

Science and Technology of Materials, Interfaces, and Processing

Topical Areas

Biomaterials
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Materials Processing
MEMS

Microelectronic Materials Nanoscale S&T Plasma S&T Quantum Science Surface Engineering Surface Science Thin Films Vacuum Technology

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7:30 - 7:40

2022 Fall Meeting Hudson Mohawk AVS Chapter Thursday, October 20, 2022 3:30 – 7:40 PM

CESTM Auditorium and Rotunda SUNY Polytechnic Institute 251 Fuller Road, Albany, New York 12203

Meeting Agenda

	3:30 - 3:50	Reception (coffee and cookies served)
	3:50 - 4:00	Welcoming Remarks
Keynote Lecture		
	4:00 - 4:30	2nm Nanosheet Technology: Overview and Patterning Challenges by Tao Li and Eric Miller (Etch Research & Development, IBM Albany)
Student Oral Presentations		
	4:30 - 4:50	Poyen Shen (Rensselaer Polytechnic Institute) Contact Resistance Measurements in Epitaxial W(001)/Mo(001) Multilayers
	4:50 - 5:10	Nicholas Stucchi (Clarkson University) Investigation of a Novel Layer-by-layer Growth Methodology for Surface Metal-organic Frameworks
	5:10 - 5:30	Alex Kaloyeros (SUNY Polytechnic Institute) Toward Scalable Telecom Single Photon Emitters for Quantum Photonics
	5:30 - 5:50	Saloni Pendse-(Rensselaer Polytechnic Institute) Van der Waals Epitaxy of Vanadium Dioxide
	5:50 - 6:10	Rajas Mathkari (SUNY Polytechnic Institute) Investigating the Effect of Oxygen Concentration Gradient Inside Tantalum Oxide on ReRAM Switching Parameters
	6:10 - 7:30	Poster Presentations (pizza and refreshments served)

Award Ceremony

CNSE Nanotechnology Complex



Parking Information

Upon entering the CNSE Nanotechnology complex on Tricentennial Drive, you will need to stop at the guard shack that is located before the access road to the NFE building. Let the guard know that you are attending the Hudson Mohawk AVS meeting. The guard will ask you to park your car in the H Lot in front of the NFE building. If the H lot is full, you will be asked to park in the F Lot, instead. After parking, you should go to the NFE rotunda to check in with security.

Visitor Information

All non-CNSE attendees will need to check in at the security desk in the NFE rotunda. Visitors need to present a government issued ID (driver's license or passport) to security in the NFE Rotunda to obtain a Visitor's badge. Non-US citizens who possess a Permanent Resident Card (green card) must present the card when they register at the security desk. After checking in, you will be escorted to the CESTM rotunda and auditorium. If you are a non-US citizen who does not possess a Permanent Resident Card, you will need to attend the meeting virtually (see next page) unless you have gone through additional security clearance procedures at the time of registration.

Virtual Access to Meeting

Virtual Access

The Fall 2022 meeting of the Hudson Mohawk Chapter of the AVS will be held in-person in the CESTM auditorium and rotunda at the College of Nanoscale Science and Engineering in Albany, NY. For those who cannot attend in-person, the oral presentations will be streamed live via Zoom.

Zoom Link

Topic: AVS Hudson Mohawk Chapter Fall 2022 Meeting Time: Oct 20, 2022 03:30 PM Eastern Time (US and Canada)

Join Zoom Meeting

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CONTACT RESISTANCE MEASUREMENTS IN EPITAXIAL W(001)/Mo(001) MULTILAYERS

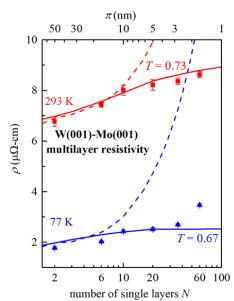
Poyen Shen and Daniel Gall

Materials Science and Engineering Department Rensselaer Polytechnic Institute Trov. New York. 12180-3590

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Epitaxial W-Mo multilayers are used as a model system to demonstrate a new contactresistance measurement method where the resistivity measured parallel to metal-metal interfaces is used to quantify the specific interface resistance perpendicular to the interfaces, circumventing sub-10-nm patterning that would be required for direct transport measurements across the interface.

