

Thin Films

Room Naupaka Salons 4 - Session TF-MoM

Nanostructured Surfaces and Thin Films: Synthesis and Characterization I

Moderator: Toshiyuki Taniuchi, The University of Tokyo

8:00am TF-MoM-1 Characteristics of ZrO_2 Films Atomic-Layer-Deposited Using $Cp-Zr(NMe_2)_3$: Effects of Oxidant and Deposition Temperature, *Wan Oh, W Lee, S Choi, Y An, C Lee, S Wi, H Kim*, Sungkyunkwan University, Republic of Korea

The ZrO_2 thin films have been actively used as a dielectric material in various nanoelectronic devices, such as transistors and memories. In achieving excellent electrical performance, uniformity, and step coverage, atomic layer deposition (ALD) is the most perfect method. Consequently, development of the ALD ZrO_2 process itself as well as dielectric engineering (nanolaminating or alloying with other dielectrics) have been largely researched to lower the leakage current while taking advantage of its relatively high dielectric constant [1].

In this study, the ALD ZrO_2 thin films were deposited using $Cp-Zr(NMe_2)_3$ as a Zr precursor, and the effects of oxidant (H_2O , O_3) and deposition temperature (200-300°C) on their electrical properties were systematically studied. Metal-insulator-metal capacitors were fabricated and their electrical properties, such as capacitance and leakage current, were evaluated. In addition, the physical properties of the ZrO_2 thin films were compared by examining them using transmission electron microscopy, atomic force microscopy, and X-ray diffractometry. Lastly, the ALD ZrO_2 films were applied to a stacked structure of $ZrO_2/Al_2O_3/ZrO_2$, which has been popularly used in memory devices and their electrical properties were evaluated.

[1] D. Panda and T.-Y. Tseng, *Thin Solid Films* 531, 1 (2013).

8:20am TF-MoM-2 Enantioselective Catalyst on Oxide Support: Study of the Chemical Nature of Tartaric Acid on Rutile $TiO_2(110)$ by XPS and HREELS, *Gregory Cabailh, E Meriggio*, Sorbonne Université, France; *R Lazzari*, CNRS, France; *C Méthivier*, Sorbonne Universit evier, France; *V Humblot, X Carrier*, Sorbonne Universit e, France

1. Objectives :

Chiral molecules play a vital role in the biochemistry of living organisms, justifying the essential challenge of controlling enantioselectivity in several fields such as the pharmaceutical and agrochemical industry. Heterogeneous asymmetric catalysis for the synthesis of enantiopure chiral compounds is a tool of choice for its many economic and ecological benefits. Several techniques have been developed, including the modification of a metal surface by an organic chiral inducer. Nevertheless, the number of systems developed successfully remains limited. Unlike monocrystalline metal surfaces, very little is known on the role of the oxide support in catalysts based on supported metallic nanoparticles. The control of the role of the oxide support and the chiral inducer is based on the knowledge of the interactions at the molecular level between the three parties involved in the reaction: the oxide, the metal nanoparticles and the chiral inducer, represented in this work by TiO_2 single crystals, nickel nanoparticles (NPs) and tartaric acid (TA). A model approach is used here, where TA molecules and NPs are deposited by evaporation in an ultra-vacuum environment and then characterized by surface analysis techniques.

2. Results :

The chemical state of TA is characterized by X-ray Photoemission Spectroscopy (XPS) and High Resolution Electron Energy Loss Spectroscopy (HREELS). TA is first deposited on single crystals of Cu (110) and Au (111), on which the chemical nature of TA is well known, in order to obtain reference XPS spectra. By analyzing the C 1s and O 1s spectra, the presence of monotartrate adsorbed species ($COO^- / COOH$) is demonstrated on copper, while the molecules are in the bi-acid form ($COOH / COOH$) on gold. The comparison of these results with the data recorded on rutile $TiO_2(110)$ (in particular the energy differences between the C1s peaks) and complementary HREELS measurements allow to conclude that TA is absorbed as monotartrate on TiO_2 in analogy with other carboxylic acids. In addition, the organization and the nucleation point on the surface can be observed by scanning tunneling microscopy (STM). TA is finally deposited on the Ni / TiO_2 system at different coverage rates and studied by XPS and

STM to characterize the interaction between the three parties of the system.

