Atomic Layer Etching
Room On Demand - Session ALE1
Plasma and/or Energy-enhanced ALE

ALE1-1 Interpretation of SiO_2 Atomic Layer Etching Based on Plasma Diagnostics*, **Youngseok Lee**, C. Cho,* Chungnam National University, Korea (Republic of)*; S. Kim,* Nanotech, Korea (Republic of)*; J. Lee, I. Seong, S. You,* Chungnam National University, Korea (Republic of)

Atomic-scale etching in semiconductor processing requires self-limiting behaviors to obtain highly precise controllability of material thickness. Achieving the self-limiting behaviors during atomic layer etching (ALE) is dominantly determined by the processing plasma parameters such as electron density and ion energy distribution, which governs the processing conditions. Knowing such fundamental parameters of the processing plasma is therefore essential in realizing ideal ALE. We analyzed our ALE data obtained by an in situ ellipsometer based on plasma diagnostics using an emissive probe and quadrupole mass spectrometer. What we focused on among various plasma parameters is plasma potential and radical density since they are directly related to ion bombarding energy and chemical reaction during the ALE process, respectively. The analysis explained how the ALE results changed according to processing condition variations. In this presentation, the validity of our plasma diagnostics and the analysis results will be discussed in detail.

Atomic Layer Etching
Room On Demand - Session ALE12
Atomic Layer Etching Poster Session

ALE12-1 On the Reactivity of SiN Surfaces Damaged by Ion Bombardment Towards CH_3F and CF_4 Precursors*, **Erik Cheng**, G. Hwang,* University of Texas at Austin*; P. Ventzek, Z. Chen,* Tokyo Electron America

Our recent studies based on extensive first-principles based simulations have revealed that a quasi-equilibrated surface of silicon nitride (SiN) under Ar^+ ion bombardment may consist of a large density of surface defects with lower coordination and that the damaged surfaces tend to be dominated by Si-containing moieties. Contrary to conventional intuition, we have found that these damaged surfaces may be far less reactive than expected towards precursor molecules under typical ALE conditions. From density-functional tight-binding molecular dynamics (DFTBMD), we have observed nearly none of the spontaneous reactions generally expected to happen on these highly damaged surfaces with coordination defects. First-principles calculations reveal that the presence of undercoordinated sites may not imply the presence of dangling bonds, as it is possible for lone pairs and multiple bonds to be present at coordination defect sites. Furthermore, this effect can be further enhanced by overcoordination of atoms within the bulk, which can result in a higher charge density near the surface. When surface reactions are induced under Ar^+ bombardment, far more Si-C bonds are produced than generally expected, while C-N and Si-F bonds are formed relatively infrequently. These findings lead us to speculate that the reactions induced by Ar^+ bombardment may be the key contributor towards the ALE effects seen in experiment and undergo pathways far from what is generally expected given typical chemical intuition.

ALE12-2 Mechanism of Thermal Dry Etching of Metallic Iron Thin Films Using Chlorine and Acetylacetone (acacH)*, **Mahsa Konh**, A. Teplyakov, A. Janotti,* University of Delaware

Thermal dry etching of metallic Iron thin films using Cl_2 and acetylacetone (acacH) was investigated. Iron metal is commonly used in magnetic random-access memory (MRAM) technology. The etching pathway was followed by detecting expected desorbing fragments during a heating ramp via temperature-programmed desorption (TPD) technique. The chemical properties of the etched surfaces were then analyzed with ex situ X-ray photoelectron spectroscopy (XPS). The morphology of the surface was studied with microscopic techniques such as scanning electron microscopy (SEM) and atomic force microscopy (AFM). To desorb volatile etch products, having an oxidized or halogenated Iron surfaces is vital, since clean surfaces resulted in decomposition of the diketone ligands. The pre-chlorination of the surfaces was shown to lead to the formation of transition metals-containing products at lower temperature compared to those on oxidized surfaces. However, halogenation makes the mechanism more complicated, and the etch product can contain both Fe^{2+} and Fe^{3+}. These products may have a combination of ligands, and their general formula can be expressed as $Fe(acac)_xCl_y$. To corroborate surface reaction mechanisms, density functional theory calculations with periodic slab geometries were performed using the Vienna Ab initio Simulation Package (VASP). Based on the computational investigations, it was concluded that the removal of iron is determined by the nature of the surface-bound acac ligand, favoring the process involving a monodentate configuration. Computational work also illustrated the effect of surface smoothing observed experimentally.

