

Atomic Scale Processing Mini-Symposium Room Central Exhibit Hall - Session AP-ThP

Atomic Scale Processing Mini-Symposium Poster Session

AP-ThP-1 Surface Bromination as a Way to Prepare an Atomic-Layer Resist: A Path Towards Area-Selective Deposition, *John R. Mason, A. Teplyakov*, University of Delaware

As the size of components in electronics is shrinking, and their designs continue to get more complex, we need to find new approaches to meet these design needs. Area-selective atomic layer deposition is a rising technology to address the requirement for reaching single-nanometer sized features, while keeping the high uniformity that is desired. Silicon bromination has been demonstrated to produce a surface that can effectively resist metal oxide deposition; however, such a substrate is difficult to prepare outside of ultra-high vacuum conditions. This study aims to provide alternative methods for brominating silicon (100) wafers without the need for expensive ultra-high vacuum equipment, with strong ability to resist deposition of titanium dioxide. The study looks at various bromine-based chemistries in liquid phase to prepare a non-growth surface and compares the resulting selectivity for TiO₂ deposition using titanium tetrachloride or tetrakis(dimethylamido)titanium as a titanium source and water as the oxygen source. The process is compared with that on the traditional non-growth surface of hydrogen-terminated silicon and on the traditional growth surface of oxidized silicon.

Surface morphology is monitored with atomic force microscopy and scanning electron microscopy. Atomic concentrations are followed with X-ray photoelectron spectroscopy to observe surface ability to serve as a resist. In addition, the deposition process, the chemical environment of the inhibitor species, and the thickness of the ultimately deposited oxide layers are observed using TOF-SIMS.

AP-ThP-2 Thermal Atomic Layer Etching Process for 2D van der Waals Material CrPS₄, *Marissa Pina, M. Whalen, J. Xiao, A. Teplyakov*, University of Delaware

CrPS₄ is a 2D van der Waals ternary transition metal chalcogenide (TTMC). CrPS₄ is an A-type antiferromagnetic semiconductor, in which spins within the same layer are aligned in same direction but spins in adjacent layers are aligned in opposite directions. Ferromagnetic and antiferromagnetic orderings are observed within the same layer and between adjacent layers, respectively. Consequently, thin flakes a few layers thick can display net or zero magnetization depending on whether there is an odd or even number of layers.

In order to understand the magnetism down to the monolayer limit and the dynamic excitations in magnons and excitons, and make devices based on 2D magnetic materials viable for industry, 2D materials with well-controlled layer structures have to be produced. The existing methods for controlling CrPS₄ thickness, such as mechanical and liquid exfoliation, are either not well controlled or introduce damage to the crystal structure. In this study, we will show that thermal atomic layer etching (ALE) can be used to controllably etch the 2D crystals of this material without contaminating them. Ultimately, using ALE to manipulate the thicknesses of these flakes will allow for controlling their magnetic and dynamic optical properties.

CrPS₄ flakes were exfoliated onto a gold film from a single crystal via mechanical exfoliation. Thermal ALE cycles were performed in an ultra-high vacuum chamber. Each cycle was performed at elevated temperature and consisted of a chlorine dose using a solid-state electrochemical chlorine source followed by an acetylacetone dose. Atomic force microscopy was used to determine an average etching rate of 0.10 ± 0.07 nm/cycle. Although the etching rate appeared to depend on the thickness of the flakes, this average removal rate was recorded for 75 different points for flakes ranging from 4 to 90 nm in thickness. ALE also removed the island defects caused by exfoliation from the top of the flakes. XPS and ToF-SIMS were used to follow chemical changes in the material and to interrogate the distribution of etchant components within the flakes. The formation of chemical species containing acetylacetone ligands was confirmed for all the components (Cr, P, S) of this TTMC, and the chlorination was followed in ToF-SIMS depth-profiling experiments. The ALE process that resulted in controlled material removal did not result in measurable surface contamination. Importantly, the etching of CrPS₄ is highly temperature-dependent, as lowering the process temperature by even 30 °C does not result in noticeable etching. Further, faster etching (above ALE regime) can be achieved using higher temperatures and higher pressures.

AP-ThP-3 Conversion of TiO₂ ALD Precursor Selectivity via Amination of Chlorinated Silicon with Primary Amines, *Tyler Parke, J. Mason, A. Teplyakov*, University of Delaware

Area-selective atomic layer deposition (AS-ALD) is a rapidly developing technique which allows for the fabrication of 3D nanoelectronic architectures. AS-ALD schemes may be made more versatile by introducing surface modification steps which 'switch' non-growth surfaces, which are unreactive to ALD precursors, to reactive growth surfaces. While several studies have demonstrated the conversion of chlorine- or hydrogen-terminated silicon to amino-terminated silicon, both in solution and gas-phase reactions, few have focused on the subsequent use of these prepared surfaces as ALD substrates. Chlorinated silicon resists were modified in vacuo with ammonia and methylamine to produce amino surface ligands and TiO₂ ALD was performed on each resulting surface to test its reactivity as a growth or non-growth surface in the presence of titanium tetrachloride or tetrakis(dimethylamino)titanium (TDMAT). Deposition was confirmed by XPS and surface species resulting from reaction of titanium precursors on each surface were probed with in situ FTIR and ex situ time-of-flight secondary ion mass spectrometry (ToF-SIMS). The experimental surface species data was paired with density functional theory (DFT) simulations of the local surface structure to propose a reaction pathway.

