PCSI

Room Ballroom South - Session PCSI-1WeA

Atomic Layer Deposition & Etching II

Moderator: Angel Yanguas-Gil, Argonne National Lab

2:00pm **PCSI-1WeA-1 Thermal Atomic Layer Etching of Silicon Using an Oxidation and "Conversion-Etch" Mechanism**, ***Steven M. George***, *A Abdulagatov,* University of Colorado at Boulder **INVITED**

Thermal atomic layer etching (ALE) is based on sequential, self-limiting surface reactions. Thermal ALE is the reverse of atomic layer deposition (ALD). Thermal ALE has been demonstrated for many materials including Al_2O_3, HfO_2, ZrO_2, TiN and W. This talk will focus on thermal Si ALE using oxidation and "conversion-etch". During this process, the Si surface is oxidized to a silicon oxide layer using O_2 or ozone. The silicon oxide layer is then converted to an Al_2O_3 layer using trimethylaluminum (TMA) [1]. Subsequently, the Al_2O_3 layer is fluorinated by HF to an AlF_3 layer prior to the removal of the AlF_3 layer by a ligand-exchange reaction using TMA [1]. This reaction sequence is shown in Figure 1.

Si ALE was studied using silicon-on-insulator (SOI) wafers in a warm wall reactor with a hot sample stage. *In situ* spectroscopic ellipsometry (SE) was employed to monitor the thickness of both the silicon and the silicon oxide layer during Si ALE. These studies observed that the silicon film thickness decreased linearly with number of reaction cycles while the silicon oxide thickness remained constant. Using an O_2-HF-TMA reaction sequence, the Si ALE etch rate was 0.4 Å/cycle at 290°C as shown in Figure 2. Comparable etching rates were observed using ozone instead of O_2 as the oxidant.

Thermal Si ALE should be useful in advanced semiconductor fabrication. Thermal Si ALE could also be utilized for atomic-scale polishing and cleaning of silicon surfaces. In addition, there may be applications in other areas such as silicon-based optoelectronics, photonics and MEMS fabrication

2:30pm **PCSI-1WeA-7 Fundamental Properties for Enhanced Etching of Ge Surfaces in Water Assisted by Single Sheets of Reduced Graphene Oxide**, ***Tomoki Hirano***, *Y Nakata, H Yamashita, S Li, K Kawai, K Yamamura, K Arima,* Osaka University, Japan

Metal-assisted chemical etching is an emerging technology for fabricating various three-dimensional nanostructures on a semiconductor surface for future electronic and optical devices . Thus far, our group has reported that a Ge surface in contact with noble metals, including Pt and Ag, is selectively etched in O_2-containing water. However, it is extremely difficult to remove residual metallic particles on the processed Ge surfaces. To resolve this issue, graphene is used, which supposedly functions as a catalyst free from metals.

In this study, fundamental properties of graphene-assisted chemical etching, which is the preferential etching method for a Ge surface in contact with single sheets of reduced graphene oxide (rGO) in O_2-containing water were described. An rGO solution was prepared by chemical reduction of a GO solution and spin-coated on a Ge(100) surface. The sample was immersed in O_2-containing water for 24 h. We show the change in surface morphology of rGO sheet-loaded Ge upon immersion in O_2-containing water. The sheet thickness ranged from 0.8 to 1.2nm and single rGO sheets were well dispersed after our sample preparation. Then the Ge surface was preferentially etched under the rGO sheets in O_2-containing water. This enhanced etching did not occur using water without dissolved O_2 molecules, indicating that rGO-assisted chemical etching is mediated by an oxidant (O_2 molecules) in a solution (water). Next, the dependence of etching rate on water temperatures was investigated. The etching rate considerably depended on water temperatures (e.g., 1.9 nm/h at 22 °C and 15.1 nm/h at 48 °C). The Arrhenius plot from this data permitted the estimation of activation energy for this etching mode.

2:35pm **PCSI-1WeA-8 Laser-patterning of Graphene Oxide Beyond the Diffraction Limit**, ***Maksim Fatkullin***, Tomsk Polytechnic University, Russia

Graphene oxide (GO), same as graphene itself, attracted a tremendous attention since its re-discovery in 2004. [1]. Main advantages of GO are: water dispersible, flexible and the greatest one its tunable conductivity. Conductivity changing due to reduction process, during which dielectric GO becomes to conductive reduced graphene oxide (rGO). Reduction could be done in different ways, but all of them are either chemical or thermal [2].

The most part of reduction methods are ex-pensive and not scalable, for example reduction using atomic force microscopy (AFM) tip or electron beam [3][4]. The other limitation of these methods is that they attracted all volume of material.

