Nanomaterials
Room Hau - Session NM-TuE
Nanofabrication and Nanodevices II

Moderator: Adam Hitchcock, McMaster University, Canada

5:40pm **NM-TuE1 Surface and Screening Effects on Optical Properties of Carbon Nanotubes**, ***Yuichiro Kato,*** RIKEN, Japan **INVITED**

Screening is limited in single-walled carbon nanotubes because of their one-dimensional nature, and the strong Coulomb interactions result in optical spectra dominated by excitons with binding energies lager than half an eV. Also because of the limited screening, a charged carrier can be bound to an exciton to form a trion that is stable at room temperature. Adsorption and desorption of molecules on the surface of nanotubes can readily modulate such interactions.

Here we discuss experiments aimed at highlighting the behaviors of excitons and trions in individual suspended carbon nanotubes. Simultaneous photoluminescence and photoconductivity spectroscopy show evidences for spontaneous dissociation of excitons [1], despite the expectation that free carrier generation from such a tightly-bound state would be difficult. As the field is increased, we observe an emergence of new absorption peaks in the excitation spectra, which can be explained by electrical activation of dark excited states [2]. Although trion formation has been thought to be difficult in suspended nanotubes due to low exciton-carrier scattering rates, we have succeeded in identifying trion emission under an application of gate voltages [3]. More recently, we have observed optical bistability of exciton emission, which is attributed to resonance shifts caused by molecular adsorption and desorption.

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6:20pm **NM-TuE3 Low-temperature Localized Growth of High Aspect-Ratio Multi-Wall Titanium Dioxide Nanotubes for Orthogonal Frequency Coded SAW Gas Sensors**, ***William Clavijo,*** *C. Castano,* Virginia Commonwealth University, USA*; W. Wilson,* NASA Langley Research Center, USA*; G. Atkinson,* Virginia Commonwealth University, USA

We expand the potential application and sensitivity of solid acoustic wave (SAW) gas sensors by incorporating ultra-high surface area, multi-wall TiO_2 nanotubes into orthogonal frequency coded (OFC) SAW gas sensors. This process relies on synthetization of multi-wall tube-in-tube polycrystalline TiO_2 nanotubes utilizing nanoporous anodic aluminum oxide (AAO) templates in a thin (2.5µm) aluminum film deposited on a lithium niobate substrate. We have demonstrated this method by integrating multi-wall nanotubes onto the delay line of an OFC SAW device to form an integrated sensor structure. The multi-wall TiO_2 nanotube growth uses a combination of multi-stage aluminum anodization, alumina barrier layer removal, TiO_2 and Al_2O_3 atomic layer deposition (ALD), and wet release etching. This growth process selectively forms TiO_2 nanotubes on the delay line while the aluminum film remains intact for interdigital transducers (IDT) and reflector banks. The self-assembled high density AAO template was selectively formed in an ultra-smooth (R_a=1.5nm) 2.5 µm thick aluminum layer deposited through e-beam evaporation. The resulting AAO template consists of nanopores of 100 nm in diameter and 1.5 µm in height with an aerial density of 1.3 x 10^{10} nanopores/cm^2. This AAO template was then filled with successive ALD nanotubes by alternating Al_2O_3 sacrificial spacers and TiO_2 at 200 ˚C. The alumina template and Al_2O_3 sacrificial spacers were then removed, leaving free standing multi-wall coaxial TiO_2 nanotubes of 1.5 µm in height and 100 nm in diameter, offering an increase in 112X the surface area over a standard flat TiO_2 film for sensing applications. The TiO_2 nanostructures were characterized by SEM, and TEM to examine internal structure, composition, and verify crystal structure. In addition, the OFC SAW gas sensor with a center frequency of 229 MHz and 3 reflectors on each side of the IDT was tested using 200 ppm NH_3 to demonstrate functionality and measure sensitivity. Mass loading induced by the NH_3 gas absorbed onto the multi-wall TiO_2 nanotube resulted in amplitude shift of 0.027 dB upon exposure to 200 ppm NH_3 at room temperature during interrogation of the 3rd reflector in sensitive channel. The sensor shows a promising room temperature operation with reproducible performance. Furthermore, OFC SAW gas sensors may be coded and implemented both passively and wirelessly in addition of taking advantages of the benefits of SAW technology.