8:40am TF-MoM-3 The Study on Flash Light Sintering Characteristics of Printed Copper Pattern Electrodes with Respect to their Width and Interval, *Yong-Rae Jang, H Kim, C Ryu, Y Hwang*, Hanyang University, Seoul, Korea

In this work, copper nano/micro-ink screen-printed on a polyimide (PI) substrate, were sintered by flash light irradiation. To find out the effects of the pattern width and interval between copper patterns on the flash light sintering characteristics, analytical thermal transfer simulation was conducted by finite difference method, where the temperature of the substrate and electrodes during the flash light irradiation could be predicted. The copper nano/micro-ink was printed with different widths and intervals and sintered via flash light. The flash white light irradiation conditions such as pulse duration, frequency, and number of pulses were optimized on each pattern sizes. To investigate the macrostructure of the copper pattern, optical microscope and alpha step were used. The microstructures of the copper pattern were observed using scanning electron microscope (SEM). Also, in-situ resistance monitoring was conducted to find the tendency of the sintering characteristics according to the Cu printed pattern. From the study, it was confirmed that the heat generated in the copper pattern by flash light irradiation, was dramatically increased as the pattern width becomes wider and the pattern interval becomes narrower. It is noticeable that the flash light irradiation condition should be designed considering the size of the pattern due to pattern dependent heat transfer phenomena.

9:00am TF-MoM-4 High Throughput XPS Surface Analysis of Novel Materials Generated by a Combinatorial Approach, *J Counsell, S Coultas*, Kratos Analytical Ltd., UK; *David Surman, C Moffitt*, Kratos Analytical Inc.

Combinatorial approaches have been widely used to discover new material phases for many years, allowing rapid exploration of composition-structure properties in complex material systems¹. The mapping of chemical properties such as oxidation state and alloying as a function of composition is an integral part of understanding the underlying physical and chemical properties. Here we apply combinatorial techniques for preparation of model systems to be characterised by X-ray photoelectron spectroscopy (XPS). Two diverse sample sets have been characterised by high throughput XPS - ternary alloy formation post thin-film deposition and polymer microarrays for biomaterial screening.

Ternary metal compounds are used in a wide range of applications; as high-performance alloy materials and electronic semiconductors. We have examined a range of thin-films of first-row transition metals co-deposited on Si wafers to form a matrix of ternary alloys. The surface composition was analysed with XPS to determine the stoichiometric mixing for different alloy compositions and the extent of oxidation and chemical bond formation during deposition. Further analysis of large datasets allows the user to determine areas of particular interest and performance for further investigation – leading to more detailed bulk/surface comparison studies by destructive and non-destructive depth profiling techniques.

Combinatorial methods are also exploited for screening of functional biomaterials. The surface composition of a series of printed polymer microarrays are analysed with XPS to correlate differences in surface chemistry with specific biological performance. This high throughput method allows for library databases to be created for parallel screening of a wide range of polymer blends.

Workflow and data-handling will be discussed for the two different systems. Data visualisation through XPS processing is also described for large datasets generated during these analyses.

1. C. J. Long, J. Hatrick-Simpers, M. Murakima, R. C. Srivastava, I. Takeuchi, V.L. Karen and X. Li, *Rev. Sci. Inst.*, 78, 072217, 2007.

9:20am TF-MoM-5 Semiconductor Nanowire Y-Junction Arrays Grown by MBE, *Esteban Cruz-Hernandez*, CIACYT, Universidad Autonoma de San Luis Potosi, Mexico

INVITED

Energetically unstable crystalline surfaces, among their uses, can be templates for the self-assembling of semiconductor structures at the nanometric level. Highly uniform structures such as quantum wires can now be fabricated from the self-assembly of nanometric facet arrays produced by using high-index substrates and epitaxial techniques such as Molecular Beam Epitaxy (MBE) [1]. However, the self-assembling of more complex nanostructures such as Y-junctions (produced by the union of two semiconductor nanowires) is a more complex problem. In MBE the growth process is carried out under non-equilibrium conditions, then the nonlinear

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evolution processes (such as step-bunching, meandering instabilities, and coarsening) that produce a very rich variety of surface morphologies have to be understood to precisely control the self-assembly of such complex nanostructures.

The control on the assembly of semiconductor Y-junctions could have great potential in technological applications (for example, in nanoelectronics as quantum logic gates) and one-dimensional physics exploration. Until very recently, related works on nanometric Y-junctions have been based on carbon nanotubes and graphene [2, 3], but not with semiconductor crystalline materials. In this contribution we report on the high-order and two-dimensional mechanisms in the MBE growth of GaAs on high-index GaAs substrates, which allow the formation of a regular alternating pattern of bifurcated nanowires [4] with suitable dimensions to form a Y-junction electron gas device.

[1] E. Cruz-Hernandez, S. Shimomura, and V. H. Mendez-Garcia, *Appl. Phys. Lett.* **101**, 073112 (2012).

[2] Zhen Yao, Henk W. Ch. Postma, Leon Balents, and Cees Dekker, *Nature* **402**, 273 (1999).

