

Monday Afternoon, November 10, 2014

Energy Frontiers Focus Topic

Room: 315 - Session EN+EM+MN+NS+TR-MoA

Energy Harvesting with Nanostructures

Moderator: Phillip Christopher, University of California - Riverside

2:00pm EN+EM+MN+NS+TR-MoA1 **Optical Engineering for Colloidal Quantum Dot Photovoltaics**, *Susanna Thon*, Johns Hopkins University **INVITED**

The next generation of photovoltaics seeks to improve both efficiency and cost through the use of flexible platforms and new materials. Colloidal quantum dots (CQDs), semiconductor nanoparticles synthesized from solution, are a particularly attractive material for solar energy. The bandgap of films composed of arrays of CQDs can be tuned via the quantum confinement effect for tailored spectral utilization. The performance of CQD solar cells is currently limited by an absorption-extraction compromise, whereby photon absorption lengths in the near infrared regime exceed minority carrier diffusion lengths. I will review several photonic and optical engineering schemes aimed at overcoming this compromise. These include nanophotonic and geometric light trapping techniques, as well as jointly-tuned plasmonic-excitonic photovoltaics. Additionally, I will discuss how nanoscale engineering of CQDs and related materials can lead to emergent optical properties for building color-tuned optoelectronic films.

2:40pm EN+EM+MN+NS+TR-MoA3 **Energy Transfer from Nanocrystal Quantum Dots to Si Nanomembranes Monitored via Wavelength Dependent Photocurrent Response**, *Weina Peng, S. Sampat, S. Rupich, B. Anand, H. Nguyen, D. Taylor, Y. Gartstein, Y.J. Chabal, A. Malko*, University of Texas at Dallas

We report the observation of wavelength dependent photocurrent in thin silicon nanomembranes (75 nm) coupled to colloidal CdSe/ZnS nanocrystal quantum dots (NQDs). The measurement was performed on back-gated, FET-type thin Si structures, which are functionalized with self-assembled monolayer (SAM) of ester termination groups to prevent surface oxidation and the formation of surface defect states. A thin film of nanocrystals is drop casted on the surface and an increase of photocurrent, up to several hundred nA, are recorded as a function of excitation wavelength on NQD/SAM/Si devices vs. plain SAM/Si structures. Quantitative analysis of photocurrent vs. NQD absorption spectrum allows us to ascribe the observed photocurrents to the photoexcited NQD excitons transferred to the underlying Si substrate via non-radiative and radiative energy-transfer mechanisms¹.

¹H. M. Nguyen, O. Seitz, W. N. Peng, Y. N. Gartstein, Y. J. Chabal, and A. V. Malko, *ACS Nano* **6**, 5574 (2012).

3:40pm EN+EM+MN+NS+TR-MoA6 **Triboelectric Nanogenerator - A New Energy Technology**, *ZhongLin Wang*, Georgia Institute of Technology **INVITED**

Triboelectrification is an effect that is known to each and every one probably ever since the ancient Greek time, but it is usually taken as a negative effect and is avoided in many technologies. We have recently invented a triboelectric nanogenerator (TEG) that is used to convert mechanical energy into electricity by a conjunction of triboelectrification and electrostatic induction. As for this power generation unit, in the inner circuit, a potential is created by the triboelectric effect due to the charge transfer between two thin organic/inorganic films that exhibit opposite tribo-polarity; in the outer circuit, electrons are driven to flow between two electrodes attached on the back sides of the films in order to balance the potential. Ever since the first report of the TENG in January 2012, the output power density of TENG has been improved for five orders of magnitude within 12 months. The area power density reaches 500 W/m², volume density reaches 490 kW/m³, and a conversion efficiency of ~50% has been demonstrated. The TENG can be applied to harvest all kind mechanical energy that is available but wasted in our daily life, such as human motion, walking, vibration, mechanical triggering, rotating tire, wind, flowing water and more. Alternatively, TENG can also be used as a self-powered sensor for actively detecting the static and dynamic processes arising from mechanical agitation using the voltage and current output signals of the TENG, respectively, with potential applications for touch pad and smart skin technologies. The TENG is possible not only for self-powered portable electronics, but also as a new energy technology with a potential of contributing to the world energy in the near future.

[1] Z.L. Wang "Triboelectric Nanogenerators as New Energy Technology for Self-Powered Systems and as Active Mechanical and Chemical Sensors", *ACS Nano* **7** (2013) 9533-9557.

[2] G. Zhu, J. Chen, T. Zhang, Q. Jing, Z. L. Wang* "Radial-arrayed rotary electrification for high-performance triboelectric generator", *Nature Communication*, **5** (2014) 3456.

4:20pm EN+EM+MN+NS+TR-MoA8 **Conflicting Roles of Charge Traps in ETA Solar Cells: The CREM Point of View**, *Hagai Cohen*, Weizmann Institute of Science, Israel

The characterization of multi-interfacial devices commonly encounters critical difficulties due to the limited access of standard electrical probes to selected inner domains. In this respect, the XPS (x-ray photoelectron spectroscopy) based CREM (chemically resolved electrical measurements) [1] is a technique proposing particularly useful capabilities. Demonstration of internal junction fields evaluation has already been provided, as well as the direct measurement of layer-specific photovoltages in ETA (extremely thin absorber) solar cells.[2] However, the complex dynamics realized during charge separation in such cells has not yet been investigated thoroughly by CREM.

The present work focuses on this issue, showing conflicting roles of charge trap states and, specifically, their different expression under controllably varied conditions. Comparison with complementary characterization techniques is further discussed, demonstrating the unique insight provided by CREM for their interpretation.

References

1. H. Cohen, *Appl. Phys. Lett.* **85**, 1271 (2004).

2. Y. Itzhaik, G. Hodes, H. Cohen, *J. Phys. Chem. Lett.* **2**, 2872 (2011).

4:40pm EN+EM+MN+NS+TR-MoA9 **Understanding Morphological and Structural Effect on Organic Photovoltaic Devices from Plasmonic Particles using Advanced Characterization Techniques**, *Nuradhika Herath, V. Lauter, J. Browning*, Oak Ridge National Laboratory

Organic electronics have been under intense scientific interest in recent years because of their attractive properties such as low cost fabrication processes, ability to performance under low light, and flexibility. Major achievements are based on use of new conjugated polymer and small molecules in bulk heterojunction (BHJ) devices to increase the inner donor acceptor interfaces of fully functional devices such as organic photovoltaics (OPVs) and organic light emitting devices (OLEDs). Many strategies have been introduced to enhance the power conversion efficiency (PCE) of organic electronics. Among them, one of the most promising solutions to enhance the absorption and device efficiencies of OPVs is incorporation of various metal nanoparticles (NPs). Metallic NPs enhanced the efficiency of the devices through local surface plasmonic responses (LSPR). This phenomenon reduced the recombination level of geminate excitons and increases the exciton dissociations, which enhanced the photocurrent and fill factors of devices. However, metallic NPs blended within the active layer can act as polaron traps detracting the device performances. In this study, we investigate layer and interfacial structure of small molecule (SM), *p*-DTS(FBTTh₂)₂ and fullerene, PC₇₀BM system incorporated with silver (Ag) NPs, using neutron reflectometry (NR), X-ray reflectometry and Atomic Force Microscopy (AFM). We present detailed composition changes with Ag NPs concentrations along the film depth to understand morphological and dynamical effects of BHJ devices incorporated with plasmonic particles. To complement and enhance the findings from NR, we report optical properties of the samples using UV-Visible absorption and Photoluminescence spectroscopy. Our findings provide unique information and clear insights into dynamics of plasmonic organic solar cells and their future applications for further enhancement of PCE.

This research was conducted at Spallation Neutron Source and at the Center for Nanophase Materials Sciences, which is sponsored at ORNL by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

5:00pm EN+EM+MN+NS+TR-MoA10 **Doped TiO₂ Based Core-Shell Structures for High Efficiency Hybrid Solar Cells**, *Jonas Weickert, J. Dorman, M. Noebels, M. Putnik, T. Pfadler*, University of Konstanz, Germany, *A. Wisnet, C. Scheu*, LMU Munich, Germany, *L. Schmidt-Mende*, University of Konstanz, Germany

Hybrid solar cells, with an inorganic/organic interface for charge separation, have been extensively investigated in the past decade in order to replace the expensive Si based technology with an inexpensive alternative. Typically, these devices incorporate a mesoporous TiO₂ film which is decorated with dye molecules and filled with a hole transport polymer, for example P3HT,

to conduct the electrons and holes, respectively. Recently, we have shown that the efficiency of nanowire based hybrid solar cells can be increased from ~1.8 % to 2.5 % through the formation of a Sn-doped TiO₂|TiO₂ core-shell device created via a hydrothermal growth and subsequent TiCl₄ treatment. However, this surface treatment presents difficulties in creating a crystalline conformal coating, limiting the control over the extent of coating and the crystallinity, directly affecting the charge injection from the polymer into the TiO₂ array. In this work, we directly deposit a controllable TiO₂ film through atomic layer deposition to conformally coat the nanowire arrays with various thicknesses. By changing the thickness and TiO₂ crystallinity, we are able to engineer the energy levels at the TiO₂-dye-P3HT interface due to the magnitude and position of the Fermi levels of the core and shell material, influencing the rate of charge injection and recombination. Furthermore, the crystallinity of the shell layer directly affects the amount of dye that can be absorbed on the surface of the nanostructures with a reduction in light absorption by roughly 30% from anatase to rutile TiO₂. Finally, a detailed mechanism will be proposed for the device performances based on the energy level alignment between the pinned Fermi-level TiO₂ structure and the HOMO of the P3HT resulting in a shifting open circuit voltage based on the crystal phases. Additionally, the core-shell structures are characterized with photovoltage decay and impedance spectroscopy measurements to study the charge transport and recombination across these various interfaces.

5:20pm **EN+EM+MN+NS+TR-MoA11 Stack Numbers Dependence of the Activation Energies for Carrier Escape from and Recombination in Strain-Balanced InGaAs/GaAsP MQW**, *Atsuhiko Fukuyama, T. Ikari, K. Nishioka, T. Aihara, H. Suzuki*, University of Miyazaki, Japan, *H. Fujii, M. Sugiyama, Y. Nakano*, The University of Tokyo, Japan

Fabrication of multiple quantum well (MQWs) in an absorption layer can extend the absorption region toward a longer wavelength and enhance the short-circuit current in the solar cells. However, MQWs function as recombination centers, leading to degradation in both open-circuit voltage and fill factor. We have already reported that the increase in stack number of QW causes the degradation of carrier collection efficiency [1]. In this study, we investigate the effects of stacks number on temperature dependences of the photoluminescence (PL), photothermal (PPT) and the surface photovoltage (SPV) signals. Although the photoexcited carriers in the barrier should relax by the radiative recombination (PL), carriers can thermally escape (SPV) or non-radiatively recombine (PPT) at the same time. Therefore, the latter two methodologies give us new insights for the carrier recombination and drift through the QW.

The present strain-balanced InGaAs/GaAsP MQWs absorption layer was composed of a 7.0-nm-thick In_{0.25}Ga_{0.75}As well and a 10.8-nm-thick GaAs_{0.66}P_{0.34} barrier. All layers were grown on an *n*-type GaAs substrate using metal-organic vapor phase epitaxy. We prepared different samples with MQW stack numbers of 10, 20, 30, and 40 in the *i*-region.

All PPT and SPV spectra showed three distinctive peaks followed by a step like function. They were decomposed into inter-subband transitions expressed by the two dimensional density of states for the QW and exciton peaks [2]. Although the PL intensity decreases with increasing the temperature, signals for PPT and SPV increases. We suppose two activation energies for the process: one is that for the carrier escape from the QW and another is for the non-radiative recombination in the QW. The three rate equations were built for PL, PPT and SPV and the temperature dependences are numerically fitted to estimate the two activation energies. As a result, we have estimated the activation energy for carrier escaping from the QW is constant as 70 meV for all samples with different stacks number. This is the same as the calculated barrier height. However, the activation energy for the non-radiative recombination increases from 6 to 49 meV for the sample with 10 and 40 stacks. This means that radiative recombination increases with increasing the stack number. The carriers thermally escape from the QW again relax into next well and may contribute to increase the radiative recombination.

[1] H. Fujii et al., Jpn. J. Appl. Phys. **51**, 10ND04 (2012).

[2] M. Kondow, A. Fukuyama, and T. Ikari et al., Appl. Phys. Express **2**, 041003 (2009).

Biomaterial Interfaces

Room: 317 - Session BI+AS+MN+NS-TuM

Biosensors

Moderator: Graham Leggett, University of Sheffield

8:20am **BI+AS+MN+NS-TuM2 An Inductive-Capacitive Sensor for Real-time Biofilm Growth Monitoring**, *Ekaterina Tolstaya, Y.W. Kim, S. Chu, K.D. Gerasopoulos, W.E. Bentley, R. Ghodssi*, University of Maryland, College Park

We present a real-time biofilm monitoring device based on inductive-capacitive (LC) sensing principles. Bacterial biofilms cause severe infectious diseases and environmental contamination. The bacterial biofilm's complex structure and composition, as well as its ability to exchange genetic information, result in a high tolerance for antimicrobial agents. As a result, established biofilms on implanted or external biomedical devices, such as catheters, are difficult to treat. Traditional antibiotic therapies for biofilm infections often require doses 500-5000 times larger than for non-biofilm infections [1]. Moreover, biofilm growth in environmental and industrial facilities causes contamination and corrosion of equipment due to the toxins generated by biofilms. Therefore, early detection of biofilm growth is critical to facilitate treatment of severe infections and prevent equipment contamination.

In this work, an LC sensor was fabricated using conventional lithography and metal deposition via E-beam evaporation (Cr/Au, 15 nm/200 nm) (Figure 1). The resonant frequency of the sensor was approximately 16 MHz in air at room temperature. A device sensitivity of 1140 Hz/dielectric was demonstrated using a known dielectric material (deionized water) (Figure 2). *Escherichia coli* W3110 biofilms were grown for 48 hours over the LC sensor and the resonant frequency of the sensor was measured every 80 seconds using a spectrum analyzer (Figure 3). As the biofilm grew over the device, an increase in the resonant frequency of the LC sensor was observed. This is due to the lower dielectric permittivity of the biofilm compared to that of the growth media (Luria Broth, $\epsilon \sim 80$), which results in decrease in the capacitance of the sensor. In control experiments with water and air as the media, a slight decrease in the resonant frequency was observed. The resonant frequency shift over time is in good agreement with the natural trend of biofilm growth (Figure 4) [2, 3]. The results validate the use of LC sensing for continuous monitoring of biofilm growth. This sensitive and reliable detection scheme, as well as the capability for flexible substrate integration and wireless interfacing, can serve as a foundation for the development of microsystems for real-time biofilm monitoring for both clinical and environmental applications.

8:40am **BI+AS+MN+NS-TuM3 The Interplay of Electrode Materials and Biomaterials in a Catechol-Modified Chitosan-Based Sensor for Clozapine Detection**, *Robert Dietrich, T.E. Winkler, H. Ben-Yoav, S.E. Chocron, E. Kim*, University of Maryland, College Park, *D.L. Kelly*, University of Maryland School of Medicine, *G.F. Payne, R. Ghodssi*, University of Maryland, College Park

We present a study of atomic layer-deposited TiN and electroplated Pt black (PtB) as candidate electrode materials to replace Au in a catechol-modified chitosan redox cycling system (Fig. 1) for the electrochemical detection of the antipsychotic clozapine (CLZ). In complex biological fluids like blood, interference from other electrochemically active species is a major challenge. The choice of electrode material is critical in addressing this challenge, as surface morphology and composition may produce a stronger and more reproducible CLZ signal, while shifting that signal away from potential interferents and improving the signal-to-noise ratio. Our electrochemical characterization results indicate that TiN is superior to Au as a sensor material, with a 2.6 times higher CLZ signal and a 3.2-fold lower variability.

