Nanoscale Science and Technology
Room 114 - Session NS1-TuM

Synthesis and Visualization of Nanostructures I
Moderator: Aubrey Todd Hanibiki, Laboratory for Physical Sciences

8:00am NS1-TuM-1 Fabrication of High Aspect Ratio Gan and AlN Nanopillar Arrays with M-Oriented Sidewalls by Combining Dry and Wet Processes for the Next Generation of Deep Ultraviolet Light-Emitting Diodes, *Lucas Jaloustre, S. Sales de mello,* CNRS-LTM, France*; L. Valera,* CEA, France*; S. Labau, C. Petit-Etienne,* CNRS-LTM, France*; G. Jacopin,* CNRS, France*; C. Durand,* CEA, France*; E. Pargon,* CNRS-LTM, France

III-N materials have emerged as promising candidates for ultraviolet (UV) light-emitting diodes (LEDs) due to their wide band gap [1]. However, the current planar architecture of III-N LEDs has demonstrated unsatisfactory efficiency, particularly for wavelengths below 250 nm where the external quantum efficiency drops below 0.1%. One strategy to address this challenge is the transition from a planar to a core-shell geometry [2], which offers many advantages (reduced defects, larger emissive area, better light extraction). This approach involves patterning organized arrays of AlN or GaN nanowires with a high aspect ratio (AR>10) and ideally *m*-plane sidewalls using plasma etching. Metalorganic Chemical Vapor Deposition (MOCVD) is then used to radially grow emissive quantum wells.

In this work, the authors developed an Inductively Coupled Plasma etching process using a Cl_2 chemistry and a hard mark, suitable for the realization of highly anisotropic and smooth GaN and AlN pillars with an aspect ratio up to 16. They demonstrate that the III-N etching using Cl_2 plasma is driven by crystallographic orientation preferential etching and ultimately leads to the formation of *a*-plane sidewalls (Fig. 1-a), and not to the desired *m*-faceting [3].

Post-etching chemical treatments have been explored to improve sidewall roughness and to favour the appearance of the *m*-planes. The authors demonstrate the feasibility of such *m*-faceting on III-N pillars with KOH wet etching and highlight two key parameters for this process[4]: 1) The presence of a HM with a suitable shape during the wet to prevent top pillar erosion and drives the etching, allowing the transfer of the HM shape onto the pillars (Fig. 1-b and 1-c). 2) A tapered pillar profile, which is mandatory to ensure the HM shape transfer.

The wet mechanisms leading to this faceting, and the significant impact of KOH concentration on the etching dynamics (Fig. 2), will be discussed.

This work provides a promising path for achieving pillar arrays that serve as the first building block for highly efficient UV core-shell LEDs. The fabrication of straight and smooth GaN and AlN pillar arrays with the desired crystalline *m*-planes sidewalls (Fig 1-d) was achieved through a two-step process combining Cl_2 plasma etching and KOH wet etching. Finally, successful MOCVD growth of AlGaN/AlN MQWs has been achieved through a collaboration with CEA-PHELIQS, demonstrating UV-C emission on such structures (Fig. 3).

1. M. Kneissl, *et al. Nat. Photonics* **13**,233–244 (2019).
2. J. Kim, *et al. scientific reports* **8**, 935 (2018)
3. L. Jaloustre, *et al. Mater. Sci. Semicond. Process* **165**, (2023)
4. L. Jaloustre, *et al. Mater. Sci. Semicond. Process* **173**, (2024)

8:15am NS1-TuM-2 Exploring Large PAH in "Stardust" by HR-AFM, *Percy Zahl,* Brookhaven National Laboratory*; M. Chacon-Patino, J. Frye-Jones,* National High Magnetic Field Laboratory

Meteorites provide a glimpse into the past of the solar system by preserving snapshots of the universe for millions to billions of years. (1) Organic material, i.e. Polycyclic Aromatic Hydrocarbons (PAH), forms over this time, creating common molecules seen on Earth such as carboxylic acids, aromatic and aliphatic hydrocarbons, and most importantly for life, amino acids. (1–4) Organic material formed in such a way is often revealed as ultra-complex mixtures, similar to fossil fuels and natural dissolved organic matter seen on Earth.

However, these ultra-complex organic mixtures require ultrahigh-resolution analytical techniques to achieve comprehensive molecular-level characterization.