AP-ThP-4 Atomic Layer Deposition of Ruthenium and Ruthenium Oxide Thin Films for Electrochemical Water Splitting, *Swapnil Nalawade, D. Kumar, S. Aravamudhan*, North Carolina A&T State University

Electrochemical water splitting is a unique and sustainable hydrogen production cycle with water and oxygen as the only by-products. However, at present, the primary hurdle for hydrogen production from water is the lack of materials that can support the reaction with high efficiency. Addressing the hydrogen challenge requires innovations in catalysis for the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), the two electrochemical reactions in water splitting. Among the many electrocatalysts, thin films of Ruthenium and Ruthenium Oxide for OER and HER are very promising because of their high catalytic activity, broad pH applicability and long-term stability. In this work, we studied as-grown and post-annealed properties of Ruthenium and Ruthenium Oxide thin films deposited by thermal atomic layer deposition (ALD) technique. ALD Ru films were deposited at 300C using Ru(EthylCycloPentaDienyl)₂ and oxygen as co-reactants and characterized for morphology, composition, and resistivity. Post-annealing at higher temperatures (400-600C) in oxygen environment resulted in phase transformation of the as-grown Ru to RuO₂. These phase changes were confirmed using XRD, XPS, Raman and resistivity measurements. Finally, repetitive redox cycling (electrochemical studies) were conducted to study thin film stability and polarization behavior.

AP-ThP-5 Fabrication of p-n Junction Photodiodes using Low-Temperature ALD grown ZnO and NiO films on Si substrates, *H. Jiang, T. Cu, S. Bin Hafiz, H. Saleh, F. Bayansal, I. Sifat, A. Agrios, Necmi BIYIKLI*, University of Connecticut

In this study, we present findings on the photodiodes made of ALD grown ZnO and NiO films. The ZnO deposition process on p-type Si substrate samples involved the use of diethylzinc as the metal precursor and H₂O as the co-reactant. The thermal ALD deposition was done at 120 °C with 20 sccm of N₂ flow, 500 ms pulse time for 400 cycles. The thickness of ZnO film was measured as ~48 nm. On the other hand, NiO deposition on n-type Si substrate samples required nickelocene (bis(cyclopentadienyl)nickel) as precursor and O₂ plasma as co-reactant. The plasma-ALD process was conducted at 200 °C with 100W RF plasma power. The plasma duration was 20 seconds and total deposition run was 800 cycles. The resulting thickness of NiO film was ~34 nm.

The p-n photodiode device layout was similar to the design of a commercial solar cell with interdigitated electrode metal contacts. We designed 1 x 1 cm devices, in which we used 5/5 μm finger-width/spacing to collect generated photocurrent. After metal-oxide deposition, we fabricated the patterned contact metals via photolithography and lift-off process. 20/30 nm Ti/Al metal layers were e-beam evaporated on n-ZnO/p-Si and p-NiO/n-Si samples. The samples were then soaked in remover solution where metal lift-off process was completed with ultrasonication.

The I-V curves of ZnO/Si and NiO/Si devices show typical characteristics of back-to-back Schottky-diode and p-n junction photodiode, respectively. ZnO/Si Schottky photodiodes typically display rectifying behavior, showing minimal current flow under reverse bias due to the presence of a Schottky barrier, followed by a steep increase in reverse current beyond the barrier height. Under forward bias, rectifying behavior is observed, with a turn-on

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voltage indicating the onset of conduction. For NiO/Si p-n junction photodiode, the curve exhibits a clear rectifying behavior with exponentially increasing current at positive bias voltage, signaling unhindered current flow. Conversely, minimal current is observed under negative reverse bias voltages. These initial results indicate promise in achieving high-performance UV photodetector characteristics using both as-grown crystalline n-type ZnO and p-type NiO layers grown via thermal and plasma-assisted ALD, respectively at substrate temperatures less than 200 °C.

AP-ThP-6 Design of Gas Flow Field for a Microchannel Flow ALD Processing Chamber, *Kyung-Hoon Yoo*, Korea Institute of Industrial Technology, Republic of Korea; *G. Song*, KUMYOUNG ENG Inc., Republic of Korea; *C. Kim*, TNG Co., Republic of Korea; *J. Hwang, H. Lee, S. Lee, J. Woo*, Korea Institute of Industrial Technology, Republic of Korea; *K. Lee*, Samasung Display, Republic of Korea

It is necessary to establish a sustainable manufacturing technology for a high-productivity, high-efficiency ALD processing chamber and cluster tool that reduce the intrinsic excessive consumption of energy and materials because semiconductor ALD processes can be a concern for economic and environmental feasibility.^{1,2} In the present study, as the part of countermeasure to the excessive consumption, a microchannel flow ALD processing chamber is considered for the optimized design with the process space volume decreased. The changes in the flow field of nitrogen in the process space of the processing chamber with the gap size of 1 mm or 10 mm respectively are observed at 400 °C, utilizing computational fluid CFD numerical analysis. For the present nitrogen flow field with a inlet static pressure of 1 or 10 Torr and a inlet mass flowrate of $4.233 \cdot 10^{-6}$, the Knudsen number $Kn=0.223$ and Reynolds number $Re=1.474$ are evaluated. The continuity, momentum and energy equations of a steady-state compressible laminar flow field are considered.^{3,4}

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