NSF grant # ECCS-0701703 "An Ultrasensitive Biosensor Integrating Semiconductor Nanowires with Plasmonic Resonators." [Report for IREE supplement]

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ABSTRACT: With the support of an IREE supplemental grant, one graduate student from the University of Cincinnati and one undergraduate student Miami University were able to participate in a collaborative research project with the Australian National University, Canberra, Australia. Over a three month period, the students were able to conduct research towards the goal of developing a biosensor, including the fabrication of Ohmic contacts on a nanowire device, learning the method of dispersal of gold nanoparticles, and orienting nanowires by using electrophoresis. In addition, we were able to learn more about the nanowire growth process, and develop closer personal relationships with our collaborators. The students were also able to experience some of the cultural aspects of Australia, such as the importance of tea time as a tool for networking.

INTRODUCTION

The primary objective of this research is to design, fabricate and test a novel semiconductor nanowire based biosensor that is mobile, easily operated by first responders, able to test for multiple pathogens, that is sensitive with few false positives, and responds rapidly. The proposed nanowire biosensor combines noble metal plasmonic resonators with nonlinear resonant excitation of carriers in semiconductor nanowires. The binding of specific pathogens (bacteria, toxins, or viruses) to attached ligands is signaled by a small frequency shift of plasmonic resonators which induces a dramatic change in the photocurrent in a semiconductor nanowire. We seek to understand both the fundamental and the technical issues involved in each component of this sensor in order to develop a portable device.

Our collaboration with the research group of Professor C. Jagadish at the Australian National University (ANU) in Canberra, Australia where the high-quality semiconductor nanowires for our biosensors are grown was strengthened and extended by the international research experience for both our graduate and undergraduate students. The specific goals of this international research experience were to the learn about the growth process for III/V nanowires, including doping and heterostructures, about device fabrication using the grown samples, and about achieving ohmic contacts on these devices. Additional goals were to learn about the use of electrophoresis for orienting the nanowires as well as understanding the process for dispersing gold nanoparticle on the surface of the devices to achieve resonant enhancement of signals. Finally the students should better understand and appreciate the different style and culture both in the conduct of research and in daily interactions in an international laboratory.

ANU's facilities provided a rich range of state of the art growth and growth characterization facilities to the visiting graduate and undergraduate researchers. The facilities available for growth include two MOCVD reactors including a state of the art Aixtron MOCVD reactor with gas foil rotation which allows the growth of a range of III-V compound semiconductor structures based on GaAs, InGaAs and InP, including nanowires and devices like lasers, photodectors and modulators. A range of thin film deposition facilities are available including a thermal evaporator, an e-beam evaporator and a plasma enhanced CVD system. Both E-beam and Photo-Lithography Labs were available for device fabrication. Clean room facilities are also available. The characterization techniques range from scanning and transmission electron microscopy to x-ray diffraction to secondary ion mass spectroscopy to deep level transient spectroscopy.

From June 15 thru September 15, 2008, Melodie Fickenscher, graduate student at the University of Cincinnati, and Colin Boyle, undergraduate at Miami University, participated in the international research program at Australian National University. Several outstanding undergraduate and graduate students were considered for selection for this international research opportunity. The selection criteria included academic performance, previous research experience, and personal recommendations. In addition, we looked for students with a genuine interest not only in the specific research project, but also in an international research experience. Melodie brought talents in both sophisticated data analysis technical capabilities and an understanding of optical spectroscopy. She has displayed all the characteristics of an "exceedingly fast learner," and was enthusiastic about our research directions and more specifically about this international research opportunity. Colin brought initial experience in spectroscopic methods from co-PI's (JYR's) lab and enthusiasm for both the science and the possibilities of an international exchange from co-PI's (JYR) lab.

The IREE program provided a unique opportunity to engage graduate and undergraduate students within an internationally-based device development cycle from nanowire growth to several varieties of characterization to feedback for new growths. Beginning with the initial growth of the nanowires, each step of the cycle has shared or prime responsibilities of the Australian (AUS) or USA groups. At each step, students in both AUS and USA are an integral part of the cycle.