ALE12-3 Atomic Layer Etching of Titanium Nitride With O_2 Plasma and CF_3I Plasma*, **Seon Yong Kim**,* Hanyang University, Korea (Republic of)*; S. Shin, I. Park, J. Ahn,* Hanyang University, Korea

Atomic layer etching (ALE) is a promising etching technology based on sequential, self-limiting surface reactions. Recently, the ALE of conducting transition metal nitrides such as TiN, VN, and TaN has been widely researched. The thermal ALE process of TiN with O_3 and HF gas was reported.[1] However, the speed of process (etched thickness per cycle (EPC) = 0.02 nm/cycle) was too slow to be commercialized. The rapid ALE (EPC = 0.6 nm/cycle) process was reported by using CHF_3 and O_2 down-stream plasma[2], but the process was environmentally problematic because of the high global warming potential of CHF_3 (GWP_{100} = 12,400).

In this work, plasma-based TiN ALE was demonstrated byusing O_2 plasma and non-global warming gas of CF_3I (GWP_{100} = 0.3) plasma. All the processes were carried out at temperature of 35 ℃. In the ALE process, a cycle consists of two steps; oxidation and subsequent removal steps. In the first oxidation step, the O_2 plasma oxidizes the surface of the TiN film.Since the surface is oxidized with O_2 plasma, there are much oxidation state of Ti of +4. This Ti state easily makes the film volatile with the form of TiF_4 for the next steps, instead of non-volatile material of TiF_3. In the second etching step, the oxidized surface of TiN film reacts with F radical in CF_3I plasma. Thenthe oxidized TiN surficial layer is completely removed through a volatile byproduct of TiF_4.

The thickness change was analyzed by spectroscopic ellipsometry and transmission electron microscopy. Also, X-ray photoelectron spectroscopy was used to analyze the TiN surface step by step, after the first oxidation step with O_2 plasma and the second removal step of oxidized surface with CF_3I plasma. Saturation characteristics of EPC were observed in ALE process. The EPC of 0.3 nm/cycle was saturated after sufficient supply of both reactive plasma. Furthermore, the EPC was modulated from 0.15 nm/cycle to 0.3 nm/cycle, which is acceptable for the precise layer control at etching process, by only changing the O_2 plasma source power.

References

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ALE12-6 Thermal Atomic Layer Etching of Cobalt with Cl_2 Plasma and Hexafluoroacetylacetone (hfacH)*, **Yongjae Kim**, D. Shim, J. Kim, H. Chae,* Sungkyunkwan University (SKKU), Korea (Republic of)

As the device dimensions continue to shrink, the back end of line (BEOL) interconnects line must also shrink. [1] Copper was used as a material for interconnect lines, but as the line width narrows, resistance increases rapidly due to surface scattering of electrons. [2] In recent studies, cobalt has been used as a substitute for W in local interconnects. As an alternative metal, cobalt has a greater bulk resistance than copper, but does not require a thick barrier/liner and has less resistance than copper as the line critical dimension decreases. [3] Cobalt deposition based on atomic layer deposition requires an ALE process because the surface roughness increases as the thickness increases. [4] In this work, cyclic thermal atomic layer etching process was performed for cobalt in an inductively coupled plasma (ICP) reactor. The process consists of two steps: surface modification with chlorine plasma and removal with lamp heating. In the first step, the surface of cobalt is modified with a layer of $CoCl_2$ using chlorine plasma. In the second step, the modified surface is removed by thermal desorption with hexafluoroacetylacetone. Etch rate were compared at various conditions of flow rate, plasma power and plasma time. The thickness of the cobalt film was confirmed by cross-sectional SEM imaging, and the roughness of the surface was observed by AFM. The etch rate could be controlled below 1 nm/cycle. Surface roughness was compared according to chlorine plasma power and desorption temperature.