We used laser irradiation to provide external energy for the thermal annealing at the local area of GO thin film (selective reduction). From other side this method is cheap, eco-friendly and easy to perform.

Using this method, anyone can make electrical circuits of different shapes at the flexible transparent substrates with carbon nanowires, made beyond the diffraction limit without special equipment and conditions. To pattern rGO conductive lines we used different substrates and different lasers: CO2 laser with λ=1064 nm and portable laser engraver with λ=405 nm. Figure 1 demonstrated rGO pattering by the laser irradiation.

The key result of this contribution came out after applying the highest laser power. Even though the patterned material was completely ablated in some regions, we still observed a significant electrical conductivity along the pattern (Figure 2). This observation implies that by optimizing the laser parameters, and under higher power than has been reported previously, it is possible to achieve confined rGO regions: the edges of the patterns. Conductive rGO patterns can thus be achieved with spatial dimensions much smaller than the laser spot size.

[1] A.K. Geim, Graphene: status and prospects, Science. 324 (2009) 1530–1534.

[2] Songfeng Pei, Hui-Ming Cheng, Carbon, 50 (2012) 3210 – 3228

[3] Jeffrey M. Mativetsky et al., Am. Chem. Soc., 132 (2010) 14130 –14136

[4] Gil Gonçalves et al., Carbon, 129 (2018) 63 - 75

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2:40pm **PCSI-1WeA-9 Maskless Si Nano-wall Formation by Wet-etching Process using a Femtosecond Laser Irradiation**, *S Lee,* Pusan National University, South Korea; ***Hyun Hwi Lee***, Pohang Accelerator Laboratory, South Korea; *H Kim,* Pusan National University, South Korea

Recently, ultrashort pulsed laser direct writing technique has been intensively investigated to develop a nanoscale fabrication enabling high aspect ratio. In the referred applications, laser induced nanostructures are formed with well manipulated laser beams in small area. On the other hand, Laser Induced Periodic Surface Structure (LIPSS) has attracted increasing attention for the possibility to generate periodic nanoscale structures in large area with relatively simple optical configurations. LIPSS is a self-organized one-dimensional periodic structure which is formed when multiple laser pulses with the laser fluence near ablation threshold are exposed. These self-induced nanostructures are often categorized into Long Spatial Frequency LIPSS(LSFL) and High Spatial Frequency LIPSS (HSFL) by their periodicity. The periodicity of LIPSS is varied by the wavelength of the laser and the material properties of the substrates. The orientation of the LIPSS is affected by the laser polarization. In case of the LSFL, the orientation is observed almost perpendicular with respect to the incident laser polarization. Therefore, LIPSS with direct-write scheme has been applied in rapid production of functional surfaces on large area such as superhydrophobic surfaces, enhanced absorption, cell adhesion, and tribological applications.

However, these demonstrations utilized the LIPSS property to increase the surface area by desirable surface roughening or enhancing surface properties. Relatively less attention was paid to the morphological changes of LIPSS followed by a chemical etching.

This presentation will introduce a new mask-free patterning technique of Si, which is combined with a conventional wet-etching process and direct-write LIPSS patterns of Si. The technique is a two-step process. First, a femtosecond laser irradiates a Si surface to generate one-dimensional LIPSS pattern on the surface. Conventional wet-etching solvents, such as KOH and TMAH (tetramethylammonium hydroxide), etch the LIPSS to form a periodic micro-cell surrounded by nanowalls with the height of a few hundred nanometers. The distance between the nanowalls was approximately one micrometer and the bottom surface of the cell was atomically flat which is sufficient to grow organic semiconducting thin films for organic devices. The bottoms of micro-cells surrounded by the nanowalls were considerably flat with a 3.10 nm surface roughness. A pentacene layer was deposited on the micro-cells of a Si surface to evaluate the film properties by grazing incidence wide angle x-ray scattering measurements.

2:45pm **PCSI-1WeA-10 Epitaxial $(Bi,Sb)_2Te_3$/Graphene/2D-Ga Heterostructures Towards Topological Superconductivity**, ***Brian Bersch,*** *N Briggs, J Jiang, Y Zhao, Y Chuang, C Li, Y Wang,* The Pennsylvania State University*; M Fu, Q Zou, Z Gai, A Li,* Oak Ridge National Laboratory*; M Chan, C Chang, V Crespi, J Zhu, J Robinson,* The Pennsylvania State University

