

Plasma Science and Technology Division Room B130 - Session PS+2D+EM+SS+TF-ThA

Plasma-Enhanced Atomic Layer Etching

Moderators: Steven Vitale, MIT Lincoln Laboratory, Mingmei Wang, TEL Technology Center, America, LLC

2:20pm **PS+2D+EM+SS+TF-ThA1 Atomic Layer Etch: Real World Utilization of an Idealized Solution, Peter Biolsi**, TEL Technology Center, America, LLC

INVITED

Atomic Layer Etch: Real World Utilization of an Idealized Solution

Critical dimensions (CD) continue to shrink driven by the quest for cheaper, faster and less power-consuming devices. If simple shrink was not enough, all of the back end, middle and front end of line (BEOL, MOL and MOL) also have introduced structural complexity and stringent topographic dimension, material property integrity and fundamental integration yield requirements. Atomic layer etching (ALE) has gained favor as an approach to extract more control over the fabrication of small CD complex topographic structures, atomic layer etching. The idea is that alternating steps of self-limiting processes (e.g., passivation layer formation) and desorption (e.g., the removal of a passivation layer) mitigate aspect ratio dependence effects that lead to the aforementioned problems. The problem is that not all passivation processes are self-limiting. For the etching of dielectric materials, a self-limiting precursor step is not available as etch processes relies on cyclic process (fluorocarbon deposition and ion bombardment steps). Fluorocarbon based processes are not self-limiting rendering them quasi-atomic layer etch. Without special consideration, quasi-ALE has the same problems that continuous processes possess with additional burden of throughput.

Even though ALE can be difficult to be utilized in real-world scenarios, the learning from ALE finds its use in many etch applications. An etch chamber which can provide wide range of radical to ion flux ratios and precise ion energy control (using pulsing techniques) is suitable for ALE or utilizing ALE learnings. Currently, new ALE techniques based on surface modification by ions (Hydrogen plasma treatment of Silicon Nitride) followed by removal of modified layer by F radicals (High pressure NF₃ or SF₆ plasma) or surface modification by NH₃/HF (to create a quasi-self-limiting diffusion barrier layer) followed by removal of modified layer by thermal means, are employed to etch critical layers where requirements are stringent. New frontier of etch technology will be the ability to achieve area selective etch without compromising etch rate of the process. Examples of such activities will be presented in this presentation.

3:00pm **PS+2D+EM+SS+TF-ThA3 Mechanism of SiN Etching Rate Fluctuation in Atomic Layer Etching, Akiko Hirata, M. Fukasawa, K. Kugimiya, K. Nagaoka**, Sony Semiconductor Solutions Corporation, Japan; *K. Karahashi, S. Hamaguchi*, Osaka University, Japan

Atomic layer etching (ALE) enables atomic-precision control of the surface reaction and low damage etching of the underlying layer for device fabrication. In this study, we investigated SiN ALE with process optimization of the surface adsorption and desorption steps, and we clarified the rate fluctuation mechanism.

A dual frequency CCP reactor (60 MHz/2 MHz) was used in this study. A SiN (50 nm) was deposited on the Si substrate by LPCVD. One etching cycle consisted of two steps. CH₃F/Ar plasma was applied to deposit the hydrofluorocarbon (HFC) polymer as the adsorption step. Then, Ar plasma was used in the desorption step. The thicknesses of SiN and the HFC polymer were measured by spectroscopic ellipsometry. The chemical bonding was analyzed by XPS.