[3] A. Jacobsen, I. Shorubalko, L. Maag, U. Sennhauser, and K. Ensslin, *Appl. Phys. Lett.* **97**, 032110 (2010)

[4] R. Mendez-Camacho, M. Lopez-Lopez, V. H. Mendez-Garcia, D. Valdez-Perez, E. Ortega, A. Benitez, A. Ponced and E. Cruz-Hernandez, *RSC Adv.* **7**, 17813 (2017).

10:20am TF-MoM-8 Controllable Bandgap Design in (2+1) D Colloidal Photonic Crystals, *Lijing Zhang*, Dalian University of Technology, China

Photonic crystals (PCs) are artificial periodic dielectric materials with the characteristic of photonic bandgap (PBG), which can control the behavior of photons in a similar manner as what semiconductors do for electrons. (2+1) D photonic crystals, as a novel photonic crystal structure, possess unique advantages in both structural tenability (control in single layer level) and optical property (PBG broadening and deepening) compared with traditional 1D, 2D and 3D photonic crystals. However, the fabrication of high quality (2+1) D photonic crystals is still a big challenge, which greatly limit the systematic study on its optical property. Here we present a simple strategy to achieve (2+1) D photonic crystal with enhanced crystalline integrity by layer-by-layer deposition of annealed colloidal crystal monolayers. By simply manipulating the diameter of PS spheres, arrangement type and repetition period of the colloidal monolayers, flexible control in structure and stopband position of the (2+1) D photonic crystals (including superlattice and heterostructure) have been realized. The optical properties of the resulting (2+1) D PCs with different lattice constants were systematically studied and a universal photonic stopband variation rule was proposed, which makes it possible to program any kind of stopband structure as required. The superlattice structure exhibits fine control in PBG position and obvious PBG resonance enhancement. While dual- or multi-stopbands and ultra-wide stopband can be achieved by fabricating heterostructures. This work may afford new opportunities for delicate engineering photonic bandgap materials. Furthermore, we explored their fluorescence (FL) enhancement ability based on their special bandgap effect and demonstrate their application in heavy metal ion detection. A multiple heterostructure photonic crystal (MHPC) with super-wide stopband improved the limit of detection of Cr(VI) to 0.2ppb. and may find significant applications for augmenting FL intensity in chemical and biochemical sensing, imaging, disease diagnosis, and environmental monitoring.

10:40am TF-MoM-9 Effects of Interface on Proton Ordering in Heteroepitaxially Grown Ice Films, *Toshiki Sugimoto*, Institute for Molecular Science, Japan

INVITED

Materials with a strongly correlated and highly frustrated degree of freedom have potential for exhibiting dramatic and unusual responses to external stimuli. In the case of common water ice, protons in the hydrogen-bond network are strongly correlated and highly frustrated under the Bernal-Fowler-Pauling ice rules. The ubiquity of water ice makes it essential to clarify the fundamental physicochemical properties of the strongly correlated many-body proton system. It is, however, extremely difficult to directly access the local configuration of protons and their ordering dynamics through traditional experimental approaches. Moreover, the strongly correlated protons inevitably lose ergodicity at low temperature. These problems prevent us from fully understanding cooperative thermodynamic and electric responses of the many-body protons to external stimuli at the low temperature.

To open up a new route to unveil hidden exotic properties of many-body protons in ice, we have investigated a possibility of interface-induced ferroelectric proton ordering by focusing on heteroepitaxially grown crystalline-ice films on metal substrates as model systems [1-3]. We have used recently developed phase-resolved sum-frequency generation (SFG) vibrational spectroscopy in an ultrahigh vacuum chamber [4]. The Im $\chi^{(2)}$ SFG vibrational spectra ($\chi^{(2)}$: the second-order nonlinear susceptibility) exhibits positive and negative sign for OH oscillators with H-up and H-down orientation, respectively. Thus, heterodyne-detected SFG has a great advantage to directly observing local configuration of protons that cannot be investigated by other traditional experimental methods.

Recently, we have demonstrated that the adsorbed first-layer water molecules prefer an net-H-down configuration on model platinum substrate: Pt(111) [1,3]. The coverage dependence of the Im $\chi^{(2)}$ SFG spectra in the hydrogen-bonded OH stretching regions clearly reveals that the H-down proton ordering in the first layer is significantly pinned by the Pt(111) substrate and is subsequently propagated to the overlayer during the multilayer film growth. Temperature dependent SFG measurement revealed that such a ferroelectric proton ordering is thermodynamically stable and has an extremely high critical temperature of ~ 175 K [1,3], which is more than twice as large as that of ferroelectric bulk ice XI ($T_c \sim 72$ K). In addition to these results, I will discuss our recent challenges on the interface engineering for modulation of the ferroelectric proton ordering.

[1] *Nature Phys.* **12**,1063(2016);[2,3] *Phys.Rev.B* **96**,115405(2017); **97**,075410 (2018); [4] *Phys.Rev.Lett.* **117**,186101(2016).

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