Nanomaterials
Room Naupaka Salon 5 - Session NM-TuM
Nanofabrication and Nanodevices

Moderator: Adam Hitchcock, McMaster University

8:00am **NM-TuM1 High-throughput, Continuous Flow Synthesis of Colloidal Nanoparticles as a Safe and Sustainable Nanofabrication Method***, Emily Roberts,* *R.L. Brutchey,* University of Southern California

In the past two decades, flow chemistry methodologies have been recognized as a step towards more green and sustainable chemical and material production. As an industrial demand for colloidal nanoparticles increases, there will be an increasing need to scale up and process intensify typical small-scale bench-top reactions. In respect to nanofabrication, continuous flow reactors have efficient heat and mass transport, excellent control of local mixing conditions, improved safety, decreased solvent waste, and are automatable. These advantages address green chemistry values by decreasing or preventing waste, improving the atom economy by increasing production yields, offering less hazardous synthetic methods, increasing throughput, and enhanced energy efficiency.

We will present our recent results on the development of high-throughput, continuous flow reactors for the synthesis of various colloidal nanoparticles. Reactor designs for a wide range of temperatures (150-320 ˚C), using various heating methods (conventional oven, microwave heating, and sand bath), reusable solvents, and one- and two-phase flow will be discussed. The differences between resulting products in terms of yield, morphology, and functionality will also be evaluated. Lastly, the continuous flow methods will be compared to analogous batch reactions to assess the viability of continuous flow nanofabrication methods.

8:20am **NM-TuM2 Nanoporous Oxide Memristive System & Artificial Synapses for Next Generation Electronic Device Application***, Gunuk Wang,* Korea University, Republic of Korea

The two-terminal oxide-based memristive switch is garnering enormous interest for the development of next-generation nonvolatile memory beyond current Si-based memory technology and is concurrently considered as an artificial synapse candidate for the neuromorphic computing hardware. In this talk, I will introduce a breakthrough and attractive approach, that is utilized a nanoporous oxide structure as a switching medium, for fabricating simple and cost-efficient high-density memory arrays with acceptable switching performances, low power consumption, and low electroforming voltage (or forming-free). I will talk a topic about the single nanopore (SNP)-based SiOx memories that enable unipolar switching through its internal vertical nanogap, which outperforms the switching ability of any other unipolar memory [1-3]. As a second part, I will briefly introduce our recent approaches and achievements for the neuromorphic device technology using two-terminal self-rectifying memristor synapse employing a Pt/Ta_2O_{5-y}/nanoporous (NP) Ta_2O_{5-x}/Ta layers [4,5].

References：

[1] S. Kwon et al., *Nano Lett,* 2017, 17, 7462.

[2] G. Wang et al., *Nano Lett*. 2014, 14, 4694.

[3] G. Wang et al., *ACS Nano*, 2014, 8, 1410.

[4] W. Huh et al., Adv, Mater. In press 2018.

[5] S. Jang et al., under review 2018.

8:40am **NM-TuM3 Synaptic Plasticity and Learning Behaviors Mimicked in Electromigrated Au Nanogaps***, Keita Sakai,* *K. Minami, S. Tani, T. Sato, M. Ito,* Tokyo University of Agriculture & Technology, Japan*; M. Yagi,* National Institute of Technology, Ichinoseki College, Japan*; J. Shirakashi,* Tokyo University of Agriculture & Technology, Japan

For many years, neuromorphic devices that can mimic functions of biological brains have been studied in the field of neuromorphic engineering. The synaptic functionality of neuromorphic hardwares originates in a gradually modified resistance. Previously, we have investigated simple methods for controlling the tunnel resistance of the nanogaps called activation. In this technique, electromigration is induced between nanogap electrodes by a field emission current, resulting in the reduction of the gap width. The tunnel resistance of the nanogaps also decreases after activation. In this study, we apply the activation procedure for Au nanogaps and demonstrate the experimental implementation of synaptic functions in Au nanogaps. First, Au nanogaps were fabricated by electron-beam lithography and lift-off process. Then, a fixed width and height voltage pulse was loaded to Au nanogaps periodically. After the applied pulse was removed, current decayed rapidly at the beginning of the time followed by a gradual fading to a stable level. By increasing the number of stimulations, the relaxation time increased, implying a slow fade in forgetting process time. Meanwhile, it was observed that current level was clearly elevated, showing a potentiation of synaptic weight. These phenomena confirm the STP-to-LTP transition in our device. These results indicate that inorganic synapses are successfully achieved using Au nanogaps controlled by the activation.

