optic integrated optical interconnects\textsuperscript{23}.

**A.2. Complex oxide-oxide composite nanoscale material:** Our objective is to uncover and understand the materials science at unit-cell oxide-oxide interfaces (Fig. 1). For instance, the electron gas at the LaAlO$_3$/SrTiO$_3$ and Zn$_{1-x}$Mn$_x$O/ZnO interfaces\textsuperscript{24}, and its quantum properties, demonstrates both the promise and challenge of these complex structures. To explore the possibilities, Chakhalian with laser MBE, and Salamo with conventional all-oxide MBE, will synthesize complex oxide interface materials and develop a correlation to structure analysis by Johnson and Freeland (Argonne). The team will determine the role of the polarity of atomic layers\textsuperscript{25}; covalent bonding\textsuperscript{26} and orbital reconstructions\textsuperscript{27}; lattice relaxation\textsuperscript{28}; exchange interactions\textsuperscript{29}; interface disorder; etc. in material properties. For example, we expect the band alignment on each side of the interface to result in charge transfer and possibly charge accumulation at the interface, enabling electronic doping without disorder. This can lead to dramatically altered states at the interface, states which do not even exist on the bulk phase diagram! Moreover, we may design the interface to be at a bi-critical point where a subtle modulation of the interface will result in a profound change of its physical properties. Xiao and Murphy will explore controlling this transition by applying external stimuli, e.g. strain, light, pressure, electric or magnetic field. Initial targets for synthesis and study are charge-transfer insulator-band insulator interfaces, such as 1SrNiO$_3$/1SrTiO$_3$ or 1SrNiO$_3$/1DyScO$_3$ (where “1” is 1 unit cell) to explore the lattice mismatch and orbital selection at the interface with an expectation to observe a high T$_c$ superconducting phase. Meanwhile, for 1LaCrNiO$_3$/1LaCrFeO$_3$, calculation\textsuperscript{30} predicts that a small distortion of the octahedra will induce a half-metallic anti-ferromagnetic phase! Such structures can potentially start a disruptive class of materials with 100% spin polarized current in the absence of uncompensated magnetism.

Another target for synthesis and study are oxide-multiferroic/oxide-ferroelectric interfaces, such as BiFeO$_3$/(Pb,Zr)TiO$_3$ which will be synthesized by Salamo and modeled by Bellaiche. For example Zou will investigate the influence of a tilt in the oxygen octahedral of BiFeO$_3$ measured by Johnson, on the Curie temperature (T$_c$) of PbTiO$_3$ and similarly the influence of PbTiO$_3$ on the Neel temperature of BiFeO$_3$. It is also known that (Pb,Zr)TiO$_3$ exhibits phase transitions\textsuperscript{32} for compositions around 50% of Zr and Ti. Such phase transitions lead to huge dielectric and piezoelectric responses. Zou will explore the effect of these transitions on the hybrid’s properties. Such transitions can make the BiFeO$_3$ lattice softer inducing a phase transition in BiFeO$_3$, which can lead to huge piezoelectric and dielectric responses as well as phenomenal magnetic susceptibilities and ME coefficients.

**B.1. Metal-semiconductor composite nanostructures:** The optical dipole interactions in composite systems comprised of metal and semiconductor nanostructures can strongly alter the optical properties of
the individual constituents, creating a new class of materials which can efficiently localize, guide and switch light on the nanoscale\textsuperscript{29-30}. For example, we envision a semiconductor quantum dot coupled to two arms of a metallic bow tie antenna (Fig. 2). Grating-coupling of incident far-field light will launch surface plasmon polaritons (SPP) wavepackets which will be spatially localized inside and tunnel through the gap of the bowtie antenna. Due to the strong light localization inside this nanogap, optical excitation of a single exciton in the QD located inside the bowtie nanogap is expected to result in a sizeable change in the transmission of the SPP wavepacket through the bowtie nanogap. Such coupled hybrid nanostructures can explore the dynamics of coupling between single excitons and single SPPs. We will probe linear-nonlinear ultrafast dynamics of optical excitations of individual coupled structures composed of a metallic nanoparticle (MNP) and semiconductor QD guided by theoretical modeling by Fu. The MNP grown by Chen will be deposited on buried QD arrays fabricated by Salamo. The composite system will be morphologically characterized by Johnson, while Xiao and Heyes will investigate if the mechanism for exciton-SPP coupling arises from an optical dipole interaction between two coupled modes, electron transfer, or tunnel-coupling induced by wave function overlap, by comparing experiment with the nonlinear effects described by the Fano model\textsuperscript{31-32}. Meanwhile, Mullen will also model core-shell QD’s (synthesized by Peng) and interactions with other QD’s and metal and semiconductor surfaces. Optically excited excitons within the shell can be stabilized by image charges on metal surfaces or by similarly polarized neighboring QD’s. Xiao will detect PL from a cascade collapse of the exciton chain.

B.2. Semiconductor-semiconductor composite nanostructures: Knowledge of the nature of coupling between semiconductor nanostructures can play a significant role in developing on-chip devices. As an example, one can imagine a QW as a huge reservoir of carriers to pump a QD laser. At the same time, coherent resonant tunneling is itself an interesting materials science question. Does the exciton tunnel or is it the electron or hole separately? To begin to probe such questions Salamo with help from Marega (Universidade Sao Paulo) will grow and Mullen will model beginning with the coherent resonant coupling\textsuperscript{33} between a QD/QW. We aim at gaining this understanding by probing, in real time, the transfer of excitons. Heyes and Mortazavi (UA Pine Bluff) will explore the coherent tunneling probability dependence on resonance using an applied electric field and on the QD/QW separation and potential barrier. We will also investigate the effect of Rabi oscillations on the tunneling probability using resonant PL, PLE, and pump probe methods for individual QD/QW. This is just the beginning since we are prepared to study the optical and transport behavior of QD chain-QW, QWr array-QW, and QWr-QD coupled nanostructures. For example, Salamo will make use of a unique instrument for growth of QDs developed at Arkansas that uses a scanning AFM tip that has a nanoscale aperture and uses an electrical pulse to place droplets of In, Ga, or Al, at precise locations before they are crystallized into QDs by an As\textsubscript{4} flux. This precision makes it easy to prepare coupled QDs of the same or different compositions and specific geometrical arrangements and study their collective properties due to the coupling between them.

B.3. Complex oxide-semiconductor composite nanostructures: In a complementary direction, Tian will synthesize hybrid nanostructures with ZnO crystallites as templates\textsuperscript{34} on which core-shell GaN/ZnO or ZnO/ZnS colloidal nanoparticles will be grown. MNPs will then be added in the cavities of ZnO crystallites forming a composite nanostructure. Using dopants the absorption spectrum of nanoscale semiconductors will be tuned over the visible range to be resonant with the SSP of the MNP. While we have had some success with this procedure it will be improved to control the properties of the resulting hybrid material. Xiao will optically probe a single structure to develop an understanding of their linear and nonlinear optical properties. Mullen will also model nanoscale tunnel junctions where Pb(Zr,Ti)O\textsubscript{3} (PZT) materials are used as the insulating barrier. A single electronic charge on a femtofarad junction produces a tenth of a millivolt potential difference across the device. At issue is how single electron tunneling events can couple to the PZT degrees of freedom within the insulating barrier.