Research Activities and Accomplishments of the International Cooperation (Limit: 1-1/2 pages)

From the first day of our arrival, our hosts at ANU were ready to accommodate our every need. The first week, a large group meeting was held to welcome us and learn more about what our research goals were. We were also introduced to the current projects of the various group members and given a tour of the facilities. During our visit, several post-docs with extensive experience in growth and fabrication helped us with our different needs. We checked in with them daily to update them on any issues we experienced with our experiments. In addition, we explained to them the methods we use for NW device fabrication and the specific challenges unique to the process, so that they could begin to create the same kind of devices independently. Weekly seminars and small project oriented group meetings were held to keep the various aspects of the project working concurrently. For example, once the optical results from University of Cincinnati (UC) were received, discussions were held to determine the best ways to alter the growth parameters to obtain the desired results. Because of this welcoming approach to our visit to their institution, our research was successful on many levels.

The efforts carried out provided our group members with a unique opportunity to understand the the nanowire growth process. In addition, we were able to utilize ANU's extensive knowledge of device fabrication and Ohmic contacts from their work in fabricating quantum dot lasers. In return, our group's deep knowledge of optical techniques to characterize the structure of nanowires (zinc-blende, wurtzite or mixed phase) and the fabrication of nanowire devices was shared with ANU's group.

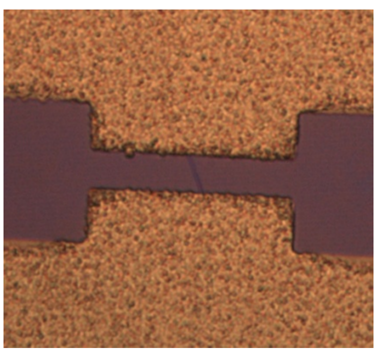


Fig 1: Fabricated device showing nanowire bridging gold-germanium contact pads

First we sought to understand the process for growing the nanocrystals and the limitations of the process. One example is the effects of changing one small parameter such as adding a dopant. This may cause a kinked or defect filled nanowire, while previous *undoped* growths exhibited very controlled samples. Understanding these limitations is important, as researchers normally involved in the characterizations of these growths, we may ask for something from the grower which is wholly impossible to achieve. Through this collaboration we are better able to understand the capabilities *and* limitations of the growth activities.

The next component of this visit was characterization by transport measurements. This was by far the most challenging. One of the major challenges was the very simple step of device fabrication. For our device, a nanowire must bridge a gap between two contact pads. Eventually, these simple devices will form the building blocks of the nanowire biosensor. The goal was to fabricate Ohmic devices and characterize the electrical properties of the wires. One limiting factor in the fabrication of this device arose from the simple issue of not achieving clean liftoff after metallization of the devices. The liftoff issue did not hinder others working in the laboratory because they could simply lightly rub the surface of the device to promote liftoff of the metalized resist. However, in our case, any mechanical contact with the surface would cause a break of the nanowire. The main cause of this issue was the resist reaching a high temperature during thermal evaporation and baking onto the surface of the wafer. Approximately 1 in 10 devices would have clean liftoff and give a clear signal when measuring its IV curve. Figure 1 one shows a device where the liftoff was successful and the nanowire remained intact.

While the successes of the device fabrication were somewhat mixed, the limited results we did achieve showed that the best candidates for transport were wires which did not exhibit a mixed phase of wurtzite and zinc blende structure. Knowing this, we selected wires by utilizing the results of optical characterization from our UC group which were received during our visit. Therefore, we were able to advance the understanding of the connections of the optical properties to the measurement of the transport properties of single semiconductor nanowires for both our ANU collaborators as well as UC.