50-nm-thick epitaxial multilayer stacks containing 2-60 individual W(001) and Mo(001) layers are deposited on MgO(001) substrates and their resistivity ρ measured as a function of superlattice period π at 293 and 77 K. ρ increases from 6.77 to 8.62 $\mu\Omega$ -cm with decreasing π = 50-1.7 nm which is attributed to increasing electron-interface scattering. The data are well described by semiclassical Fuchs-Sondheimer model for surface scattering for $\pi \ge 10$ nm, but the model overestimates the resistivity for π < 10 nm. Small superlattice periods require revision of the classical transport model to account for coherent electron transmission across multiple interfaces. Data analyses using this revised model yields an electron transmission probability T of 0.73 and 0.67 at room temperature and 77 K, respectively. indicating a temperature-independent $T = (70 \pm 3)\%$ for W(001)-Mo(001) interfaces, corresponding to a specific Mo-W



interface resistance of $3.35 \times 10^{-16} \ \Omega \text{-m}^2$ for a bulk ballistic conductance of $1.28 \times 10^{15} \ \Omega^{-1} \text{-m}^{-2}$.

Acknowledgements:

The authors acknowledge funding from the Semiconductor Research Corporation under tasks 3085.001 and 2966.003, and the NY State Empire State Development's Division of Science, Technology and Innovation (NYSTAR) through Focus Center-NY–RPI Contract C150117.

INVESTIGATION OF A NOVEL LAYER-BY-LAYER GROWTH METHODOLOGY FOR SURFACE METAL-ORGANIC FRAMEWORKS

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The fabrication of highly ordered and crystalline surface-confined metal-organic frameworks (SURMOFs) has garnered interest in applications such as catalysis, gas storage, and gas separation. At present, the state of the art is a layer-by-layer (LBL) growth, wherein a functionalized substrate undergoes sequential immersions in solutions of the desired metal or ligand. This LBL growth is commonly performed using gold substrates modified with carboxylate-terminated self-assembled monolayers (SAMs) which act as an initial nucleation site for the metal cluster. Careful control over deposition conditions and reaction times results in the formation of crystalline SURMOFs with tunable thicknesses. However, this technique is limited to substrates that can undergo the necessary SAM functionalization as well as being highly sensitive to the deposition conditions. I will discuss the development of a new LBL methodology that utilizes a pre-formed covalent-organic framework (COF) on the surface of highly oriented pyrolytic graphite (HOPG) as the template for SURMOF growth. The COF template should have the same geometry and a lattice parameter close to that of the desired SURMOF to minimize the strain of the first few layers. As such, COF-366-Zn was chosen as the template for UiO-67, which has a 3% lattice mismatch. The COF was reacted with isonicotinic acid (INA) in which the pyridine moieties axially coordinate to the zinc centers of the COF leaving the exposed carboxylate moieties to serve as nucleation sites for the zirconium acetate clusters of UiO-67. The SURMOF was formed following several sequential reactions in the cluster and benzene-1,4-dicarboxylic acid (BDA) ligand solutions. The COF and initial INA binding will be characterized by micro-Fourier transform spectroscopy (micro-FTIR). Atomic force microscopy (AFM) will be used to characterize the LBL growth of UiO-67. The crystallinity of the SURMOF will be determined using diffraction techniques.

