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A Study of Material and Optical Properties of Nano Diamond Wires

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A study of Material and Optical Properties of Nano Diamond Wires

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Abstract

This Korea-USA collaborative project, sponsored by AOARD for 2 years (April 18th, 2013 - April 17th, 2015), "A study of material and optical properties of nano diamond wires (AOARD-134085)", aspired to find a way to synthesize a new form of carbon, crystalline diamond nanowires, and then to characterize them for device applications in nanophotonics, nanoelectronics, and quantum information processing. Reproducible synthesis of the crystalline diamond nanowires has proven to be extraordinarily challenging, to us as well as to the field in general. Our lab has so far had the only reported success. However, if a method is successfully developed with reproducibility, it would bring yet another new member into the family of carbon allotropes, this time on the sp³ side. It would also generate new insights into the phases, stability, and functionalization of diamond altered under nanoscale confinement, and pave way for a broad range of applications in nanoelectronics and nanophotonics, e.g., quantum information processing.

Enabled by the AOARD support, the Korean-US collaborative team has taken on this challenge to investigate the feasibility of reproducible growth of diamond nanowires during the period of performance. As a result, progresses have been made on techniques for improving the reproducibility of diamond nanowires and the unexpected discovery of vet another new carbon allotrope – graphite nanowires. Specifically, the concept of catalyst engineering was proposed and tested with successes to provide ultrasmall (sub-5-nm) noble metals or iron-family catalysts and to support sufficiently high capillary pressure (> 4 GPa) associated with the small diameter during atmospheric chemical vaporliquid-solid (VLS) growth of diamond nanowires. In addition to the catalyst engineering, painstaking efforts have been made for careful optimization of growth parameters, such as temperature, time, and gas flow ratios. Such modifications and numerous experimental growth trials resulted in the growth of carbon nanowires from the high melting point Pt catalyst, ultrathin iron-family catalysts, and the Ni-Fe multilayered (or alloy) catalysts. It also led to the unexpected discovery of crystalline graphite nanowires from the ultrasmall iron-family catalysts. These findings will significantly improve the reproducibility of crystalline carbon wires and lay a foundation for those wires to be integrated into emerging optoelectronic devices. Due to the ending of the WCU program at the host institution -SNU, the project was transitioned after two years along with the PI-role to Professor N-M Hwang at SNU whose group has been collaborating with us on this front for a few years. The pursuit, however, continues just the same in the new setting.

1. Introduction

By all accounts, diamond is a material of extremes. Besides its beauty and attraction as glamorous jewelry, it is the hardest, thermally most conductive, highest in break-down field, and greatest in atomic density of any known material. Adding to this list, it is likely the most stable source in single-photon emission even at room temperature. Despite the tremendous attention and publicity given to discoveries of new carbon forms such as C60, carbon nanotubes, and graphene, diamond and graphite have remained two most successful carbon allotropes exploited in technologies and science

to date. The chance discovery of crystalline diamond nanowires, in the PI's lab at Brown University, signified a step forward in diamond research. However, reproducible synthesis of the crystalline diamond nanowires has remained challenging. In this project supported by AOARD, we took steps to meet this challenge of the reproducible growth and pursued an investigation of the material and optical properties and device potential of single-crystalline diamond nanowires, including specific device-enabling effects such as microwave manipulation and control of single-photon emission and low-threshold electron field emission. The PI of this project is Prof. Jimmy Xu, and the project prime is Dr. Do-Joong Lee, assisted by Dr. Jin Ho Kim with the utilization of the extensive expertise and the state of the art characterization facilities at Seoul National University and Brown University.