Identifying electrode materials with high CLZ signal-to-noise ratio will greatly aid in translating our detection approach into a point-of-care monitoring system. Such a device will reduce the burden currently associated with CLZ due to safety and efficacy monitoring requirements [1], thereby improving the quality of life for people affected by schizophrenia. Our previous work [2] has relied on gold electrodes as a substrate for our catechol-modified chitosan films. These $5 \times 5 \text{ mm}^2$ micro-fabricated planar gold electrodes serve as controls, which we further modified here with: TiN for its inert properties; and PtB for its high surface area and potential electrocatalytic activity (Fig. 2).

The fabricated electrodes were characterized using cyclic voltammetry. Bare Au yields an oxidative CLZ peak signal of $1.06 \pm 0.20 \mu\text{A}$, compared to $5.20 \pm 2.26 \mu\text{A}$ when coated with chitosan-catechol (Fig. 3). TiN electrodes

produce a signal of $2.00 \pm 0.26 \mu\text{A}$ bare, and $13.7 \pm 0.7 \mu\text{A}$ when modified. The combination of higher signal and lower variability with the TiN is likely due to its inert chemical properties which also propagate more repeatable biomaterial modification. We observed a secondary peak with gold as well as bare TiN electrodes, likely due to interference related to chloride or oxygen. Modified TiN revealed only a single, CLZ-related peak. Results show that, as expected, signals from the bare PtB electrodes were 3370 times higher than from Au. However, they exhibited large variation between experiments, indicating the need for electroplating optimization. Testing the PtB electrodes with the chitosan-catechol film should increase both CLZ signal and resolution. Ongoing work is also focused on glassy carbon electrodes, which are expected to yield high repeatability by eliminating potential interfering oxygen signals in the redox cycling system.

9:00am **BI+AS+MN+NS-TuM4 Characterization of an Amperometric Glucose Sensor on a Flexible Polyimide Substrate for Continuous Glucose Monitoring and Insulin Delivery through Single Device**, *X. Du, J.R. Motley, A.K. Herman, Liney Arnadottir, G.S. Herman, X. Tan, J.F. Conley, Jr., Oregon State University, W.K. Ward, R.S. Cargill, J.R. Castle, P.G. Jacobs*, Pacific Diabetes Technologies

Type 1 diabetes affects over one million people and every year more than 30,000 children and adults are diagnosed with type 1 diabetes in the United States alone. Patients with type 1 diabetes cannot produce their own insulin and depend upon glucose sensors to monitor their blood glucose and adjust insulin levels either by injection or an insulin pump. The continuous monitoring of glucose blood levels and automatic insulin release by an artificial pancreas is a promising alternative to current treatment options, and can significantly improve the comfort and quality of life for the patient. Here we introduce a flexible catheter with an integrated glucose sensor capable of both continuously measuring glucose levels and deliver insulin through a single catheter. The amperometric glucose sensor includes multiple Pt indicating electrodes, Ag/AgCl reference electrode, electrohydrodynamic jet (e-jet) printed glucose oxidase enzyme layers, and permselective membrane for optimal glucose response from the interstitial tissue. The compact design is integrated on a flexible polyimide substrate and requires high durability for all the components due to the small radius of curvature of the catheter. The e-jet printing provides digital patterning flexibility and highly precise deposition of the enzyme layer, which allows improved uniformity and accuracy of the glucose sensor. Here we will discuss characterization and optimization of the indicating and reference electrodes using electrochemical methods, scanning electron microscopy, X-ray photoelectron spectroscopy (XPS), and time of flight secondary ion mass spectrometry. XPS was used to confirm full glucose oxidase coverage of the indicating electrode. Electrochemical testing indicates that e-jet printed glucose oxidase inks are still active towards glucose oxidation after printing and subsequent deposition of the permselective membrane. The operation and characterization of a fully functional glucose sensor integrated onto a catheter will also be discussed.

9:20am **BI+AS+MN+NS-TuM5 Chemically Modifying Graphene for Biosensing and Interfacing with Biology**, *Paul Sheehan*, Naval Research Laboratory, *S.C. Hernandez*, National Research Council, *N. Long*, Nova Research, *S.P. Mulvaney, J. Robinson*, Naval Research Laboratory, *R. Stine*, Nova Research, *C.R. Tamana, S.G. Walton*, Naval Research Laboratory

INVITED

Graphene has many properties that are highly suited for biological studies. For instance, its atomic thinness, high electrical conductivity, and simple production methods are ideal for biosensing. As another example, graphene can be attached to arbitrary substrates to lend them the chemical flexibility of carbon while adding only an ultrathin coating. For both biosensing and biofunctionalization, it is critical to produce high quality films that are precisely modified with the desired chemistry. For biosensing, the sensor must be functionalized for specific receptor-ligand recognition such as DNA-DNA or antibody-antigen binding. We will discuss our strategies for functionalization and the successful detection of specific DNA hybridization biologically-active field-effect transistors (BioFETs) based on chemically modified graphene. We will then discuss our use of graphene to interface biology with materials ranging from polymers to dielectrics to semiconductors. Graphene's incredible thinness enables its inclusion in more traditional sensing platforms as a non-intrusive functionalization layer, discreetly lending its chemical flexibility to other, more inert materials without otherwise impacting the sensing device.

11:00am **BI+AS+MN+NS-TuM10 Bioresorbable Sensors and Electronics**, *John Rogers*, University of Illinois at Urbana Champaign
INVITED

A remarkable feature of the modern integrated circuit is its ability to operate in a stable fashion, with almost perfect reliability. Recently developed classes of electronic materials create an opportunity to engineer the opposite outcome, in the form of devices that dissolve completely in water, with harmless end products. The enabled applications range from 'green' consumer electronics to bio-resorbable medical implants – none of which would be possible with technologies that exist today. This talk summarizes recent work on this physically 'transient' type of electronics and sensors, from basic advances in materials chemistry, to fundamental studies of dissolution reactions, to engineering development of complete sets of device components, sensors and integrated systems.

11:40am **BI+AS+MN+NS-TuM12 Surface Chemistry Enhanced Microbial Bioelectrocatalysis**, *Kateryna Artyushkova, C. Santoro, S. Babanova, J. Cornejo, L. Ista, A. Schuler, P. Atanassov*, University of New Mexico

Bioelectrochemical oxidation carried out by bacteria attached on a solid electrode is capturing the attention of scientists all over the world. Different species of bacteria have been shown as electroactive and being able to oxidize organic compounds releasing electrons that can be transferred to a conductive solid support. If the oxidation reaction is coupled with the oxygen reduction reaction (ORR), the degradation of organics could lead to a production of useful electricity and water. Those related aspects are currently utilized in the development of alternative and cost effective bioelectrochemical systems (e.g. microbial fuel cell (MFC)) for simultaneous organics removal and electricity production. Understanding the bioelectrocatalytic nature of organics dissimilation by bacteria and the subsequent internal and external electron transfer is of a high importance for the further development of these systems and a key moment in their future application.

In this work, an artificial approach for enhanced microbial bioelectrocatalysis was explored along with study of the parameters promoting bacteria external electron transfer. This approach consisted of artificial modification of electrode surfaces having, as a result, different surface chemistries. Mixed bacterial culture development, biofilm growth and electrochemical performance have been studied. Smooth gold surfaces were modified with organic thiols to form self assembled monolayers (SAMs) with various functional groups (-CH₃, -OH, -N(CH₃)₃ and -COOH).

Power curves and single electrode polarization curves have been taken to evaluate the performance of the MFC as a whole and of the electrodes separately. XPS analysis of electrodes was used to study the effect of chemistry on the performance. Confocal and SEM microscopy was used to study the bacteria biomass and biofilm development was tracked over time .

MEMS and NEMS

Room: 301 - Session MN+NS-TuA

Multi-Scale Phenomena and Bio-Inspired MEMS/NEMS

Moderator: Philip Feng, Case Western Reserve University, Meredith Metzler, Cornell University

2:20pm MN+NS-TuA1 MEMS-Enabled Multiscale Nanolaminated Magnetics, *Mark Allen*, University of Pennsylvania **INVITED**

The manufacture of materials with bulk volumes and precisely controlled nanostructure has led to the creation of materials with surprising and useful mechanical and electrical properties. Recently we have developed a 'top-down' fabrication technique that allows the creation of highly-structured multilayer metallic materials, with precisely designed characteristic lengths in the hundreds of nanometers scale, but volumes of manufactured material in the macro range. The fabrication relies on automated and repeated multilayer electrodeposition of multiple metallic materials, followed by sacrificial etching of one metal. The resultant structure consists of individualized high-lateral-aspect-ratio sub-micron metallic films. The application of these multiscale materials to ultracompact energy conversion is investigated. Metallic magnetic materials have desirable magnetic properties, including high permeability and high saturation flux density, when compared with their ferrite counterparts. However, eddy current losses preclude their use in many switching converter applications due to the challenge of simultaneously achieving sufficiently thin (100-500 nm) laminations such that eddy currents are suppressed while simultaneously achieving overall material thicknesses (0.1-1 mm) such that substantial power can be handled. Sequential electrodeposition of multiple nanoscale 'sheets', or laminations, of magnetic materials such as permalloy and NiFeCo offers an approach to fabricate the desired nanostructured magnetic core. Tests of toroidal inductors with nanolaminated cores showed negligible eddy current loss relative to total core loss even at a peak flux density of 0.5 T and a frequency of 10 MHz. The ability to operate at such high flux levels offers the possibility of dramatically shrinking the physical size of power inductors in energy converters. DC-DC converters with efficiencies of up to 93% and power handling of approximately 40W have been achieved in ultracompact form based on these materials.

3:00pm MN+NS-TuA3 Fabrication and Electrical Performance of Through Silicon Via Interconnects Filled with a Copper/Carbon Nanotube Composite, *Y. Feng, Susan Burkett*, The University of Alabama

Three-dimensional integrated circuit (3D-IC) technology has been developed using copper (Cu) filled through silicon vias (TSVs). The vertical interconnects pass through a set of stacked die and enable many applications that benefit from increased bandwidth, reduced signal delay, and improved power management. However, the reliability of Cu interconnects is a serious concern since the performance is affected by electromigration and stress associated with mismatch in thermal expansion coefficients. Carbon nanotubes (CNTs) are nanoscale materials which possess a high Young's modulus, a low coefficient of thermal expansion, and high thermal conductivity. Compared to Cu, CNTs exhibit low resistivity due to the existence of ballistic conduction and they are capable of carrying a higher current density. In this work, we fabricated TSVs using a novel materials system consisting of a composite of Cu and CNTs as a possible solution to the problems encountered in Cu-based interconnects. First, blind TSVs were fabricated using a Bosch process. After etching, an insulating layer, a metallic seed layer, and a catalyst layer were deposited previous to CNT growth. Vertically aligned CNTs were grown by chemical vapor deposition method. Finally, Cu was deposited by periodic reverse pulse electroplating inside the vias to form a Cu/CNT composite. Polishing completed the fabrication and allowed measurement of electrical performance for TSV interconnects. The experimental results were compared for interconnects filled with Cu and those filled with the Cu/CNT composite. The results are encouraging for the Cu/CNT composite having potential application as a TSV interconnect material.

3:20pm MN+NS-TuA4 Meso Scale MEMS Motion Transformer and Amplifier Electrostatically Actuated by Parallel Plate Electrodes, *Y. Gerson, S. Krylov*, Tel Aviv University, Israel, *Tali (T.) Nahmias, R. Maimon*, Microsystems Design Center, RAFAEL LTD, Israel

Meso scale microelectromechanical structures found on the upper scale of microelectromechanical systems (MEMS) can potentially replace conventional mechanical devices produced by common for the macro-engineering approaches such as machining and assembly of individual parts. When realized as a compliant mechanism containing a single flexible

member rather than multiple parts attached by joints they provide smooth frictionless motion without backlash and exhibit improved reliability and robustness. Batch fabrication using micromachining processes established in MEMS allows improved yield and significantly lower cost. However, actuation of these devices remains challenging. Electrostatic actuation, which is the most widely used in smaller MEMS devices, is viewed to be less suitable for the actuation at the meso scale due to unfavorable scaling laws, namely quadratic reduction of the actuating force with the distance between the electrodes. For this reason, most of the meso scale micro devices are actuated by thermal transducers, distinguished by slow response and high power consumption or by piezoelectric or magnetic motors, which cannot be integrated within the device and require post-fabrication assembly.

In this work we report on the design, fabrication and characterization of an electrostatically actuated meso scale microelectromechanical motion transformer and amplifier. The actuator incorporate a transducer with multiple parallel plate electrodes and is realized as a compliant mechanism relying on flexible pseudo hinges. The $5000\ \mu\text{m} \times 4000\ \mu\text{m}$ device converts linear motion of the transducer into mechanically amplified angular motion of a rotating lever. By combining a highly efficient small-gap parallel plate electrode and a motion amplification the device is designed to provide a lever tip displacement of $60\ \mu\text{m}$, an initial blocking force of 0.001N at zero displacements and a blocking force of 0.012N in the maximal displacement configuration when the parallel plate actuator is in its closed position. The devices were fabricated using DRIE from a SOI wafer with (111) front surface orientation and a $150\ \mu\text{m}$ thick device layer. The devices were operated in ambient air conditions and the functionality of the device was demonstrated experimentally. The voltage-displacement dependence and resonant curves were built using image processing procedure implemented in Matlab. Excellent agreement between the results provided by the Finite Elements models and the experimental data was observed. The results of the work demonstrate an ability to achieve both large displacements and high blocking forces in an electrostatically actuated meso scale compliant mechanism.

4:20pm MN+NS-TuA7 Bio-Inspired Microlenses and Their Biomedical Applications, *Hongrui Jiang*, University of Wisconsin - Madison **INVITED**

Optical detection and imaging have wide applications in biomedicine and biological and chemical analyses. With continuing miniaturization effort to realize integrated microsystems, micro-scale optical components become more and more important. For any optical system, lenses are critical elements. In this talk, I will present our work on liquid microlenses. I will first introduce a few types of microlenses and microlens arrays, including tunable liquid microlenses actuated by temperature-, pH- and infrared light-responsive hydrogels, microlens arrays for light-field imaging, microcamera arrays mimicking compound eyes, and artificial reflecting superposition compound eyes. Then, I will discuss about potential applications of these lenses in medical instruments. I will describe miniaturized cameras capable of multiple viewpoints, prototype flexible endoscopes implementing infrared-light responsive liquid microlenses at their distal ends, and prototype multiple-camera laparoscopes.

5:00pm MN+NS-TuA9 The Development of a Valve Based Microfluidic Biofilm Reactor for Biofilm Studies with Reliable Controls, *Sowmya Subramanian, M.T. Meyer, Y.W. Kim, W.E. Bentley, R. Ghodssi*, University of Maryland, College Park

We present a multi-experiment PDMS based biofilm analysis platform using a valve-actuated microfluidic system, designed to reduce growth variance of *in-vitro* biofilms to less than 10%. This was achieved by integrating hydraulic push-down valve actuators to section a uniform biofilm grown in a channel by maintaining a single source of bacterial suspension [1, 2]. In this work, we establish a simplified process flow for the fabrication of a multi-depth device mold and demonstrate the high throughput capability of the microfluidic biofilm reactor.

Bacterial biofilms are the primary cause of infections in medical implants and catheters. The widespread use of high doses of antibiotics to treat biofilm infections is leading to the emergence of antibiotic resistant strains, necessitating the development of alternative methods of treatment [3]. However, the experimental evaluation of new treatment techniques is strongly hindered by the stochastic nature of biofilm growth [1]. Therefore, it is required to develop a microsystem that can not only facilitate multi-experiment studies for new treatment evaluation but also enable the growth of uniform biofilms that can be used as reliable controls.

Figure 1 shows a single uniform biofilm grown in the horizontal center channel of the device is sectioned into multiple sections, by hydraulically

actuating the push-down valves thereby enabling multi-experiment studies on the same biofilm. Figure 2 shows the schematic of the operation of a “push-down” valve [4], the schematic of the CAD layout of the two-level microfluidic device and its two modes of operation. The two-step photolithography of the molds (Figure 3) using negative photoresists, SU8-2015 and KMPR1050, allows for the patterning of the multi-depth microfluidic mold without the need for additional passivation of the first resist layer, thereby simplifying fabrication. The mold can be reused to produce multiple devices; a photograph of the valve region of a used multi-depth mold is shown in Figure 4. Photographs of the device operating in different modes are shown in Figure 5.