References

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Atomic Layer Etching
Room On Demand - Session ALE2
Gas-phase and/or Thermal ALE

ALE2-1 Anomalous Etch Behavior of NHC-Containing Gold Precursor*, **Eden Goodwin**,* Carleton University, Canada*; M. Griffiths,* Wayne State University, Canada*; A. Kadri,* McMaster University, Canada*; S. Barry,* Carleton University, Canada

N-Heterocyclic carbenes (NHCs) have been shown to reconstruct gold surfaces by dislocation and displacement of individual atoms on the surface (Amirjalayer, Bakker, Freitag, Glorius, & Fuchs, 2020). When NHCs are used as ligands for gold precursors, the role of NHC could be two-fold; they saturate surface sites and promote self limiting growth like phosphines (Van Daele et al., 2020) or they could abstract gold atoms and reorganize or etch the film.

In this work we analyze the surface behaviour of a newly reported NHC-containing gold precursor – 1,3-diisopropylimidazol-2-ylidene)methylgold(I) – on a gold coated quartz crystal microbalance (QCM). For a 100-cycle pulse sequence (60s pulse, 20s N_2 purge). In situ QCM data demonstrates frequency growth that begins at a rate of 19.6Hz/cycle, gradually decreases to 2.0Hz/cycle, and has an overall rate of 3.9 Hz/cycle (Figure 1). This figure demonstrates the stepwise etch, where the frequency increases during the precursor pulse and plateaus during the purge. Based on the QCM crystals intrinsic mass to frequency ratio of $17.7 \mathrm{ng/cm}^{-2}\cdot\mathrm{Hz}$, we observe an initial etch rate of 8.9 Au atoms/$\mathrm{nm}^{2}\cdot$cycle, a final rate of 1.1 Au atoms/$\mathrm{nm}^{2}\cdot$cycle, and an overall rate of 2.1 Au atoms/$\mathrm{nm}^{2}\cdot$cycle (compared to 13 atoms/nm^2 in a gold closest packed layer).

Etched QCM crystals were analyzed by atomic force microscopy (AFM) and compared against a standard. The QCM standard had a root mean square roughness of 1.42 nm, while an etched crystal had an enhanced roughness of 2.04 nm. The presence of NHCs on the surface was confirmed by energy dispersive X-Ray analysis (EDX). Changes in surface morphology were also apparent by scanning electron microscopy.

The magnitude of mass loss and its dependence on the presence of the NHC-containing gold precursor, combined with the increased roughness of the surface suggests that surface NHCs induce gold mobility leading to surface reorganization and mass loss of newly-formed gold-containing species. The precursor-surface interaction will be discussed, and in situ mass spectrometry will be shown to support potential surface mechanisms of this precursor.

ALE2-2 Thermal Cyclic Etching of Non-Volatile Material by Self-Stabilizing Organometallic Complex Formation*, **Yoshihide Yamaguchi**, S. Fujisaki, K. Shinoda,* Hitachi, Japan*; K. Sato, M. Izawa,* Hitachi High Technologies, Japan

Remarkable progress on the thermal cyclic etching of non-volatile materials has been made in recent years. The typical procedure for thermal cyclic etching of non-volatile materials such as HfO_2 is cyclic repetitions of formation and desorption of the organometallic complex at a constant temperature [1]. The key steps in thermal cyclic etching is the formation and the desorption of the volatile organometallic complex layer on the surface. The organometallic layer will prevent the diffusion of etching species into the deep at the formation step and it must be easily removed at the desorption step. Our previous study on the thermal cyclic etching of La_2O_3 reported that thermal instability of the corresponding organo-lanthanum complexes must be suppressed in the essential presence of a stabilizer material [2]. In the current study, we present a novel thermal cyclic etching of non-volatile material via a self-stabilizing organometallic complex formation without any additional stabilizer.