TOWARD SCALABLE TELECOM SINGLE PHOTON EMITTERS FOR QUANTUM PHOTONICS

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Single-photon emitters (SPEs) associated with point-defects and ions in semiconductors are currently considered a significant resource for the solid-state implementation of photonic quantum information processing, quantum imaging, and quantum key distribution technologies. Specifically, non-classical single-photon light sources emitting in the nearinfrared region of the electromagnetic spectrum around 1.5 µm, falling in the lowest loss wavelength range of fiber optics networks, are critical chip-scale building components for the development of fiber-based quantum networks. The realization of scalable on-chip quantum devices, such as single-photon sources and quantum memories, requires novel nanostructured materials that must be compatible and can be integrated with existing electronic circuits, waveguide architectures, and current chip-scale and silicon process technology. Here, we present nanophotonic structures composed of arrays of silicon carbide (SiC) nanowires (NWs) and nanocylinders (NCs) based on a novel and fab-compatible nanofabrication process. These nanophotonic nanostructures enable the deterministic positioning of erbium (Er³⁺) ions with a state-of-the-art accuracy of ~10 nm and are pivotal in engineering the Er³⁺-induced 1.54 μm emission. They exhibit high Er³⁺ photoluminescence (PL) emission at 1.54 µm and near-radiative-limited lifetimes and efficient excitation characteristics with an absorption cross-section ($\sim 2 \times 10^{-18}$ cm²) two-orders larger than typical benchmark values for direct absorption in rare-earth-doped quantum materials. Additionally, we study the polarization properties of the Er:SiC NW structures, which is important for efficient coupling to optical cavities for applications in quantum photonics. Finally, we benchmark and optimize our state-of-the-art near-infrared single-photon detector system, which will be used to characterize the single-photon character from these scalable nanophotonic structures.

VAN DER WAALS EPITAXY OF VANADIUM DIOXIDE

<u>Saloni Pendse</u>¹, Jie Jiang¹, Yuwei Guo¹, Lifu Zhang¹, Ru Jia¹, Zhizhong Chen¹, Yang Hu¹, Zonghuan Lu¹, Yuandong Wang^{2,3}, Toh-Ming Lu⁴, Yi-Yang Sun², and Jian Shi¹

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With the influx of flexible electronics as well as the emergence or prediction of unique phenomena in two-dimensional forms of materials, epitaxy at weakly coupled interfaces is gaining momentum as a feasible technique to develop nanostructured and two-dimensional materials. The weak substrate-film interaction expected in this method of epitaxy has been believed to be crucial in enabling not only the formation of sharp, defect-free heterostructures but also the mechanical exfoliation of the epilayer. Vanadium dioxide (VO₂) is a strongly correlated oxide widely studied for applications in electronics due to its metal-insulator transition at approximately 68°C. While thin films and nanostructures of VO₂ have been grown on common rigid substrates like Al₂O₃, TiO₂, and Si, strong chemical interaction between the substrates and VO₂ can induce significant strain during the metal-insulator transition. This not only broadens the temperature range of transition but also leads to the formation of alternating insulating and metallic domains, hence complicating room temperature device applications. Here, we present our efforts to grow VO₂ wires by conventional as well as van der Waals epitaxy. We unravel an unconventional understanding of epitaxy at weakly coupled interfaces, entailing ions of the van der Waals substrate being scavenged by the growing film, resulting in the formation of a distinct and uniform unit-cell-thick interfacial layer. By revealing metalinsulator transition proceeding via a single domain within a narrow temperature range of 2°C. we present van der Waals epitaxy as an effective tool to tune phase transition kinetics in VO₂ or similar systems.

Oral Presentation

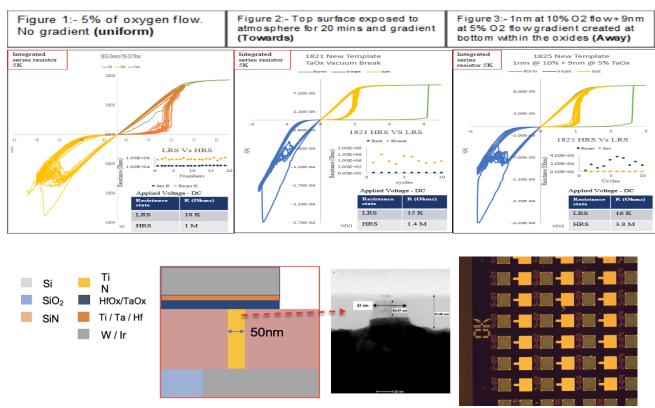
INVESTIGATING THE EFFECT OF OXYGEN CONCENTRATION GRADIENT INSIDE TANTALUM OXIDE ON RERAM SWITCHING PARAMETERS