The unique capability of this valved microfluidic biofilm reactor to section uniform biofilms can facilitate high-throughput biofilm studies, including new drug discovery. The push-down valve configuration allows for easy integration of electrodes for the study of alternative treatment methods like electric fields. Furthermore, the integration of the biofilm reactor with a real-time measurement system will enable high-throughput continuous analyses on uniform biofilms while ensuring tight and reliable controls.

5:20pm MN+NS-TuA10 Multimode Silicon Carbide (SiC) Microdisk Resonator in Liquid, Hao Jia, P.X.-L. Feng, J. Lee, Case Western Reserve University

We experimentally demonstrate, for the first time to our knowledge, the operation of silicon carbide (SiC) microdisk resonators in fluidic and viscous environments (particularly in water) with robust multiple flexural-mode resonances in the high and very high frequency (HF/VHF) radio band. We observe ~8 resonance modes in a 20 μ m-in-diameter SiC microdisk resonator with resonance frequencies up to ~120 MHz and quality Q factors as high as ~40 in water.

SiC is a highly attractive material for microelectromechanical systems (MEMS) due to its superior mechanical (*e.g.* high elastic modulus, $E_V \sim 450$ GPa), optical (wide bandgap, >2.3 eV) and thermal properties (thermal conductivity of 320-490 W/[m \times K])^[1]. These advantages make SiC especially suitable for sensing applications in liquid for its transparency from visible to mid-infrared light and high optical power handling ability, facilitating efficient laser actuation and detection. Meanwhile, two dimensional (2D) microdisk structure exhibits multiple flexural-mode resonance characteristics, which can enhance sensing performances in liquid with the additional degrees of freedom and larger sensing area. Further, the unique biocompatibility of SiC allows potential in-liquid biosensing applications be developed.

In this study, we demonstrate the operation of high frequency SiC microdisk resonators in liquid. The SiC microdisk resonators are completely immersed in water, and are optically driven by an amplitude-modulated 405nm laser. The multimode resonances are detected with optical interferometry using a 603nm He-Ne laser. We observe ~8 resonance modes up to ~120 MHz with Q s as high as ~40 in water. To our best knowledge, both the number of resonance modes and Q s measured are the highest among flexural-mode resonators operating in water reported to date^{[2],[3],[4],[5]}. Such high frequency SiC microdisk resonators with robust multimode resonances and high Q s in water may provide an appealing platform for particle and biological sensing applications in liquid.

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- [1] X. Lu, J. Y. Lee, P. X.-L. Feng, and Q. Lin, *Opt. Lett.* **38**, 1304 (2013).
 - [2] S. S. Verbridge, L. M. Bellan, J. M. Parpia, and H. G. Craighead, *Nano. Lett.* **6**, 2109 (2006).
 - [3] S. Sawano, T. Arie, and S. Akita, *Nano. Lett.* **10**, 3395 (2010).
 - [4] J. H. Park, T. Y. Kwon, D. S. Yoon, H. Kim, and T. S. Kim, *Adv. Func. Mater.* **15**, 2021 (2005).
 - [5] C. Vancura, Y. Li, J. Lichtenberg, K.-U. Kirstein, A. Hierlemann, and F. Josse, *Anal. Chem.* **79**, 1646 (2007).

5:40pm MN+NS-TuA11 Development of CMOS-based Capacitive Micromachined Ultrasonic Transducers Operated in Collapsed Mode, Wei-Cheng Chung, M.-C. Tsao, P.-C. Li, W.-C. Tian, National Taiwan University, Taiwan, Republic of China

In this work, experimental results of complementary metal-oxide-semiconductor (CMOS)-based capacitive micromachined ultrasonic transducers (CMUTs) operated in the collapsed mode will be reported. Our CMUT is fabricated by TSMC 0.35 μ m two poly Si and four metal layer (2P4M) CMOS-MEMS standard process followed by a post customized wet etching. Conventionally, the applied DC bias is 80% of the collapse voltage during the CMUT operation. Compared to the conventional operation, the CMUT membrane will be snapped-down on the bottom electrode and this will change the center frequency of the transducers. The collapsed voltage of our CMUT is designed at approximately 40V. The center frequency (in immersion) of our CMUT in conventional mode operation is 2.89MHz

while the frequency is shifted to 9.12MHz in collapsed-mode operation. The sensitivity is proved to be 4-times larger in the collapse-mode operation because the increased electrical-mechanical coupling efficiency.

The comparison of single-electrode and double-electrode design will be reported as well. With the double-electrode design, the collapse voltage is first applied to the center electrode while a separated DC bias is applied to the side electrode to actuate our CMUTs. The maximum displacement of the CMUT membrane will be appeared on the side electrode. It is proved that CMUTs with the double-electrode design can transmit a higher output pressure and receive signals with a higher sensitivity compared to CMUTs with the single-electrode design. It is believed that the our CMUTs with standard CMOS-based process will broaden the application spaces such as in biomedical imaging and nondestructive evaluation.

6:00pm MN+NS-TuA12 Development of Micro Gas Preconcentrator Using Electroless Gold Deposition for Human Breath Analysis, ChunYen Kuo, C.-L. Hsu, National Taiwan University, Taiwan, Republic of China, H.-Y. Kuo, C.-J. Lu, National Taiwan Normal University, Taiwan, Republic of China, W.-C. Tian, National Taiwan University, Taiwan, Republic of China

The detection of the volatile organic compounds (VOCs) in human breath can be analyzed by gas chromatograph (GC) as a non-invasive diagnosis for lung diseases. However, the gas concentration of the VOCs in human breath is low, approximating in the ppb to sub ppb range, and thus a gas preconcentrator (PCT) must be placed before a GC to collect and preconcentrate trace compounds. Early μ PCTs using commercially available adsorbents and microheaters were demonstrated. However, the heating efficiency of the device is limited either by a large thermal mass or a poor heat transfer.

In this study, we present a gas PCT using a simple one-photomask micromachined process and the electroless gold deposition method to form the gold film, serving as a thin film microheater, on the inner surface of the microchannel. An amorphous and porous carbon film that functions as an adsorbent is grown on microheaters inside the microfluidic channel followed by the electroless gold deposition. The developed gas PCT can be heated to $>300^\circ\text{C}$ by applying a constant electrical power of ~5W with a heating rate of $60^\circ\text{C}/\text{sec}$. Four suspected lung cancer biomarkers, acetone, benzene, toluene and xylene, are collected through the proposed gas PCTs and separated successfully using a 17-m-long gas chromatography (GC) column. Compared with previous works, the more simple fabrication process, more stable heating element, more uniform temperature distribution and more efficient heating rate of the micro gas preconcentrator are developed demonstrated.

Wednesday Morning, November 12, 2014

MEMS and NEMS

Room: 301 - Session MN-WeM

Optomechanics, Photonics, and Quantum Nanosystems

Moderator: Susan Burkett, The University of Alabama,
W.K. Hiebert, University of Alberta and The National
Institute for Nanotechnology

8:40am MN-WeM3 Diamond Quantum Nanophotonics and Nanomechanics, Marko Loncar, Harvard University **INVITED**

Diamond possesses remarkable physical and chemical properties, and in many ways is the ultimate engineering material - "the engineer's best friend!" For example, it has high mechanical hardness and large Young's modulus, and is one of the best thermal conductors. Optically, diamond is transparent from the ultra-violet to infra-red, has a high refractive index ($n = 2.4$), strong optical nonlinearity and a wide variety of light-emitting defects. Finally, it is biocompatible and chemically inert, suitable for operation in harsh environment. These properties make diamond a highly desirable material for many applications, including high-frequency micro- and nano-electromechanical systems, nonlinear optics, magnetic and electric field sensing, biomedicine, and oil discovery. One particularly exciting application of diamond is in the field of quantum information science and technology, which promises realization of powerful quantum computers capable of tackling problems that cannot be solved using classical approaches, as well as realization of secure communication channels. At the heart of these applications are diamond's luminescent defects—color centers—and the nitrogen-vacancy (NV) color center in particular. This atomic system in the solid-state possesses all the essential elements for quantum technology, including storage, logic, and communication of quantum information.

I will review recent advances in nanotechnology that have enabled fabrication of nanoscale optical devices and chip-scale systems in diamond that can generate, manipulate, and store optical signals at the single-photon level. Examples include a room temperature source of single photons based on diamond nano wires [1] and plasmonic apertures [2], as well as single-photon generation and routing inside ring [3] and photonic crystal resonators fabricated directly in diamond [4]. In addition to these quantum applications I will present our recent work on diamond based on-chip frequency combs [5], diamond nano mechanical resonators [6].

1 TM Babinec, et al, "A bright single photon source based on a diamond nanowire," *Nature Nanotechnology*, 5,195 (2010)

2 JT Choy, et al, "Enhanced Single Photon Emission by Diamond-Plasmon Nanostructures," *Nature Photonics*, 5,738 (2011)

3 BJM Hausmann, et al, "Integrated Diamond Networks for Quantum Nanophotonics", *Nano Letters*, 12,1578 (2012)

4 MJ Burek, et al, "Free-standing mechanical and photonic nanostructures in single-crystal diamond", *Nano Letters*, 12,6084 (2012)

5 B Hausmann et al, "Diamond Nonlinear Photonics", *Nature Photonics*, 8,369 (2014)

6 M Burek et al, "Nanomechanical resonant structures in single-crystal diamond", *Appl. Phys. Lett.*, 103,131904 (2013)

9:20am MN-WeM5 A Compact Footprint Nano-Opto-Mechanical System with Evanescent Interaction, Marcel Pruessner, D. Park, T.H. Stievater, Naval Research Laboratory, D.A. Kozak, NRC Postdoc (Naval Research Lab), W.S. Rabinovich, Naval Research Laboratory

We present a compact footprint, fully-integrated nano-opto-mechanical system with strong evanescent field interaction. Silicon nitride films with sub-wavelength thickness ($t_{\text{Si}_3\text{N}_4} \ll 4n_{\text{Si}_3\text{N}_4}$) enable low-loss waveguides [1] as well as complex photonic circuits [2], e.g. directional couplers, Mach-Zehnder interferometers, microring cavities [3], nanobeam cavities [4], etc. Furthermore, the thin core layer and air top cladding allow access to the waveguide's evanescent field, which can be tailored by simply varying the Si_3N_4 core layer deposition thickness. We previously demonstrated evanescent field interactions in these structures using a tapered fiber as an *off-chip* perturber [2] and by performing absorption spectroscopy on a number of chemical analytes present near the waveguide [3].

We now build upon our previous work [2,3] by fabricating a suspended tensile microbridge (Si_3N_x) just above the waveguide surface ($\text{gap} \approx 100\text{-}300\text{nm}$) to achieve strong interactions between optical and mechanical structures in a *fully-integrated* device. For example, displacement of the mechanical perturber (microbridge) modifies the waveguide's effective

index so that the nano-opto-mechanical system acts as a high-resolution displacement sensor in which determination of the change in effective index is a measurement of displacement. At the same time, the change in the waveguide effective index as a function of displacement implies an optical force that acts on the microbridge [5].

Our nano-opto-mechanical system is compact and occupies a footprint that is essentially determined only by the waveguide since the mechanical structure is suspended directly above it. This vertical architecture enables us to optimize the optical and mechanical structures independently. Although simple, the opto-mechanical system enables complex interactions with a variety of potential applications including displacement sensing, optical-force reconfigurable photonics, and opto-mechanical oscillators. The compact footprint enables large-scale integrated opto-mechanical systems on a chip.

We will present the basic approach of our nano-opto-mechanical system, design and fabrication details, simulations to support strong evanescent field interaction, and initial experimental results demonstrating a strong interaction in chip-scale opto-mechanical structures.

9:40am MN-WeM6 GaAs Disks Optomechanical Resonators in Liquid, I. Favero, Eduardo Gil-Santos, Université Paris Diderot, CNRS, France

Vibrating nano or micromechanical structures, such as cantilevers, have been the subject of extensive research for the development of ultrasensitive mass sensors for mass spectrometry, chemical sensing and biomedical analysis. In liquids, the energy losses due to viscous damping, acoustic losses and squeeze film effects are high and the mass sensitivity diminishes dramatically. Additionally, viscous damping in a fluid is often larger when the devices are miniaturized.

To circumvent these problems, novel structures have been proposed, such as microchannels, where the liquid is placed directly inside the resonator. They have indeed shown lower energy losses, but they can hardly be miniaturized. External feedback loops have been applied as well in order to diminish artificially energy losses [4]. Besides this, another technique to reduce mechanical losses in a liquid has been to use higher order modes or contour/extensional modes. On one hand, these modes indeed show lower dissipation, on the other hand the related displacement is extremely small, making it more difficult to detect, especially in a liquid.

Here we study the potential of GaAs disk resonators in this context, in particular focusing on mechanical radial breathing modes. GaAs mechanical disks, with their high mechanical Q even in air ($>10^5$), their low mass (pg) and high mechanical frequency (GHz), have been shown to be potential powerful sensors. Their use in liquids has been never investigated or even suggested, and it is still uncertain what energy losses and sensitivity they will present in such environment. GaAs disks support optical whispery gallery modes (WGMs), with high optical quality factor (several 10^5). This fact, together with the outmost optomechanical coupling that they possess (up to 4 MHz), provide them with an extremely high displacement sensitivity in the 10^{-18} m/√Hz range, allowing measuring the thermomechanical noise of the resonator even in a liquid.

We measure for the first time a GaAs mechanical disk vibrating in a liquid, directly in the Brownian motion regime. Employing finite element simulations and an analytical fluid-structure model, we investigate the mechanical damping mechanisms at play in this situation. We study the fluidic dissipation as a function of disk's dimensions and of the physical properties of the liquid, such as density and viscosity, performing experiments in a family of different liquids. We finally analyze the sensing capabilities of this object and compare it to other existing approaches.

11:00am MN-WeM10 Photonic Actuation and Detection of Higher Order Modes in Nanomechanical Resonators, Jocelyn Westwood, V.T.K. Sauer, University of Alberta and The National Institute for Nanotechnology, Canada, Z. Diao, National Institute for Nanotechnology and University of Alberta, Canada, W.K. Hiebert, University of Alberta and The National Institute for Nanotechnology, Canada

All-optical actuation and detection of nanomechanical devices has recently emerged as a high-bandwidth technique with high displacement sensitivity [1],[2],[3],[4],[5]. We explore optical actuation and detection of higher order vibrational modes, including even modes, in nano-optomechanical doubly clamped beams. Higher order modes have increased resonance frequencies, thereby increasing the mass sensitivity for sensing purposes and increasing the measurement bandwidth [6], [7]. Currently, higher order modes are not well studied since the symmetry of the modes causes a zero effective index shift over the vibrating beam, limiting the sensitivity of the all-optical technique. We demonstrate the fabrication of doubly clamped beams with the symmetry broken, due to a step in the substrate height under

the doubly clamped beam. The doubly clamped beams are embedded in an optical racetrack resonator. This allows for the all-optical actuation and detection of the first through fifth modes of the doubly clamped beams. Additionally, the thermomechanical noise floor of the first few modes is observed.

- [1] F. Marquardt and S. Girvin, *Physics*, vol. 2, pp. 40, 2009.
- [2] T. J. Kippenberg and K. J. Vahala, *Science*, vol. 321, pp. 1172–6, 2008.
- [3] J. Chan et al., *Opt. Express*, vol. 17, no. 5, pp. 3802–3817, 2008.
- [4] M. Li et al., *Nature*, vol. 456, pp. 480–4, 2008.
- [5] V. T. K. Sauer et al., *Appl. Phys. Lett.*, vol. 100, no. 26, pp. 261102, 2012.
- [6] K. L. Ekinci, Y. T. Yang, and M. L. Roukes. *J. Appl. Phys.*, vol. 95, no. 5, pp. 2682–2689, 2004.
- [7] M. K. Ghatkesar et al., *Nanotechnology*, vol. 18, no. 44, pp. 445502, 2007.