The project was launched on April 15, 2013, with the focus being on uncovering the growth mechanism of nano diamond wires and on characterizing material and optical properties of those. Finding a pathway for reproducible growth of the diamond nanowires was a most critical part of this study. It was also the most challenging in general. Its success could be most rewarding as well, when one considers what the introduction of each of the new forms of carbon, from C60 to carbon nanotube to graphene, has done to science in the last three decades. Yet, all these prior discoveries of new carbon allotropes were on the sp² side of the carbon family. On the sp³ side of the family, we have had the same old one member – diamond, that is, until our chance find of crystalline diamond nanowires in a CVD process in 2010 (Figure 1). However, it has proven to be extremely difficult to reproduce them. It turned out that we were not alone, as remarked by Ian Snook, a well-known name in diamond research: "It is interesting that in 0D you can grow everything from graphitic onions to bulky diamonds to nano-diamonds. In 2D you can grow diamond thin films but which are largely polycrystalline and often contain graphite, but in 1D it is so hard to get sp³ diamond." To meet the challenge, we have invited to join us in the pursuit a research team led by Professor Nong-Moon Hwang in Seoul National University.

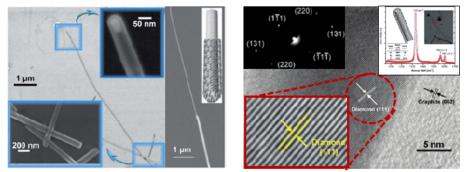


Figure 1. Representative results of diamond nanowires by a chance discovery in PI's group. (left) SEM image of the diamond nanowires and (right) corresponding high-resolution TEM image of the wire. Inset figures show selective area electron diffraction pattern and Raman spectra.

Enabled by the AOARD support, the Korean-US collaborative team has taken on this challenge to investigate the feasibility of reproducible growth of diamond nanowires. During the two years period of exploratory research, this project has produced a number of outcomes which could be highlighted. These outcomes include new techniques for improving the reproducibility of diamond nanowires and the unexpected discovery of yet another new carbon allotrope – graphite nanowires. Specifically, the concept of catalyst engineering was proposed to provide ultrasmall (sub-5-nm) noble metals or iron-family catalysts and to support sufficiently high capillary pressure (> 4 GPa) associated with the small diameters during atmospheric chemical vapor-liquid-solid (VLS) growth of diamond nanowires. In addition to the catalyst engineering, painstaking efforts have been made for careful optimization of growth parameters, such as temperature, time, and gas flow ratios. Such modifications and numerous experimental growth trials resulted in the growth of straight carbon nanowires from the ultrasmall Pt catalys and the Ni-Fe multilayered (or alloy) catalysts and led to the unexpected

discovery of crystalline graphite nanowires from the ultrasmall iron-family catalysts. The introduction of the ultrasmall, noble metal catalysts and the establishment of the new characterization protocols demonstrated in this project proved effective in accelerating the synthesis processes, the yield, and the subsequent sample selection. In addition, the discovery of the graphite nanowire would enrich understandings of 1-D carbon nanomaterials, the Li atom intercalation process that is vital for Li-ion batteries, and the electron field emission and possibly light emission in graphite. Details on such accomplishments are described in the following section.

2. Results and Discussion

2.1. Strategies for the reproducible synthesis of diamond nanowires

Atmosphere-pressure chemical vapor deposition (APCVD) of diamond nanowires involves many growth parameters, including, but not limited to, heating rate, growth temperature, growth time (duration), pressure, gas composition, gas flow ratios, and preparation of catalysts (materials, preparation methods, and initial sizes or thicknesses), and cooling rate and cooling gas flow rates. It would take unrealistically long time to test through all combinations of those parameters to find the right window of growth parameters. Taking cue from the growth conditions that brought to us the chance find of diamond nanowires, we decided to focus on preparation of sub-10-nm catalysts and the introduction of hydrogen flow.

It has been well known that diamond is a high-pressure (> 40 katm at 1,000 °C) stable carbon phase. While the growth of diamond nanowires has been experimentally demonstrated at the atmospheric pressure (1 atm) in our previous works, such the growth pressure cannot provide the required thermodynamic pressure for the growth in diamond phase. Instead, several studies, including the study by the PI's lab, have pointed to the surface stress/tension or capillary pressure, as the possible reason that allowed the diamond phase to be stable in the nanowire morphology. A higher capillary pressure (ΔP) would result if the size (r: radius) of the nanowire is smaller and the surface energy (y) is higher, $\Delta P=2\gamma/r$. The capillary force of diamond nanowires can be as high as that meets the thermodynamic stability criterion (3-4 GPa) owing to the extremely high surface energy (>5 J/m^2) if the wire is narrow enough (< 10 nm). Based on the known surface energy of diamond ($\gamma_{(111)}=5.1$ J/m² and $\gamma_{(110)}=6.3$ J/m²), we estimated the capillary pressure as a function of diameters. As shown in Figure 2(a), the capillary force becomes significantly higher than 5 GPa once the diameter of diamond nanowire gets smaller than 5 nm (and still higher than 2 GPa at 10 nm diameter). Such high capillary pressures are sufficient for the diamond phase to be thermodynamically stable to nucleate and grow, as in Figure 2(b). Our estimation suggests that, if the capillary force indeed plays the enabling role, one of the key prerequisites for the reproducible synthesis of diamond nanowires would be in the preparation of sub-5nm nanocatalysts.