Rajas Mathkari, Ross Pareis, Pramod Ravindra, Karsten Beckmann, Natalya Tokranova, Nathaniel Cady

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Resistive random-access memory (ReRAM) is a form of non-volatile memory that has potential applications in high-density memory and as embedded memory for many non-Von Neumann computing architectures. However, reliability issues are a significant concern for such applications. In this work, we introduced an oxygen concentration gradient in tantalum oxide switching layers and studied its effect on memristor performance. All devices were fabricated on 50 nm diameter TiN bottom electrodes. PVD produced three stacks: uniform oxygen distribution and the gradient in oxygen concentration towards and away from the Ta oxygen exchange layer (OEL). This was followed by the deposition of OEL and the top electrode. Device performance was evaluated by current-voltage switching characteristics. Ongoing work is focused on further reducing the leakage current and using different OEL materials for better switching characteristics to improve the ReRAM memory window, forming voltage, retention, and endurance.



Left: Cross-section schematic of the nanoscale ReRAM bottom electrode template used for device development and testing. Right: Top-down view of patterned and etched ReRAM stacks (using contact lithography) fabricated on top of nanoscale bottom electrode templates.

ADVANCED TECHNIQUES IN AFM FOR DEVICE CHARACTERIZATION and MEASUREMENT OF ELECTRONICA MATERIALS

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SRAM yield is a key metric in semiconductor technology node qualifications. Much effort in failure analysis and device characterization occurs at the contact level. The results of Conductive AFM analyses on a commercially available 7 nm SRAM, using an in-situ AFM inside a SEM, are presented. Current maps are shown which demonstrate the ability to find defects and even analyze noise margins in device engineering. This analysis capability provides a quick visual indication of the health of junctions across a wide field of view, and as such will be critical not only to yield management in industry, but also device improvement in a research setting. Results are also shown which demonstrate the benefit of a "bake and scrape" technique which can improve sample surface quality and expose new areas, one that would only be possible with an AFM in a SEM.

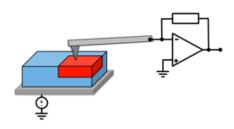
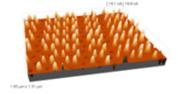


Diagram of basic principle for conductive AFM. As the needle scans the surface, the current making it to the op-amp from the backside is measured.



SEM view showing the relative arrangement of the AFM tip to a delayered block of 7 nm SRAM



CAFM results of a block of SRAM, displayed as a 3D height field proportional to the current map. Higher (positive values) are shown as peaks, and negative values as holes. The junction health is shown across a wide field of view.

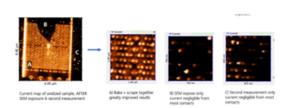


Diagram showing results of a method of improving sample surface that is only possible in SEM-based systems.