11:20am **MN-WeM11 Dynamic Range Effect on the Mass Sensitivity of Optomechanically Transduced NEMS Devices with a Poorer Q Value.** *S.K. Roy, V.T.K. Sauer, W.K. Hiebert*, University of Alberta and The National Institute for Nanotechnology, Canada

Suitable control over the oscillatory properties and tunable nonlinearities has made nanomechanical resonators attractive to the research community not only for their ultra-sensing ability but also for rich physics behind their optomechanical properties. Optomechanical transduction of these devices has become promising for optimizing device applications. The present work is aimed at studying the interplay between dynamic range (DR), mass sensitivity, and mechanical quality factor (Q), and measurement bandwidth in state-of-the-art optomechanical NEMS devices. While poorer Q is normally assumed to lead to degradation in mass sensing performance, there are situations where performance can be recovered, and even improved, through the dynamic range dependencies on Q. This is welcome news for applications at atmospheric pressure such as sensitive gas sensing. In quest of an appropriate mass or gas sensor, nonlinear oscillatory behaviour was studied on a doubly clamped beam of $8.75\mu\text{m}\times 220\text{nm}\times 160\text{nm}$ which is 160 nm away from a racetrack resonator optical cavity. To get the upper end of DR, the resonator was driven close to nonlinearity, i.e. to the amplitude where 1dB compression was observed. Thermomechanical noise signals were measured to achieve the bottom end of the DR. At high vacuum ($<10^{-5}$ torr), 6 torr and 1atm the obtained experimental DR values are 53, 64 and 55 respectively. The corresponding Q values are 2866, 944 and 26. According to these experimental results, calculated mass sensitivity for the device were found 0.3, 0.2 and 28 Zepto g at high vacuum, 6 torr and 1atm respectively. An atmospheric pressure room temperature mass sensitivity of 28 zeptogram for Q value of 26 is an intriguing value. Such a surprising result of better mass sensitivity with poorer Q can be explained based on existing theories.

12:00pm **MN-WeM13 Scanning Optical Interferometric Spectromicroscopy for Mapping Multimode Resonant Motions in Planar Silicon Carbide (SiC) Micromechanical Resonators with $f\times Q$ Approaching 10^{13}Hz .** *Zenghui Wang, J. Lee, P.X.-L. Feng*, Case Western Reserve University

Higher-order and multiple modes in vibrating micro/nanomechanical resonators are of great interest and promise for both fundamental research such as exploring and understanding quantum mechanics in these man-made structures, and for technological applications such as signal processing and multi-modality sensing (e.g., simultaneously detecting mass and position of a physisorbed particle on resonator surface)[1][2]. It is therefore important to understand such multimode behavior in micro/nanomechanical resonators down to their fundamental limits, i.e. in their completely-undriven Brownian motions, at all conditions (e.g., ranging from cryogenic to elevated temperatures). This demands ultrasensitive motion transduction schemes that would allow us to attain more comprehensive information from the devices, far beyond what can be extracted from the conventional frequency-domain resonance curves.

Over the recent few decades, various motion transduction technologies (e.g., electrostatic, piezoelectric, piezoresistive, optomechanical, etc.) have been developed to read out small displacements in micro/nanomechanical resonators. While the commonly-used motion readout schemes have their respective advantages and have achieved many milestones, they lack multimode capabilities, and particularly, experimental visualizations of these multiple modes. For example, optomechanical technique has demonstrated excellent displacement sensitivity (better than $\text{fm}/\text{Hz}^{1/2}$), but is unable to experimentally determine the spatial mode shapes of 2D planar resonators, which is highly desired for determining and engineering high-order modes.

Optical interferometric techniques have been continuously advancing over the recent years [3][4]. Here, we report on the design and implementation of a scanning laser interferometry and spectromicroscopy technique, and we demonstrate direct visualization of multimode resonances in SiC micromechanical resonators with various geometries, including membranes, plates, trampolines, torsional resonators, and center-supported disks, with many resonances up in the VHF and UHF bands. Besides setting a new record of $f\times Q$ product in all SiC flexural-mode resonators ($\sim 1.0\times 10^{13}$), our devices effectively enable high-order resonances with clearly distinguishable mode shapes through their 2D nature and high-aspect-ratios.

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- [1] Dohn, S., Sandberg, R., Svendsen, W. & Boisen, A. *Appl. Phys. Lett.* **86**, 233501 (2005).
 - [2] Hanay, M. S. et al. *Nature Nanotech.* **7**, 602 (2012).
 - [3] Hiebert, W. K., Vick, D., Sauer, V., & Freeman, M. R. *J. Micromech. Microeng.* **20**, 115038 (2010).
 - [4] Lee, J., Wang, Z., He, K., Shan, J., & Feng, P. X.-L. *ACS Nano* **7**, 6086 (2013).

Wednesday Afternoon, November 12, 2014

2D Materials Focus Topic

Room: 310 - Session 2D+AS+EM+MI+MN+NS+TF-WeA

Properties of 2D Materials

Moderator: Guy Le Lay, Aix-Marseille University

2:20pm **2D+AS+EM+MI+MN+NS+TF-WeA1 Tuning Excitons in Two-Dimensional Semiconductors**, Kirill Bolotin, Vanderbilt University
INVITED

Monolayer molybdenum disulfide (MoS₂) is a two-dimensional crystal comprising a single layer of molybdenum atoms sandwiched between two layers of sulfur atoms. Monolayer MoS₂ differs from its celebrated all-carbon cousin, graphene, by the presence of a direct band gap leading to robust light absorption and by strong electron-electron interactions leading to formation of rightly bound excitons. In this talk, we demonstrate that both electrical and optical properties of MoS₂ can be widely tuned via external influences.

In the first part of the talk, we study changes in the bandgap and phonon spectra in strained MoS₂. We investigate the transition from direct to indirect band gap in MoS₂ under uniaxial strain. The experimental signatures of this transition include strain-induced changes in the PL wavelength and intensity.

Second, we examine the influence of the environment of MoS₂ on its properties. We demonstrate substrate-induced scattering is suppressed in suspended MoS₂ specimens. We use photocurrent spectroscopy to study excitons in pristine suspended MoS₂. We observe band-edge and van Hove singularity excitons and estimate their binding energy. We study dissociation of these excitons and uncover the mechanism of their contribution to photoresponse of MoS₂.

3:00pm **2D+AS+EM+MI+MN+NS+TF-WeA3 Electron-Phonon Coupling and Photoluminescence in Single Layer Transition Metal Dichalcogenides**, Neha Nayyar, V. Turkowski, D.T. Le, T.S. Rahman, University of Central Florida

Single layer MoS₂ and other transition metal dichalcogenides have been the subject of numerous investigations because of their unusual optical, electronic and transport properties. To understand and thereby tune their photoluminescent properties, we have analyzed the role of electron-phonon interactions. Density functional perturbation theory is used to calculate the dispersion of system phonons, while electron-phonon coupling is obtained using the Eliashberg approach. Time-dependent density-functional theory based calculations using the density-matrix approach is employed to study the exciton and trion excitations which are found to appear as peaks in the absorption spectrum in the visible range with binding energy ~0.5 – 1 eV and ~0.02-0.03 eV, correspondingly. The emission peak is found to also lie in the visible spectrum and is sensitive to the value of the electron-phonon coupling, which depends on the nature and extent of doping. The position of the spectral peaks may thus be manipulated by doping. Calculations of the self-energy and spectral functions of doped systems show excitations to have 10-100 fs lifetime, which makes the system interesting for ultrafast applications. Comparison will be made of these optical properties of several single layer dichalcogenides and contact will be made with available experimental data. Work supported in part by DOE Grant No. DOE-DE-FG02-07ER46354

3:20pm **2D+AS+EM+MI+MN+NS+TF-WeA4 Temperature Dependent Photoluminescent Spectroscopy of MoS₂**, Michael Watson, J.R. Simpson, Towson University & NIST, R. Yan, H. Xing, University of Notre Dame, S. Bertolazzi, J. Brivio, A. Kis, EPFL, Switzerland, A.R. Hight-Walker, NIST

We report temperature and power dependent photoluminescence (PL) of molybdenum disulfide (MoS₂). Mechanical exfoliation of MoS₂, from bulk provides single-layer flakes which are then transferred either to sapphire substrates or suspended over holes in Si/SiO₂. We measure temperature dependence from ~100K to 400K and power dependence from ~6μW to ~7mW using an Argon laser at 514.5nm and a HeNe laser at 632.8 nm. The PL spectrum exhibits a main excitonic peak(A) at ~1.87eV which consist of both neutral excitons and charged trions (A- or A+) [1]. The A exciton peak and the A- exciton peak redshift and broaden with increasing temperature and power. Along with the A peak, we observe a lower energy bound exciton (BE) that is likely related to defects. The BE, a broad peak centred at ~1.7eV, linearly redshifts and narrows with increasing power. The power dependence of both the main and bound peak saturates above 0.5mW. Raman temperature and power dependence will also be discussed [2].

[1] K.F. Mak et al. Nat. Mat 12,207(2013)

[2] R.Yan and J.R.Simpson, S. Bertolazzi and J. Brivio, M. Watson, X.Wu and A. Kis, T.Luo, H.G.Xing, A.R. Hight Walker, ACS Nano 8,1 (2013)

4:20pm **2D+AS+EM+MI+MN+NS+TF-WeA7 Effects of Dimensionality on the Raman and Photoluminescence Spectra of and TaSe₂ and TaS₂ Dichalcogenides**, Danilo Romero, University of Maryland, College Park, M. Watson, J.R. Simpson, Towson University, H. Berger, Ecole Polytechnique Federale de Lausanne, Switzerland, A.R. Hight Walker, NIST

We investigate the effects dimensionality on the electronic properties through the optical spectra of the transition-metal dichalcogenides 2H-TaSe₂ and 1T-TaSe₂, and 1T-TaS₂. In bulk, these materials exhibit electronic states from Mott insulator, commensurate and incommensurate charge-density phases, and superconducting ground state as function of temperature. We explore the evolution of these properties as the materials approach a few layers, achieved via mechanical exfoliation of bulk single-crystals. Raman and photoluminescence spectroscopy of 2H-TaSe₂ and 1T-TaSe₂, and 1T-TaS₂, carried out over a wide-range of temperature, were used as a probe of the change of the electronic properties from the bulk to single-layer phases of the materials. Comparison of the phonon and excitonic transitions as a function of temperature and dimensionality will be presented.

4:40pm **2D+AS+EM+MI+MN+NS+TF-WeA8 Few-Layer and Symmetry-Breaking Effects on the Electrical Properties of Ordered CF₃Cl Phases on Graphene**, Josue Morales-Cifuentes, T.L. Einstein, Y. Wang, J. Reutt-Robey, University of Maryland, College Park

An effective potential mechanism for breaking the inherent sublattice symmetry of graphene has been studied using DFT calculations on hexagonal boron nitride.¹ Electrical detection of CF₃Cl phase transitions on graphene shows the existence of a commensurate ordered phase in which this can be tested.² We study the electronic properties of similar phases varying coverage and orientation of CF₃Cl with respect of the graphene substrate using VASP ver 5.3.3, with ab initio van der Waals density functionals (vdW-DF1, vdW-DF2).^{3,4} Consistent with a physisorbed phase, binding energies are calculated to be on the order of 280meV, and insensitive to coverage and orientation of the CF₃Cl molecules. Charge transfer was calculated to be sensitive with coverage, but not orientation, which is qualitatively consistent with experiment. For low coverages, sublattice symmetry breaking effects are responsible for gap openings in the order of 4meV, whereas for large coverages it is the formation of ordered overlayers that opens gaps of 15meV. Furthermore, in bilayer graphene at low coverage we estimate an enhanced gap of 20meV.

[1] Gianluca Giovannetti et al. , PRB **76**, 073103(2007)

[2] Yilin Wang et al. , APL **103**, 201606 (2013)

[3] Jiri Klimes et al. , PRB **83**, 195131 (2011)

[4] Kyuho Lee et al. , PRB **82**, 081101(R) (2010)

5:00pm **2D+AS+EM+MI+MN+NS+TF-WeA9 Optical Anisotropies in Layered Nanomaterials**, Jon Schuller, UC Santa Barbara
INVITED

In nanomaterials optical anisotropies reveal a fundamental relationship between structural and optical properties. In layered materials, optical anisotropies may result from in-plane and out-of-plane dipoles associated with intra- and inter-layer excitations respectively. In this talk, I describe a novel method wherein we resolve the orientation of luminescent excitons and isolate photoluminescence signatures from distinct intra- and inter-layer excitations, respectively. We compare photoluminescence anisotropies in materials with weak or strong interlayer coupling, MoS₂ and the organic semiconductor PTCDA respectively. We demonstrate that photoluminescence from MoS₂ mono-, bi- and trilayers originates solely from in-plane excitons, whereas PTCDA supports distinct in-plane and out-of-plane exciton species with different spectra, dipole strengths and temporal dynamics. The insights provided by this work are important for understanding fundamental excitonic properties in layered nanomaterials and designing optical systems that efficiently excite and collect light from exciton species with different orientations.

5:40pm **2D+AS+EM+MI+MN+NS+TF-WeA11 Mechanical Properties of 2D-Materials**, J.M. Gonzales, University of South Florida, R. Perriot, Los Alamos National Laboratory, Ivan Oleynik, University of South Florida

Graphene and other two-dimensional (2D) materials possess extraordinary mechanical properties, which are currently being explored in various novel applications. Atomic force microscopy (AFM) nanoindentation experiments

on both pristine and polycrystalline samples of 2D materials, while being successful in measuring overall mechanical performance of graphene, require some theoretical input to extract the important mechanical properties. Large-scale atomistic molecular dynamics simulations are used to predict the mechanical properties of 2D materials, such as the elastic moduli, breaking strength, stress/strain distributions, and mechanisms of fracture under conditions of AFM nanoindentation experiments. Perfect, defective, and polycrystalline samples are investigated using large-scale molecular dynamics simulations with a screened environment-dependent bond order (SED-REBO) potential. The mechanisms of crack propagation in both perfect and defective samples will also be presented.

6:00pm **2D+AS+EM+MI+MN+NS+TF-WeA12 Mechanical Control of Structural Phase Transitions in Two-Dimensional Mo- and W-Dichalcogenide Monolayers**, *Evan Reed, K.-A.N. Duerloo, Y. Li*, Stanford University

Mo- and W- dichalcogenide compounds have a two-dimensional monolayer form that differs from graphene in an important respect: it can potentially have more than one crystal structure. Some of these monolayers exhibit tantalizing hints of a poorly understood structural metal-to-insulator transition with the possibility of long metastable lifetimes. If controllable, such a transition could bring an exciting new application space to monolayer materials beyond graphene. Here we discover that mechanical deformations provide a route to switching the thermodynamic stability between a semiconducting and a metallic crystal structure in these monolayer materials. We employ density functional and hybrid Hartree-Fock/density functional calculations including vibrational energy corrections to discover that single layer MoTe₂ is an excellent candidate phase change material. We identify a range from 0.3% to 3% for the tensile strains required to transform MoTe₂ under uniaxial conditions at room temperature. We elucidate the appropriate thermodynamic constraints for monolayers, which can differ from bulk materials. The potential for mechanical phase transitions is predicted for all six studied compounds. The potential application space ranges from catalysis to information storage and nanoscale electronics.

MEMS and NEMS

Room: 301 - Session MN+PS-WeA

Emerging Materials and Fabrication Technologies for MEMS/NEMS

Moderator: Sushma Kotru, The University of Alabama, Meredith Metzler, Cornell University

2:20pm **MN+PS-WeA1 Organic Sensors and Actuators Patterned by Inkjet Printing**, *Tse Nga (Tina) Ng*, PARC (Palo Alto Research Center), a Xerox Company, *J. Kim, W.S. Kim*, Simon Fraser University, Canada, *K.S. Kwon*, Soonchunhyang University, South Korea **INVITED**

Organic materials have been demonstrated as good candidates for large-area sensors, because they allow wide tolerance of sensor geometry and thickness, which would ease fabrication problems such as strain induced cracking on deformable plastic platforms. Organic electronic materials can be deposited and patterned by low-cost printing tools such as inkjet printers. Notably, the printing process is compatible with many substrates ranging from plastics to fibers, to potentially integrate electronics on any surface. At Palo Alto Research Center, we have developed processes for printed electronics that enable new form factors and applications in flexible sensors and circuits. In conjunction with university collaborators, here we present examples of organic mechanical sensors and actuators fabricated by facile solution processes.