According to these assumptions, we have focused on the catalyst materials engineering to prepare sub-5-nm nanoparticles as catalysts. Specifically, to inhibit agglomeration and subsequent surface- and bulk-diffusion of catalyst materials during the heating and growth stages, we tested the use of high melting point noble metals (Pt), ultrathin iron-family catalysts (Fe, Ni, Co), and alloy of those catalysts (Ni-Fe). A higher melting point means a greater resistance to agglomeration and to surface migration. The ultra-thinning (below 1-nm thick) can significantly reduce an overall volume of catalyst material. The alloying approach can reduce an inter-diffusion coefficient and limit both bulk- and surface-diffusion. In our approaches, these strategies have been utilized in a combinatorial manner so that it can maximize an efficiency of the researches.

Another process parameter deemed as equally important or enabling is the introduction of hydrogen during the growth and/or cooling processes. Hydrogen may take a role of preferentially etching amorphous carbon and other sp^2 carbon species over diamond, *via* dissociate adsorption on a metal surface and decompose into atomic hydrogen. Indeed our previous work demonstrated that a

slow cooling rate in the hydrogen ambient increased the chance of finding diamond nanowires in otherwise a denser jungle of other carbon species. The preferential etch of other carbonates by hydrogen injection has also been observed in microwave plasma CVD of diamond films as a hydrogen-rich and CH₄-lean condition resulted in the formation of high quality sp^3 diamond (nanocrystalline diamond) while a hydrogen-free (Ar-rich) condition gave ultrananocrystalline diamond embedded within amorphous carbon and other sp^2 carbon species. The recent results on a CVD growth of a graphene have demonstrated the catalytic etch of a graphene on a metal substrate by high hydrogen flow even at a temperature as low as 700 °C. In this project, effects of hydrogen injection (flow rate) have been systematically studied to control quality and phase of carbon species grown on those catalysts. The flow rate ratios of argon, hydrogen and methane were varied during the growth stage, and various samples were grown.

Based on the catalyst engineering and the hydrogen flow control approaches, various catalysts materials, including high melting point noble metal (Pt), ultrathin iron-family elements (Fe, Ni, Co), and alloyed (multilayered) iron-family catalysts (Ni-Fe), have been tested to reproducibly grow crystalline diamond and graphite nanowires.

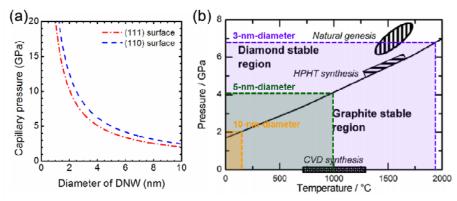


Figure 2. (a) Estimated capillary pressure of a diamond nanowire as a function of a diameter. (b) Pressure - temperature phase diagram of carbon. Colored boxes indicate the capillary pressure (top) and thermodynamically stable temperature (right) of the diamond nanowires with various diameters.

2.2. Nanowires growth on noble metal catalysts

The first trial growth tests made with high melting point noble metals as catalysts have yielded straight nanowires that bear the resemblance in morphology of the first diamond nanowires we found by chance earlier. Compared to the conventional iron-family catalysts (Fe: 1538 °C, Ni: 1455 °C, Co: 1495 °C), the noble metals, such as Pt (1769 °C), Pd (1555 °C), Ru (2334 °C), and Ir (2447 °C), have excellent chemical stability and much higher melting points. Those noble metals can withstand better harsh hydrogen-rich (or pure) ambient during the growth. Higher melting points help reduce agglomeration and surface migration during the pre-heating and extend coalescence time of catalysts. Such properties motivated us to test the noble metals as catalysts.

