FINAL TECHNICAL REPORT

Project Narrative

Materials Science and Physics at Micro/Nano-Scales

DE-FG02-01ER45911

The University of Kansas Center for Research, Inc.

2385 Irving Hill Road, Lawrence, KS 66045-7563

Judy Wu (PI),

University of Kansas, Department of Physics & Astronomy

1251 Wescoe Hall Drive, room 1082 Malott Hall

Lawrence, Kansas 66045

Ph: 785-864-3240; Email: jwu@ku.edu

DOE Office of Basic Energy Sciences, Division of Materials Sciences & Engineering

Program Manager: Dr. Bonnie Gersten

1. PROGRESS REPORT = Final

1.1. Overall Project Summary

The DOE support for Judy Wu (DE-FG03-01ER45911, “Material science and physics at a microscopic scales”, \$377k/3year) started on August 15, 2005. This grant supports two graduate students, one undergraduate and one faculty-summer month each year through the whole three-year project period. A 12 month no-cost extension was applied and approved for one the graduate students to complete her PhD thesis. No significant amount of remaining funds is expected by the end of the project period. The **scope** of this project is to study nanostructures of semiconductors and superconductors, which have been regarded as promising building blocks for nanoelectronic and nanoelectric devices. The emphasis of this project is on developing novel synthesis approaches for fabrication of nanostructures with desired physical properties. The ultimate goal is to achieve a full control of the nanostructure growth at microscopic scales. The major experimental achievements obtained will be summarized in the following. The details can be found in a US patent awarded, 23 papers published, and 15 invited talks at national and international workshops and conferences. Many of our publications were selected to publish in online AIP Virtual Journals of Application of Superconductivity and Nanoscale Science & Technology. Our paper on nanopores [*Appl. Phys. Lett.* **93**, 062506 (2008)] was featured as a Technology Update on the IOP Nanotech Web on October 17, 2008.

Education has been a major component of this project. Several graduate students—Hua Zhao (PhD 2007), Xiang Wang (PhD 2008), Rose Emergo (PhD expected in 2009), Guowei Xu, Caitlin Rochford, Alan Elliot, Gary Malek (current PhD students) have been supported partially over the project period. In addition, four undergraduate researchers have also been supported by this project. They are Jesse Noffsinger, Alan Dibos, David Jones, and Greg Gaumer. The first three are physics majors and the last one is from mechanical engineering. All of them were/are honor students at KU. The involvement of research in their early career has greatly enhanced their interest in sciences and most of them have co-authored multiple publications. Many of our students have won various awards. Caitlin Rochford is the recipient of 2008 NSF graduate scholarship and Jesse Noffsinger, 2005 recipient and has been in PhD program of physics at UC Berkeley since the Fall of 2005. Alan Dibos, who received honorable mention from the 2006 Goldwater and 2007 NSF graduate scholarships, began his graduate study at Harvard in the Fall of 2006 continuing on his research interests in nanoscience. This project has also involved local high school students in research. Ruilong Hu from Free State High, who worked several terms at our laboratory and will

be co-author for several of our publications, has been admitted by the Washington University (St. Louis) on science major in 2007. The PI has also hosted/participated in many other K-12 outreach activities, women in science and engineering. One recent event is a nanotechnology lab tour of 26 gifted 7th and 8th graders from the Hocker Hill middle school in Kansas City. In addition, the PI has been serving as the SPS (society for Physics students) advisor and the principal for the Lawrence Chinese school (volunteer) since 2001, the latter has attracted a large number of K-12 students (typically ~35-40 students) from Chinese, American and other families. Besides offering weekly Chinese lessons, the school has organized seminars of in math, science, economy, history, etc.

1.2. Major Research Results

Topic 1. Semiconductor nanostructures

Semiconductor nanowires (SMNWs) have attracted much attention during the past few years because of their potential in nanoelectronics and many exciting process has been achieved. Our interests in B nanowires (BNWs) are several folds. Boron is the third lightest element in the solid form, but has a high melting temperature near 2300 °C. Its hardness is very close to the diamond. These unique features make boron and boron-related compounds attractive for various applications including high-temperature lightweight coatings and high-temperature semiconductor electronic devices. Boron typically forms three-center electron-deficient bonds and B₁₂ icosahedron serves as the building block for many boron-related compounds. In the bulk or thin film forms, boron has low electrical conductivity in the semiconductor regime. High conductivity in the metal regime, however, may be achievable in novel boron structures such as layered, tubular and fullerene-like solids built from elemental subunits may exhibit novel physical properties. For example, boron nanotubes (BNTs) may have metallic density of states that may lead to higher electrical conductivity in boron nanotubes than in carbon nanotubes. This has motivated considerable efforts recently in growth of BNWs. Some of our work in BNW and BNT synthesis are highlighted in the following. Unfortunately, the conductivity we have measured on single BNWs and BNTs is extremely low, not consistent with theoretical expectation. So in the last year or so, we have shifted part of the effort to synthesis of InN nanostructures with emphasis on understanding the growth mechanism in a self-catalytic process.