A 1.2-nm-thick HFC polymer was deposited on SiN as the adsorption step. Next, we investigated the desorption step by using Ar plasma. The etched amount for 1 cycle was 0.58 nm. However, we found the etch-stop of SiN after 10 cycles of ALE, owing to the deposition (>6 nm) of a protective film on the surface. The etch-stop could be caused by sputtering of the Si upper electrode and/or re-deposition of the HFC film. To investigate the etch rate fluctuation, the SiN surface after ALE was analyzed. C-C and C-N bonds were detected after 1 cycle, and C-C bonds increased after 10 cycles. It was clear that the excess HFC polymer deposition suppressed the ALE reactions. Ar⁺ ion bombardment during the desorption step selectively eliminated the H and F in the HFC polymer, because the bonding energies of C-H and C-F were low. As the bonding energies of C-C (6.4 eV) and C-N (7.8 eV) are relatively high, these bonds remained after the desorption step. We

speculated that excess C-rich polymer deposition after ALE started from the residual C-C bond. Residual Si-C bond is also possible reason, since the MD simulation revealed that the formation of Si-C bond was promoted in the fluorocarbon layer during SiO₂ ALE. [1] These results clearly showed that the initial adsorption kinetics of HFC polymer was strongly affected by the residual carbon on the SiN surface. To suppress the C-rich polymer deposition, we studied stable SiN ALE using the desorption step of Ar/O plasma (0.36 nm/cycle) and the two-step sequential desorption step of Ar and O plasma (0.6 nm/cycle). Although the effect of O adsorption in SiO ALE has been studied previously, [2] few studies have been reported for the case of SiN. Because the surface condition is able to fluctuate with the number of cycles, precise surface control is strongly required to achieve stable ALE.

[1] S. Hamaguchi et al., 2018 AVS, PS-FrM6. [2] T. Tsutsumi et al., JVST A 35 (2017) 01A103.

3:20pm **PS+2D+EM+SS+TF-ThA4 Effect of Polymerization on Ar+ Bombardment Modification of SiO₂ and Si₃N₄ Substrates: Molecular Dynamics Simulation Study, Hojin Kim, Y. Shi, Y.-H. Tsai, D. Zhang, Y. Han**, TEL Technology Center, America, LLC; *K. Taniguchi*, TEL Miyagi Limited, Japan; *S. Morikita*, TEL Miyagi Limited; *M. Wang, A. Mosden, A. Metz, P.E. Biolsi*, TEL Technology Center, America, LLC

To understand the selective removal of silicon oxide (SiO₂) against silicon nitride (Si₃N₄) with gaseous reactants for advanced etch process, we have studied the surface modification of both SiO₂ and Si₃N₄ substrates with Ar⁺ bombardment by using molecular dynamics (MD) simulation. The substrate samples was prepared with and without carbon (C) and hydrogen (H) polymerization to investigate the effect of polymerization on surface modification. C and H atoms were deposited with low ion energy not to disrupt the surface much. After preparation of substrate, Ar⁺ bombardment with various ion energy (IE) were performed. We obtained a damage depth with a wigner-seitz defect analysis as a function of IE and compared the cases with and without polymerization to check the role of the added polymer layer on surface modification. In pristine Si₃N₄ and SiO₂ case, at IE=25eV, both substrates starts to show the damage with penetration of Ar⁺ and follows with an exponential raise as the IE increases. Damage depth at Si₃N₄ is deeper than that at SiO₂. In polymerization, simulations show that H is more deposited than C on Si₃N₄ while on SiO₂, C is more deposited than H. no silicon-hydrogen bonds appear on both substrates and in Si₃N₄, nitrogen-hydrogen bond is dominated while oxygen-carbon bond is popular in SiO₂. For damage analysis, in Si₃N₄ case, CH polymerization helps to lower about 30% in the damage depth with exponential behavior. However, SiO₂ case shows the opposite effect of CH polymerization in the damage depth. Formed polymer layer leads to increase the damage depth by comparing with pristine SiO₂ and helps more clear exponential behavior as a function of IE. Finally, analyzed results using XPS and/or SIMS from blanket SiO₂ and Si₃N₄ films etched in a Capacitively Coupled Plasma (CCP) chamber are compared with the MD simulation results.

