Atomic Scale Processing Mini-Symposium
Room C124 - Session AP+PS-FrM

Atomic Scale Processing Late Breaking Atomic Layer Etching and Area Selective Deposition

Moderator: Eric Joseph, IBM T.J. Watson Research Center

8:20am **AP+PS-FrM-1 Atomic Layer Etching of SiO_2 via H_2/SF_6 Plasma and TMA***, **David Catherall**, A. Minnich,* California Institute of Technology

The quality factor of ultrahigh Q silica microdisk resonators has reached values exceeding one billion but remains at around an order of magnitude below intrinsic upper limits due to surface-roughness scattering. Atomic layer etching (ALE) has potential to mitigate this scattering because of its ability to smooth surfaces to sub-nanometer length scales. Here, we report an ALE process for etching of SiO_2 using sequential exposures of TMA and $Ar/H_2/SF_6$ plasma. The $Ar/H_2/SF_6$ plasma has been reported to enable in-situ production of HF, enabling HF exposures in the ALE process without the need for an external source of HF vapor. We observe etch rates up to 0.6 Å per cycle and examine the effect on surface roughness. This work advances a process of relevance to ultrahigh Q silica resonators which are fundamental elements of on-chip photonic devices such as frequency combs.

8:40am **AP+PS-FrM-2 Area Selective Deposition of HfO2 on Oxide and Nitride Surfaces***, **ByungChan Lee**,* Incheon National University, Republic of Korea*; C. Nguyen,* Incheon National University, Viet Nam*; S. Shim, Y. Kang, H. Lee,* Incheon National University, Republic of Korea

Due to the scaling down in the Si device fabrication, the aspect ratio and complexity of 3D device structures is rapidly increased, leading to the limitation of the conventional fabrication process including deposition, etching, lithography and so on. Area selective deposition (ASD) has received great attentions from the Si industry as one of the unit processes to overcome the limitations. ASD is developed based on the atomic layer deposition (ALD) which has the unique self-saturation surface reaction mechanism. The surface chemical properties are modified by using the promoter or inhibitor which promotes or inhibits the thin film growth, respectively. Accordingly, the ALD thin films are selectively deposited on the desired area. At the beginning of the ASD research, the self-assembled monolayers (SAMs) were commonly used as an inhibitor. But the inherent size of SAMs has potential problems for the pattern interference in nm-size scale. In this study, we investigated the ASD using a small molecule inhibitor (SMI). We selected the aldehyde molecules as SMI to inhibit the nitride surface but not on oxide surface. By using density functional theory (DFT) calculation, adsorption behaviors and energetics of the aldehydes was studied on nitride and oxide surfaces. From the experiments, it was observed that the aldehyde selectively adsorbs on only nitride surface but not on oxide surface and block the HfO_2 deposition until 15 cycles. The inhibition of nitride surface using SMI can contribute to many unit processes of Si device fabrication by simplifying the process scheme.

9:00am **AP+PS-FrM-3 Surface Functionalization of SiN_x over SiO_2 with Aldehydes to Enable Area-Selective Atomic Layer Deposition***, **Andrew Kaye**,* Colorado School of Mines, USA*; S. Agarwal,* Colorado School of Mines*; B. Zope, A. Derecskei, R. Pearlstein, X. Lei,* EMD Electronics, USA

As the semiconductor device dimensions continue to shrink, area-selective atomic layer deposition (AS-ALD), which is a bottom-up technique, can address the challenges associated with device fabrication. SiO_2 and SiN_x are two of the most commonly used dielectrics in semiconductor devices, and deposition on one dielectric with minimal deposition on the other can simplify processing. For example, in 3D-NAND structures, there are alternating layers of SiO_2 and SiN_x, and during processing, it is desirable to grow a metal oxide on SiO_2 with no growth on SiN_x. In AS-ALD, inhibitor molecules can be used to functionalize SiN_x because very few ALD precursors have an inherent binding selectivity to SiO_2 over SiN_x. Finding inhibitor molecules that selectively adsorb on SiN_x over SiO_2 is also challenging since on SiO_2 films contain SiOH groups, which react readily with many compounds such as chlorosilanes, alkoxides, and aminosilanes. We have previously shown that aldehydes selectively adsorb on SiN_x with minimal adsorption on SiO_2.

