Plasma Science and Technology
Room 315 - Session PS-FrM

Novel Chemistries and Materials in Plasma Processing

Moderators: Prof. Kenji Ishikawa, Nagoya University, Japan, **Dr. Thorsten Lill**, Lam Research Corporation

8:15am **PS-FrM-1 Low Energy Remote Plasma and Non-Plasma Methods for Highly Selective Etching of Advanced Nanodevices**, ***Mark Kawaguchi***, LAM Research **INVITED**

In the pursuit of higher performance semiconductors, device length scales continue to shrink down to nanometer dimensions with emerging chip designs increasingly dependent on 3D structures to maintain scaling. Memory manufacturers have already deployed 3D NAND devices with ongoing development for 3D DRAM devices. Advanced logic manufacturers have already deployed 3D FinFET devices and are beginning to deploy more complex GAA (Gate-All-Around) 3D devices as well. Building 3D structures has increased the need for more sophisticated selective etching. As these selective etches have become critical to the formation of the device, atomic precision material loss is required with low contrast materials. We review exemplary materials systems where insufficient selectivity control necessitates innovative approaches such as remote-plasma radicals with atomic layer passivation & ultra-low residual ions as well as plasma-less low energy thermal chemical etching.

Dummy polysilicon removal requires full removal of the polysilicon with minimal film loss to dielectric films such as silicon oxide and silicon nitride. Remote-plasma radical etch removes the polysilicon, but it is desirable to improve film damage control due to higher energy reactants reaching the surface. The first approach applies atomic layer passivation to modify the top monolayer of an oxide encapsulation layer. Epitaxial film damage is improved by hindering diffusion of halogen radicals through the encapsulating film. The second approach reduces the higher energy reactant flux to the surface. We characterize the intensity of higher energy reactants by measuring the residual ion flux to the wafer surface.By modifying flow geometry above the wafer, the residual ion flux is reduced over 2 orders of magnitude, in the range of nA/cm^2, and results in improved material loss.

GAA device integration relies on depositing and subsequently removing SiGe layers to form Si-nanowires or nanosheets. Besides the bulk SiGe etch, we highlight strict film loss requirements that require highly selective native oxide removal prior to removing SiGe layers. We describe a thermal chemical etching approach that applies wet etch mechanisms in a vacuum environment. Etch rates are tunable over a wide range from 2-200 A/min as well as high selectivity to both silicon and silicon nitride materials. In addition, we have applied a Langmuir-Hinshelwood surface kinetics model to extract steady state reactant surface coverage.We find that the surface coverage is sub-monolayer, and over a broad surface coverage range, localized etching characteristics are well-behaved as measured by AFM roughness.

8:45am **PS-FrM-3 A Novel Si Etch Chemistry for CFET Fin Definition**, ***Yifeng Zhou***, *Hiroto Ohtake,* Applied Materials, Inc.

CFET channel design requires upper ~75% fin etch profile to be straight and smooth, in addition to the traditional requirements for profile loading, etch depth loading, line edge roughness, and mask selectivity. New etch chemistry and process structure are necessary to meet those challenges as the conventional Cl2- and SF6-based fin etch chemistries ran out of steam.

This study introduces a cyclical process featuring a BCl3/NF3 based etching step and a CH4/SO2 based passivation step that provides straight and smooth upper 85% profile, with minimal profile and depth loading among various pattern pitches.

Profile control: NF3 is the main etchant and BCl3 provides effective passivation for Si and SiGe sidewalls. HBr can provide more passivation, via re-deposition of less volatile SiBrx etch products. NF3:BCl3 and NF3:HBr gas flow ratios are the main knobs for profile control.

Si/SiGe scalloping: Scalloping results from relatively higher lateral etch rate of SiGe compared to that of Si. While SO2/CH4 passivation step helps reduce scalloping by forming Ge-S bonds, standalone H2 trim steps eliminates scalloping by trimming Si faster than SiGe.

Profile loading: iso/dense profile loading roots from sidewall passivation delta between spaces with difference widths. Directional breakthrough step removes more passivation from more sloped sidewalls to allow for more taper correction in subsequent etch steps.

Depth loading: SO2/CH4 passivation step deposits thicker carbon polymer on wider trenches, negating the higher etch rate from higher neutral fluxes.