9:00am **NM-TuM4 Preparation and Corrosion Properties of Bulk Nanocrystalline Two-phase Ag-25Cu Alloys***, Zhongqiu Cao,* *X.T. Yin, Q.Y. Tian, Y. Wang, K. Zhang, J. Lu,* Shenyang Normal University, China

In this paper, two bulk nanocrystalline LPRAg-25Cu and MAAg-25Cu (at.%) alloys were prepared by liquid phase reduction and mechanical alloying methods, respectively, and afterwards hot pressing process. Fig. 1 depicts the X-ray diffraction (XRD) pattern (a) and the transmission electron microscopy (TEM) photograph (b) of LPRAg-25Cu alloyed powders. These alloyed powders have no impurities with about 10 nm average grain sizes. The densities of two bulk nanocrystalline Ag-25Cu alloys exceed 99%. The average grain size measured by XRD is about 13 nm after liquid phase reduction and about 27 nm after hot pressing, about 8 nm after mechanical alloying and about 19 nm after hot pressing.

Fig. 2 depicts the microstructures of two nanocrystalline alloys and a coarse grained counterpart (PMAg-25Cu). They all are composed of two phases. One is α phase rich in Ag, the other is β phase rich in Cu. The microstructure of coarse grained PMAg-25Cu alloy is extremely inhomogeneous. The microstructure of nanocrystalline LPR or MAAg-25Cu alloys is more homogeneous than that of coarse grained PMAg-25Cu alloy, while the microstructure of nanocrystalline LPRAg-25Cu alloy is most homogeneous.

Fig. 3 depicts Open Circuit potential (a), polarization (b), EIS (c), and Mott-Schottky (d) curves of three Ag-25Cu alloys. Corrosion rates of three Ag-25Cu alloys increase in the range of PMAg-25Cu, MAAg-25Cu and LPRAg-25Cu alloys. The corrosion rate of nanocrystalline alloy is faster than that of corresponding coarse grained alloy. The faster corrosion rates are attributed to the different microstructures of three Ag-25Cu alloys prepared by the different processes including the grain size as well as phase distribution and compositions. EIS plot of coarse grained PMAg-25Cu alloy is composed of a single capacitive loop. The corrosion process is controlled by electrochemical reactions. EIS plots of nanocrystalline MAg-25Cu and LPRAg-25Cu alloy are composed of a single capacitive loop with diffusion tail. The corrosion processes of two nanocrystalline Ag-25Cu alloys are controlled by diffusion. The passive films formed on three Ag-25Cu alloy surface exhibit n-type semiconducting properties. The passive current density of LPRAg-25Cu alloy is lower than that of PMAg-25Cu alloy, but higher that of MAAg-25Cu alloy. Thus, the chemical stability of passive films on MAAg-25Cu alloy surface is highest.

Acknowledgements

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9:20am **NM-TuM5 Nanomaterials-enabled Advances in Microfabricated Sensors for Environmental and Health Monitoring***, Roya Maboudian,* University of California at Berkeley **INVITED**

Accurate detection of toxic and flammable gases is critical to public health and the environment, and to the safe operation of many industrial processes. This presentation will discuss our efforts in low-power gas sensing for health, environmental and process monitoring. The core technology is a suspended polycrystalline silicon microheater functionalized with a number of nanotechnology-based sensing materials, targeting various analytes. Our microheater platform will be described and the latest results in sensitive, selective, and stable detection of several target gas molecules (including H_2, propane, CO and NO_2) will be presented. The talk will end with plans for future directions.