6:40pm **NM-TuE4 Epitaxial Graphene Based Sensors for Gigahertz Detection**, ***Anthony Boyd,*** US Naval Research Laboratory, USA*; A. El Fatimy, P. Barbara,* Georgetown University, USA*; A. Nath, PM. Campbell, M. Currie, R.L. Myers-Ward, K.M. Daniels, D.K. Gaskill,* US Naval Research Laboratory, USA

There is a clear need for fast, high efficiency, and broadband sensitive detectors. Graphene demonstrates great promise to fill this void, possessing high room temperature carrier mobility, up to 60000 $cm^2V^{-1}s^{-1}$, and absorption of incoming radiation, ~2.3%. This absorption is impressive considering graphene is a single atomic layer thick. In the gigahertz (GHz) frequency range, the absorption is enhanced due to the Drude contribution of the free carriers. Synthesizing epitaxial graphene (EG) on SiC has the advantages of wafer scale size, low defect density, and being single crystal.[1] Growing high quality, conformal dielectric films with Atomic Layer Deposition (ALD) on EG is challenging due to the lack of dangling bonds which serve as nucleation sights for film growth. Researchers at this laboratory have developed a fluorine functionalization approach to overcome the challenge without negatively impacting graphene's morphology and electronic properties to enable ALD of high-κ dielectrics onto EG for gated devices.[2]

We investigate two types of GHz detectors fabricated on EG. The first is an antenna coupled device. It utilizes two dissimilar contact metals, one for the source and the other for the drain, and the metal work function difference translates into asymmetric Seebeck voltages at each contact. We fabricated these devices with two types of EG: 1) a quasi-free standing bilayer graphene (QBLEG) and 2) a standard one monolayer EG (1ML). The second device is a field effect transistor constructed using 1ML EG with an asymmetric top gate that creates a PN junction and facilitates tuning the photovoltaic response . Both device types were fabricated using a lift off resist-based clean lithography process, have low contact resistance [3] and use metal work function asymmetry for detection, consistent with recent studies of the photothermoelectric effect mechanism.[4]

The devices were electrically characterized and then irradiated with a Backwards Wave Oscillator from 100 to 177GHz. The antenna coupled devices response varies with frequency, incident power, and demonstrates a distinct antenna coupling. The QBLEG shows a 3 to 4X increase in response over the standard 1ML. The response of the PN junctions depends on the radiation frequency and the gate voltage. At a fixed frequency, the device response can be doubled by tuning the gate voltage, consistent with the known dependence of the Seebeck coefficient with charge concentration.

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7:00pm **NM-TuE5 Structural and Electrical Properties of Electromigrated Au Nanogaps**, ***Tomoyuki Ito,*** *K. Inoue, J. Shirakashi,* Tokyo University of Agriculture & Technology, Japan

Au nanogaps have been attractive for the fabrication of single-molecule devices. For this reason, many different approaches of Au nanogaps have been reported, including electromigration [1], break junction [2] and electroplating [3]. We have already reported on fabricating narrower Ni nanogaps by controlling tunnel resistance of the nanogaps using field-emission-induced electromigration. We call this method "activation" [4, 5]. In this report, the application of activation to Au nanogaps is investigated in comparison with that of Ni nanogaps.

Under room temperature and vacuum condition, the activation was applied to initial Au nanogaps with a separation of around 50 nm. The initial Au nanogaps showed high tunnel resistance of more than 500 TΩ. After performing the activation with the preset current I_s of above 300 nA, the tunnel resistance of Au nanogaps gradually decreased to less than 10 MΩ. Activation properties of Au nanogaps are quite similar to those of Ni nanogaps ever reported [4, 5]. Thus, the results imply that the tunnel resistance of Au nanogaps can be controlled in the same way as that of Ni nanogaps using activation.

References

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8:00pm **NM-TuE8 Investigation of Electromigration Induced by Field Emission Current Flowing through Au Nanogaps in Ambient Air**, ***Kazuki Inoue**, T. Ito, J. Shirakashi,* Tokyo University of Agriculture & Technology, Japan

We have proposed a simple method for the fabrication and control of nanogaps, called "activation" [1]. In the activation scheme, electromigration (EM) is induced by field emission current passing through the nanogaps. Hence, the control of tunnel resistance of Ni nanogaps was achieved using the activation method [1, 2]. As expected, the activation method has been applied to Ni nanogaps in vacuum conditions. On the other hand, controlled EM technique is generally applicable to Au nanowires in ambient air conditions [3]. Here, we investigate activation properties for Au nanogaps in ambient air conditions, from the point of view of practical use of activation method. First, initial nanogaps of Au, separated by several tens of nanometers, were fabricated on SiO_2/Si substrate by electron-beam lithography and lift-off process. Then, the activation method was performed in ambient air at room temperature. The tunnel resistance of the Au nanogaps after performing the activation became smaller than that of before performing the activation, resulting in a decrease in the separation of the Au nanogaps. Thus, these results suggest that the activation method can be applied to Au nanogaps even in ambient air conditions.