9:00am **PS-FrM-4 Creation and Recovery of Defects in Lead Zirconate Titanate Thin-Films introduced by Inductively Coupled Plasma Reactive Ion Etching**, ***Madeleine Petschnigg***, *Marco Deluca,* Silicon Austria Labs GmbH, Austria; *Susan Trolier-McKinstry,* The Pennsylvania State University

Due to their excellent actuation performance, with an $|e_{31,f}|$ coefficient of about 15 Cm^{-2}, lead zirconate titanate (PZT) based thin-films are widely adopted for actuator type piezoelectric micro electromechanical systems (piezoMEMS), including inkjet printer heads[1–4], micro speakers[5,6], micro coolers[7,8] and auto focus devices[9,10].In the fabrication of piezoMEMS devices, accurate patterning of the active layer plays a key role. By combining physical and chemical mechanisms, inductively coupled plasma reactive ion etching (ICP-RIE) allows the fabrication of highly anisotropic profiles at high etch rates while maintaining a high selectivity against masking and stop-layer materials.

Plasma assisted dry etching techniques, like ICP-RIE, however, can degrade the patterned PZT and alter its dielectric and piezoelectric properties, which manifests itself in a decreased permittivity, and/or a decreased remanent polarization [11–14]. Degradation is a concern not only when the PZT surface is directly exposed to etching conditions, but alsothrough the introduction and migration of defects at etched side walls [14,15].Potential sources for degradation include changes in surface chemistry due to selective etching or contamination, crystallographic damage due to bombardment, and potential liberation of hydrogen from organic resist masks.Althoughthe electromechanical properties may be recovered by annealing treatments [11,16,17]at 500°C and above, a comprehensive study of the required temperature and time for recovery has yet to be done.

This work aims to uncover the primary mechanism responsible for the degradation of PZT during ICP-RIE patterning, including the effect of pre- and post-etch electrode deposition as well as the presence of hydrogen-containing gases during the plasma etch. Based on this, a targeted recovery treatment procedure will be defined, and the patterning process flow optimized.

Nb-doped PZT films will be deposited by sputtering on Pt-coated Si wafers and patterned by ICP-RIE. The electric properties as well as the aging behavior of pristine samples will be compared to samples right after the etch and after recovery. The potential incorporation of hydrogen will be assessed by Raman spectroscopy. Thermally stimulated depolarization current (TSDC) measurements and charge-based deep level transient spectroscopy (Q–DLTS) will provide insight on the difference in the films defect chemistry.

9:15am **PS-FrM-5 Plasma-Surface Interactions of Polyurea Deposited on SiO2 and SiNx with HF Plasmas**, ***Wallis Scholl***, Colorado School of Mines; *Mingmei Wang, Thorsten Lill, Wenyu Zhang, Louis Kim, Harmeet Singh,* Lam Research Corp; *Sumit Agarwal,* Colorado School of Mines

Fluorocarbon plasmas have been traditionally used to etch SiO_2 and SiN_x during semiconductor processing. Because fluorocarbon radicals inherently lower the etch rate by depositing a polymer on the SiO_2 or SiN_x surface, the industry is transitioning to C-free reactive plasmas, such as HF. As a result, new techniques are needed to enhance surface passivation and etch selectivity during HF plasma etching. During etching of high aspect-ratio (HAR) features, sidewall passivation is needed to preserve the profile. Molecular layer deposition (MLD) is a technique for depositing organic and hybrid organic-inorganic films. We studied the HF plasma interactions after a polyurea film deposited by MLD on top of SiO_2 or SiN_x. We have shown in previous work that MLD polyurea film deposited on top of SiO_2 or SiN_x can protect the underlying material from etching. During HF plasma etching of blanket films on a planar substrate, the polyurea film acted as a sacrificial layer and prevented SiO_2 or SiN_x etch while the polyurea was present. When the polyurea was completely consumed by reaction, the SiO_2 or SiN_x film was etched at its baseline etch rate (see Figure 1). The presence of polyurea also delayed the formation of ammonium fluorosilicate on the SiN_x surface, which is known to form on the surface in the presence of HF, and SiF_4 and NH_3 generated as etch products.