Very little work has been done so far using High Resolution non-contact Atomic Force Microscopy (HR-AFM) (5). Here we analyze highly enriched PAH meteorite sample extracts using our preliminary extraction method similar to that used for fossil fuels. Acetone assists in the extraction of highly aromatic compounds out of a powdered form of meteorite specimens that have already been extracted in a polarity gradient from methanol to toluene. The resulting fraction is enriched in highly aromatic/hydrogen-deficient compounds, as suggested by ultrahigh resolution FT-ICR mass spectrometry.

Comparison with a fraction extracted with chloroform demonstrates a drop in the H/C ratio (a measure of aromaticity) from an average 1.6 for chloroform species down to 0.6 for acetone-extracted compounds. This correlates with the images observed in HR-AFM, where more aliphatic species were observed in the chloroform extract compared to the highly aromatic compounds observed in the acetone fraction. The selected motifs observed highlight the highly aromatic composition of species from the acetone fraction, containing complex ring systems.

References:

[1] Sephton, M. A.,Phil. Trans. R. Soc. A: Mathematical, Phys. and Eng. Sci., 363(1837), 2729–2742 (2005)

[2]Pizzarello, S.; Cooper, G. W.; Flynn, G. J.,Meteorites and the Early Solar System II,625–651 (2006)

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[4] Pizzarello, S.; Shock,Cold Spring Harb Perspect Biol, 2(3), 1–19 (2010)

[5] Kaiser K.;Meteoritics & Planetary Science 57, Nr 3, 644–656 (2022)

8:30am NS1-TuM-3 Direct Atomic Manipulation of a Buried Graphene Interface, *Marek Kolmer,* Ames National Laboratory*; J. Hall,* Iowa State University*; S. Chen,* Ames National Laboratory*; S. Roberts, Z. Fei,* Iowa State University*; Y. Han,* Ames National Laboratory*; M. Tringides,* Iowa State University

Controlling the two-dimensional (2-d) materials via interlayer interactions is a promising strategy for synthesizing novel electronic and topological phases. These interactions may be tuned locally via atomic-scale manipulations using scanning tunneling microscopes (STMs). However, the practical application of STM manipulation encounters fundamental problems in protecting the designer structures formed atop the surface. We will present a material platform and experimental protocol for precisely manipulating the buried epitaxial graphene interface, which can serve as a template for further targeted synthesis. The covalent bonds between a graphene buffer layer and the silicon carbide substrate may be reversibly broken and restored using the electric field from the STM tip. The charge separation resulting from covalent bond redistribution is used to pull or push the interface atoms by controlling the polarity of the tip-sample bias voltage. The reported effect propagates to the top graphene layer to form a pattern of nanoprotrusions with lateral precision, reaching the dimension of a single unit cell of the interface moiré lattice (~1.8 nm).

Local and reversible electric-field-induced patterning of the epitaxial graphene heterostructures from the bottom interface presents an alternative architecture to synthesize metastable configurations at the interface. The decoupled interface could be locally arranged in ordered superstructures, creating a new 2-d phase with long-range periodic potential experienced by the Dirac electrons in the top graphene layer(s). The location of the voltage pulses controls the period of these superstructures. It allows exploring novel, rich 2-d quantum phases with low-energy electronic excitations of tailored superlattice minibands. This band structure control is realized directly within the epitaxial graphene-based tunable heterostructures on the technologically relevant silicon carbide substrate.

8:45am NS1-TuM-4 Effect of Methanol and Photoinduced Surface Oxygen Vacancies on the Charge Carrier Dynamics in TiO_2, *B. Guner,* **Omur E. Dagdeviren,** École de technologie supérieure, University of Quebec, Canada

The migration of holes in metal oxides such as TiO_2 plays a vital role in (photo)catalytic applications. The dynamics of charge carriers under operation conditions can be influenced by both methanol addition and photoinduced surface oxygen vacancies (PI-SOVs) [1]. Nevertheless, the existing knowledge of the effect of methanol as a function of PI-SOVs solely concentrates on the chemical reduction process. For this reason, the fundamental understanding of the time-dependent charge carrier-vacancy interactions with the presence of methanol is impaired. To overcome this

challenge, we performed time-resolved atomic force microscopy measurements to quantitatively disclose the dynamics of charge carriers in a rutile-terminated, single-crystal TiO_2 (100) sample under the influence of methanol as a function of high-energy ultraviolet (UV) surface irradiation [2-4]. We have three major experimental findings: (I) The addition of methanol decreased the time constant, and hence, the mobility of the charge carriers. (II) The energy barrier within the system was decreased by UV irradiation; however, the presence of methanol did not alter the corresponding barrier. (III) The reversibility of the charge carrier dynamics was observed upon the termination of UV irradiation. Our analysis of methanol's role in hole mobility as a function of surface irradiation contributes to the understanding of surface interactions and charge carrier dynamics, offering valuable insights for (photo)catalytic applications.