The experimental apparatus we used is a tool for thermal gas phase cyclic etching equipped with a single liquid source vaporizer. A La_2O_3 thin film sputtering deposited on a SiO_2/Si wafer was used as a sample. In the first step, the La_2O_3 film was exposed to the vapor of a non-diketonate ligand liquid as the etchant that had a self-stabilizing moiety in the molecule. The sample was then annealed up to 350°C to remove the corresponding organo-lanthanum complex layer from the surface. After consecutive processes of complex formation and its desorption, the La_2O_3 film thickness remaining on the sample surface was evaluated using ellipsometric measurements.

The results showed that the cumulative etched thickness of La_2O_3 film increased linearly in proportion to the number of cycles and that no additional stabilizer was needed. The etching selectivity of La_2O_3 to some other oxides was also confirmed.

From these findings, we conclude that a novel thermal cyclic etching of La_2O_3 by self-stabilizing organometallic complex formation without an additional stabilizer has been successfully demonstrated.

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Atomic Layer Etching
Room On Demand - Session ALE3
Solution-based including Wet ALE

ALE3-1 Novel Electrochemical Concepts for Enabling Atomic Layer Etching of Metals*, Y. Gong, **Theodore Phung**, R. Akolkar,* Case Western Reserve University

In this talk, we will outline electrochemical concepts for achieving atomic layer-by-layer etching of interconnect materials such as copper and ruthenium used in semiconductor devices. By employing a two-step process comprising surface-limited electrochemical oxidation followed by selective etching of the surface oxide monolayer, we will demonstrate the atomic layer etching (electrochemical ALE) of copper and ruthenium. Characteristics of the electrochemical ALE process steps will be outlined using a suite of in situ and ex situ techniques including electrochemical measurements, quartz crystal micro-gravimetry, and high-resolution TEM or AFM. Finally, the critical role of the electrode potential in enabling layer-by-layer etching without surface roughness amplification will be highlighted. Underlying electrochemical mechanisms and thermodynamic considerations will be explained leading to guidelines for optimal electrochemical ALE process design.

Atomic Layer Etching
Room On Demand - Session ALE8
Integration of ALD + ALE

ALE8-1 Simultaneous Selective Deposition and Etching of Ru for Atomic Layer Processing of SiO_2*, **Sumaira Yasmeen**, B. Ko, B. Gu, H. Lee,* Incheon National University, Korea (Republic of)

Nanofabrication is facing multiple challenges, such as patterning limits and transition to 3D structures, with the downscaling of devices to sub-5nm scale. To overcome the existing challenges, area-selective atomic layer deposition (AS-ALD) has surfaced as a promising candidate for a toolbox of nanofabrication. In our previous work, we introduced a Si precursor type inhibitor using bis(methylamino)dimethylsilane (DMADMS) and it showed reliable AS-ALD with high process compatibility with current unit processes of nanofabrication. In this work, the AS-ALD is extended to a multipurpose process that DMADMS is used as a Si inhibitor as well as precursor for SiO_2 ALD using ozone as an oxidant. In addition, AS-ALD Ru process is also integrated into the SiO_2 process as a supporting layer for oxidation protection and lateral growth control. In a detailed process, the experiments are designed in such a way that DMADMS inhibitor is first adsorbed selectively on SiO_2 surface. After DMADMS inhibitor adsorption, Ru AS-ALD process is carried out and Ru is selectively deposited on Cu surface only, given that DMADMS can efficiently block Ru ALD. In the following process, SiO_2 AS-ALD process is performed by oxidizing DMADMS inhibitor by ozone counter reactant. A SiO_2 film nucleates solely on SiO_2 surface, while ozone etches out the AS-ALD Ru from the Cu surface simultaneously. In this way, self-aligned nanopatterns can be formed without additional plasma dry etching processes and photolithography. This combined atomic layer processing is believed to be an example to show effective integration and applicability of AS-ALD into the current nanofabrication technology.

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