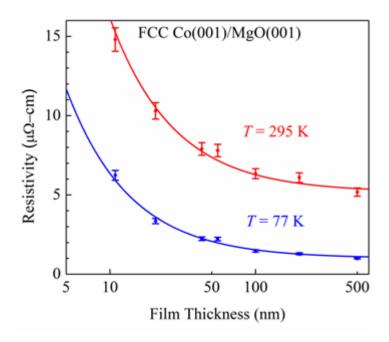
EPITAXIAL CUBIC Co(001)/MgO(001) LAYERS AS POTENTIAL INTERCONNECT CONDUCTOR

Anshuman Thakral, Atharv Jog, and Daniel Gall

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Metastable face-centered cubic (fcc) cobalt layers are deposited to determine the potential of fcc Co as interconnect metal to replace Cu in future integrated circuits. The stabilization of cubic Co is achieved using reactive sputtering in 5.0 mTorr pure N₂. Growth at T_s = 400 °C on single-crystal MgO(001) substrates results in epitaxial phase-pure fcc Co(001) layers, as confirmed by X-ray diffraction θ -2 θ scans, ω -rocking curves, and φ scans. The resistivity size effect is quantified with transport measurements as a function of layer thickness d = 5 – 500 nm at 295 and 77 K, as plotted in the figure. Data fitting with the Fuchs-Sondheimer model for diffuse surface scattering yields a room-temperature bulk resistivity ρ_o = 5.2 ± 0.3 $\mu\Omega$ -cm and an effective electron mean free path λ_{eff} = 56 ± 3 nm. At 77 K, the resistivity is reduced to ρ_o = 1.0 ± 0.1 $\mu\Omega$ -cm while λ_{eff} = 140 ± 7 nm. The overall results indicate that fcc Co has a 18% lower resistivity than the stable hcp phase, but that the resistivity scaling as quantified by the product $\rho_o\lambda_{eff}$ = (29 ± 3) ×10¹⁶ Ω -m² is 2.3 times larger suggesting that fcc Co cannot outperform hcp Co for narrow interconnect lines.



GROWTH AND PROPERTIES OF EPITAXIAL TIN(001)-TIC(001) SUPERLATTICES

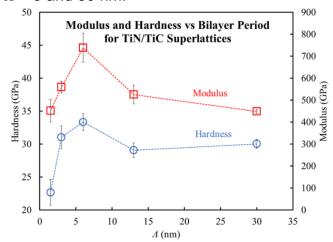
Elie Azoff-Slifstein and Daniel Gall

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Superlattices of epitaxial TiN(001)-TiC(001) layers are deposited on MgO(001) in order to explore superlattice hardening in a cubic nitride-carbide materials system. Superlattices are of widespread interest for enhancing mechanical properties through local strain variations and dislocation pinning at interfaces of alternating layers within nanoscale composites. Transition metal nitrides and carbides are particularly promising due to their high intrinsic mechanical strength and hardness. Reactive magnetron sputtering in Ar/N₂ and Ar/CH₄ mixtures at 1100 °C is employed to grow 1- μ m-thick TiN-TiC superlattice films with a superlattice bilayer period Λ = 1.5-30 nm. X-Ray diffraction θ -2 θ scans, ω -rocking curves, and reciprocal space maps (RSMs) confirm a cube-on-cube epitaxy of alternating rock-salt structure TiN(001) and TiC_{0.5}(001) on MgO(001). Superlattice peaks in θ -2 θ scans with $\Delta\theta$ = 0.15° and 0.36° provide accurate measurements of Λ = 30 and 13 nm, respectively. The ω -rocking curve full width at half-maximum is narrow and increases from 0.1 - 0.6° with decreasing Λ , indicating good crystalline quality. RSMs show partial relaxation of TiN(001)-TiC(001) layers for Λ = 6 and 13 nm, but fully-strained coherent superlattices for Λ = 3 and 30 nm.

Scanning electron microscopy analyses show surface protrusions due to misoriented grains which increase in density from ρ = 0.4 to 1.0 μ m⁻² for Λ = 1.5 to 3 nm but then decrease back to $\rho = 0.06 \ \mu \text{m}^{-2}$ for Λ Misoriented cause 30 nm. grains nanoindentation measurements to exhibit a depth dependence such that 20, 80, and 10% of indentations are depth-dependent for Λ = 1.5, 6, and 30 nm, respectively, reflecting the trend of the measured misoriented grain density. The superlattice system demonstrates hardness Н and elastic modulus E enhancements with H = 34 GPa



and E = 750 GPa maxima at $\Lambda = 6$ nm as shown in the figure.

DEVELOPMENT OF VOLTAGE-TUNABLE IR PHOTODETECTOR

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Quantum Well Infrared Photodetectors (QWIPs) provide the means to control their spectral sensitivity with an applied bias. We have designed and demonstrated an adaptable sensor that contains an asymmetrically doped double quantum well (QW) structure (Fig.1). The structures were designed using a finite element 1D Schrodinger-Poisson solver, to define electronic transition energies responsible for IR photosensitivity (Fig.2) with adequate responsivity control. The design, growth, and characterization of QWIPs have been performed aiming at the detection wavelength from 8 μ m to 12 μ m. The structures were grown by molecular beam epitaxy and contain double GaAs QWs and Al_xGa_{1-x}As barrier (x~ 0.2) inside and between the double-QW elements (Fig. 1). One of the QWs in the pair was modulation-doped to provide asymmetry of potential. The sensing region contained 25 periods of double QWs. The spectral photo response at various biases (Fig. 3) shows two bands at 5.5 μ m and 8 μ m with tunable sensitivity. The ratio of the sensitivity of the two bands is controlled over an order of magnitude (Fig. 4). The proposed design is adequate for the adaptive "2-color" sensors which can be driven by the Artificial Intelligence agent for improved object recognition.