10:20am **NM-TuM8 Nature-Inspired Approaches to Nanotechnologies***, Jong-Souk Yeo,* Yonsei University, Republic of Korea

Biomimetics, Biomimicry, Nature-Inspired, or Biologically Inspired technologies are all referring to the emerging fields where innovations are strongly influenced by the wisdom from nature or biological systems.

Biomimetics is the scientific approach of learning new principles and processes based on systematic study of living organisms, plants, or animals in order to develop novel engineering systems through the convergence of biology, materials science, cognitive science, robotics, and nanotechnology. Especially, the multi-functionality offered by nature can enable various applications with the help of nanotechnology. Multiple levels of approaches are feasible from nature-inspiration – adaptation of how nature works, adoption of what nature provides, or replication of natural processes and functionalities for eco-friendly, sustainable, and highly efficient technologies. In this talk, nature-inspired approaches to nanotechnology will be introduced for next generation technologies in omniphobic surfaces, color reflective displays, neuromorphic semiconductors, stretchable electronics, biomaterials and biosensors enabled by biomimetic surface, optical, electronic, or bio functionalities.

This research was supported by the MIST (Ministry of Science and ICT), Korea, under the "ICT Consilience Creative Program" (IITP-2018-2017-0-01015) supervised by the IITP (Institute for Information & communications Technology Promotion) and also under the "Mid-career Researcher Program" (NRF-2016R1A2B2014612) supervised by the NRF (National Research Foundation) and by the MOTIE (Ministry of Trade, Industry & Energy (project number 10080625) and KSRC (Korea Semiconductor Research Consortium) support program for the development of the future semiconductor device.

10:40am **NM-TuM9 A Reproducible Assay for Versatile Biosensing by Surface-enhanced Raman Scattering***, M. Al Mamun, N.A. Cole, S. Juodkazis,* ***Paul Stoddart****,* Swinburne University of Technology, Australia

Over the forty years since its discovery, surface-enhanced Raman scattering (SERS) has attracted significant attention as a sensitive technique for surface analysis. The high sensitivity of SERS and compatibility with microfluidic techniques makes it an attractive option for point-of-care sensing applications. However, we are not aware of any routine analytical applications of SERS that have emerged to date. In particular, SERS substrates are subject to variability due to high sensitivity to nanometre scale structure, complex surface interactions in real-world samples, susceptibility to environmental contamination, and a limited substrate shelf life. Here we report a versatile biosensing technique, where the target analyte is labelled with biotin, and is in turn reliably captured by a streptavidin-coated substrate. Subsequent exposure to an excess of biotin saturates the remaining binding sites and provides an internal intensity reference to assist quantification. Once the analyte has been immobilized via the biotin-streptavidin interaction, a photochemical reduction process is used to deposit silver nanoparticles over the surface. This generates a SERS substrate on demand, with high sensitivity and high reproducibility, while protecting the surface from environmental contamination. Using atto-488 as a model analyte, it has been shown that the process can deliver nanomolar sensitivity. The fluorescent emission of the atto-488 was used to confirm the surface immobilization, but is quenched by the presence of the metal coating in the SERS measurements. With appropriate extensions to an integrated microfluidic platform, the developed technique has the potential to be used to detect a wide range of small molecule targets of interest in body fluids .

11:20am **NM-TuM11 Molecular Dynamics Investigation for Chemical Effects of Nanobubble Collapse on Precision Polishing***,* ***Yoshimasa Aoyama****, N. Miyazaki, Y. Ootani, N. Ozawa, M. Kubo,* Tohoku University, Japan

For manufacturing high-performance semiconductor devices, the fabrication of a highly-planar surface is important. As the planarization method, chemical mechanical polishing (CMP) is used for efficient processing. The efficient process leads cost-savings. Therefore, the design of more efficient and more precise CMP process is required. Then, Aida et al. have recently reported that the nanobubble contributes to CMP process[1]. In this polishing process, the water hammer shock is regarded as the elemental process, which brings the jet stream when the nanobubble collapses[2]. From their study, effects of the jet would depend on the solvents around the nanobubble and the inner gaseous species of the nanobubble. However, the details of chemical relationship among CMP process, solvents, and gaseous species are unclear. Therefore, understanding the atomistic CMP mechanism with nanobubble and the chemical effects of solvents and gaseous species in nanobubble collapse phenomenon are required to establish more efficient CMP process. In this study, we performed nanobubble collapse simulation by molecular dynamics method using reactive force field, which is possible to simulate the formation and dissociation of chemical bonds.

