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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