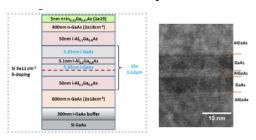


Fig 1: (left) Schematic of the QWIP with asymmetrically doped double quantum wells, and (right)TEM micrograph of the double QW structure.

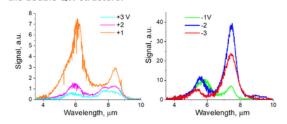
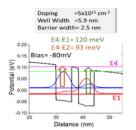


Fig 3: Experimental FTIR spectral response of QWIPs at 77K as a function of applied bias for positive and negative voltages.



The work is supported by ARO, contract No. W911NF 2110251

Fig. 2: Example of calculated potential and wavefunctions in the double quantum well under bias with indicated transitions

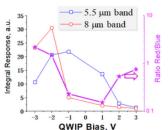


Fig 4: Integral response of the two bands controlled by the applied bias to the QWIP structure, and the sensitivity ratio of the two bands.

DEVELOPMENT OF A MICROCONTROLLER-DRIVEN TESTING PLATFORM FOR LOW-POWER, RESISTIVE MEMORY-BASED COMPUTING

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Resistive Random Access Memory (ReRAM), an emerging non-volatile memory technology with in-memory processing capabilities, has shown promising outcomes for the implementation of energy-efficient artificial intelligence hardware. In this work, we designed a microcontroller-based, printed circuit board (PCB) interface to perform device level testing and in-memory computation on packaged chips with 8 rows and 8 columns of hafnium oxide based ReRAM. The test board was designed to generate variable control pulses including: electroforming (+3.3V, 1ms to 125ms) and programming (-2.5V to +2.5V) with adjustable pulse width (1us to 125us), as shown in the block diagram. Additionally, the board enables the simultaneous application of different voltages to all 8 devices in a column, for demonstration of in-memory computation and column-based vector operations. ReRAM performance was strongly affected by chip packaging parameters and initial electrical noise in the test board, which was resolved to enable low-power implementation of error correcting codes as an operational test case.

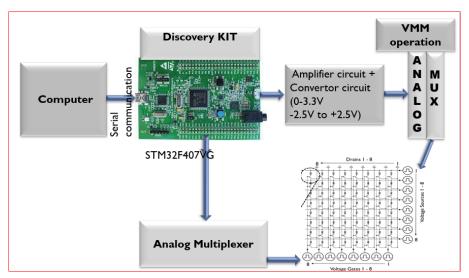


Fig: Block Diagram representing the test board test-up

ANALYSIS OF THE OXIDATION OF Ru THIN FILMS

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Ruthenium is often used as an electrical contact material because of its resistance to oxidation at elevated temperatures. In addition, the most stable stoichiometry of ruthenium oxide under ambient conditions is RuO₂, which is an electrically conductive oxide. The goal of this study is to determine the stoichiometry and measured thickness of the surface oxide on Ru formed by typical semiconductor fabrication processing techniques such as reactive ion etch, plasma ashing processes, and annealing in various environments. In addition, changes in the surface topography induced by these processing techniques is monitored. The primary analysis techniques used for this study are X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The Ru thin films were deposited on SiO₂/Si(100) substrates. Angle-resolved XPS data were collected at takeoff angles of 10°, 20°, 30°, 40°, 50°, and 60°, where the takeoff angle is measured from the plane of the surface. The acceptance angle of each of the angle-resolved measurements was 10°. Angle-integrated XPS data were collected at a takeoff angle of 45° and acceptance angle of 40°. Analysis of the Ru-3d XPS spectrum of the as-grown Ru film indicates that the native oxide is in a 2+ state and is less than a nm thick. Annealing at atmosphereic pressure results in the formation of Ru in a 4+ state (RuO₂) at the surface that is ~2 nm thick. In addition, the presence of higher order oxides and surface carbon is detected after the anneal. Performing either a RIE or ashing process on the as-deposited Ru film also results in the formation of RuO₂ but with a thickness of ~1 nm. Higher order oxides (Ru_xO_y) and carbon are also present in the surface region after these processing techniques have been performed but at a lower surface concentration than the sample annealed in air. Analysis of the O-1s XPS spectra of the samples indicates the presence of an ~1 nm thick water layer on top of each sample during the measurements. AFM measurements of the as-deposited films, the films annealed in air, films after the RIE, and films after the ashing process show rounded surface features with a topography or about 2 nm.