First, we prepared the simulation model with vacuum nanobubble in the water solvent and the simulation model without nanobubble. A vacuum nanobubble is modeled by removing the water molecules as the spherical shape. Then, we performed nanobubble collapse simulation and applied a shock for the substrate surface by using "momentum mirror"[3]. From these simulations, we found that the jet was generated in the model with a nanobubble, and this jet brought larger plastic deformation on the substrate, indicating that the nanobubble increased the efficiency of CMP process. Second, in order to investigate the effects of gaseous species in the nanobubble, we prepared nanobubble models with various gaseous species. By determining the density of gas molecules in the nanobubble to satisfy the Young-Laplace law, we succeeded in creating oxygen and nitrogen nanobubble stably. By this procedure, we got to be able to fabricate various gaseous nanobubbles stably and simulate nanobubble collapse process under various solvents and gaseous species. In the conference, we are going to report the atomistic CMP mechanism and chemical effects of solvents and gaseous species in nanobubble collapse simulation.

[1] H. Aida et al., Precision Engineering, 40 (2015) 81.

[2] C. D. Ohl et al., Phys. Rev. Lett., 90 (2003) 214502.

[3] B. L. Holian et al., Phys. Rev. A, 37 (1988) 2562.

11:40am **NM-TuM12 Determination of Anisotropic Diffusion Ratio on Si(110)-16×2***,* ***Masahiro Yano****, T. Terasawa, S. Yasuda, S. Machida, H. Asaoka,* Japan Atomic Energy Agency, Japan

Establishing bottom-up nanofabrication-techniques are required to develop electronic devises and create novel functional devices because further miniaturization using top-down techniques is becoming hard due to fundamental physical and technological limitation. The anisotropic material-diffusion, which dominates the formation of the nanostructures, should be clarified to control the nanofabrication using template surface more precisely. Si(110)-16×2 reconstructed structure has been used as a template for fabricating several types of nanowires and nanodots due to the one-dimensional structure in which the one-atomic-layer steps are arranged at a period of 2.5 nm. However, the influence of the anisotropic material-diffusion on the Si(110)-16×2 surface has not been clarified because of difficulty determining the anisotropic material diffusion ratio on the reconstructed structure.

In this study, we focused on a nano-hole, called as "void", formed during the thermal decomposition of oxide layer on Si, where the pure Si was exposed due to the desorption of the oxide layer to determine the anisotropic Si diffusion rate ratio on the Si(110)-16×2. The void is grown by the Si atoms which was created and diffused on the void bottom decomposed the oxide layer following the reaction, $Si + SiO_2 \rightarrow 2SiO\uparrow$. The voids were observed by scanning tunneling microscope (STM) at room temperature because the oxide layer is decomposed by STM at high temperatures.

The void sidewall exposed the (17, 15, 1) plane, meaning that the void is surrounded by crystallographically equivalent planes. This indicated that the anisotropic void growth rate ratio depends on only the density ratio of diffusing Si supplied to oxides between the void edges because the reaction and desorption rate of oxide were uniform around the void. The length of the voids along to the step rows of the 16×2 reconstructed structure was longer than that of perpendicular to the step rows. We found that the anisotropy of the void shape decreased as the void became deeper, indicating the reduction of the Si density ratio during the diffusion on the sidewall. Taking the migration of diffusing Si atoms between the adjacent sidewalls and the creation of diffusing Si atoms on sidewalls into account, we determined that the diffusion parallel the step rows of the reconstructed structure at the void bottom was 7 times faster than that perpendicular to the step rows. This diffusing ratio will help to realize the precise control of the nanodots and nanowires formation on the Si(110)-16×2 reconstructed structure.

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