- **Two-liquid VLS process for inclined BNW bundles**—In the VLS process typically employed for SMNWs growth, nucleation and anisotropic crystal growth of single nanowires are achieved with generation of a solid/liquid alloy interface using metal catalysts. The nucleation and growth mechanism of nanowires may be greatly altered when a second liquid is introduced into the solid/liquid alloy interface. In this work, we demonstrate bundled BNW array growth on Au coated Si substrates by introducing a second liquid of B₂O₃ onto the solid (B)/liquid alloy (Au-B) interface. The BNWs in each bundle are straight but inclined with respect to the normal of the substrate. A study of BNW morphology and chemical elemental distribution using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDS) suggested that the catalyst Au provided the nucleation site for BNW bundles while the liquid B₂O₃ modified the initiation of BNWs from each nucleation site, resulting in multiple initiations of the BNWs from each site.

- **Fused BNW Y-junctions**—In this work, we demonstrated that BNW Y-junctions can be synthesized in a self-assembled manner by fusing two individual BNWs grown inclined towards

each other. The presence of a second liquid (low melting B_2O_3 in BNW case), in addition to the liquid Au catalyst, was found critical to the inclination of the BNW. The interplay between the low melting B_2O_3 with the Au liquid metallic catalyst resulted in inclination of BNWs. This provides an essential condition for fusing BNWs (see Fig. 1). The structure of the BNW Y-junction arrays may allow construction of three or multiple-terminal nanowire devices directly on Si-based readout circuits through controlled nanowire growth. The approach of the self-assembled growth of the nanowire junctions developed in this work has also provided a viable strategy for formation of large-scale nanowire functional devices.

Fig. 1. Left panel: SEM image of a boron nanowire Y-junction obtained by fusing two BNWs together. Right panel: EDS mapping of boron, oxygen and fold on the junction.

- **Clone semiconductor nanowires using *in situ* switch from VLS to OA growth mode²²**—The VLS process has a well-defined mechanism in determining the morphology of SMNWs, but suffers a major difficulty in achieving high growth rate needed for commercialization. The OA growth process, on the other hand, typically has high growth yield of more than an order of magnitude higher, but does not have a well-defined nanowire nucleation mechanism. The morphology of the SMNWs made in OA is not as uniform as in VLS process achieved with the metal catalytic tips. To combine the advantages of the VLS and OA processes, we have developed a two-step process. The first step is a typical VLS process to generate well-defined short stubs of SMNWs. These stubs continue growing with the same diameters in the second-step OA process at a much higher growth rate. Although we have only demonstrated this scheme in B and Si nanowires, the same scheme may be applied to other SMNWs.

- **VLS and OA bimodal competition growth of metal/semiconductor core-shell nanocables²¹**—Metal/semiconductor core-shell coaxial nanocables are promising building blocks for nanoelectronic devices while *in situ* growth of these nanocables remains challenging due to the distinctly different synthesis temperature ranges required for metals and semiconductors. To overcome this difficulty, we have developed a VLS-OA bimodal competition growth strategy for *in situ* metal/semiconductor core-shell nanocable growth. Using this process, gold/boron core-shell nanocables were obtained. A core-shell Au-B/ BO_x eutectic droplet formed via hydrogen gas-assisted rapid cooling was found critical for initiation of the nanocable growth. In addition, the large difference in the BNW growth rates in the VLS and OA mechanisms facilitates the layered growth in the nanocables. The compatibility of this method with the VLS process applied widely for SMNW growth allows *in situ* connection of metal/semiconductor nanocables with SMNWs. Finally, BNTs could be obtained by dissolving gold core in the gold/boron core/shell nanocables.