Acknowledgements: This project was funded in part by the New York State Center for Advanced Technology in Nanomaterials and Nanoelectronics (CATN2).

Poster Presentation

INFLUENCE OF HAFNIUM AND TITANIUM THICKNESS RATIOS ON RESISTIVE RANDOM ACCESS MEMORY (ReRAM) PERFORMANCE

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Resistive random-access memory (ReRAM) is a novel form of non-volatile memory, compatible with CMOS technology, with potential to solve bottlenecks in current memory technology if properly optimized. We integrated ReRAM with CMOS transistors (1T1Rs) using TiN electrodes, a Ti oxygen exchange layer, and an HfO $_{\rm x}$ insulator, and altered the thickness of the Ti and HfO $_{\rm x}$ layers to observe performance differences. Five 300mm wafers were tested with HfOx:Ti ratios of 1.14:1, 1.33:1, 1.5:1, 1.66:1, and 2:1. 1T1Rs were formed, pulsed, and underwent endurance testing. Differences in forming voltage, set/reset voltage, resistance values, and device yield were observed. Yield and forming voltage varied most significantly, a 0.1 increase in HfO $_{\rm x}$:Ti corresponded with an approximate 1.9% decrease in yield (R²=0.763). This yield difference could potentially be explained by devices with higher HfO $_{\rm x}$:Ti requiring higher forming voltages, resulting in greater electric field and more destructive electroforming, and switching. Memory window also varied with HfOx:Ti, with thicker hafnium layers corresponding to a larger memory window, and thus better performance. This leads to a tradeoff between having higher yields or better energy efficiency and performance.

Poster Presentation

DYNAMIC COVALENT CRYSTALIZATION OF COVALENT ORGANIC FRAMEWORKS BETWEEN PLANAR SUBSTRATES

Jennifer M. O'Brien¹, Joshua S. Roys¹, Adam D. Hill², Jingyun Ye³, and Ryan D. Brown¹

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Covalent organic frameworks (COFs) are materials that can form large crystalline domains with tunable physical and chemical properties, and they can be grown in solution or using solid surfaces as a growth template. To date, COF growth when confined at solid-gas interfaces, solid-liquid interfaces, and liquid-liquid interfaces has been well characterized, but COF growth under confinement between planar substrates has not been investigated. We explored the growth of a simple COF (COF-1) confined between mica and graphene, and observed extraordinary crystallinity compared to COF-1 growth on bare mica. Atomic Force Microscopy (AFM) and micro-Fourier Transform Infrared Microscopy (micro-FTIR) measurements demonstrated formation of COF-1 from its molecular precursors both outside of and beneath exfoliated graphene, as well as the presence of water confined between graphene and mica. We argue that there are two major factors at play causing the increased crystallinity: (1) that the material under graphene confinement produces larger crystalline domains due to greater exposure to water and thus greater error correction through dynamic covalent crystallization, and (2) the decrease in mobility of the precursor molecules under graphene inhibited the erosion of crystals from this high level of water exposure, which allows for large crystalline domains to form and persist.