In this work, we also deposited polyurea onto 65:1 aspect ratio holes in SiO_2-SiN_x stacks, which were then exposed to an etching plasma to evaluate sidewall passivation. Scanning electron microscopy images show that the polyurea film reduced the diameter throughout the entire depth, showing both the conformality of the MLD film as well as successful passivation of

the sidewalls. Subsequent etching of these features preserved the critical dimension compared to etching without the polyurea film (see Figure 2). Further, *in situ* infrared spectroscopy was used to monitor polyurea interactions with plasma species to better understand the etch mechanism. We exposed the films to a remote HF plasma and HF gas to mimic the conditions in HAR structures. While the radical species in the remote HF plasma gradually removed the polyurea film, it remained largely intact during exposure to HF gas. Fluorination of the polymer film was observed prior to its removal, suggesting that polyurea is removed as volatile hydrofluorocarbon fragments during HF plasma etching. Additionally, we show that during etching at a higher substrate temperature of 150 C, the presence of polyurea enhanced the SiO_2 etch rate: we attribute this to activation of HF through hydrogen-bonding interactions with the amines in the polyurea film.

9:30am **PS-FrM-6 Long-Term Influence of Fluorine Containing Plasmas and Gases on Sapphire (Single-Crystal Al2O3) and Ni-Based Alloy Surfaces**, ***Takuya Ishihara***, *Nozomi Kida, Hidenobu Tochigi, Keigo Iwamoto,* Azbil Corporation, Japan*; Kazuo Karahashi,* Nagoya University, Japan*; Satoshi Hamaguchi,* The University of Osaka, Japan

In semiconductor manufacturing processes such as dry etching or chemical vapor deposition, capacitance manometers are widely used as essential vacuum pressure sensors to monitor and control the pressures of process gases. These gauges must be corrosion-resistant against process gases such as halides and their radicals generated by the plasmas. The diaphragm material of the manometer is especially important because, if its surface is altered by such corrosive gases, the sensor would send imprecise output signals possibly with the zero-point drift or pressure sensitivity shift. The errors are caused by the changes in mechanical properties of the diaphragm arising from the formation of the modified surface layer. For this reason, Ni-based alloys or polycrystalline ceramics of aluminum oxide (Al_2O_3) are typically used as the diaphragm material of capacitance manometers. More recent capacitance manometers employ sapphire (single-crystal α-Al_2O_3) as their diaphragm material, which is of specific interest in this study [1]. Recent studies on the interactions of polycrystalline Al_2O_3 with fluorine-containing plasmas indicated the formation of aluminum fluoride layers on Al_2O_3 exposed to such plasmas [2,3,4,5,6]. We have reported the results of ion beam experiments to understand the surface modification mechanisms of Ni-based alloys and polycrystalline Al_2O_3 film by fluorine-containing plasmas [7,8]. In addition, Ni-based alloy samples were exposed to xenon difluoride (XeF_2) gases for 3 and 6 months and their fluorinated surfaces were analyzed [9]. In this study, we obtained 12 months XeF_2 exposure data of Ni-based alloys, in which fluorine continued to diffuse even after one year, unlike in sapphire.Furthermore, the differences in surface states between sapphire and nickel-based alloys upon exposure to XeF_2 or NF_2 remote plasma will also be reported.

[1] T. Ishihara, *et al*, 35th Sensor Symposium (2018)

[2] Chen Chien-Wei, *et al*, J. Vac. Sci. Technol. A Vol.41 No.1 Page.012602(pp9) (2023)

[3]Kim Yewon, *et al*,Appl. Surf. Sci. Vol.641 Page. Null (2023)

[4]Vos Martijn F. J., *et al*,J. Phys. Chem. C Vol.125 No.7 Page.3913-3923 (2021)

[5]Chittock Nicholas J., *et al*,Appl. Phys. Lett. Vol.117 No.16 Page.162107(pp5) (2020)

[6]Fischer Andreas,et al, J. Vac. Sci. Technol. A. Vol.38 No.2 Page.022603(pp7) (2020)

[7] T. Ishihara, *et al*, the AVS 70th International Symposium & Exhibition (2024)

[8]H. Kang, *et al* Jpn. J. Appl. Phys. Vol. 64 Page: 046001(pp8) (2025)

[9] T. Ishihara, *et al*, the AVS 71st International Symposium & Exhibition (2025)

9:45am **PS-FrM-7 Investigations of Oxygen-Containing Plasma Etching of Diamond**, ***Justin Boles***, University of Houston*; Louis E. S. Hoffenberg, Jack S. Draney, David. B. Graves,* Princeton University*; Vincent M. Donnelly,* University of Houston