Fig. 2. Left: HRTEM image a gold/boron core-shell nanocable with crystalline gold core and amorphous boron shell. EDS mapping of elements boron, oxygen and gold is shown. Right: Schematic diagram of the VLS/OA bimodal competition growth process. (a) A boron nanowire is initiated via VLS mode from an Au-B eutectic droplet. In (b), a rapid cooling is applied which leads to the formation of an Au-B/ BO_x core-shell tip after condensation of B_2O_3 vapor around the original Au-B eutectic droplet. A boron nanotube is precipitated from the BO_x outer layer due to a much higher growth rate in OA mode accompanied by the Au-B eutectic liquid filling in the nanotube. In the later stage of the rapid cooling (c), the eutectic liquid inside the boron nanotube solidifies when temperature decreases below its pseudo eutectic point, which drives gold to the center while boron nucleates on the inner wall of the boron nanotube. This completes the formation of a gold/boron core-shell nanocable in stage (d). Temperature decreases from left to right. The inset shows a boron nanowire with a core-shell tip which was formed in a two-step growth. The second step OA growth temperature was 950 °C.

- **Building SMNW 3D nano-architectures**— 3D nano-architectures with SMNWs as building blocks are promising for multiple terminal electronic devices if a precise control could be achieved in assembling them. We have exploited several processes for (a) growing “trees” of SMNWs (Si and B) through multiple steps of evaporation of metal catalyst followed by growth of SMNWs; and (b) junctions of SMNWs via evaporation of oxides on crosses of SMNWs (Fig. 3).

Fig. 3. Left: SEM image of boron (yellow)/silicon (green) tree; middle and right: SEM images of junction of two boron nanowires (middle) and three boron nanowires (right) connected by SiO_x beads.

- **InN-based III-Nitride alloy nanowires**²⁴—A Plasma-enhanced chemical vapor deposition (PECVD) system was assembled recently for synthesis of InN nanowires (NWs). There are several unique features of this system. First, the system allows feeding of both individual source lines of In, Ga and N, etc, and pre-mixed solid sources, allows, which is necessary to obtain the desired chemical composition in $\text{In}_{1-x}\text{Ga}_x\text{N}$ (x can be changed between 0 and 1) NWs and multiple band axial and core-shell. The growth chamber at the feeding point of the vapor sources is connected to the main chamber through a gate of controllable opening, which allows a systematic adjustment of the growth pressure from vacuum (10^{-7} Torr to overpressure of up to 1.6 Atm.) in the growth zone. This feature is important for investigation of the growth mechanism of InN NWs in a wide range of growth pressure. Finally an RF plasma generator (13.56 MHz, 500W) was

recently implemented to the growth zone for enhancement of the nanowire growth, in particular, to generate vertically aligned growth.

We have made a systematic study on InN NW growth window (growth temperature, pressure, flow rate of different gases-NH₃, N₂, etc) and two pressure windows were identified. One is at lower indium partial pressure in which aligned InN columns grow first followed by NWs. This is similar to the observation in PE-MBE growth, which will be discussed in more details in Theme 1, topic 2. The higher pressure window overlaps with that reported in CVD growth by other groups, in which we have made an investigation on the InN NW nucleation and evolution in the self-catalyzed growth by quenches at the early stage of the growth followed by characterization (Fig. 4). It was revealed that amorphous InN_x micro-particles of cone shape form in the initial stage of the growth. InN crystallites later formed inside the cone may experience highly anisotropic growth along the favorable (0001) orientation, resulting in InN NW bundles protruding out from the micro-particle. The micro-particles are most probably in liquid phase, which is supported by the observation of disappearance of the micro-particles after InN NWs form and the alignment of the InN NWs protruding out from the same micro-particle. The liquid phase micro-particle may eventually evolve into the amorphous sheath. The sheath at the NW tip serves as an interface between growing InN NWs and the incoming vapors of indium and nitrogen and supports fast growth of NWs in a similar way to the oxide sheath in the oxide-assisted growth of other semiconductor NWs such as Si. This result presents critical clues towards understanding of the self-catalysis nucleation and evolution of InN NWs.²⁴ A thorough understanding of the microscopic mechanism of the self-catalyzed growth of InN nanostructure is critical to achieve a precise control of the physical properties of the InN nanostructures including morphology, dimension, crystallinity and electrical transport properties.

Fig. 4: Schematic description of nucleation and evolution of InN nanowires in the self-catalyzed growth process. (a) The formation of liquid InN_x micro-particles and nucleation of multiple InN crystallites inside the liquid InN_x micro-particles. (b) Anisotropic growth of InN nanowires from the crystallites along (0001) direction out of the InN_x micro-particles. (c) Further growth of InN nanowires with the help of amorphous InN_x sheath in liquid phase after InN_x micro-particles diminish and (d) a magnified view of one InN nanowire in (c). The attachment of In and N from the vapors, occurs mostly at the tip (see the TEM images at the center) through the liquid InN_x amorphous sheath around the tip.

