Nanomaterials
Room: Hau - Session NM-MoM

Nano Fabrication
Moderator: Adam Hitchcock, McMaster University, Canada

8:40am **NM-MoM1 Polymers, Peptides and Proteins as Pattern Generators and Switches for Functional Nanostructures**, ***David Williams***, *Malstrom, Wason, Papst, Roache, Strover, Hackett, Pei, Leung, Brimble, Evans, Travas-Sejdic, Gerrard*, The University of Auckland, New Zealand **INVITED**

We have explored self-assembling proteins and block co-polymers, rationally designed peptides, and switchable polymer brushes as design elements for functional nanostructures.

Block co-polymers can self-assemble to form interesting regular nanostructures. Indeed, micro-phase separation in block copolymers has been fairly extensively explored as a means of patterning high-density memory elements. Similarly, proteins self-assemble: individual subunits can assemble into doughnuts, stacks, fibres and scaffolds. We have explored the idea of combining the two, using micro-phase separation of a block copolymer as a means to organise a protein stack which may then be used to organise something else. In the RNA-binding protein Lsm-α, monomeric subunits assemble into doughnuts. The doughnuts can then be induced to form stacks by a combination of protein engineering and changes in solution conditions such as pH and metal ion concentration. These nanoscale tunnels can then potentially acts as a template to organise metal ion or nanoparticle columns. In order to organise the protein stacks, we have explored the segregation of the protein into the hydrophilic domains of a hydrophobic-hydrophilic block copolymer. We illustrate the idea using thin films of poly(styrene)-b-poly(ethyleneoxide) – PS-b-PEO, with the Lsm-α doughnut incorporated into self-assembled hexagonally packed cylinders of PEO. The issues are choice of a solvent system that promotes structuring of the polymer, and functionalization of the protein to convey compatibility with the solvent system necessary for formation of the micro-phase separated structure, whilst still retaining the structure, function and organisation of the protein.

In a different approach to building up the elements needed to construct functional nanostructures, we have been exploring the use of rationally designed peptides as templates for nanoparticle growth, and surface-grafted polymer brushes as switchable sub-units. Peptides offer great flexibility in molecular design. We have been able successfully to incorporate, in defined spatial organisation, sites that specifically adsorb to metal surfaces, sites that control inter-particle interaction, and sites that complex the particle precursor species and thus control particle nucleation. Separately, we have been able to synthesise co-polymer brush systems that are electrochemically switchable. We present initial approaches towards integrating all these structural and functional elements and studying their interaction with living cells.

9:20am **NM-MoM3 Si, C and SiC_x Nanostructures and Nano Devices Fabricated Using In Situ Liquid Cell TEM Technology**, ***Xin Chen***, East China University of Science and Technology, China, *L.H. Zhou, P. Wang, H.L. Cao, X.L. Miao, F.F. Wei*, East China University of Science and Technology

Silicon, carbon and SiC_x nano structures were fabricated using liquid phase electron beam induced deposition (LP-EBID) technology . $SiCl_4$, CH_2Cl_2, and $SiCl_4$ in CH_2Cl_2 solutions of different concentrations were used as the liquid precursors, which were sealed between two Si_3N_4 window grids in home made in situ TEM liquid cells. JEOL TEM systems operating under a 200 keV electron acceleration voltage were used for the deposition. Focused electron beams of 0.28 to ~40 nA were used to decompose the precursors and deposit the nano structures on the Si_3N_4 window substrates.

With the beam focused on a fixed location for a certain time, nano dots have been deposited, with sizes ranging from <60 nm to ~500 nm depending on the deposition parameters, with well size controllability. Generally, the nano dot diameter increases with beam exposure time and beam intensity, but was insensitive to the composition ratio of these precursors. Under the higher beam current, the nano particle growth was observed to be retarded. The general growth trend is attributed to a secondary electron effect, while the retarded growth is attributed to the influence of the primary electrons.

By using scanning electron beams, nano wires of different sizes have been deposited. Besides a uniform straight line growth, we have also observed a branched growth behavior under certain deposition conditions. The secondary electron mechanism can be used to explain these growth behaviors.

The in situ cells were later dissembled, with platinum nano electrodes deposited on the two ends of the SiC_x nano wires using a FEI Dual Beam 235 focused ion beam system, forming nano electronic devices. SEM and AFM imaging analysis showed good structural morphology of the devices, and I-V property test have been made on the devices. Issues of liquid bubbling under electron beam irradiation, image resolution and structural stability of the deposited nano structures made by in situ liquid cell TEM technology have been further discussed.