[1] Orcun Dincer, Bugrahan Guner, and Omur E. Dagdeviren, APL Materials **12** (2) (2024).

[2] Bugrahan Guner, Simon Laflamme, and Omur E. Dagdeviren, Review of Scientific Instruments **94** (6) (2023).

[3] Bugrahan Guner and Omur E. Dagdeviren, ACS Applied Electronic Materials **4** (8), 4085 (2022).

[4] Bugrahan Guner, Orcun Dincer, and Omur E. Dagdeviren, ACS Applied Energy Materials **7** (6), 2292 (2024).

Funding information:

9:00am **NS1-TuM-5 Single Nanofabrication Step of Low Series Resistance Silicon Nanowire-Based Devices for Giant Piezoresistance Characterization**, *K. Shao Chi, L. Spejo,* University of Campinas (UNICAMP), Brazil*; R. Minamisawa,* Institut für Mathematik und Naturwissenschaften Fachhochschule, Switzerland*; J. Diniz, **Marcos Puydinger,*** University of Campinas (UNICAMP), Brazil

Strained silicon nanowires (NWs) are essential in sensor applications and in the microelectronics industry, as they exhibit giant piezoresistance and variable carrier mobility as a function of stress. In this work, individual NWs were fabricated from strained silicon-on-insulator (sSOI) thin films with 0.8% biaxial strain. After a lithographic step, the buried oxide (BOX) was removed from the SOI film, thus suspending the NWs. The new boundary condition induces mechanical stress amplification, now uniaxial in the NW longitudinal direction (Fig. 1a). Finite element method simulations show that before the removal of SiO2, the nanowires exhibit predominantly uniaxial strain of around 0.8%, while the peripheral pads show a 0.8% biaxial strain. In this sense, the proposal is to stress the NWs to levels higher than those employed in industry.

The solutions proposed in the literature usually require external actuators or complex multi-step nanofabrication infrastructure [1], [2]. Here, we present a method for prototyping sSiNWs without external actuators and measuring their piezoresistance directly in a 2-probe setup (Figs. 1b and 1c) without further lithographic or metal deposition steps for the electrical contacts. We were able to simplify the steps involved in the fabrication, thus making fast prototyping of strained NWs possible using a single-step protocol and electrical characterization with optimized contact resistance.

In addition, Raman spectroscopy was used to measure the NW uniaxial stress. Figure 2 shows an example of the fabricated suspended sSiNW and its spectrum. We have measured the uniaxial mechanical stresses of around 2.9 GPa for 200 nm-wide sSiNWs, which vary depending on the NW dimension. Parameter optimization can further result in the fabrication of MOSFETs based on a single ultra-strained NW in gate-all-around (GAA) topology, as well as chemical and physical sensors for various technological applications.

[1] F. Ureña-Begara et al. J Appl Phys, vol. 124 (9), 2018.

[2] H. Ando and T. Namazu. J. Vac. Sci. Technol. B, vol. 41 (6), 2023.

9:15am **NS1-TuM-6 Size-Dependent Oxidation of Supported Pd and Pd-Pt Nano-Catalysts Under Methane Oxidation Conditions**, *A. Large,* Diamond Light Source, UK*; H. Hoddinott, R. Palmer,* University of Swansea, UK*; **Georg Held,*** Diamond Light Source, UK

The importance of cluster size effects in heterogeneous catalysis has been recognized for some time and numerous studies have addressed this issue. XPS is a well-established technique to study changes in the chemical composition and electronic structure of catalyst nanoparticles. However, as XPS is an averaging technique and based on the detection of electrons, experiments require a narrow distribution of cluster size and a conducting homogeneous support in order to avoid sample charging, which would prevent accurate measurements of chemical shifts. Traditional methods of catalyst synthesis by impregnation/calcination of support powders lead to very large particle size distributions (typically ±50 %) and insulating samples, which fail on both the above criteria. Here we present an operando XPS study of Al_2O_3-supported Pd and Pd-Pt nanoparticles under various dry and wet reaction conditions for methane oxidation (CH_4 + O_2 [+ H_2O]). In order to create a system as close to industrial catalysts as possible, the support consists of 5-10 nm thick alumina films electrochemically grown on Al foil. The nanoparticles (1 to 10,000 atoms) were produced by gas condensation and size-selected within 4-5%. TEM confirms the narrow size distribution. The XPS spectra of the clusters before the reaction show clear chemical shifts as function of particle size. Under dry reaction conditions larger clusters tend to oxidize fully (Pd II) whereas smaller particles show a mix of oxidation states (Pd 0-II).The situation is less clear under wet conditions, which could be due to sintering.