4:00pm **PS+2D+EM+SS+TF-ThA6 Advanced Cyclic Plasma Etch Approaches for Metal Patterning: Synergy and Surface Modification Effects, Nathan Marchack**, IBM T.J. Watson Research Center; *K. Hernandez*, University of Texas at Dallas; *J. Innocent-Dolor, M.J.P. Hopstaken, S.U. Engelmann*, IBM T.J. Watson Research Center

INVITED

Atomic layer etching or ALE is a burgeoning research area of plasma processing that offers critical advantages needed for future advancements in semiconductor devices, namely lower damage and enhanced selectivity, through its self-limited reaction cycles separated by purge steps.[1] ALE processes offer a significantly higher degree of tunability over traditional continuous-wave (CW) plasma etching, due to the fact that parameters such as gas flows, pressure, and bias power can be adjusted on a step-specific basis rather than as a global setting for the length of the process.

Our previous work investigated the effect of varying the purge step times in a quasi-ALE process using alternating Cl₂/H₂ exposures on the etched profiles of titanium and tantalum nitride.[2] Titanium and tantalum-based conductive films have been previously evaluated as gate materials for CMOS devices but more recently have been incorporated as top electrodes for novel technologies such as magnetoresistive RAM (MRAM) and hard masks for carbon electrodes utilized in biological sensing. As the trend of downscaling device size continues, the ability to pattern these films at tight pitches with minimal redeposition becomes highly important.

Sub-surface modification of films such as Si₃N₄ and indium-doped tin oxide (ITO) by low atomic weight (LAW) ions such as H⁺ has been discussed in literature as facilitating self-limited etch behavior.[3,4] We present new

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data exploring the incorporation of LAW species into cyclic etch processes, namely penetration depth into these metal nitride films and their role in surface oxide formation, the latter of which can contribute to novel pitch multiplication schemes.[5] SIMS measurements reveal that the depth of penetration of H⁺ for TaN films can be >40 nm and can occur through a native oxide layer that inhibits etching by Cl species. Pressure variation is a significant factor in tuning this effect, which can potentially modify the etch resistance of these films and enable novel integration schemes.

[1] K. J. Kanarik, T. Lill, E. A. Hudson, S. Sriraman, S. Tan, J. Marks, V. Vahedi, R. A. Gottscho, *J. Vac. Sci. Technol. A*. 2015, 33, 020802.

[2] N. Marchack, J. M. Papalia, S. U. Engelmann, E. A. Joseph, *J. Vac. Sci. Technol. A*. 2017, 35, 05C314.

[3] S. D. Sherpa, A. Ranjan, *J. Vac. Sci. Technol. A*. 2017, 35, 01A102.

[4] A. Hirata, M. Fukasawa, K. Nagahata, H. Li, K. Karahashi, S. Hamaguchi, T. Tatsumi, *Jpn. J. Appl. Phys.* 2018, 57, 06JB02.

[5] N. Marchack, K. Hernandez, B. Walusiak, J.-I. Innocent-Dolor, S. U. Engelmann, *Plasma Process Polym.* 2019, e1900008.

4:40pm PS+2D+EM+SS+TF-ThA8 Surface Modification and Stability of Plasma-assisted Atomic-layer Etching (ALE) of Si based Materials; Analysis by Molecular Dynamics (MD) Simulation, Satoshi Hamaguchi, M. Isobe, E.J.C. Tinacba, S. Shigeno, Y. Okada, T. Ito, K. Karahashi, Osaka University, Japan

A plasma-assisted atomic-layer etching (ALE) process typically consists of alternating application of chemically reactive species (adsorption step) and Ar ion bombardment with low bias energy (desorption step) to the surface to be etched. In the adsorption step, a modified layer is formed on the material surface and, in the desorption step, the modified layer is removed with the original material underneath being intact. In this presentation, using the results of MD simulation of ALE for Si, SiO₂, and SiN, together with experimental observations, physical mechanisms of the formation and removal of surface modified layers in typical ALE processes will be discussed.