The first example is a capacitive pressure sensor patterned by block copolymers. Different microstructures (hemisphere, cones, nano-needles) are explored for the dielectric film, and the dielectric with nano-needles showed the highest sensitivity, with the relative capacitance change up to 176%/kPa. The capacitor with the nano-needle filler was integrated with an inkjet printed OTFT to provide current output. The device sensitivity is comparable to the sensitivity of human skin and will be useful for tactile sensing applications on a wide range of surfaces.

In a second example, we have fabricated a bimorph actuator from electroactive polymer blends with ionic liquid. The polymer blends allow low-voltage operation, and we found that the actuator displacement increases with larger gradient difference in ionic liquid content. A maximum strain of 0.48% was observed. The electroactive polymers are compatible with extrusion printing and have the potential to be patterned through layer-by-layer printing for incorporation into 3d structures.

3:00pm **MN+PS-WeA3 Microfabrication by Etching for Carbon Nanotube Composite Sheets**, *Nathan Boyer, J. Rowley, D.D. Allred*, Brigham Young University, *S. Liddiard*, Moxtek, Inc, *R.R. Vanfleet, R.C. Davis*, Brigham Young University

We have prepared extremely smooth carbon nanotube (CNT)/polymer composite sheets and patterned them with holes and trenches using a process of photolithography and plasma etching. The high strength patterned CNT/polymer composite could be used in MEMS applications. A CNT sheet was impregnated with polyimide and the composite was cured in a vacuum hot press at 400°C. A film of amorphous silicon nitride was deposited on the composite sheet and patterned to act as a hard mask during oxygen plasma etching. Structural and mechanical testing of the CNT composite sheets will be presented along with plasma etching results.

3:20pm **MN+PS-WeA4 High Aspect Ratio Magnetic MEMS Fabricated using Carbon Nanotube Templated Microfabrication**, *Robert Davis, L. Barrett, D. Barton, R.R. Vanfleet, D.D. Allred*, Brigham Young University

We have fabricated nickel microstructures with aspect ratios greater than 20-1, and feature sizes as small as 5 μm . The process involves growing a forest of carbon nanotubes in the desired pattern, and coating the tubes with an additional layer of carbon by CVD. Then the remaining space in the forest, approximately 90%, is filled with nickel by pulsed electroplating. Because the resulting composite has a magnetic response, it is ideal for MEMS magnetic sensors and actuators. To demonstrate this, we constructed a simple MEMS scale sensor with a frame, two flexures and a proof mass. Optical measurement of the proof mass's displacement as a function of applied magnetic field will be shown.

4:20pm **MN+PS-WeA7 Sub-100nm Thin Polycrystalline Diamond Nanomechanical Torsional Resonators**, *Rui Yang, Z. Wang, J. Lee, C.A. Zorman, P.X.-L. Feng*, Case Western Reserve University

We report experimental demonstration of high-frequency (HF) torsional nanomechanical resonators based on nanoscale polycrystalline diamond thin films. We fabricate devices with tethers as thin as 100nm \times 50nm in cross section, measure their multi-mode resonances with frequency (f_{res}) into the HF band (up to \sim 10MHz, while most existing sensitive torsional devices are at kHz or low-MHz), and quality (Q) factors exceeding 2000 at room temperature. We also perform temperature-varying measurements, and observe strikingly different temperature coefficients of frequency (TCf) between the torsional and flexural resonant modes.

Diamond is particularly interesting for micro/nanoelectromechanical systems (MEMS/NEMS), because of its exceptional mechanical properties (Young's modulus greater than 10¹²Pa), relatively low mass density (3500kg/m³), very high thermal conductivity (22W/(cm \cdot K)), and excellent wear/corrosion resistivity¹. Especially, its high sound velocity is attractive for making high frequency mechanical resonators². Resonators based on diamond thin films from microwave plasma chemical vapor deposition have been demonstrated, showing mechanical properties comparable to single crystal. However, *torsional resonators* based on diamond thin films showing resonance in HF band and exceptional force and torque sensitivities have not been explored. While we demonstrated torsional resonators using 1.2 μm -thick SiC film³, *much thinner and smaller devices* are required for higher sensitivities.

Here we fabricate torsional resonators on 50 to 100nm thin polycrystalline diamond films with focused ion beam. We perform Raman spectroscopy to confirm the nanocrystalline diamond nature of the membrane. The mechanical resonances are measured by driving the mechanical motion with a modulated laser (405nm), and detecting the resonant motion with laser interferometry (633nm). These devices show force sensitivity down to the sub-fN/ $\sqrt{\text{Hz}}$ range, and torque sensitivity on the order of 10⁻²² (N \cdot m)/ $\sqrt{\text{Hz}}$, which is similar to the best reported results in other materials⁴. This opens up the possibility for fabricating ultrasensitive devices for force/torque, inertia, and thermal sensing, based on nanocrystalline diamond platform. TCf measurement shows clear and intriguing anti-crossing behavior, which vividly illustrates cross-mode mechanical coupling.

¹ O. Auciello, *et al.*, *J. Phys.-Condens. Mat.* **16**, R539 (2004).

² L. Sekaric, *et al.*, *Appl. Phys. Lett.* **81**, 4455-4457 (2002).

³ R. Yang, P. X.-L. Feng, *et al.*, *Appl. Phys. Lett.* **104**, 091906 (2014).

⁴ X. C. Zhang, *et al.*, *Nano Lett.* **13**, 1528 (2013).

4:40pm **MN+PS-WeA8 Temperature Compensated Graphene Nanomechanical Resonators**, Jaesung Lee, Case Western Reserve University, H.-Y. Chiu, University of Kansas, P.X.-L. Feng, Case Western Reserve University

Graphene-based atomically-thin two-dimensional (2D) nanostructures have emerged as new building blocks for novel nanoelectromechanical systems (NEMS) [1], which can enable nanodevices with unprecedented performances such as ultrasensitive detectors and highly tunable oscillators [2] In addition to its excellent mechanical properties, such as ultralow areal density ($r_A=0.74\text{fg}/\mu\text{m}^2$), ultrahigh strain limit ($\sim 25\%$), and large Young's modulus ($E_Y\sim 1\text{TP}$), graphene has superior thermal properties, which can enable large temperature range operations and ultra-stable high temperature performances. In addition, the unique negative thermal expansion coefficient of graphene can be employed to tune the device tension and thus its resonance behavior through controlling the device temperature. To date, most experimental investigations of graphene resonators are at room temperature or below, with high temperature operation remaining largely unexplored.

In this work, we experimentally study graphene resonators from room temperature to $\sim 600\text{K}$ and study their resonance characteristics by measuring the thermomechanical noise. Our graphene resonators show relatively small frequency shifts from 300K to 600K due to natural temperature compensation from the different thermal expansion coefficients of graphene and other structural metals. We further examine temperature profile in graphene resonators, and establish resonator models with wide range temperature operation, elucidating temperature compensation mechanisms in graphene resonators. This study will help improve the understanding and development of both temperature-sensitive and insensitive 2D NEMS resonators, which can lead towards future large temperature range and high temperature application of 2D NEMS.

References:

- [1] J. Lee, P. X.-L. Feng, *IEEE International Frequency Control Symposium (IFCS'12)*, DOI: 10.1109/IFCS.2012.6243742 (7 pages), Baltimore, MD, May 21-24 (2012).
- [2] C. Chen, J. Hone, *Proc. IEEE***101**, 1766-1779 (2013).
- [2] C. Chen, S. Rosenblatt, K. I. Bolotin, W. Kalb, P. Kim, I. Kymissis, H. L. Stormer, T. F. Heinz, and J. Hone, *Nature Nanotech.***4**, 861- 867 (2009).

5:00pm **MN+PS-WeA9 A Porous Material for Improving Cantilever Q in Air and Liquid for Resonant Mechanical Sensing**, Steven Noyce, R.C. Davis, R.R. Vanfleet, Brigham Young University, H.G. Craighead, Cornell University

Nanoporous cantilever resonators have potential performance advantages for cantilever based sensing. For porous cantilevers a high surface area leads to a high adsorbed mass which is independent of the cantilever dimensions. Larger cantilever dimensions can lead to higher quality (Q) factors in air and liquid sensing environments. Here we present work on the fabrication of nanoporous carbon/carbon nanotube composite cantilevers. Our results include characterization work on tuning the composite materials properties and cantilever geometries for high Q in fluid.

5:20pm **MN+PS-WeA10 XPS to Investigating Spatial and Temporal Modification of PDMS Platforms for Micro-Fluidic Devices**, Marshal Dhayal, CSIR- Centre for Cellular and Molecular Biology, India

Spatial and temporal changes in surface chemical composition silicon (Si), carbon (C) and oxygen (O) of polydimethyl siloxane (PDMS) surfaces before and after plasma treatment were estimated from quantitative elemental analysis of X-ray photoelectron spectroscopy (XPS) wide scan spectra. Theoretical ratio of Si/C/O in repeating unit $(-\text{Si}(\text{CH}_3)_2\text{O})_n-$ of PDMS were calculated and were compared to experimentally obtained ratio for Si/C/O obtained from untreated and plasma PDMS surfaces used for micro-fluidic devices. The contact angle measurements have shown that (PDMS) surfaces treated by air plasma can recover up to about 50% of its hydrophobic nature in less than 30 min of air exposure. These plasma modified surfaces were functionalized with poly(ethylene glycol) (PEG) silane to obtained PDMS surface as hydrophilic in nature for micro fluidic application. The surface chemistry of PEG-functionalized PDMS substrate has been studied using XPS. These different types of surfaces were used fabricate micro-fluidic devices and effects of surface nature of micro channels on fluid velocity were observed in PEG grafted micro channel in PDMS base micro fluidic devices. The effect of different pH of the fluids on the fluid velocity in PDMS-based micro channel was also studied.

5:40pm **MN+PS-WeA11 A Microplasma-based Sputtering System for Direct-Write, Micropatterning of Metal Structures**, Edwin Burwell, A.C. Barnes, P.X.-L. Feng, M. Sankaran, C.A. Zorman, Case Western Reserve University

Patterning metal as a contact or interconnect is a critical processing step for device fabrication in a wide range of applications ranging from conventional electronics on silicon chips to implantable biosensors on flexible polymeric substrates. Traditionally, physical vapor deposition is combined with photolithography to deposit patterned metal films. Although this subtractive approach produces high pattern fidelity and conductivity, low throughput, materials wastage, and need for vacuum lead to high production costs and limited scalability. The emergence of flexible devices has stimulated the desire for additive approaches such as ink-jet printing for depositing patterned conductive materials. Ink-based printing is carried under ambient conditions and can be integrated with roll-to-roll systems for large-scale manufacturing. However, the inks can be expensive and the variety of materials that are available as printable inks is very small. In addition, the organic capping agents that are used to stabilize the particles are difficult to remove, which can compromise conductivity and mechanical integrity. Removal of the organics requires high annealing temperatures that limit the usage of certain polymers and other temperature-sensitive substrates. Adhesion of the printed structures to the substrates can also be a significant issue, especially in flexible applications.

In this paper, we describe a microplasma-based process to deposit patterned structures with micro- to nanoscale dimensions on rigid or flexible conducting and insulating substrates. This direct-write, additive process uses plasma-based sputtering to generate a physical vapor comprised of the material of interest. The plasma is generated within a small capillary tube that is capped with a micron-sized orifice. The sputtering target consisting of a micron-sized wire is positioned inside the capillary. Forced Ar flow aids in the ejection of the resulting physical vapor through the orifice, which is positioned in close proximity to the substrate. The process is performed at atmospheric pressure, thereby addressing the most significant limitation associated with conventional magnetron sputtering and thermal evaporation, and is low temperature, allowing deposition on temperature-sensitive substrates such as polymers and paper. To date, we have successfully deposited patterned Au structures that are submicron in thickness and 150 microns in width on glass substrates. Our presentation will detail the apparatus, the principal of operation, and the most current results in creating and characterizing micropatterned metal structures on insulating substrates.

Thursday Morning, November 13, 2014

Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Focus Topic

Room: 317 - Session QC+AS+BI+MN-ThM

Fundamentals and Method Development of QCM

Moderator: Ralf Richter, CIC biomaGUNE & MPI for Intelligent Systems, W.K. Hiebert, University of Alberta and The National Institute for Nanotechnology

8:40am **QC+AS+BI+MN-ThM3 High-Frequency Contact Mechanics Studies with a QCM.** *Diethelm Johannsmann*, Clausthal University of Technology, Germany **INVITED**

Studying particulate objects with a QCM is challenging with regard to interpretation, but also of outstanding interest. Potential samples would be (bio-) colloids, vesicles, granular matter, bacteria or technical multi-contact interfaces. The analysis must build on the small-load approximation, which states that the shifts in resonance frequency and resonance bandwidth are proportional to the in-phase and the out-of-phase component of the area-averaged stress at resonator surface. For realistic modeling, a numerical code is needed which predicts this stress field from the geometry and all materials parameters involved. There is such a model in two dimensions, building the finite element method.

On a simpler level, the behavior of particles on a resonator surface can also be understood from the coupled resonance model. The particles in contact form small resonators of their own, where the “particle resonance frequency” is determined by the mass and the stiffness of the contact. If the particle resonance frequency in the range of frequencies amenable to the QCM one observes a coupled resonance, meaning that the shifts of resonance frequency and resonance bandwidth themselves form a resonance curve when plotted versus overtone order. Depending on whether the particle resonance frequency is higher or lower than the QCM frequency, the frequency shift can be positive or negative. From the particle resonance frequency, one can assess the stiffness of the contact between the particle and the surface.

The detailed investigation of the coupled resonance picture reveals a problem. though. FEM models of the corresponding geometries reveal two coupled resonance, occurring at different frequencies. They corresponding to a rotation of the particle about the point of contact (the “rocking mode”) and a rotation about the center of mass (the rotational mode”). The problem complicates the interpretation of experimental data, but it points to an intriguing analogy between QCM experiments a vibrational spectroscopy. A QCM experiment amounts to a vibrational spectroscopy on surface-attached colloids.

The last part of the talk is concerned with a novel sensing dimension of the QCM, which is the dependence of frequency and bandwidth on amplitude. Such dependences are ubiquitous in contact mechanics experiments and can be understood in terms of partial slip. The contacts behave nonlinearly. Nonlinear behavior can also be observed in liquids, where it is caused by the nonlinear term in the Navier-Stokes equation. The nonlinear term drives a steady flow of liquid along the direction of oscillation towards the center of the plate.

9:20am **QC+AS+BI+MN-ThM5 Study of Water Adsorption and Capillary Bridge Formation for SiO₂ Nanoparticle Layers by Means of a Combined In Situ FT-IR Reflection Spectroscopy – QCM-D Set-up.** *Boray Torun, C. Kunze*, University of Paderborn, Germany, *C. Zhang, T.D. Kühne*, Johannes Gutenberg University Mainz, Germany, *G. Grundmeier*, University of Paderborn, Germany

During the past decade nanoparticles attracted a great deal of attention and found many applications in various fields ranging from pigments and antibacterial agents to highly effective catalysts. In this context, the handling and processing of nanoparticle powders play an important role. In contrast to macroscopic particles, nanoparticle flow properties are mainly governed by the particle-particle interactions. The forces determining these interactions strongly vary not only with the material properties but also with surface chemical composition as well as the environmental conditions. Hence, a fundamental understanding of the processes and forces involved plays a key role for the prediction of nanoparticle powder behavior.