Plasma etching of single-crystal diamond is vital for the development of next-generation power electronics and quantum platforms based on nitrogen-vacancy complexes (NV-centers). Despite this, little has been reported on the fundamental etching mechanisms, including the roles of ions and neutrals. Here we report a detailed study of the etching of single-crystal diamond (100) in O_2/Ar magnetically-confined, inductively-coupled plasmas, using a combination of optical emission spectroscopy, ion flux measurements, etching rate measurements, and simulations. Fluxes of positive ions (O^+, O_2^+, Ar^+) to the (100) diamond surface were determined from ion saturation current measurements and Langmuir probe measurements, while O and O_2 number densities were determined using optical emission actinometry. Optical emission spectroscopy was further employed to measure gas temperature (via N_2 rotational spectroscopy) and identify CO and CO_2 reaction products. Etch rates were measured via masking and optical profilometry as functions of ion energy and $\%O_2$ in Ar. In "pure" (98% or 100%) O_2 plasmas, with an O-to-O_2^+ flux ratio of about 25:1, the etch rate and product optical emission intensities obeyed a square root of ion energy dependence, with a threshold near 11 eV. The etching yield (C atoms-per-ion) was 7.5 at a mean ion energy (DC self-bias voltage plus plasma potential) of 215 eV. If CO were the only product, and since physical sputtering yields are much lower, O atoms must be playing a dominate role in etching at this energy. As the feed gas ratio was changed from pure O_2 to 20%O_2/Ar at constant pressure (10 mTorr), ICP power (300 W), and ion energy (215 eV), the total positive ion flux remained nearly constant (1-2 $X10^{16}cm^2s^{-1}$) and the O-to-ion flux ratio actually increased to between 40:1 and 50:1, while the yield decreased monotonically to about 3.5 C-per-ion, still much larger than the sputtering yield of 0.16 C-per-Ar^+. The yields as a function of O-to-ion flux ratio and $\%O_2$ in Ar compare favorably with molecular dynamics simulations.

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10:00am **PS-FrM-8 The Effect of Remote Ar Plasma Exposure on the Crystalline Structure of VO_2**, ***Peter Litwin***, *Neeraj Nepal,* U.S. Naval Research Laboratory*; Marc Currie,* US Naval Research Laboratory*; Andrew Lang, Luis Carrillo, David Boris, Michael Johnson, Scott Walton, Virginia Wheeler,* U.S. Naval Research Laboratory

The effect of chemically inert plasmas on the surface of thin film materials is of interest because it allows for an additional means to deliver energy to a material beyond increasing the material's temperature. This could be of use in cases where energy needs to be delivered to specific layers or interfaces in a heterostructure without subjecting the entire material stack to higher temperatures or to overcome energetic barriers, such as those associated with material crystallization (or amorphization) or the formation of metastable phases. However, plasmas make for a complex environment due to the various energy contributions from ions, electrons, excited species, and photons. Despite this complexity, an increased understanding of energy transfer by controlling the fluence and energy of ions at the plasma-surface interface opens additional avenues in material engineering. This may be particularly true for plasma-enhanced atomic layer deposition (PEALD) processes where thin films are cyclically exposed to plasmas during deposition and thus could benefit from an increased understanding of the interaction between plasmas and material surfaces.

In this work, we look at the impact of remote Ar plasmas on crystalline VO_2 thin films deposited by ALD as a function of plasma power and substrate bias. Thermal ALD of VO_2 was carried out at 150 °C using TEMAV and O_3 and subsequently crystallized in a dedicated thermal annealing vacuum system following a previously established process[1]. We find that the Raman signature of the equilibrium monoclinic phase of VO_2 (m-VO_2) decreases after exposing the sample to a remote Ar plasma beyond a minimum power or substrate bias threshold. Interestingly, this process is reversible, i.e., the signature of m-VO_2 can be recovered by exposing the sample to a subsequent Ar plasma of decreasing power or bias starting below the initial threshold required to reduce the m-VO_2 signature. These results suggest one of two possibilities: either amorphization of the film and subsequent recrystallization or selective stabilization of different VO_2 phases based on the plasma condition used. TEM analysis indicates the plasma-treated material is in fact highly crystalline despite the decreased signature of m-VO_2, which suggests the latter of the two explanations. This presentation will discuss the details of these experiments and, with the aid of in situ plasma diagnostics, attempt to elucidate the plasma parameters responsible for the behavior observed.

[1] J. Phys. Chem. C 2017, 121, 19341−19347

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