9:40am **NM-MoM4 Quantum Chemical Molecular Dynamics Approach to Chemical Mechanical Polishing Processes of Gallium Nitride by SiO_2 Abrasive Grain**, ***Kentaro Kawaguchi***, *T. Aizawa, Y. Higuchi, N. Ozawa, M. Kubo*, Tohoku University, Japan

Gallium nitride (GaN) is a next-generation semiconductor material with a wide band gap and high electron conductivity. Although the atomic-level planar polished surface is essential for practical GaN devices, it is difficult to polish efficiently the GaN substrate because of its high hardness and chemical stability. The chemical mechanical polishing (CMP) is promising for efficient polishing of the GaN substrate. However, the detailed CMP mechanisms are unclear, and then the design of the processes is difficult. In this study, in order to design the efficient and precise GaN CMP processes, we investigate the GaN CMP via our tight-binding quantum chemical molecular dynamics (TB-QCMD) method.

We perform CMP simulations of a GaN(0001) surface by a SiO_2 abrasive grain in aqueous H_2O_2 solution and aqueous NaOH solution to clarify the chemical reactions of each solution. We reveal that OH radicals and OH^- ions are adsorbed on the GaN surface in aqueous H_2O_2 solution and aqueous NaOH solution, respectively. According to the analysis of the atomic bond population between the Ga atoms in the first layer and the N atoms in the second layer, we elucidate that Ga-N bonds of the GaN substrate in aqueous H_2O_2 solution are weaker than those in aqueous NaOH solution. Therefore, we suggest that the OH radicals are effective for GaN CMP. To confirm the effectivity of OH radicals, we add one OH radical into the solution every 4.0 ps until 64.0 ps during polishing simulation under pure water environment. After 8 OH radicals are added, the 8 added OH radicals are adsorbed on the GaN surface. After 10 OH radicals are added, a surface-adsorbed O atom is generated by the chemical reaction between the surface-adsorbed OH species and a OH radical in the solution. At the friction interface between the GaN substrate and the abrasive grain, the surface-adsorbed O atom is mechanically pushed into the GaN substrate by the abrasive grain. This O atom intrusion induces the dissociation of Ga-N bonds of the GaN substrate. The N-N bond in the GaN substrate is generated due to the Ga-N bonds dissociation. After 16 OH radicals are added, the Ga atom in the first layer binds with 3 OH radicals. Subsequently, $Ga(OH)_3$ is generated and desorbed from the surface. N_2 molecules are also generated and desorbed from the surface due to the dissociation of Ga-N bonds. We suggested that the GaN CMP process efficiently proceeds by the mechanically induced chemical reactions: a surface-adsorbed O atom is generated and pushed into the GaN bulk by the abrasive grain.

10:20am **NM-MoM6 Expanding Scalability of Scanning Probe-Based Nanofabrication**, ***Wooyoung Shim***, Yonsei University, Republic of Korea

Massively parallel scanning-probe based methods have been used to address the challenges of nanometer to millimeter scale printing, and thus revolutionize the conventional scanning probe-based nanofabrication. Such tools enable simple, high-throughput, and low-cost nano-patterning, which allow researchers to rapidly synthesize and study systems ranging from nanoparticle synthesis to biological processes. In this regard, we have developed a novel scanning probe-based cantilever-free printing method termed hard-tip, soft-spring lithography (HSL), which uses an massive array of Si tips to transfer materials and energy in a direct-write manner onto a variety of surfaces. Various related techniques such as graphene-coated and actuation of HSL are also discussed.

References

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10:40am **NM-MoM7 Mueller Matrix Ellipsometry for Detection of Foot-like Asymmetry in Nanoimprinted Grating Structures***, **Xiuguo Chen**,* Huazhong University of Science and Technology, China*, C.W. Zhang, H. Jiang,* Huazhong University of Science and Technology*, S.Y. Liu*, Huazhong University of Science and Technology, China

Nanoimprint lithography (NIL), in which features on a prepatterned mold are transferred directly into a polymer material, represents a promising technique with the potential for high resolution and throughput as well as low cost. Although symmetric imprint resist profiles are expected in most cases, errors could occur in actual NIL processes and will result in undesired asymmetry and pattern transfer fidelity loss in downstream processes. Detection of imprint resist asymmetric defects leads to improvement of the template, imprint process, and imprint tooling design, and therefore guarantees pattern transfer fidelity in template replication. Both cross-sectional scanning electron microscopy (X-SEM) and atomic force microscopy (AFM) are capable of identifying imprint resist profile asymmetry, but they are in general time-consuming, expensive, complex to operate, and problematic in realizing in-line integrated measurements. Being nondestructive, inexpensive and time-effective, optical scatterometry, which is traditionally based on reflectometry and ellipsometry, has been successfully introduced to characterize nanoimprinted grating structures. However, conventional optical scatterometry techniques have difficulties in measuring asymmetric grating structures due to the lack of capability of distinguishing the direction of profile asymmetry.