In the presented study^[1], water adsorption and capillary bridge formation within a defined layer of SiO₂ nanoparticles was studied by means of a novel *in-situ* analytical setup allowing for combined quartz crystal microbalance with dissipation analysis (QCM-D) and Fourier

transformation infrared reflection absorption spectroscopy (FT-IRRAS). On the one hand, the QCM-D gave insights on both, mass change (Δf) and changes in the contact mechanics, indicated by dissipation changes ($\Delta \Gamma$), whereas on the other hand FT-IRRAS allowed for the characterization of the adsorbed water structure. Employing peak deconvolution to the OH-signal in the region of 3400 cm⁻¹, “ice-like” and “liquid-like” water structures could be clearly identified.

Combined measurements show that for a monolayer of monodisperse SiO₂ particles with a diameter of about 250 nm the adsorption of water leads to a linear increase in dissipation for relative humidity (RH) values up to 60%. Subsequently, the strong increase in dissipation between 60% and 80% RH was attributed to the actual liquid bridge formation. This result was supported by the predominant growth of “liquid-like” water during the bridge formation phase indicated by the corresponding FT-IR data. Furthermore, for RH > 90% a decrease in dissipation was detected indicating the merging of capillaries and the onset of a water film formation. Overall, our results indicate that combined *in-situ* QCM-D and FT-IRRAS analysis enables the qualitative and quantitative analysis of water adsorption and capillary bridge formation in particle layers.

[1] Torun, B. et al., *Phys. Chem. Chem. Phys.*, **2014**, 16, 7377-7384

9:40am **QC+AS+BI+MN-ThM6 On the Role of Acoustic Streaming in Particle Detachment Events at a QCM Surface.** *Rebekka König, A. Langhoff, D. Johannsmann*, Clausthal University of Technology, Germany

A steady flow of liquid was observed above the surface of a quartz crystal microbalance (QCM) under conditions, where the oscillation amplitude exceeded 10 nanometers. The streaming flow occurs parallel to the displacement vector and is directed towards the center of the plate. It is expected to have applications in acoustic sensing, in microfluidics, and in micromechanics in a wider sense. The flow is caused by the nonlinear term in the Navier-Stokes equation, which can produce a nonzero time-averaged force from a periodic velocity field. Central to the explanation are the flexural admixtures to the resonator's mode of vibration. Unlike pressure-driven flows, the acoustically driven steady flow attains its maximum velocity at a distance of a few hundred nanometers from the surface. It is therefore efficient in breaking bonds between adsorbed particles and the resonator surface. As a side aspect, the flow pattern amounts to a diagnostic tool, which gives access to the pattern of vibration. In particular, it leads to an estimate of the magnitude of the flexural admixtures to the thickness-shear vibration.

[1] R. König, A. Langhoff, D. Johannsmann, *Physical Review E* **2014**.

11:00am **QC+AS+BI+MN-ThM10 QCM for Particle Sizing and Beyond.** *Adam Olsson, I.R. Quevedo, D. He, M. Basnet, W. Lee, N. Tufenkji*, McGill University, Canada **INVITED**

The dissipative energy loss of a quartz crystal microbalance (QCM) sensor is typically ascribed to the viscoelastic nature of the adsorbed material. While such an interpretation is suitable for thin homogeneous films, it is not *a priori* valid for discrete objects. As demonstrated recently, dissipation due to nanoparticle deposition can be described by the relative movement of the particles attached to the oscillating sensor surface. This particular dissipation behavior of nanoparticles gives rise to new experimental approaches to study colloidal transport, particle-surface interactions and particle properties.

In this presentation, we focus on QCM-D as a method to determine the size of deposited nanoparticles. The approach involves analysis of the change in dissipation per attached mass (i.e., the “ $\Delta D/\Delta f$ -ratio”) to predict a hypothetical full particle surface coverage that can be used to calculate an effective layer thickness of the particulate film; and this quantity, in turn, can be related to the average particle diameter. To validate the approach, we determined particle sizes using various types of nanoparticles with diameters ranging from ~ 5 nm to ~ 110 nm and compared the results with sizes obtained from dynamic light scattering (DLS) and transmission electron microscopy (TEM). We found that accurate particle sizing is possible, but requires firm coupling between the particle and the sensor surface. Hence, if the particle size is known, the approach can also be used to investigate the strength of the nanoparticle-surface interaction.

We will also describe our ongoing work where we are studying the QCM-D response to the deposition of anisotropic bacteriophage to determine their orientation on the surface. Bacteriophages are viruses that bind to and infect bacteria with high specificity and, thus, can be exploited in antimicrobial and biosensor applications. One challenge in functionalizing surfaces with bacteriophages is to control their orientation such that their binding sites remain exposed to the ambient medium. By studying how dissipation changes with phage surface coverage, it is possible to identify at which surface coverage phage-phage interaction occurs. This event compromises

the phages ability to bind to bacteria, as evidenced by subsequent bacterial “capture” experiments and imaging, and thus is crucial for the performance of QCM-D based biosensors that utilize bacteriophage as a biorecognition element.

11:40am **QC+AS+BI+MN-ThM12 Full Experimental Proof of the Relationship between the Intrinsic Viscosity of DNA and the Acoustic Ratio of SAW and TSM Sensors**, *Achilleas Tsortos*, IMBB-FORTH, Greece, *G. Papadakis*, NCSR-Demokritos, Greece, *E. Gizeli*, IMBB-FORTH & Univ. of Crete, Greece

Acoustic wave sensors are extensively used in biotechnology and biophysics in order, for example, to detect molecules in a solution, study an antibody-antigen interaction or the hybridization of DNA. Today, data analysis includes (a) the use of the Sauerbrey equation, in order to calculate the mass of the molecules attached on the surface of the acoustic device by use of frequency data and (b) the use of complicated mathematical models of the assumed ‘film’ formed by the attached molecules. In the second case information such as the rigidity modulus and viscosity of the ‘film’ can be calculated and comments can be made on the softness (viscoelasticity) of the added layer.

Here, we present an entirely different approach. Based on a theory developed earlier^{1,2} we correlate the acoustic ratio R , to the intrinsic viscosity $[\eta]$ of the attached molecule. The acoustic ratio is the ratio of the amount of energy loss per attached unit mass – this is given as $(\Delta D/\Delta F)$ in the TSM acoustic mode notification, or as $(\Delta A/\Delta Ph)$ in the SH-SAW mode and is readily obtained in each experiment. The *intrinsic* viscosity on the other hand, is a hydrodynamic quantity directly related to the size and shape of a biomolecule and can be determined independently through viscometry. In this study we present collected experimental data from a variety of case studies proving for the first time the semi-empirically assumed relationship $R \sim [\eta]$ in a general form. Data are presented for various shapes and sizes of DNA and other systems of biological interest. The case is made for two acoustic modes (thickness shear and surface horizontal) and for various frequencies in the range of 5-155 MHz.

Our analysis presents a paradigm shift and challenge; we claim that (label-free) structure probing is a much more improved method offering higher flexibility in design and interpretation of experimental assays. Detecting and monitoring in real time processes that involve structural changes but not necessarily mass changes and/or ‘film’ formation is a novel concept that can be readily applied in anything from DNA, RNA hybridization and detection of mutations to molecular machines (e.g. DNA Holliday junction) and protein/DNA/RNA interactions in the broad areas of biophysics, structural DNA nanotechnology and diagnostics.

Acknowledgement: the REGPOT-InnovCrete/EU-FP7 (Contract No. 316223) for financial support.

References:

1. A. Tsortos, et al., *Biophys. J.* 2008, 94:2706
2. A. Tsortos, et al., *Biosens. Bioelectron.* 2008, 24:836

12:00pm **QC+AS+BI+MN-ThM13 Characterization of the Conformation of Linker-Suspended Proteins at Surfaces through Acoustic Ratio Measurements**, *Electra Gizeli*, IMBB-FORTH & Univ. of Crete, Greece, *D. Milioni*, IMBB-FORTH, Greece, *G. Papadakis*, NCSR-Demokritos, Greece, *A. Tsortos*, IMBB-FORTH, Greece

Characterization of protein shape and orientation following surface binding is an area of great interest in biophysics with many applications in chemistry and nano/biotechnology. Techniques such as ellipsometry and AFM have been extensively used for providing such information. A lot of effort has also been put with acoustic sensors; results in this case though depend greatly on the data interpretation model employed. An important question is always the preservation of protein integrity/form.

In this work we employ acoustic devices based on a QCM geometry at 35 MHz. The acoustic ratio $\Delta D/\Delta F$, i.e., the dissipation over frequency change of the shear wave has been employed in our analysis. We have previously shown¹ that as a tool, this ratio provides valuable information regarding the conformation of surface attached DNA molecules; we have also employed this approach in the design of DNA assays for diagnostic purposes, including detection of sequence targets in real samples².

Here we expand this methodology in proteins; streptavidin is used as a case study for characterizing spherical protein immobilization on an acoustic device. Good control of the binding mode was achieved by changing the distance of the protein from the surface, ranging from zero (direct physisorption) to several nm, using anchor molecules. In this way we can manipulate the degree of surface interference to the protein structure. Our results clearly show that direct protein adsorption is a multistep process resulting in very low acoustic ratio, in agreement with the literature. However, we show for the first time that suspending the protein away from the surface from a single point through a variable-length linker, gives an

entirely different picture; the process is a single-step event, as judged from D-F plots, and the resulting acoustic ratio is much higher (order of magnitude) than that obtained in physisorption. The effect of the linker length on the apparent acoustic ratio is analyzed. This approach gives more reliable and different information regarding the protein shape than do simple physisorption protocols and interpretation models involving notions such as ‘film’ formation etc.

References:

1. A. Tsortos, et al., *Biosens. Bioelectron.* 2008, 24:836; A. Tsortos et al., *Biophys. J.* 2008, 94:2706
- G. Papadakis et al., *Anal. Chem.* 2012, 84:1854; G. Papadakis et al., *Scientific Rep.* 2013, 3:2033

Thursday Afternoon, November 13, 2014

2D Materials Focus Topic

Room: 310 - Session 2D+EM+MI+MN+NS+SS+TF-ThA

Novel Quantum Phenomena in 2D Materials

Moderator: Alexander Sinitskii, University of Nebraska-Lincoln

2:20pm **2D+EM+MI+MN+NS+SS+TF-ThA1 Optoelectronics of Two-Dimensional Semiconductors, Xiaodong Xu, University of Washington**
INVITED

Two dimensional transition metal dichalcogenides are a recent addition to the 2D electronic materials family. They have shown outstanding electrical and optical properties for new optoelectronic device concepts. In this talk, we will first discuss the unique interplay between spin, valley, and layer pseudospins in bilayer WSe_2 . Such coupling effects lead to electrical control of spin states and optical generation of valley coherence through interlayer triions, where electrons and holes are localized in different layers. We will then talk about optoelectronic devices based on monolayer WSe_2 , including p-n junctions as light emitting diodes and hybrid monolayer semiconductor/photonic crystal cavity devices. We will conclude the talk with a discussion of the optoelectronic properties of MoSe_2 - WSe_2 heterostructures.

3:00pm **2D+EM+MI+MN+NS+SS+TF-ThA3 Theory of Graphene Transport Barriers in the Specular Limit, Daniel Gunlycke, C.T. White, Naval Research Laboratory**

Offering room-temperature ballistic electron transport well over one micron, while being atomically thin and planar, graphene is undeniably a promising material for future nanoelectronic devices. Presently, however, switchable devices have normally low on-off ratios, a reflection of the challenge of selectively blocking electron and hole carriers from propagating across the graphene surface. This has stimulated a lot of research on different methods for making graphene nanoribbons that exhibit suitable band gaps. An alternative way to obtain a controllable gap takes advantage of resonant tunneling across a pair of transport barriers. For the latter approach, the key is to find a barrier that is fairly reflective but not so much as to effectively cut off all transport across it.

In this presentation, we present a model for straight transport barriers in graphene in the specular limit. Using the Lippmann-Schwinger equation, we obtain the wave function, from which we derive the reflection and transmission probabilities, as well as the local density of itinerant states. This local density of states exhibits fluctuations arising from quantum interference between incoming and outgoing matter waves that allow the transport properties of a barrier to be estimated without explicitly probing the current across the barrier. Our model is tested against exact multi-channel, tight-binding quantum transport calculations for graphene with weak local potentials, local strain, local adsorption, and a locally defective structure. As the model parameters are related to observable quantities, they could be obtained from theory and/or experiment, allowing the model to be adopted even when the precise details of the barrier are unknown.

3:20pm **2D+EM+MI+MN+NS+SS+TF-ThA4 Tip-induced Potential Confinement on Graphene in Scanning Tunneling Microscopy Measurement, Yue Zhao, J. Chae, J.E. Wyrick, NIST/CNST, F.D. Natterer, Ecole Polytechnique Fédérale de Lausanne (EPFL), France, S. Jung, Korea Research Institute of Standards and Science (KRISS), A.F. Young, C.R. Dean, L. Wang, Y. Gao, Columbia University, J.N. Rodrigues, Graphene Research Centre, NUS, Singapore, K. Watanabe, T. Taniguchi, National Institute for Materials Science (NIMS), Japan, S. Adam, Graphene Research Centre, NUS, Singapore, J.C. Hone, K. Shepard, P. Kim, Columbia University, N.B. Zhitenev, J.A. Stroscio, NIST/CNST**

Graphene is a two-dimensional-electron-gas(2DEG) system with exposed surface, which allows scanning tunneling microscopy (STM) to investigate the electron-electron interaction associated with the Dirac nature on a local scale, with a variety of tuning knobs, such as carrier density, spatially varying disorder potential, and applied magnetic field. However, the electron-electron interaction in graphene is sensitive to the disorder details. Moreover, tip induced potential confinement can significantly complicate the interpretation of STM experiment. Utilizing a high mobility graphene device with low residual disorder, we can minimize the effect of local potential fluctuation, to better understand the role tip-induced potential plays in the measurement. We observed the emergency of large spectra gaps, modification to graphene Landau levels (LLs), and quantum dots with changing size due to the spatially inhomogeneous tip gating.

4:00pm **2D+EM+MI+MN+NS+SS+TF-ThA6 Topological Phase Transitions and Spin-orbit Density Waves, Hugo Dil, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland**
INVITED

In recent years systems where the spin-orbit interaction (SOI) is not just a perturbation but the main energy scale have received increasing attention. In combination with a broken inversion symmetry in the crystal structure or at interfaces, SOI will lift the spin degeneracy and induce a complex Fermi surfaces and spin textures with spin momentum locking [1,2]. Furthermore, the SOI can drive the system through a phase transition to a so-called topological insulator. Being an insulator in the bulk these systems are characterized by spin-polarized, topologically protected interface states.

After a short introduction to the role of topology in the band structure of solids I will give an overview of our main spin- and angle-resolved photoemission (SARPES) results on a variety of non-interacting topological insulators [3]. One of the questions is how the spin texture evolves around a topological transition. We explored the occurrence of spin polarized states around a SOI driven topological transition [4] and around a structure driven topological transition [5]. In both cases we observe spin-polarized precursor states, which indicate that although the topological transition is sharp, the response of the system is more gradual.

From a fundamental point of view the truly interesting aspect of non-trivial spin textures lies in their combination with other interactions. This can result in a variety of phenomena, cumulating in the creation of the elusive Majorana Fermion. An example of a combination of interactions is our recent verification with SARPES of SbB_6 as a topological Kondo insulator [6]. In topologically trivial systems, interactions can lead to the formation of a so-called spin-orbit density wave. I will show how the combination of a large spin-splitting and Fermi nesting leads to the formation of such a state and can explain the anisotropic behavior of Pb nanowires [7]. Furthermore, I will present our recent SARPES results for transition metal oxide surfaces where a subtle interplay between ferroelectricity and magnetic order results in the formation of a single spin-polarized energy contour. The occurrence of superconductivity in such systems could render it a 2D Majorana platform.