Our molecular dynamics (MD) simulation of SiO₂ ALE by fluorocarbon adsorption and Ar⁺ ion bombardment shows that preferential sputtering of oxygen takes place by Ar⁺ ion bombardment and a Si rich layer mixed with fluorine and carbon atoms is formed on the SiO₂ surface. Ideally this modified layer should be removed completely in the subsequent desorption step, but in general it is not. In such a layer, the atomic number ratio of Si to O can be as high as unity and carbon provided in the subsequent adsorption step tends to be deposited rather than removing O atoms from the surface by forming CO molecules. Therefore as the ALE cycles proceed, the adsorbed fluorocarbon layer thickens and eventually an etch stop may occur. With fine tuning of incident Ar⁺ ion energy, an etch stop may be avoided but the process window to achieve both continuous ALE cycles (by sufficiently high Ar⁺ ion energy) and ideal self-limit in each cycle (by sufficiently low Ar⁺ ion energy) may still be small or even nonexistent. The incompleteness of the modified surface removal in each ALE cycle seems universal phenomena for plasma-assisted ALE for most materials. For other plasma-assisted ALE processes that we examined by MD simulation, the surface modified layer formed during the adsorption step could not be removed completely by low-energy Ar⁺ ion bombardment, either. Indeed low-energy Ar⁺ ion bombardment contributes to the formation of a deeper modified layer by pushing down adsorbed species into the bulk, rather than simply removing it.

5:00pm PS+2D+EM+SS+TF-ThA9 Innovative Future Etch Technology by Atomic-order Control, Yoshihide Kihara, T. Katsunuma, S. Kumakura, T. Hisamatsu, M. Honda, Tokyo Electron Miyagi Ltd., Japan **INVITED**

In recent years, with the progress of device miniaturization and increased challenges in the scale of integration of semiconductor devices, ultra-high selectivity and atomic layer-level critical dimension (CD) control techniques are required in the fabrication processes.

In the conventional etching, using a fluorocarbon (FC) gas, the high selectivity is obtained by taking advantage of the difference of the FC protective film thickness due to the difference of materials.^[1] However, adopting the conventional approach to cutting-edge pattern structure becomes difficult due to the excessive FC film clogging the micro slit facet. To meet the highly complex requirements, alternative process was developed by using ion modification and chemical dry removal.^[2] We have made several improvements on this new approach and applied it to SiN and SiC etching. The improved new approach achieves ultra-high selectivity without FC protective film and we also confirmed this process has the

characteristics of a self-limiting reaction based on ion depth profile as well as ALE.

In the patterning processes, lower pattern densities have a larger CD shrinking due to micro-loading. Hence, we developed the new process flow that combines atomic layer deposition (ALD) technique and etching. With this method, we achieved CD shrinking at atomic-layer level precision for various patterns, without causing CD loading.^[3]

Moreover, Quasi-ALE can etch the pattern while maintaining the mask CD for different pattern density. This is because Quasi-ALE precisely controls the surface reaction by controlling the radical flux and ion flux independently.^[3] Also, it was necessary to control oval CD size between X and Y respectively. We found that X-Y CD control can be easily performed by changing the balance of FC adsorption and Ar desorption in Quasi-ALE. However, there are concerns about mask selectivity and ion damage in this approach. To solve these problems, we introduce the Advanced Quasi-ALE technique which combines mask protection together with Quasi-ALE. The Advanced Quasi-ALE achieves wider X-Y CD control margin.

On the other hand, as aspect ratio is increased in the memory fabrication process, the occurrence of bowing profile is a serious problem. To address the issue, the new improvement technique has been developed that combines the concept of ALD and etching. With this method, we are able to etch profile more vertically in high A/R feature.

Reference

[1] M. Matsui et al., *J. Vac. Sci. Technol. A* 19 1282 (2001)

[2] N. Posseme et al., *Applied Physics Letters* 105 051605 (2014)

[3] M. Honda et al., *J. Phys. D: Appl. Phys.*, Vol.50, No.23 (2017)

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