9:30am **NS1-TuM-7 Evidence from Molecular Force Microscopy of Magnetic Monopole-Like Behavior in Chiral Molecule-Coated Superparamagnetic Nanoparticles** *, **Sidney Cohen,** Q. Zhu,* Weizmann Institute of Science, Israel*; J. Fransson,* Uppsala University, Sweden*; O. Brontvein, R. Naaman,* Weizmann Institute of Science, Israel

Ever since Dirac's proposition[1] nearly a century ago that magnetic monopoles should exist, experimentalists have searched for them without success. A flurry of work starting about 50 years ago eventually showed magnetic *monopole-like* behavior in very limited and extreme conditions. The potential for tunable energy storage and stable information storage makes such structures interesting technologically. Here, we use atomic force microscope (AFM)-based molecular force microscopy to show that superparamagnetic iron oxide nanoparticles (SPIONs) coated with an amino acids of opposing chirality (D and L-cysteine) exhibit monopole magnetic behavior whose polarity depends on the chirality of the molecular entity. The effect is governed by the chiral-induced spin selectivity effect (see for instance references 2-4). Attractive magnetic forces were measured between a magnetized Ni film and an SPION attached to the AFM tip through a polyethylene glycol linker. Experiments were performed in a phosphate-buffered saline solution. A thin Ti (oxide) layer covered the Ni to prevent chemical interaction between the cysteine thiol and Ni. The direction of the field was changed between up and down by flipping a magnet held under the substrate. The magnetic force is comprised of spin-exchange interactions (short range) and magnetic monopole interactions (longer range). The interaction force was observed to vary with chirality of the molecule and magnetic field direction. A significant difference was measured in the pulling force for the D vs. L cysteine and up/down magnet orientations when the Ti (oxide) layer was about 2 nm thick. Thicker layers (of Ti oxide or aluminum oxide) result in significant reduction of the magnetic force, allowing estimation of the range of the force interaction.

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[2] Naaman, R., Paltiel, Y., Waldeck, D.H. Chiral induced spin selectivity gives a new twist on spin control in chemistry *J. Phys. Chem. Lett.* **11**, 11, 3660-3666 (2020).

[3] Banerjee-Ghosh, K. et al. Separation of enantiomers by their enantiospecific interaction with achiral magnetic substrates *Science* **360,** 1331-1334 (2018).

[4] Adhikari, Y., et al. Interplay of structural chirality, electron spin and topological orbital in chiral molecular spin valves *Nat. Commun.* **14**, 5163 (2023).

9:45am **NS1-TuM-8 Mapping the Slow-Decay of End States in a Laterally Extended Graphene Nanoribbon**, ***Umamahesh Thupakula,*** CEMES-CNRS, France

End states (ESs) of quasi one-dimensional (1D) graphene nanoribbons (GNRs) have become a central focus in recent years because of their inclusion into the classification of topological tailor-made quantum systems.[1] So far, the topological phases of the GNRs are solely characterized by an integer parameter, called Z_2 invariant originating from the Zak phase, which takes values of 0 or 1 corresponding to topologically trivial or nontrivial configurations, respectively.[1] In these calculations, an infinite nanoribbon is always considered after defining the unit cells structure long the ribbon.[2] However, finite length nanoribbons are mainly observed and characterized experimentally. The tracking of the step-by-step building-up of ESs from a few unit cells to the formation of desired

1D/quasi-1D GNR molecular wire electronic band structure remains elusive. Combining picometer scale precision scanning tunneling microscopy, dI/dV spectroscopy mapping (STM and STS) with topological Hückel molecular orbital (HMO) calculations, we explain how topological quantum states are emerging or not with respect to the length 'N' (number of repeating molecular units) of the GNR starting from the basic polyene to the 1D polyacetylene chain and by a step-by-step enlargement of the nanoribbon width.

References

[1] Ting Cao, Fangzhou Zhao, & Steven G. Louie, Phys. Rev. Lett. 119, 076401 (2017)

[2] Daniel J. Rizzo, Gregory Veber, Ting Cao, Christopher Bronner, Ting Chen, Fangzhou Zhao, Henry Rodriguez, Steven G. Louie, Michael F. Crommie & Felix R. Fischer, *Nature* **560**, 204-208 (2018)

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