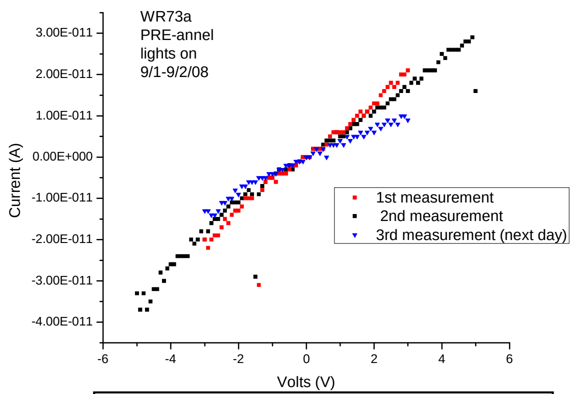


Fig 2: I-V curve on InP device showing an approximate Ohmic behavior

Another accomplishment of our visit was that we were able to learn the process by which gold nanoparticles are dispersed. By dispersing these particles atop a nanowire, we will be able to enhance the signal from the nanowire devices on a future biosensor using resonant enhancement. In addition, we can bind specific liguinds to these gold nanoparticles which are functionalized to detect specific pathogens, and give an enhanced signal only when this pathogen is present. The major issue is that the gold particles when dispersed alone, tend to bunch up. We would like to achieve an even dispersal of particles across the nanowires in our future biosensor. ANU's group uses gold nanoparticles with diameters from 20nm-100nm in their growth process and has eliminated this problem of clumping with two methods. The two methods they use are applying a layer of poly-l-lysine or immersing a weak solution of HCl. We learned the two methods during our visit, and are actively adapting them for our specific needs.

Our undergraduate student Colin Bolye focused on investigating the effects of using electrophoresis to orient the nanowires using an applied electrical field. Several gold-germanium patterns were fabricated using the same mask as was used for our nanowire devices. We used a blank substrate, without nanowires dispersed. Then we applied an electrical voltage (up to 10 V) across the pattern using a probe station setup and dispersed the InP nanowires. The wires did show some evidence of orienting themselves across the angled corners of the masks; however, the wires tended to clump in the same area. With these partially successful initial steps, we can move forward and alter the design of this mask to allow for a more even distribution of wires. Then we can fabricate metal contacts atop the wires and create array of wires within our biosensor.

Fig. 3: Colin Boyle uses electrophoresis to orient nanowires

BROADER IMPACTS OF THE INTERNATIONAL COOPERATION

The international research experience directly involved the interaction and training of a graduate student and an undergraduate student in multidisciplinary work involving nanoscale science and engineering with a fully international context and an exposure to a range of experiences. In addition, the ANU group is composed of not only Australians, but researchers from every part of the globe including China, Pakistan, and Germany,

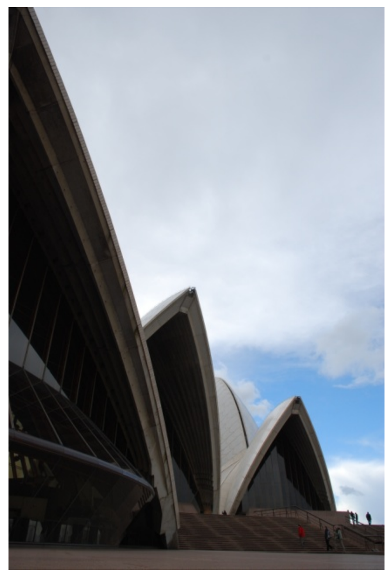
During the visit, daily interactions between the awardees and the host institution promoted the development of personal relationships. Our collaborators are no longer just names existing on the opposite end of the world, but are now friends. When we talk about the next round of growths, we have a greater awareness of what is technically possible. Finally, the awardees participated in group meetings at the host institution, allowing them to see the direction of future nanowire growths desired by the institution.

One practice of ANU's research group was the practice of bi-weekly student seminars which were titled "off the cuff". These were low pressure meetings where students presented their current research results in front of their peers. Mistakes were expected and allowed the students to learn and to react to unexpected questions. It also allowed for a more relaxed approach to presenting their work, which translated into more informative presentations during the International Conference on Electronic Materials conference in Sydney. Melodie was able to participate in the Sydney conference and give an oral presentation of her work on the optical characterization of nanowires. While in attendance, she was able to explore the rich cultural diversity of Sydney's art and music scene. Colin enjoyed modern art in Melbourne, diving on the barrier reef and camping in the "outback."