Our preliminary results on using Pt catalyst were more surprisingly good than ever expected. As shown in Figure 3, the initial thickness of Pt catalyst played a critical role on producing straight nanowires that have similar morphology at a high temperature of 900 °C. It is surprising that straight nanowires were grown on ultrathin, sub-1-nm-thick Pt catalyst, while there were no nanowires grown on 2- and 3-nm-thick catalysts. Our subsequent SEM and TEM analyses revealed that the ultrathinning initially 1nm thick catalysts resulted in the agglomerated nanoparticles with a very small size of 5.7 nm, which is sufficiently small to provide high capillary pressure over 4 GPa. The selective growth of the nanowire morphology has been achieved by rigorously selecting process parameters.

Figure 4 shows an example of the effects of carbon source flows. By controlling a flow rate ratio of methane (CH₄), we could obtain ultrahigh density (>10⁸ cm⁻²) nanowires on both 0.5-nm- and 1-nm-thick Pt catalyst at the optimal flow ratios (20-30 %). In this case, it should be noted that our growth has been made without flowing hydrogen gas (H₂), suggesting a possible self-formation of radical atomic hydrogens during the decomposition of methane precursors.

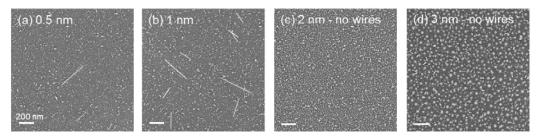


Figure 3. SEM images of nanowires grown on Pt nanocatalysts. Initial thicknesses of the catalyst are (a) 0.5 nm, (b) 1 nm, (c) 2 nm, and (d) 3 nm.

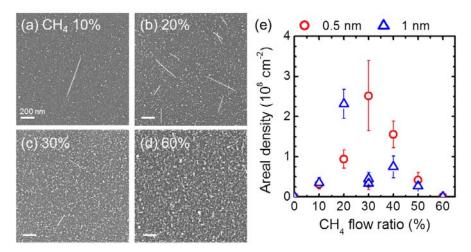


Figure 4. SEM images of nanowires grown on 1-nm-thick Pt catalysts at 900 °C. Gas flow ratios of CH_4 were (a) 10%, (b) 20%, (c) 30%, and (d) 60%. (e) Areal density of the nanowires with respect to CH_4 flow ratio.

Further studies have been made on the samples with ultrathin Pt catalysts (initial thickness: 0.5 nm) to optimize process parameters of the APDVD process and to understand underlying growth mechanism. Figure 5 shows the SEM images of the carbon nanomaterials grown on ultrasmall Pt catalysts (initial thickness of Pt: 0.5 nm) at various substrate temperatures. The results clearly demonstrated a transition of growth mode from the growth of curly, bundled carbon nanotubes at low temperatures (500 - 700 °C) to the formation of straight nanomaterials at higher temperatures of 800 - 900 °C. These nanomaterials were further characterized by transmission electron microscopy (TEM) in Figure 6. This analysis was made possible by the development of a new methodology: direct growth on a SiO_x-supported TEM grid. These preliminary characterizations suggested the grown nanomaterials are either single-walled nanotubes or amorphous carbon nanowires. A new set of the experiments and analyses is to be completed very soon and the results will be published in a due course of time.

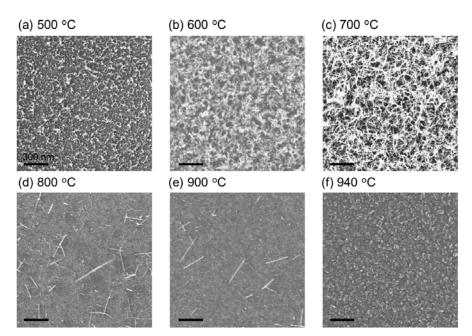


Figure 5. Carbon nanomaterials grown on ultrasmall Pt catalysts at various substrate temperatures.