Rreferences

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8:20pm **NM-TuE9 Nanoparticles and Nanostructures Synthesis by High-Power Pulsed Hollow Cathode Sputtering**, ***Ulf Helmersson**, S. Askari, N. Brenning, S. Ekeroth, R. Gunnarsson,* Linköping University, Sweden

The use of high-power pulses for synthesis of nanoparticles in the gas phase is of interest because of the effective ionization of the supplied gases and the sputtered source material. The advantage of ionizing the source material is the effective trapping of positive ions onto the negatively charged nanoparticles in the plasma resulting in a significant increase in growth rate and utilization of material. A cylindrical metal hollow cathode was used where sputtering occurs on the internal surface of the cylinder. Apart from that a cathode configuration with a linear slit was employed suitable for roll-to-roll deposition. The sputtered material of ions and neutrals is ejected from the cathode due to the the pressure buildup by the high voltage pulse, due to the outward directed ambipolar electric field structure at the hollow cathode opening and due to the flow of the gas through the cathode. This results in rapid expansion of the sputtered material and it leads to nucleation and growth of nanoparticles. A range of materials has been synthesized by this technique including Fe, Cu, Ti, Ag, Mo, In and Zn. By adding a reactive gas to the process nanoparticles containing Ti-O, Ti-N Zn-O and In-N has been synthesized. Several process parameters were identified to affect the size, size distribution, shape and structure of the nanoparticles. These parameters include pulse power, pulse frequency, sputtering gas composition, gas pressure and geometry of the setup. By tuning these parameters, the nanoparticle size can range from a few nm to more than 250 nm in diameter. Depending on the employed process parameters, the crystal structure of nanoparticles varies from a single crystal with well-defined crystallographic faces to polycrystalline and amorphous cauliflower structures consisting of randomly oriented agglomerates of nano-crystals. In the presentation it will also be shown that the nanoparticles can be used for assembling of different nanostructures.

8:40pm **NM-TuE10 Out of the Plane: Graphene-based Vertical Transistors for Realistic Applications**, ***Anindya Nath**, George Mason University, USA; B.D. Kong, A. Koehler,* US Naval Research Laboratory, USA*; V.R. Anderson,* U.S. Naval Research Laboratory, USA*; V.D. Wheeler,* US Naval Research Laboratory, USA*; E.R. Cleveland,* US Naval Research Laboratory,USA*; A.K. Boyd, K.M. Daniels, R.L. Myers-Ward, D.K. Gaskill, K.D. Hobart, F.J. Kub, G.G. Jernigan,* US Naval Research Laboratory, USA

The graphene gold rush for electronic applications has been subdued due to the lack of an energy-gap in the graphene band structure which impedes utilization of graphene-based lateral field effect transistors for switching applications. Alternatively, graphene based vertical devices, such as hot electron transistors (GHETs), have been proposed to overcome the band-gap bottle neck. HETs utilize high energy tunneling injected electrons (hot electrons) to achieve high performance. High on-off ratio can be achieved by biasing the emitter-base and collector-base junctions. For traditional metal-based HETs, the cut-off frequency are limited by base transit time (for thick base metal) or high RC delay (for thin base metal). Graphene offers the ideal solution for HETs due to its ultimate thinness and high conductivity. Epitaxial graphene grown on conducting SiC is an attractive choice for GHETs due to the naturally occurring Schottky barrier between SiC-graphene interface, which can be exploited as the collector barrier. The integration of an emitter-base junction dielectric, however, possess significant challenges due to the low wettability of the graphene sp^2 structures. Previous efforts to integrate ultra-thin dielectric layer often lead to metal rich seed layers with pinholes, graphene lattice damage, restricted ALD growth temperature or the inability of wafer scale process integration.

In this work, the amphiphilic nature of graphene oxide is exploited as a seed layer to facilitate ultrathin and conformal high-κ metal oxide deposition on epitaxial graphene by atomic layer deposition at growth temperatures as high as 300°C. Three different high-κ metal oxides (Al2O3, HfO2 and TiO2) with various thicknesses (4 -20 nm) were grown on ultrathin (1.5 nm) GO seed layers on EG. The uniformity and stoichiometry of the films were confirmed by atomic force microscopy and X-ray photoelectron spectroscopy. Additionally, metal-insulator-graphene tunnel devices were fabricated and temperature dependant tunneling behavior is studied. No defect/trap assisted conduction behavior was observed, and a transition from direct to fowler-nordheim tunneling was observed at low temperatures. For graphene field effect transistors (GFETs) with metal oxide on GO seed layer demonstrated high on-state current, low gate leakage current and good channel modulation. Capacitance voltage measurement of the GFETs exhibited low hysteresis and nearly ideal dielectric constants for respective dielectrics. These results demonstrate a simple yet cost-effective universal way of wafer-scale ultrathin high-κ dielectrics deposition on epitaxial graphene by ALD.

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