Another cultural practice was the importance of tea-time. Tradition requires that everything halts two times a day for a group gathering of tea and chats. This allowed for daily updates on research issues and goals, and it also allowed more personal relationships to develop. If someone had a manuscript accepted for publication or a birthday, cupcakes were on hand. Tea time is one of the most missed aspects of the international exchange.

Finally, the EME group understood the importance of fun in the development of a cohesive research group. There were random grill-outs, Friday night beer socials, and even a mini-olympics where the various research groups formed teams and competed in a variety of humorous tasks. All of these activities allowed our participants to form close friendships with the ANU group members which continue even after their return.

In addition to developing closer personal and professional ties to the ANU group, the experience also helped to expand the original scope of the award in a major way byallowing the introduction of new semiconductor nanowire materials, namely GaAs and InP, beyond CdS to be considered for our biosensors.



Sydney's famous opera house

DISCUSSION AND SUMMARY

Institutional mug exchange between Melodie Fickenscher and Lan Fu (ANU Postdoc)

The supplemental travel award allowed our two institutions to develop a more personal face to our collaborative efforts. Our students were able to successfully carry out several research accomplishments which will progress the goal of developing a biosensor, such as fabrication of ohmic contacts on a nanowire device, dispersal of nanoparticles, and orienting the nanoparticles using electrophoresis.

Although somewhat limited by resist liftoff issues, we were able to utilize the expertise of ANU in the area of device fabrication and successfully achieved the fabrication of Ohmic contacts. Upon returning to UC, we were able to implement some of these techniques without the same fabrication problems. However, there was an important lesson to be learned in this experience. One of the difficulties of working with chemicals in an overseas institution is the inability to obtain the ones needed, or are familiar with. At UC, our group uses a positive photoresist. We have had much success with fabrication of nanowire devices using this resist in the past, and have never experienced an issue with the resist baking onto the substrate. However, a different resist was used at ANU which functioned as both a positive and negative resist, and we experienced numerous issues with the resist baking to the substrate, as described earlier. We were unable to obtain the positive resist which we normally use to test its effect. Therefore, it would be highly advisable to inquire about the specific chemicals available at the host institution. With this knowledge, one could check the success of their processing methods before leaving to avoid these unwelcome surprises.

One of the most unexpected and pleasant surprises of the trip was being greeted with a group meeting where each member of the host institutions group gave a short description of their work. The discussion then flowed into how they could best accommodate our needs, who would be the most appropriate person to deal with for specific issues. Our undergraduate felt that a more structured "pairing" of him with a specific graduate student or post-doc would have made his work proceed in a more timely manner. Implementing the immediate incorporation of the US students with the full group definitely falls into the category of "Best Practices" as would a bit more structure for the undergraduate until he became more accustomed to the ANU research envinronment. Overall, the willingness of researchers to assist our students created a highly efficient practice which saved our students the uncertainty and effort of seeking out help for a variety of highly specified tasks.

In conclusion, the travel award was successful both professionally in terms of developing our collaborative relationship with ANU, and personally in terms of broadening the experience of our students. The ANU group was very accommodating to all of the needs of our students, and went above and beyond to make us feel welcome and incorporate us into their group.

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BRIEF BIOGRAPHIES OF RESEARCHERS

Melodie Fickenscher received the B.S. degree in Physics and Mathematics from the Northern Kentucky University in 2002. She received a M.S. degree in Physics from the University of Cincinnati, where she continues to work towards a Ph.D. Her research interests include optical characterization of III/V nanowires, and micro fabrication of nanowire devices.

Colin Boyle expects to receive his B.S. in Physics from Miami University in Oxford, Ohio in 2009. He plans on attending graduate school. In the summer of 2008 he researched electrophoresis of nanowires at the Australian National University. His research interests include electrical and optical properties of nano-scale materials.