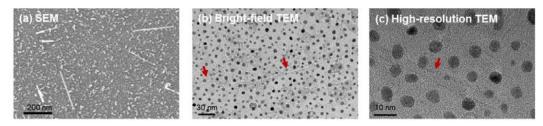


Figure 6. (a) SEM, (b) bright-field TEM, and (c) high-resolution TEM images of carbon nanomaterials directly grown on Pt catalysts / SiO_x-supported TEM grid.

2.3. Nanowires growth on iron-family and alloy catalysts

The iron-family elements, including, Fe, Ni, and Co, have been widely used as catalysts for 2-D, 1-D, and 0-D carbon materials. Extremely high catalytic activity for the carbon precursor decomposition and perfect lattice match to the hexagonal carbon lattice (< 2%) make those catalysts ideal for the growth of carbon nanotubes, and possibly for diamond nanowires as well. Even though the previous successes by the PI's and Prof. Nong-Moon Hwang's labs at SNU have been made using the Fe and Ni catalysts, one of their drawbacks is a relatively weak thermal stability to the agglomeration owing to their low melting points (below 1,600 °C). For instance, even at low temperature around 700 °C, thin Ni and Fe films were known to readily agglomerate into scattered large particles (several tens of nanometers to even larger than 100 nm) and this large size may translate into insufficient capillary pressure.

In order to overcome the severe agglomeration problem of the iron-family catalysts, we have tried to use both ultrathin (1 nm or below) iron-family catalysts (Fe, Co, Ni) and alloy of those (Ni-Fe). The use of ultrathin catalyst films may reduce the grain size of as-deposited catalyst films and, at the same time, reduce an overall volume of source catalyst materials. Thereby the ultra-thinning in catalyst evaporation may result in smaller nanoparticles after the agglomeration. The agglomeration can be further inhibited by alloying two or three elements among those. For instance, Ni and Fe make

a complete solid solution owing to the same crystal structure (FCC) and atomic radius, as expected from the Hume-Rothery rules and evidenced by a binary phase diagram (between γ -Fe and Ni) for entire compositions. Such alloying would also hinder the inter-diffusion and agglomeration of metal catalysts and produce sub-5-nm nanocatalysts.

Several attempts have been made by using ultrathin Fe, Co, Ni and alloy [multilayer of ultrathin (5 Å-thick each) Ni /Fe catalysts]. An example of the nanowires grown on the ultrathin (5 Å-thick) Fe and Ni catalysts is in Figure 7. By carefully controlling a gas flow ratio of hydrogen (~20 %, with a CH₄ flow ratio of 10 %), both straight and curved nanowires were observed on those ultrasmall iron-family catalysts. This result might suggest that the preferential etch of carbon species indeed worked by the catalytic dissociation of molecular hydrogen. The grown materials are under investigation using a new analysis protocol demonstrated in the Pt catalysts case.

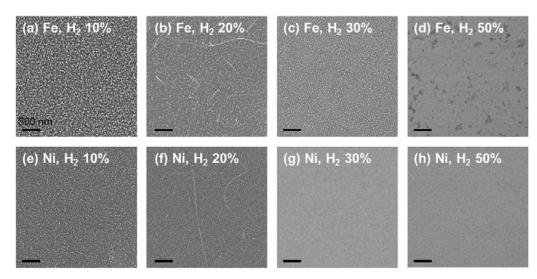


Figure 7. SEM images of nanowires grown on ultrathin (a-d) Fe and (e-h) Ni catalysts at 950 °C. Hydrogen flow ratio was varied from 10 % to 50 %, while methane flow rate was fixed to 10 %.

The results of introducing 1 nm thick Ni-Fe catalsyts were comparatively shown in Figure 8. While single-element Fe and Ni catalysts of the same thickness produced relatively low density of nanowires, the Ni-Fe multilayer catalyst was effective for nucleation and growth of ultrahigh density ($\sim 10^8 \text{ cm}^{-2}$), straight wires. Such density is 2- and 1-order of magnitude higher than the one on the single-element Fe and Ni catalysts, respectively. It opens an interesting question of its possible origin, which is under investigation by using plan-view TEM, EDS, EELS and EFTEM.