Topic 2. Superconductor Nanostructures

A fundamental issue related to the current carrying capability of high temperature superconductor (HTS), which has been commercialized for electric power applications,²⁵ is that the best critical current density J_c achieved is still an order of magnitude lower than the theoretical depairing current density J_d .^{26,27} It should be realized that J_d is the thermodynamic depairing limit, which cannot be reached in the presence of dissipation of magnetic vortex motion. In conventional superconductors, J_d was observed in extremely narrow bridges of superconductors of the transverse dimension much smaller than the London penetration depth λ .²⁸⁻³¹ In such narrow bridges, magnetic vortices cannot form inside the superconductor since its dimension (comparable to λ) is larger than the bridge. For HTS materials, such as $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO), the transverse λ_a (in the ab-plane) is on the order of 300 nm at 77K. It is therefore critical to synthesize HTS NWs of transverse dimension much smaller than λ_a and to investigate their transport properties.

- **HTS nanowires**— Fabrication of ceramic HTS thin narrow bridges is by no means trivial. This has presented a major experimental challenge because material degradation, typically showing in decreased superconducting transition temperature T_c and broadened transition width, occurs to the HTS thin narrow bridges made with lithographic methods.³²⁻³⁴ To generate single HTS nanowires, we have developed a multiple step lithography process that involves both

photolithography (PL) and electron-beam lithography (EBL) in combination with ion milling or reactive ion etching. Fig. 5 shows the images of a four-bridge circuit we have made on a YBCO thin film with the bridge width w varying from above to much below λ_a . The YBCO films with thickness of 10-50 nm are sandwiched with 3-5 nm thick $\text{PrBa}_2\text{Cu}_3\text{O}_7$ layers. No degradation in T_c was observed on these samples. The transport J_c characterization is ongoing.

Fig. 5. An SEM image of a four-bridge circuit on an $\text{YBa}_2\text{Cu}_3\text{O}_7$ film with the bridge width varying from above to below λ . The overall circuit is on a $3.5 \times 3.5 \text{ mm}^2$ film. A blowup view of one of the four bridges of width 230 nm is shown in the inset.

YBCO sponge films—In wide bridges of width $\gg \lambda_a$, the presence of strong pins on the magnetic vortices can prevent vortex motion hence support a high J_c . Nanopores have a unique advantage over their nanoparticle counterparts for vortex pinning due to the chemical-contamination free interface with HTS matrix, which is critical to achieve the optimized pinning potential energy and not to degrade the HTS matrix. Motivated by this, we have developed a PONSE process (**P**ores by **n**anoscale **s**train **e**ngineering, US patent pending). Nanopores have been obtained via nanoparticle (NP)-facilitated strain manipulation on YBCO lattice. In our process, a large number of NPs are inserted either near the film/substrate interface or during the YBCO film growth. The local tune of the strain by the inserted NPs over the globally strained YBCO lattice on vicinal substrates plays a critical role in pore nucleation and evolution. A large number of pores of dimension from few to hundreds of nanometers formed uniformly via self-assembly growth. The density of the nanopores in the range of $5 \pm 3 \text{ pores}/\mu\text{m}^2$ corresponds to an accommodation field $H_m \sim 4.1\text{-}16.6 \text{ mT}$. Significantly enhanced J_c up to $8.3 \text{ MA}/\text{cm}^2$ at 77K and SF has been obtained on these samples, which is twice of the standard YBCO film's J_c and

~17-20% of J_d , the highest so far achieved in YBCO films. A close correlation between J_c and the magnetic pinning potential U_p of the nanopores has been demonstrated below the accommodation field H_m , confirming that nanopores are strong pins on the magnetic vortices (Fig. 6). This work was featured as a Technology Update on the IOP Nanotech Web on October 17, 2008.

Fig. 6. Left: transport J_c measured on several YBCO sponge films in comparison with a regular one made using the same YBCO target under the same processing condition. Upper-inset: AFM image of an YBCO sponge film and lower-inset: a TEM image of the film/substrate interface of a porous YBCO film on a 15° STO substrate. AFM images were taken on an 8 nm thick (middle) and a 16 nm thick (right) YBCO film on a 20° vicinal STO substrate, respectively. The nanoparticles (NPs) are observed on the former and pores just initiated atop NPs are circled on the latter. The scales both figures are the same. The insets show the AFM image (bottom) and depth profile (top) on a selected pore. The x-direction in the top inset is the scan direction defined by the green line in the bottom inset. An NP at the bottom of the pore can be clearly seen.

Invention (US patent awarded 7902119, 2011):

J. Wu, R. Emergo, T. Haugan and P. Barnes, "POROUS CERAMIC HIGH TEMPERATURE SUPERCONDUCTORS AND METHOD OF MAKING SAME"

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