The interface of a conventional BCS superconductor (SC) and a topological insulator (TI) is predicted to host an exotic state of matter known as a topological superconductor, the elemental excitations of which could potentially enable quantum computing schemes that are robust against error produced by decoherence. The direct synthesis of a SC-TI heterostructure, however, is challenging due to structural dissimilarities and high interface reactivities between common superconductors and topological insulators. Here, we report on the synthesis and properties of wafer-scale $(Bi,Sb)_2Te_3$/graphene/2D-Ga heterostructures grown in-part via a new method, i.e. confinement heteroepitaxy (Chet), pioneered by the Robinson group [1]. Chet enables us to intercalate and form atomically thin gallium (Ga) layers at the interface of 2L epitaxial graphene (Gr) and its native SiC (0001) substrate. The graphene-encapsulated 2D-Ga films are predominantly 2-3L thick, crystalline, and epitaxially registered to the SiC, as confirmed by high-resolution scanning transmission electron microscopy (HR-STEM) (Fig. 1a). The Gr/Ga films exhibit a superconducting state with zero resistance at a transition temperature of $T_c \sim 4$ K (Fig. 1c), which is higher than that of bulk α-Ga (T_c = 1.08 K). In addition to serving as a capping layer for the 2D-Ga film, the Gr layer is both a reaction barrier and an ideal substrate for the subsequent molecular beam epitaxial (MBE) growth of a TI material $(Bi,Sb)_2Te_3$. HR-STEM and energy-dispersive X-ray spectroscopy (EDS) mapping shown in Fig. 1b demonstrates the atomically sharp interfaces and high-quality layer-by-layer growth of all constituent layers in a heterostructure of 6 quintuple-layer $(Bi,Sb)_2Te_3$ grown on Gr/Ga. Reflection high energy electron diffraction pattern and angle-resolved photoelectron spectroscopy measurements verify its crystalline integrity and the Dirac surface bands of the TI film. First-principles calculations reveal the electronic band structure of the heterostructure, which is conducive to proximity-induced superconductivity in the TI film. Our approach circumvents several key challenges in making high-quality SC-TI heterostructures to offer a new route towards the realization of topological superconductivity.

[1] Nature Materials 15, 1166–1171 (2016)

3:00pm **PCSI-1WeA-13 Tracking Defects through Ultra-Thin Layered Complex Oxides**, ***B.A. Noesges,*** The Ohio State University*; J Lee, C Eom,* University of Wisconsin-Madison*; L Brillson,* The Ohio State University

Improving ultra-thin films and devices requires characterization techniques capable of resolving defects at near-nanoscale depths. Defect formation in and nearby ultra-thin layers can produce effects that permeate the layer and alter interface properties. Resolving defects on this scale is especially important for complex oxide heterostructures like $LaAlO_3/SrTiO_3$ where just nanometers thick layers of LAO and STO produce a highly conductive interface between the insulating materials. Interfacial majority carriers are controlled through choice of neighboring atomic planes at the interface. These interfaces are referred to as two-dimensional electron or hole gases (2DEG/2DHG) depending on carrier type since conduction is confined in-plane. The performance of the 2DEG is strongly influenced by nearby defects like oxygen vacancies which are donors and increase carrier concentration while reducing mobility. The 2DHG interface is even more strongly affected and can't form unless nearby oxygen vacancies are sufficiently suppressed [1]. We used depth-resolved cathodoluminescence spectroscopy (DRCLS) alongside advanced growth techniques designed to carefully control defect formation to systematically study the interplay between native point defects, defect complexes and interface carrier conductivity. DRCLS is an ideal technique to investigate defects in ultra-thin layers since probe depth is tunable on the near-nanoscale by adjusting voltage of an incident electron beam. With this control, cathodoluminescence can be obtained from nanometers below the film surface, through interfaces and hundreds of nanometers into the substrate providing information about the defects present in each layer. DRCLS guided by DFT calculations can identify oxygen vacancy (V_o) defects as well as assorted metal cation related defects like Sr vacancies and Ti on Sr anti-site (Ti_{Sr}) defects [2]. Certain defects can suppress others, i.e., Ti_{Sr} formation suppressing oxygen vacancy defects creating extremely clean, high mobility 2DEG interfaces. DRCLS is a unique tool for tracking defect concentration through ultrathin oxide layers to determine the role of defects in space charge regions. Growth control combined with near-nm DRCLS distribution measurements inside complex oxide heterostructures provides a powerful approach to achieve advanced electronic features and improved device quality. Support by NSF DMR-18-00130.

[1] H.Lee, et al, Direct observation of a two-dimensional hole gas at oxide interfaces. Nature Materials 17, 231–236 (2018)

[2] D. Lee, et al, Identification of a functional point defect in SrTiO3. Phys. Rev. Materials 2, 060403® (2018)

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