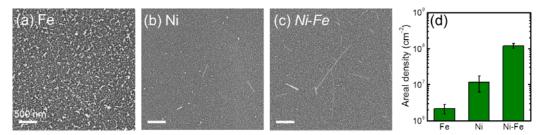


Figure 8. SEM images of nanowires grown on (a) Fe, (b) Ni, and (c) Ni-Fe multilayer catalysts. Initial thicknesses of the catalysts were 1 nm. (d) Areal density of nanowires measured from the SEM images.

In growing straight carbon nanowires on the Ni-Fe multilayer catalysts, the control of hydrogen gas flow was seen to play an important role for the selective growth, as proven in the case of ultrathin

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iron-family catalysts. As shown in Figure 9, the straight nanowires were selectively grown only in a narrow window of 20 % H₂. For lower H₂ flow rate [10% in (a)], poly-domains (grains) of bulk carbonates, probably mixed with amorphous and graphitic phases, were observed. Increasing the hydrogen flow above 20% H₂, curly, graphitic tubes were grown [30% in (c)], or no growth at all along with a partial etch of the catalyst particles [50% in (d)]. These results indicate that ultra-small nanoparticles may catalytically decompose molecular hydrogens (H₂) into atomic hydrogens (H) that can preferentially etch weakly-bound sp² carbon byproducts, such as CNTs and fibers.

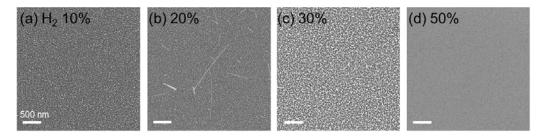


Figure 9. SEM images of as-grown samples on 1-nm-thick Ni-Fe multilayer catalysts. Flow rate ratios of H_2 were varied to (a) 10%, (b) 20%, (c) 30%, and (d) 50%.

2.4. Discovery of graphite nanowires

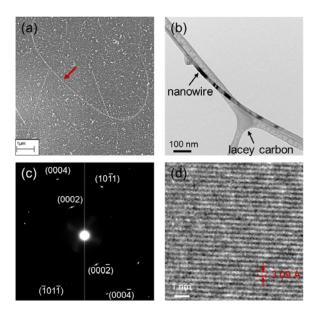


Figure 10. (a) SEM and (b-d) TEM images of a graphite nanowire grown on ultrathin Fe catalysts. (b) bright-field, (c) selected area electron diffraction, and (d) high resolution TEM images.

Like what often happens in exploratory research, the effort has likely resulted in an unexpected discovery. In this case it is likely yet another allotrope of carbon: "graphite nanowires". A representative SEM and TEM images of the graphite nanowire grown on an ultra-small Fe catalyst is shown in Figure 10. Due to the long-range coherence of pi-electrons and the small diameter, a graphite nanowire would more likely be a semiconductor than a semimetal, and would still retain a low spin-orbital coupling. As such, the graphite nanowires may exhibit efficient and diameter- and stress-tunable photoluminescence and Raman signals, and spin coherence. They would absorb and

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diffract light more like a dielectric object than a metallic one. Electronic and optical characterizations will be performed on the graphite nanowires to probe and validate the expectations. The growth conditions will continue to be optimized post the AOARD program. Structural / spectroscopic properties of the graphite nanowire will be studied and such results will be published in due course. The discovery of the graphite nanowire would enrich understandings of 1-D carbon nanomaterials grown via the VLS growth mechanism and be utilized for potential studies of Li-ion batteries, electron field emission, and optoelectronic devices.

List of Publications and Significant Collaborations that resulted from your AOARD supported project: In standard format showing authors, title, journal, issue, pages, and date, for each category list the followings:

a) papers published in peer-reviewed journals

[1] D.-J. Lee, K.-J. Kim, S.-H. Kim, J.-Y. Kwon, J. Xu, and K.-B. Kim, "Atomic layer deposition of Ti-doped ZnO films with enhanced electron mobility", *J. Mater. Chem. C* **1** (31), 4761-4769 (2013) [Date: June 5th, 2013].