[1] J.H. Dil, J. Phys: Cond. Mat. 21, 403001 (2009)

[2] G. Landolt et al. Phys. Rev. Lett. 109, 116403 (2012)

[3] D. Hsieh et al. Science 323, 919 (2009); D. Hsieh et al. Nature 460, 1101 (2009); S.Y. Xu et al. Science 332, 560 (2011); S. Ereemeev et al. Nature Comm. 3, 635 (2012)

[4] S.Y. Xu et al. arXiv:1204.6518

[5] G. Landolt et al. Phys. Rev. Lett. 112, 057601 (2014)

[6] N. Xu et al. Nature Materials (2014)

[7] C. Tegenkamp et al. Phys. Rev. Lett. 109, 266401 (2012)

4:40pm **2D+EM+MI+MN+NS+SS+TF-ThA8 The Symmetry Dependent Band Structure of MoS_2 , Duy Le, University of Central Florida, T. Komesu, University of Nebraska-Lincoln, Q. Ma, University of California, Riverside, E.F. Schwier, H. Iwasawa, Hiroshima University, Japan, M. Shimada, Higashi-Hiroshima, Japan, T.S. Rahman, University of Central Florida, L. Bartles, University of California, Riverside, P.A. Dowben, University of Nebraska-Lincoln**

We will present results of density functional theory (DFT) based calculations of symmetry dependent band structures of single crystal $\text{MoS}_2(0001)$ surface together with symmetry-polarized angle resolved photoemission spectroscopy (ARPES) derived experimental band structure. The good agreement of the DFT band structure with the experimentally derived bands with even and odd symmetries, attests to the reliability of the results. We performed ARPES at the Hiroshima Synchrotron, determining the MoS_2 band structure separately for both p- and s-, polarized to distinguish even and odd symmetry, and the experimentally determined dispersion, in accordance with expectations and experimental confirmation of C_{3v} symmetry, argues in favor of an experimental band structure obtained from single domains. The comparison of theory and experiment provides strong indications that the bands at the top of the valence band are dominated by Mo 4d states. These states and indeed placement of the valence band can be perturbed by adsorbates. Indeed, we find that, under the effect of Na adsorption, the changing placement of the valence band structure of MoS_2 clearly indicate the Na atoms donate electrons to MoS_2 and that the Fermi energy level shifts as much as 0.5 eV with respect to the top of MoS_2 's valence band. Surprisingly, Na adsorption does not perturb the MoS_2 band dispersion significantly. We will discuss these results in the light of those obtained for single layer MoS_2 for insights and clarity.

5:00pm **2D+EM+MI+MN+NS+SS+TF-ThA9 CuIn_{1-m}P₂S₆ - Room Temperature Layered Ferroelectric**, Alex Belianinov, P. Maksymovych, Oak Ridge National Laboratory, A. Dziugys, Vilnius University, Lithuania, Q. He, Oak Ridge National Laboratory, E. Eliseev, National Academy of Sciences of Ukraine, A. Borisevich, Oak Ridge National Laboratory, A. Morozovska, NAS of Ukraine, J. Banys, Vilnius University, Lithuania, Y. Vysochanskii, Uzhgorod University, Ukraine, S.V. Kalinin, Oak Ridge National Laboratory

We have utilized ambient and Ultra High Vacuum Scanning Probe Microscopy tools to explore ferroelectric properties in cleaved 2D flakes of copper indium thiophosphate, CuIn_{1-m}P₂S₆ (CITP), and report on size effect and presently achievable limits of ferroelectric phase stability. CITP is an unusual example of a layered, anti-collinear, uncompensated, two-sublattice ferroelectric system. These are the only materials known to display “2-D” ferroelectric semiconductor behavior in a van-der-Waals crystal. The material exhibits a first-order phase transition of order–disorder type from the paraelectric to the ferroelectric phase at $T_c = 315$ K. Our observations suggest the presence of stable ferroelectric polarization as evidenced by domain structures, rewritable polarization, and hysteresis loops. These observations suggest that flakes above 100 nm have bulk-like polarization and domain structures, whereas below 50 nm polarization disappears. Furthermore, the materials have measurable ionic mobility, as evidenced both by macroscopic measurements and by formation of surface damage above tip bias of 4 V, likely due to copper reduction. We ascribe this behavior to well-known instability of polarization due to depolarization field, along with internal screening by mobile Cu ions, as suggested by their high ionic mobility.

Acknowledgement:

Research for (AB, PM, QH, AB, SVK) was supported by the US Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division. Research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy.

5:20pm **2D+EM+MI+MN+NS+SS+TF-ThA10 Doping Efficiency and Mechanisms of Single and Randomly Stacked Bilayer Graphene by Iodine Adsorption**, Hokwon Kim, A. Tyurnina, Univ. Grenoble Alpes/CEA, LETI, France, J.-F. Guillet, J.-P. Simonato, J. Dijon, Univ. Grenoble Alpes/CEA, LITEN, France, D. Rouchon, D. Mariolle, N. Chevalier, O.J. Renault, Univ. Grenoble Alpes/CEA, LETI, France

The precise control of graphene's conductivity and work function is crucial in developing practical applications of graphene based electronics. In order to enhance the conductivity of graphene, we employed a simple doping method where graphene films produced by chemical vapor deposition and transferred onto SiO₂, Al₂O₃, and WO₃ substrates are p-doped with iodine vapor through physisorption at temperature of ~ 100 °C [1-3]. The work function values and iodine to carbon ratios of the one-layer (1L) and two-layer (2L) folded regions were analyzed by high spatial- and energy resolution X-ray photoelectron emission microscopy (XPEEM) on a NanoESCA instrument. After the iodine doping, the work function values were significantly increased up to ~0.4 eV and ~0.5 eV, respectively, for 1L and 2L graphene on SiO₂/Si. This higher degree of doping by iodine was corroborated by I 3d_{5/2} core level imaging of the same area where the 2L graphene exhibited significantly larger concentration of iodine (2 at. % versus 1 at. %) likely due to the intercalation of iodine at the inter-layer space.

The main iodine species identified by high resolution core level X-ray photoemission spectroscopy and Raman spectroscopy were I₃⁻ and I₅⁻ polyiodide anionic complexes with slightly higher concentration of I₅⁻ in 2L than 1L graphene possibly due to different doping mechanisms. Temperature dependent ultra-high-vacuum, in-situ annealing of the doped films has demonstrated that most of iodine is removed above 300 °C for the both 1L and 2L regions, although a significant removal of iodine is observed for 2L graphene at temperature as low as 100 °C. Surprisingly, after the complete removal of iodine by annealing, the work function value did not return to the original one before the doping treatment and remained at a much higher value. This can be ascribed to the residual hydrocarbon contaminations interacting with the atomic defects within the graphene layer that lead to unintentional n-type doping in our samples[4].

Acknowledgement: The XPEEM and KFM measurements were performed at the Nanocharacterization Platform (PFNC).

References

- [1] L. Grigorian, K.A. Williams, S. Fang, G.U. Sumanasekera, A.L. Loper, E.C. Dickey, S.J. Pennycook, P.C. Eklund, Phys. Rev. Lett., (1998) 5560-5563.
- [2] A.B. Kaiser, Rep. Prog. Phys., (2001) 1.

[3] S.W. Chu, S.J. Baek, D.C. Kim, S. Seo, J.S. Kim, Y.W. Park, Synth. Met., (2012) 1689-1693.

[4] B.H. Kim, S.J. Hong, S.J. Baek, H.Y. Jeong, N. Park, M. Lee, S.W. Lee, M. Park, S.W. Chu, H.S. Shin, J. Lim, J.C. Lee, Y. Jun, Y.W. Park, Sci. Rep., (2012).

5:40pm **2D+EM+MI+MN+NS+SS+TF-ThA11 Use of XPS for Device Characterization**, P. Aydogan, E.O. Polat, C. Kocabas, Sefik Suzer, Bilkent University, Turkey

A noncontact chemical and electrical measurement technique of XPS is utilized to investigate a number of devices made of graphene. The main objective of the technique is to trace chemical and location specific surface potential variations as shifts of the XPS peak positions under operating conditions. Devices consisting of graphene; (i) acting as a simple resistive element between two gold electrodes, (ii) a semiconducting sheet controlled by a back-gate, and (iii) between the source and the drain metal electrodes in a full transistor geometry, have been analyzed by recording the Au4f of the metal electrodes, the C1s of the graphene layer, and the O1s (or N1s) peaks of the silicon oxide (or nitride) of the substrate. The advantage of this technique is its ability to assess element specific surface electrical potentials of devices under operation based on the deviations of the core level peak positions in surface domains/structures. Detection of the variations in electrical potentials and especially their responses to various stimuli gives unprecedented information about the chemical nature as well as the location of structural and/or other types of defects as a result of doping, oxidation, reduction, etc.

Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Focus Topic

Room: 317 - Session QC+AS+BI+MN-ThA

Applications of QCM

Moderator: Electra Gizeli, IMBB-FORTH, Heraklion, Crete, Greece, Adam Olsson, McGill University, Canada

2:20pm **QC+AS+BI+MN-ThA1 Permeability of a Model Stratum Corneum Lipid Membrane**, Daeyeon Lee, University of Pennsylvania
INVITED

The stratum corneum (SC), composed of corneocytes and intercellular lipid membranes, is the outermost layer of the epidermis, and its main function is the regulation of water loss from the skin. The major components of the SC lipid membranes are ceramides (CER), cholesterol (CHOL), and free fatty acids (FFA), which are organized in multilamellar structures between corneocytes. The intercellular SC lipid membrane is believed to provide the main pathway for the transport of water and other substances through the skin. While changes in the composition of the SC lipid membranes due to intrinsic and/or extrinsic factors have been shown to affect the organization of the lipid molecules, little is known about the effect of compositional changes on their water permeability. In this talk, I will present our results on the effect of composition on the permeability of a model SC lipid membrane consisting of ceramide, palmitic acid, and cholesterol using a quartz crystal microbalance with dissipation monitoring (QCM-D). The QCM-D method enables the direct determination of the diffusivity (D), solubility (S), and permeability (P) of water through the model SC lipid membranes. In the first part, I will discuss the effect of membrane composition on the water permeability of the model SC lipid membrane. We find that D and S weakly depend on the chain length of saturated fatty acids, while P shows no significant dependence. In contrast, the saturation level of free fatty acids and the structure of ceramide have significant influence on D and S, respectively, resulting in significant changes in P. In the second part of the talk, I will present our recent work on the effect of common anionic surfactants on the water permeability of the model SC lipid membrane. Particularly, the effect of sodium dodecyl sulfate (SDS) and sodium lauryl ether sulfate (SLES) with one or three ethoxy groups on the water permeability of the model SC lipid membrane is compared.

3:00pm **QC+AS+BI+MN-ThA3 Investigation of Interaction between Monoclonal Antibody and Solid Surfaces via Multiple Surface Analytical Techniques**, Xia Dong, C.A.J. Kemp, Z. Xiao, Eli Lilly and Company

The interaction between proteins and surfaces is an important topic in the field of biomaterials. With the development of monoclonal antibody products, there is increasing interest in understanding the nature of the interactions between antibodies and the solid surfaces they contact during manufacturing processes and storage. In this study, a monoclonal antibody

was introduced to quartz crystal microbalance (QCM) substrates coated with gold, stainless steel and silicon carbide. The samples were characterized by multiple surface analytical techniques, including TOF-SIMS and XPS. The preliminary XPS results suggest that the protein adsorbed at higher concentration on gold than on stainless steel and silicon carbide, while nitrogen concentration detected on stainless steel is slightly higher than on silicon carbide. This is generally consistent with the QCM results. TOF-SIMS spectra also suggest that the interaction between the antibody and three substrates is not the same. The fragmentation patterns detected in the TOF-SIMS spectra obtained from silicon carbide and stainless steel are similar to each other, but they are different from those detected on gold. The interaction between the antibody and stainless steel coupons will be further studied to understand the influence of surface morphology.

3:20pm **QC+AS+BI+MN-ThA4 Combining Spectroscopic Ellipsometry and Quartz Crystal Microbalance to Study Biological Hydrogels – Towards Understanding Nucleo-Cytoplasmic Transport.** *N.B. Eisele, S. Ehret, R. Zahn, CIC biomaGUNE, Spain, S. Frey, D. Gorlich, MPI Biophysical Chemistry, Germany, Ralf Richter, CIC biomaGUNE & Université Grenoble Alpes & MPI Intelligent Systems, Spain*

Nature has evolved hydrogel-like materials that are exquisitely designed to perform specific biological functions. An example of such a material is the nuclear pore permeability barrier, a nano-sized meshwork of intrinsically disordered proteins (so called FG nups) that fills the nuclear pores (i.e. the roughly 40 nm wide channels across the nuclear envelope) and controls the entry of macromolecules into the nucleus of eukaryotic cells. The permeability barrier exhibits a unique selectivity in transport: very small molecules can cross the barrier efficiently, while larger objects are delayed or blocked unless they are bound to specialized proteins, so called nuclear transport receptors (NTRs). How size and species selectivity are encoded in the hydrogel-like properties of the permeability barrier is currently not well understood.

We have developed monolayers of end-grafted FG nups as a nano-scale model system of the permeability barrier. The planar geometry of this well-defined biomimetic film affords detailed and quantitative characterization – not accessible for the native system – with a toolbox of surface-sensitive characterization techniques. In particular, we present the application of the *in situ* combination of quartz crystal microbalance (QCM-D) and spectroscopic ellipsometry (SE) to quantify film thickness, hydration and viscoelastic properties as a function of protein surface density.

We will present how this experimental data, combined with polymer theory, allows us to better understand the relationship between the supramolecular organization and dynamics of the permeability barrier, its physico-chemical properties and its biological function. We demonstrate that attractive interactions between FG nups play an important role in tuning the assembly and morphology of FG nup meshworks, and highlight that even rather weak interactions – typically a few *kT* per biopolymer chain – have functional importance. We show also how the interaction between NTRs and FG nup meshworks is tuned to afford strong enrichment and at the same time rapid entry and exit of NTRs in the permeability barrier, thereby facilitating NTR translocation.

Taken together, these studies contribute important information to understand the mechanism of size- and species-selective transport across the nuclear pore permeability barrier. The mechanistic insight gained should be useful towards the design of bioinspired species-selective filtering devices. Moreover, the presented procedures for the acquisition and analysis of combined QCM-D/SE data are broadly applicable for the characterization of ultrathin biomolecular and other polymer films.

4:00pm **QC+AS+BI+MN-ThA6 Probing Nanoparticle-Biofilm Interactions using Quartz Crystal Microgravimetry and Complementary Surface-sensitive Methods.** *Kaoru Ikuma**, University of Massachusetts, *Z. Shi, A.V. Walker*, University of Texas at Dallas, *B.L.T. Lau*, University of Massachusetts

The environmental fate and transport of nanoparticles (NPs) have been a rising topic of concern due to the increased use of nanotechnology. Recent studies have shown that NPs are likely to interact readily with and accumulate in environmental biofilms. Biofilms are a ubiquitous form of microbial presence where cells attached on solid surfaces are surrounded by a sticky matrix of extracellular polymeric substances (EPS). The EPS matrix is considered to be highly heterogeneous and chemically complex. Polysaccharides and proteins are known to be major constituents of EPS and may greatly impact the likelihood of interactions occurring between NPs and biofilms.

In this study, we examined the deposition of NPs onto surface-immobilized proteins to determine the importance of protein-rich domains in the interfacial interactions between NPs and biofilms. Such interfacial processes are the initial and potentially rate-limiting step in NP-film interactions. The deposition kinetics and extent of model hematite ($\alpha\text{-Fe}_2\text{O}_3$) NPs onto protein-coated silica surfaces were quantitatively measured by quartz crystal microbalance with dissipation (QCM-D). Model proteins including bovine serum albumin (BSA) and lysozyme as well as bacterial total proteins were used herein. The proteins were initially adsorbed onto either negatively-charged bare or positively-charged poly-L-lysine (PLL)-precoated silica sensors to assess the effects of the orientation of surface-immobilized proteins. In addition to QCM-D, other complementary surface-sensitive techniques such as Kelvin probe force microscopy and time-of-flight secondary ion mass spectrometry (TOF SIMS) were used to characterize the mechanisms of interaction between the NPs and the protein-coated surfaces.