This work focuses on the adsorption mechanisms of two aldehydes, 3,5,5-trimethylhexanal (TMH) and dodecanal (DDA), on plasma-deposited SiN_x films characterized with *in situ* attenuated total reflection Fourier transform infrared spectroscopy. We show that TMH adsorbs on SiN_x forming silyl ethers, amino alcohols, enamines, and imines with surface -SiH_x and -NH_x groups being the reactive sites. Reaction of DDA with SiN_x leads to the formation of similar surface species except for enamines. Amino alcohols are reaction intermediates formed due to the reaction of surface amines with aldehydes — the complete reaction should result in the formation of imines with H_2O as the byproduct. The presence of amino alcohols is not desirable since the -OH group may react with metal ALD precursors and reduce selectivity. We show that once the amino alcohols are formed on the surface, they cannot be converted to imines by increasing the substrate temperature. The surface composition of the underlying SiN_x film greatly affects the uptake of the aldehyde and the relative ratio of the surface species formed after adsorption of both aldehydes. The aldehydes desorb from the surface when the substrate temperature is increased, and further desorption occurs over time at elevated temperatures. After desorption at a constant temperature, TMH can be replenished by redosing. In practical applications the SiN_x surface is partially oxidized upon exposure to the atmosphere. To understand the effect of surface oxidation, the plasma-deposited SiN_x films were exposed to the atmosphere for several days. The atmosphere exposed SiN_xfilms were then cleaned with D_2 plasma to possibly etch the surface oxide layer to enhance reactivity by restoring -SiD_x and -ND_x surface species.

9:20am **AP+PS-FrM-4 Surface Reactions During Atomic Layer Etching of Platinum by High-Density Nitrogen-Oxygen Plasma and Organic Acid Vapor***, **Thi-Thuy-Nga Nguyen**,* Nagoya University, Japan*; D. Akagi, T. Uno, T. Okato,* AGC Inc., Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Anisotropic patterning process of metal layers in complex nanostructures is a big challenge. Pt is a promising material, but it is a hard-to-etch material. Dry etching of Pt thin film has been developed by using halogen-based plasmas of SF_6, CF_4, or Cl_2 gas. However, the anisotropic etch profiles of Pt films in most cases have not achieved due to the redeposition of the etch residues that produces fences or tapered sidewall. Recently, non-halogen chemistry for noble metal etching has been developed using atomic layer etching (ALE) with surface modification by oxidation and removal of the oxide layer by vapor of organic compounds [1].

Our developed floating wire-assisted high-density plasma at medium pressure significantly increases the chemical reaction rate to the sample surface, that was applied in the reduction of SnO_2 [2] and dry etching of TiAlC [3]. Here, we have demonstrated ALE of Pt via high-density plasma oxidation and removal of the modified layer by organic acid vapor or organic acid plasma. High-density nitrogen-oxygen based plasma (N-O plasma) was generated to fully oxidize Pt surface and form a dominant oxidation state (Pt^{4+}). Surface modifications after the reactions of Pt with N-O plasmas and the modified layer with organic acid vapor or plasma were analyzed by X-ray photoelectron spectroscopy. The film thickness was characterized by ellipsometry and X-ray reflectivity. Surface roughness was analyzed by atomic force microscopy, and patterning profiles were observed by transmission electron microscopy. The N-O plasmas and organic acid plasmas were diagnosed by high-resolution optical emission spectroscopy.

The formation and desorption of organometallic compounds on Pt surface are able to be atomic-level controlled at low temperature (less than 100 ^oC). A smooth surface of Pt film was obtained with the etch depth per cycle from 0.3 to 0.7 nm/cycle. The exposure of Pt film to N-O plasmas determines the dominant oxidation state, surface roughness, and thickness of the modified layers, that strongly affects to etching performance of Pt film. The non-halogen atomic layer etching of Pt has been successfully developed in this study.

[1] J. Chang and J.P. Chang, J. Phys. D: Appl. Phys.50, 25 (2017).

[2] T.T.N. Nguyen et al., Plasma Process. Polym. 19, 6 (2022).

[3] T.T.N. Nguyen et al., Sci. Rep. 12, 1 (2022).

9:40am **AP+PS-FrM-5 Isotropic Plasma-Thermal Atomic Layer Etching and in-Situ Atomic Layer Deposition Passivation of Aluminum Films for Superconducting Quantum Devices***, **Haozhe Wang**,* Duke University*; I. Chen, D. Catherall, A. Hossain, A. Minnich,* California Institute of Technology

Metallic and dielectric film surface imperfections negatively impact the performance of superconducting quantum devices, including qubits and microwave kinetic inductance detectors. Despite considerable exploration into the effects of these imperfections on decoherence and low-frequency fluctuations, contemporary microfabrication methodologies fall short in rectifying them. Here, we report an atomic layer etching and in-situ

deposition (ALE/ALD) process that enables the etching of the native oxide and passivation of aluminum films, all in high vacuum. The process for both ALE and ALD involves sequential exposures to SF_6 plasma and TMA at temperatures around 300 °C; whether the exposures lead to deposition or etching is controlled by adjusting the duration of each dose at the selected temperature. The resulting films are characterized using x-ray photoelectron spectroscopy, high-resolution transmission electron microscopy, and energy-dispersive spectroscopy. The characterization methods indicate that the ~ 40 Å thick native oxide was removed and the resulting surface passivated with ~ 10 Å of AlF_3. Using x-ray photoelectron spectroscopy, we confirmed that the films are resistant to re-oxidation after exposure to the atmosphere for nine months. Our approach to engineer the surfaces of superconducting films at the atomic scale may enable superconducting quantum devices with improved performance.

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