[2] D.-J. Lee, J.-Y. Kwon, J. Kim, Y.-H. Cho, S.-Y. Cho, S.-H. Kim, J. Xu, and K.-B. Kim, "Ultrasmooth, high electron mobility amorphous In-Zn-O films grown by atomic layer deposition", J. Phys. Chem C **118** (1), 408-415 (2014) [Date: January 9th, 2014].

b) papers published in peer-reviewed conference proceedings

(see below)

c) papers published in non-peer-reviewed journals and conference proceedings

(see below)

d) conference presentations

[1] (Invited talk) Jimmy Xu, "Diamond nanowires - a challenge from the extremes", 2nd International Congress of Advanced Materials, Zhenjiang, China, May 16-19, 2013.

[2] (Invited talk) Jimmy Xu, "Challenges from the extremes: diamond nanowires, metamaterials, plasmonic oxides, etc", Nano-KISS (Korean International Summer School on Nanoelectronics), Daejeon, Korea, July 5, 2013.

[3] (Invited talk) Jimmy Xu, "Diamond nanowires - a challenge from the extremes", Rutgers University's Physics, Material Science, Electrical Engineering Joint Colloquium, New Jersey, USA, October 10, 2013.

[4] (Invited talk at DoD Institutions, acknowledging AOARD) Jimmy Xu, "Thermal Diode and Artificial Sweating – for one-way heat insulation and self-regulated cooling", Sigma Xi Research Seminar, US Army Institute for Environmental Medicine and US Army Natick Soldier Rsearch Development Engineering Center, Natick, MA, August 15, 2013.

[5] (Invited talk) Jimmy, "Diamond nanowires - a challenge from the extremes", Rutgers University's Physics, Material Science, Electrical Engineering Joint Colloquium, New Jersey, USA, October 10, 2013.

[6] (Invited talk at DoD Institutions, acknowledging AOARD) Jimmy Xu, "Enhancing thermoelectric energy harvesting via phonon engineering of flexible films and composites", Mini-Colloquium on Novel Electronics, Power, and Sensors, US Army Natick Soldier Engineering Research Development Center, Oct 24, 2013.

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[7] (Invited talk, acknowledging AOARD) D.-J. Lee, J.-Y. Kwon, S.-H. Kim, H.-M. Kim, J. Xu, and K.-B. Kim, "Doping mechanism in transparent conductive ZnO films grown by atomic layer deposition", 2014 ECS and SMEQ Joint International Meeting, October 5-10, 2014.

[8] (Invited talk) Jimmy Xu, "Diamond nanowires for quantum optics – challenges from the extremes", International Conference on Small Science (ICSS) meeting, December 8-11, 2014, Hong King.

e) manuscripts submitted but not yet published

None.

f) provide a list any interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work

[1] Part of the characterization performed in collaboration with the group of Michael Check and Luke Bissell, led by Gail Brown, at the Wright-Patterson Base of AFRL (July-August 2014, and on-going).

g) other accomplishments

<u>Honors</u>

[1] RIAM Professorship, 2014, Seoul National University, Korea (A special appointment. Of all the WCU professors when the WCU program ended, the PI was the only one received such an appointment. It is recognition of the extensive and productive collaborations my group had with the many SNU groups, and in recognition of the on-going AOARD-funded research.)

[2] Chang-Jiang Chair Professorship (visiting), 2014, Optoelectronics School, UESTC, China (A program similar to the WCU program of Korea. It comes with a research funding of \$50K/yr plus travel support for 3 years. But the research funds have to stay within the university UESTC, also modeled after the WCU program of Korea.)

[3] Professeur Invite', 2014 (and being renewed for 2015-16), CNRS-Institut d'électronique de microélectronique et de nanotechnologie and Universite de Lille, France. (An honorary professorship appointment for establishing France-USA collaborative researches on quantum optics and nano-devices. It covers travel and living expenses, ~10K Euro per year).

Awards of funds received related to this research effort

[1] NSF EAGER grant, "Synthesis, Material Investigation and Device Effect Demonstration of Nano Diamond Wires", \$206K, July 2013-June 2015.