ENHANCED CRYSTALLINITY SURFACE REACTIONS AT THE SOLID-SOLID INTERFACE

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The condensation reaction of covalent organic frameworks (COFs) on the mica surface demonstrated enhanced crystallinity when physically confined by an exfoliated graphene capping layer. This talk discusses the condensation reaction of 1,4-benzenediboronic acid (BDBA) on mica to form COF-1, the impact of solid-solid interfacial confinement on twodimensional COF growth, and the integral role of water in the polymerization process. Atomic force microscopy imaging observed COF-1 growth when confined beneath an exfoliated graphene capping layer, which exhibited exceptional growth with domains reaching square micrometers in size and highly geometric hexagonal domain habit. Unconfined COF-1 domains lacked the long-range structural order or geometric domain habit observed in confined COF-1, instead maintaining similar morphology as observed prior to reaction. Micro-Fourier transform infrared spectroscopy and density functional theory calculations were performed to elucidate the origins of the enhanced growth of confined COF domains. COF-1 formation was confirmed by micro-FTIR spectra both under and outside of graphene flakes, suggesting non-covalent self-assembly of unreacted BDBA domains was not the cause of the differential morphology observed in confined and unconfined domains. DFT calculations of confined and unconfined diffusion barriers determined the enhanced crystalline effect was not due to increased precursor mobility under graphene confinement. The most probable origin of the greater crystallinity observed in confined COF-1 domains is therefore enhanced dynamic covalent crystallization (DCC) due to constant exposure to water trapped beneath the exfoliated graphene flake, enabling heightened recrystallization and defect correction during the condensation reaction. The resulting water-rich confined environment can be imagined as a 2D-flask for COF reactions and enhanced crystallinity should be a universal behavior of condensation reactions at the solid-solid interface. Future work endeavors to develop a clear understanding of confined water dynamics at reaction conditions as well as quantify the total volume of water accessible by a 2D-flask system.

DESIGN AND DEVELOPMENT OF QUANTUM DOT SCINTILLATOR WITH MONOLITHICALLY INTEGRATED PHOTODETECTOR FOR RADIATION DETECTION

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Picosecond-scale radiation detection technologies are important in various fields such as medical imaging, high-energy physics experiments, and homeland security. Scintillating materials convert incoming radiation into light by the luminescence process, and therefore, have been the core element of many detectors. Traditional scintillating materials are known to have either low light yield or suffer from slow luminesce. Here we design a novel epitaxial scintillating material with an artificial luminescence center, namely InAs quantum dots (QDs) in a GaAs matrix. This epitaxial heterostructure has been demonstrated to have ultrafast luminescence decay, higher light yield (Fig.1), and promises to provide ps-scale time resolution for the detection of charged particles and x-ray photons. Due to the high refraction index of GaAs (n=3.5), it is essential to integrate a monolithic InGaAs photodetector (PD) matched to the QD spectrum for photon collection and provide low attenuation in waveguiding (WG). A 25 mm thick heterostructure was designed and grown by molecular beam epitaxy (Fig.2) and lifted off from the GaAs substrate using the epitaxial lift-off Preliminary response measurements from 5.5 MeV alpha-particles have shown 10 photoelectrons per 1keV of the deposited energy as collected with the integrated PD and readout electronics with a charge-sensitive preamplifier, and σ/mean equal to 17%. To understand the optical losses in the WG, a laser-scanned 2D photoluminescence map was collected with the integrated PD (Fig. 3). The attenuation in the WG was calculated to be 1-2.5 cm⁻¹. The photoluminescence collected from the area of the bottom contact metal layer show ~50% reduction in PL intensity. The work is supported by the DOE Office of Science, award # DE-SC0022344.

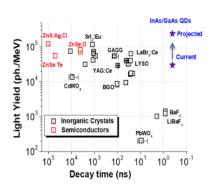


Fig. 1. Light yield vs decay time of some widely used solid-state scintillators and InAs/GaAs QD material.

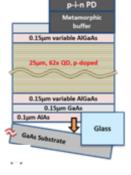


Fig.2. Schematic of InAs/GaAs waveguide and monolithically integrated InGaAs photodiode

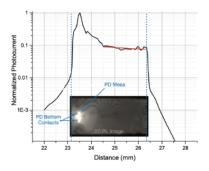


Fig. 3. 2D luminescence map and intensity profile along the center of the scintillator captured by the integrated PD.