In this work, we apply Mueller matrix ellipsometry (MME, sometimes also referred to as Mueller matrix polarimetry) to characterize nanoimprinted grating structures with foot-like asymmetric profiles that were encountered in our NIL processes when the processes were not operated at optimum conditions. Compared with conventional optical scatterometry, which at most obtains two ellipsometric angles Y and D, MME-based scatterometry can provide up to 16 quantities of a 4×4 Mueller matrix in each measurement and can thereby acquire much more useful information about the sample. In our recent work, MME was applied to characterize nanoimprinted grating structures with symmetric profiles. We experimentally demonstrated that improved accuracy can be achieved for the line width, line height, sidewall angle, and residual layer thickness measurement by using the additional depolarization information contained in the measured Mueller matrices. The present work will further show that MME not only has good sensitivity to both the magnitude and direction of profile asymmetry, but also can be applied to accurately characterize asymmetric nanoimprinted gratings by fully exploiting the rich information hidden in the measured Mueller matrices.

11:00am **NM-MoM8 Positioning of Catalyst-Free Vapor-Solid Growth of Highly Crystalline ZnO Nanowires by Inkjet-Printing.***, **PaulinaR. Martinez-Alanis**, F. Güell,* Universitat de Barcelona*, S. Khachadorian, A. Franke,* Technische Universität Berlin*, M.R. Wagner,* Institut Catala de Nanotecnologia*, A. Hoffmann,* Technische Universität Berlin*, G. Santana,* Universidad Nacional Autónoma de México*, J.R. Morante*, Institut de Recerca en Energia de Catalunya

High-density arrays of uniform ZnO nanowires, with a high crystal quality have been synthesized by a catalyst-free vapor-transport method. First, a ZnO thin film on a Si substrate was used as the nucleation site. In a second approach we demonstrate spatially selective, mask-less ZnO nanowires growth using ZnO inkjet-printed patterned islands as the nucleation sites on a SiO_2/Si substrate. Raman spectroscopy measurements were performed to characterize the ZnO nanowires, which reveals the high crystal quality of the grown nanowires and a tensile stress was observed in the inkjet-printed nanowires. Photoluminescence measurements demonstrate that only the ZnO nanowires were emitting and there is no contribution from the ZnO thin film or the ZnO inkjet-printed patterned islands. Two emission bands were observed at room-temperature, one strong and narrow peak in the ultraviolet region associated with the near band-edge transition, and a reduced broad band in the green-yellow visible region.

11:20am **NM-MoM9 Rheological and Electrical Properties of Sn-Ag-Cu Solder Paste for Reverse Offset Printing by the Particle Size Distribution***, **Min-Jung Son**,* Sungkyunkwan University, Korea, Republic of Korea*, I. Kim, T.M. Lee,* Korea Institute of Machinery & Materials (KIMM), Republic of Korea*, S.S. Yang,* Korea Institute of Materials, Republic of Korea*, H. Lee*, Sungkyunkwan University, Korea, Republic of Korea

For flip-chip packaging technologies, which gain popularity in semiconductor packaging, forming fine solder bumps with a high aspect ratio at a low cost is an integral part. A promising alternative to the conventional methods (screen printing and electroplating) is reverse offset printing owing to its high throughput.

In the present study, we developed Sn-Ag-Cu paste customized for the reverse offset printing process to use as solder bump with a high aspect ratio.

In fabrication of the pastes, we controlled the particle size distribution using Sn-Ag-Cu particles with two different sizes (2 µm and 100 nm in diameter) and the particles were mixed with various ratio (100 : 0, 75 : 25, 50 : 50, 25 : 75, and 0 : 100) to control the rheological properties without using viscosity-increasing agents, which usually degrade the electrical properties. Various tools were used for measurement of rheological properties such as viscosity, thixotropy index (TI), storage modulus (G'), loss modulus (G"), crossover point of G' and G". The TI and crossover point of G', G" gradually increased with the ratio of the nano particles increasing. In other words, if the initial viscosity increases with the increase of the amount of the nano particles, the shear thinning behavior and elasticity of the paste are dominant and the paste becomes suitable for the formation of the fine solder bumps with high aspect ratio. TI, which is related to the shear thinning behavior, increased from 0.08 to 0.53, and crossover point of G', G", which is related to the shear thinning behavior, increased from 0.15 to 148 Pa. In addition, we measured the electrical resistance of the paste to check the influence of the particle size on it. The resistance increased with the increase of the ratio of the nano particles. As a result, we obtained the lowest resistance in the paste made from only micro solder particles. Considering these results in terms of printability and electrical resistance, we used the paste with the particle ratio of 75 : 25 to fabricate solder bumps. We obtained 6 ~ 30 µm height, 100 µm pitch Sn-Ag-Cu solder bumps.

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