QCM-D results indicated that for all tested proteins, the total deposition extent of hematite NPs was significantly greater on protein layers that were adsorbed onto bare silica compared to PLL-precoated silica sensors. TOF SIMS results showed that the amino acid profiles of the topmost surface of the protein layers on bare and PLL-precoated silica sensors were distinctly different, suggesting that NP deposition was greatly influenced by the orientation of the surface-immobilized proteins. Both the extents and rates of NP deposition were also dependent on the type of model protein. Based on the surface charge, topography, and hydrophobicity characterization results, the observed interfacial interactions between hematite NPs and surface-immobilized proteins appeared not to be controlled by one dominant interaction force but by a combination of electrostatic, steric, hydrophobic, and other interactions.

4:20pm **QC+AS+BI+MN-ThA7 Association and Entrapment of Membrane-Targeted Nanoparticles with Different Binding Avidity: A QCM-D and single Particle Tracking Study.** *Anders Lundgren**, *B. Agnarsson, S. Block, F. Höök*, Chalmers University of Technology, Sweden
Nanoparticles specifically targeted to receptors in the cell membrane are interesting for various applications such as intracellular delivery and visualization of diffusing membrane proteins, so-called single particle tracking. These diverse applications require particles optimized to display different binding properties: In this model study we investigated the effect of particle size and ligand density on the association rate and mobility/entrapment of biotin functionalized core-shell nanoparticles to supported lipid bilayers sparsely modified with streptavidin. Gold-PEG core-shell nanoparticles were synthesized with two different core sizes, 20 and 50 nm in diameter, and a shell (10 nm) of mixed uncharged, negatively charged and biotinylated PEG-ligands, the biotin content varied from one to several hundreds per particle. Particle binding was examined on the ensemble level using QCM-D and on single particle level using novel light scattering microscopy that will be detailed. At physiological salt conditions, binding of 50 nm particles were weakly dependent on the number of displayed biotin ligands, whereas the association of 20 nm particles were strongly attenuated in direct relation to the ligand density. At low salt conditions, binding of the larger particles resembled that of the smaller particles, with a strong dependence on ligand density. PEGylated particles without biotin-ligands did not bind at any condition. Thus, it was concluded that specific particle affinity is strongly attenuated by particle size and surface charge due to different interaction potential between the particle and the surface. On the contrary, no dependence on particle size was observed for the mobility of single particles displaying diffusion constants close to 0.4 or $0.8 \mu\text{m}^2/\text{s}$ irrespective of particle size, which was similar to ensemble measurements using FRAP data on FITC-labelled streptavidin ($0.5 \mu\text{m}^2/\text{s}$). Only particles with a single surface tether show continuous diffusion; after formation of a second surface bond particles got quickly entrapped and formed additional bonds. In QCM-D measurements, this was manifested by a continuously decreasing dissipative response per particle for binding of particles with increasing ligand density. Together, QCM-D and particle tracking data indicates that two different mechanisms may lead to particle trapping and ultimately particle wrapping: For very high ligand densities membrane receptors in the membrane diffuse to and partly wraps around immobile particles, whereas for intermediate ligand densities the diffusion and dynamics of the particles themselves facilitate the formation of additional surface bonds and eventual wrapping.

4:40pm **QC+AS+BI+MN-ThA8 Complementary Chemiresistor and QCM Studies of Biomacromolecules as Sorptive Materials for Vapor Sensing.** *Kan Fu, X. Jiang, B.G. Willis*, University of Connecticut
Biomolecules are integral components of current sensing and diagnostic technologies including enzymatic glucose sensors, DNA microarrays, and antigen-antibody assays. The use of biomolecules in non-biological situations, however, is a burgeoning new field that may break the existing boundaries of biomolecule applications in exclusively biological context.

* QCM Focus Topic Young Investigator Award

Extensive studies have already been performed in bioelectronics using small biomolecules and biomacromolecules, revealing promising results regarding charge transport and conformation dependence. In the area of sorptive chemical sensors, biomacromolecules have inherent advantages over conventional synthetic polymers. DNA oligomers have precisely defined sequences through synthesis, they are monodisperse, and they can self-assemble into nanoscale structures. These features make them interesting for vapor sensing of small molecules.

In this work, a series of 8 custom-designed, single-strand DNA (ssDNA) were integrated with chemiresistors and QCM to make sensors. Chemiresistor sensors were made by depositing gold nanoparticles functionalized with ssDNA molecules onto microfabricated electrodes, and QCM sensors were made by depositing films of ssDNA on quartz crystals. While chemiresistors give high signal-to-noise ratios and significantly better limits of detection (LODs) and may eventually be the transducer for practical applications, QCM is a purely mass-sensitive technique that reveals fundamental absorption properties in terms of partition coefficients. By exposing these sensors to a series of organic vapors, the resistance change and mass change of the two sensor platforms can be compared. It is demonstrated that, similar to previous comparative studies of gold nanoparticles functionalized with small organic thiols and synthetic polymer modified QCM crystals, the nanoparticle-based chemiresistor response follows the QCM-traced mass change. The studies show that sorption and conductance modulation mechanisms of vapors on biomolecules are similar to sensors with small organic molecules, but the polarity preference is very different. A model relating partition coefficients K in and chemiresistor responses $\Delta R/R$ is thereafter suggested to account for the links between these 2 sensing systems. It needs to be noted that points which deviate from the modeled trends are likely the result of more complex vapor-material interactions. From here, we demonstrate that DNA oligomers are rich in diversity, which may qualify these materials for array-based and specific sensing applications. It also establishes QCM as a useful complementary tool for evaluating materials for various sensing systems.

5:00pm **QC+AS+BI+MN-ThA9 The Evolution of Complex Artificial Cell Membranes: Combining Patterned Plasma Polymers and Supported Lipid Bilayers**, *Hannah Askew, S.L. McArthur*, Swinburne University of Technology, Australia

Supported lipid bilayers (SLBs) have provided researchers with stable and reproducible platforms to recreate cell membrane environments. Such models are useful for studying a variety of processes including cell signalling and drug-membrane interactions. Unfortunately, current models are lacking in their ability to mimic complex micro and nanoscale architectures found within native cell membranes. Many methods of SLB patterning have emerged to form these complex structures. In particular pre-patterned substrates combined with vesicle collapse are of great interest as they eliminate complications associated with preserving membrane integrity during patterning. Plasma polymerisation provides a versatile, one step, dry method of creating thin films of different chemistries on almost any substrate. Successful bilayer formation on such coatings would be beneficial for promoting specific organisation in complex SLB systems using patterned surface chemistries. In the initial stages of this work we studied the effect of plasma polymer chemistry on the lipid structures formed using vesicle collapse. DOPC lipid vesicles were introduced to commonly used coatings formed from plasma polymerised allylamine (ppAAm) and acrylic acid (ppAAc). The coatings were characterised using X-Ray Photoelectron Spectroscopy (XPS), contact angle and Quartz Crystal Microbalance with Dissipation (QCM-D) techniques. Lipid interaction kinetics and lipid mobility were characterised using QCM-D and Fluorescence Recovery after Photobleaching (FRAP) respectively. It was shown that a variety of lipid structures including mobile bilayer can be formed on ppAAc using pH alone to control electrostatic interactions. ppAAm formed immobile vesicular layers under all conditions tested and could therefore be used as a barrier to confine fluid areas of bilayer. Work is now being undertaken to create single and dual plasma polymer patterns on both glass and silicon wafer. Standard photolithography and ion beam methods will be employed to pattern on both a micro and nanoscale. In this way plasma polymer patterns may enable the formation of increasingly complex SLB architectures.

5:20pm **QC+AS+BI+MN-ThA10 Applications of QCM in Industrial R&D**, *Andrey Soukhovjak*, The Dow Chemical Company

An overview of diverse applications of QCM enabled by its unparalleled sensitivity to mass and viscoelastic properties of thin samples in R&D of The Dow Chemical Company will be presented.

Thursday Evening Poster Sessions

MEMS and NEMS

Room: Hall D - Session MN-ThP

MEMS and NEMS Posters

MN-ThP1 Study on Aspect Ratio Characterization of Polydimethylsiloxane (PDMS) Pillar Arrays for Mechanobiological Traction Forces, Yu-Hsiang Tang, National Applied Research Laboratories, Taiwan, Republic of China, *Y.H. Lin,* Instrument Technology Research Center, Taiwan, Republic of China

This paper describes a PDMS-based microchip, which consists of a uniform array of ordered arrangement, vertical, elastomeric micropillar(MP), to study the effects of substrate rigidity for mechanobiological traction forces. The PDMS substrates used have the advantage that their stiffness can be easily adjusted by altering their geometry and can precisely detect the biological activities. We developed the micropillar array substrates that a flexible polymer microfabrication technique was applied for manufacturing the elastomeric microstructures of various aspect ratios with height of 2, 4, 8, 12 μm and radius: period ratios of 1:4, 1:5, 1.5:7, and 2:7 mm. The PDMS micropillar was fabricated by replica molding technique for the standard and combines different steps including photolithography, deep reaction ion etching (DRIE) and soft lithography. The experiment result shows that the micropillar array is clean and in good situation. Meanwhile, more complex patterns of pillar rigidity will help us to study the physical and topographical effect of the substrate on mechanobiological behavior. This has significant implications when designing pillar arrays or comparing lateral forces measured on different pillar geometries. Furthermore, the results presented by this research are believed to be useful for biologists who are clarifying similar mechanobiological processes. Consequently, it was investigated how the substrate contribution to the total pillar deflection depends on the Poisson ratio of the material.

Keywords: PDMS, Soft lithography, Micropillar arrays, Aspect-ratio structure

MN-ThP2 Mixing Effect of PDMS Microchannel with Biaxial Orientation Entry and Various Arrangements of Microstructures, Po-Li Chen, Y.H. Tang, ITRC, NARL, Taiwan, Republic of China, *Y.S. Lin,* Hungkuang University, Taiwan, Republic of China, *C.N. Hsiao, M.H. Shiao, Y.H. Lin,* ITRC, NARL, Taiwan, Republic of China

Most active micromixers have the problem of high fabrication cost and low reliability since external actuators and stirrers were involved. In passive mixers, the mixing effect was obtained by changing channel geometry to enlarge the contact surface between different fluids, including serpentine, herringbone, zigzag, twisted, rotating, T-shape and Y-shape channels; and they were preferred due to their easy fabrication and integration in the actual micro system. However, most literatures focused on the studies for mixers with entries on the same plane (i.e. flow directions were all parallel to horizontal plane); in this study, we report a micromixer design with biaxial orientation entries (i.e. flow directions were parallel and vertical to horizontal plane) and investigate the mixing performance by placing various arrangements of rectangular microstructures with Computational Fluid Dynamics (CFD) techniques.

This study aims on achieving good mixing by changing the arrangements of microstructures to activate the interaction between different fluids. In this paper, several major parameters, including the width and height of microstructures, and the inline or staggered arrangements of various rectangular obstacles on the overall mixing channel pressure drop and mixing efficiency all were well predicted and compared. Simulated and experimental results showed that the microstructures played an important part and resulting in good fluid mixing at low Reynolds numbers.

MN-ThP3 An Integrated Volatile Organic Compounds Sensing Module for Exhaled Air Analysis, Po-Kai Huang, C.-Y. Kuo, P.-H. Kuo, T.-H. Tzeng, S.-S. Lu, W.-C. Tian, National Taiwan University, Taiwan, Republic of China

The detection limit for the gas sensor has been an important factor for the low concentration compound measurement, especially for the detection of disease biomarkers from exhaled human breath air. In this study, we developed a CMOS-based volatile organic compounds (VOCs) sensor with either by a system on chip (SOC)-enabled negative feedback calibration (NFC) readout circuit or a custom-made voltage divider.

The sensor and the SOC-enabled NFC chip were both fabricated by the commercial TSMC 0.35 μm two poly Si and four metal (2P4M) layer process. The sensing module included a stacked of interdigitated electrodes

(IDEs) with polysilicon microheater and the sensing material of monolayer protected gold nanoclusters (MPCs) coated on the electrodes.

In order to conquer the sensor resistance variation created by the MPCs spraying process, the NFC readout circuit was used to overcome the resistance value fluctuation of the VOCs sensor. The sensitivity of our sensing module, consisting of the CMOS-based sensor and the SOC-enabled NFC readout circuit, was increased by approximately two times compared to the previous design. With our sensing module, a wide dynamic range of toluene detection from 30 ppm to 6000 ppm was demonstrated. The sensor responded rapidly, with the rising time and the recovery time both less than six seconds.

With this VOCs sensing module, the detection of lung disease biomarkers from exhaled human breath air could be achieved. Ultimately, the VOCs sensor and NFC readout circuit will be integrated on the same chip to further miniaturize the systems and to minimize the noises in the future.

Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Focus Topic

Room: Hall D - Session QC+AS+BI+MN-ThP

Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Poster Session

QC+AS+BI+MN-ThP1 In Situ Toxic Nano-Material Sensing Method Using DNA Immobilized Quartz Crystal Microbalance, Kuewhan Jang, S. Lee, J. You, C. Park, J. Park, S. Na, Korea University, Republic of Korea
Nano-material has grown from scientific interest to commercial products and there are more than 1600 nano-material products on the market. Among those nano-materials, single-walled carbon nanotube (SWNT) and silver ion have been shown great interest due to their extraordinary properties. Since SWNT and silver ion production capacity increases each year, its contamination to the environment water system will increase in the form of industrial waste. Moreover, toxicity assessment of those materials is required for human health and environmental issue since the toxicity of those materials has been reported. In this study, we propose the in-situ detection of SWNT and silver ion. The detection mechanism is based on the measurement of the resonance frequency shift arisen from the binding on the DNA immobilized quartz crystal microbalance. We are able to detect SWNT and silver ion less than an hour with the detection limit of 100 ng/ml of SWNT and 100 pM of silver ion, respectively. Moreover, the DNA immobilized quartz crystal microbalance enables the detection in real tap water. This work shows the potential of DNA immobilized quartz crystal microbalance as the in-situ toxic nano-material screening tool.

QC+AS+BI+MN-ThP2 Mechanics of Multicontact Interfaces Studied with a QCM, R. König, S. Hanke, J. Vlachová, D. Johannsmann, Arne Langhoff, Clausthal University of Technology, Germany

The contact stiffness and the contact strength at interfaces between rough surfaces are of outstanding relevance in many different fields, including mechanical engineering, bio-lubrication, and technical tribology.

Individual sphere-plate contacts have been previously investigated with a QCM and it was found that the contact stiffness can be inferred from the frequency shift, where the latter is positive because contact increases the overall stiffness of the composite resonator. At elevated amplitude of oscillation, the apparent contact stiffness decreases because of partial slip. Partial slip (also: "microslip") describes the situation, where a contact partly sticks and partly slips. Sticking mostly is observed in the center. Slip is found at the edges, where the local stress is large.

The presentation describes the extension of this work to multicontact interfaces as well as the new results which were found with the single contacts. Generally speaking, multicontact interfaces differ from individual contacts by, firstly, a broad distribution of contact size and contact strength and, secondly, by an elastic coupling between neighboring load-bearing asperities.

Different materials (aluminum, PMMA) and different characteristic scales of roughness (all in the range of many microns) were studied. The focus is on polymer surfaces, which were treated with an abrasive paper. A novel geometry, where the resonator is symmetrically loaded with the same type of sample from both sides, has allowed to increase the normal force by a factor of 10, compared to previous experiments.

At small amplitudes, the frequency response of the QCM to a contact with rough PMMA surfaces is similar to the behavior observed with individual sphere-plate contacts. There is an increase in resonance frequency, which can be converted to an interfacial stiffness. Interestingly, the contact stiffness observed with MHz excitation was found to be much higher than what has been found in similar samples with excitation frequencies in the kHz range.

At elevated amplitudes, the behavior is variable. Often one finds partial slip. Occasionally, however, there is a sharp increase in contact stiffness at a certain threshold in amplitude. The bandwidth goes through a maximum at that same amplitude. The behavior is reversible; the threshold is the same for decreasing and increasing amplitude ramps. We tentatively associate the increased apparent stiffness with an oscillation-induced increase in contact area.

[1] S. Hanke, J. Petri, D. Johannsmann, *Phys. Rev. E* **2013**, 88.

[2] P. Berthoud, T. Baumberger, *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* **1998**, 454, 1615–1634.

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