Atomic Layer Etching
Room Baekeland - Session ALE1-TuA

ALE of Si-based Materials

Moderators: Thorsten Lill, Lam Research Corporation, Tetsuya Tatsumi, Sony Semiconductor Solutions Corporation

1:00pm **ALE1-TuA-1 Realizing Selective Material Removal in Plasma-Based Atomic Layer Etching (ALE)*, Gottlieb Oehrlein,*** University of Maryland **INVITED**

In atomic layer etching (ALE) one applies iteratively sequences of cycles consisting of reactant supply and surface reaction steps to establish self-limited material removal approaching atomic scale. Since for ALE the reactant is injected only during the surface functionalization step, the surface changes continuously which has important implications for achieving materials etching selectivity. We will discuss several examples of how high materials etching selectivity in ALE may be achieved. In a first approach we describe the use of complex fluorocarbon film precursors to achieve highly selective ALE of SiO_2 over various underlayers. Additionally, reactants during the deposition step may exhibit substrate-selective deposition based on the chemical affinity of precursor gases to the substrate and nature of interfacial bonding. Combining substrate-selective deposition with a surface reaction step provides a new approach for achieving material-selective ALE, and we will describe results selective removal of HfO_2 over Si surfaces. Another material system that can be improved via ALE processing is that of maximizing the etching selectivity of a hard mask material like SiO_2 to extreme ultraviolet (EUV) photoresists in a pattern transfer process, and will be briefly reviewed.

Acknowledgements

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1:30pm **ALE1-TuA-3 Atomic Layer Etching of SiO_2 and Si_3N_4 with Fluorocarbon, Hydrofluorocarbon, Fluoroether and Fluoroalcohol Compounds*, Yongjae Kim,*** *S Kim, H Kang, Y Lee, H Chae,* Sungkyunkwan University, Republic of Korea

Highly precise etching technologies are required to etch nanometer scale patterns and to achieve high selectivity in atomic level etching. [1-3] In this work, cyclic plasma atomic layer etching process was performed for SiO_2 and Si_3N_4 with surface modification in an inductively coupled plasma (ICP) reactor with fluorocarbon, hydrofluorocarbon, fluoroether and fluoroalcohol plasmas. Etch rate were compared at various conditions of plasma power and reaction gases. The process consists of two steps of surface modification and removal step. In the first step, fluorocarbon(FC) layers were deposited on SiO_2 and Si_3N_4 surface with fluorocarbon, hydrofluorocarbon, fluoroether, and fluoroalcohol plasmas. In the second step, the modified layers are removed with ions or radicals generated from Ar or O_2 plasmas. The etch rate was correlated with the fluorine-carbon (F1s/C1s) ratio determined from XPS peaks. Fluoroether and fluoroalcohol plasma generated FC layers having the lowest F1s/C1s ratio, and C_4F_8 plasmas produced the highest F1s/C1s ratio. Constant etch rates were observed in the bias voltage range of 55–60 V, which is identified as the ALE window. Self-limiting etch rate was confirmed with the etching process time and the etch rate could be controlled below 10 Å/cycle. High selectivities of SiO_2/Si and Si_3N_4/Si were obtained with fluoroether precursor having low F1/C1s ratio and the higher carbon on surface is attributed to the lower Si etch rate.

References

[1] V. M. Donnelly and A. Kornblit, J. Vac. Sci. Technol., A 31, 050825 (2013).

[2] H. Zhu, X. Qin, L. Cheng, A. Azcatl, J. Kim and R. M. Wallace, ACS Appl. Mater. Interfaces 8, 19119 (2016).

[3] Y. Lee and S. M. George, ACS Nano 9, 2061 (2015).

Keywords: Cyclic plasma etching, Fluorocarbon polymer, Selectivity

1:45pm **ALE1-TuA-4 Strategies to Enhance the Etch Selectivity During Plasma–Assisted Atomic–Scale Etching of SiO_2 over SiN_x*, Ryan Gasvoda,*** Colorado School of Mines*; Z Zhang, E Hudson,* Lam Research Corp.*; S Agarwal,* Colorado School of Mines

Atomic layer etching (ALE) and its derivatives can provide high etch fidelity, atomic–scale precision, directionality, and high selectivity that is required for manufacturing of sub–7–nm node semiconductor devices. Specifically, plasma–assisted ALE of SiO_2 and SiN_x with ultra–high selectivity of SiO_2 to SiN_x is required in the self–aligned contact etch step. Generally, high selectivity can be achieved through manipulating the process and plasma parameters (similar to continuous etching). To further increase overall etch selectivity, we selectively functionalize the SiN_x surface with benzaldehyde prior to the start of etching. This pre–functionalization retards the net etch of SiN_x in the subsequent ALE process leading to higher SiO_2 to SiN_x etch selectivity. This etch selectivity can be reversed by selectively functionalizing the SiO_2 surface.

In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy in combination with *in situ* 4–wavelength ellipsometry to monitor surface reactions, film composition as well as etch per cycle during ALE. Further, the ion energy distribution (IED) in the Ar plasma activation half–cycle is characterized with a retarding field energy analyzer. We have shown previously that cyclic azasilanes can be used to selectively functionalize the SiO_2 surface from the gas phase. Figure 1 shows the infrared active region of a SiN_x (green) and SiO_2 (blue) surface exposed to benzaldehyde which selectively functionalizes the SiN_x surface with sp^2–hybridized–carbon. Figure 2 shows the infrared absorbance change for 15 sequential ALE cycles on a) bare SiN_x surface and b) benzaldehyde functionalized SiN_x. In both cases, we observe a broad increase in absorbance from ~1200 – 1800 cm^{-1} which indicates the formation and accumulation of an etch inhibiting graphitic fluorocarbon film. An etch stop is observed at cycle 13 for both SiN_x surfaces, however the net etch of SiN_x is ~20% less (~2 nm) for the benzaldehyde functionalized SiN_x than the net etch of the bare SiN_x. This shows that pre–functionalizing a SiN_x surface, selective to a SiO_2 surface, can reduce the overall SiN_x etch loss. Further, we discuss the role of maximum ion energy and IEDs in the activation step on overall etch selectivity with specific focus on non–ideal Ar plasma activation steps where the maximum ion energy is above the sputtering threshold of both SiO_2 and SiN_x.

2:00pm **ALE1-TuA-5 Cryo-ALE of SiO_2 with C_4F_8 Physisorption: Process Understanding and Enhancement*, Gaëlle Antoun,*** *T Tillocher, P Lefaucheux, R Dussart,* GREMI Université d'Orléans/CNRS, France*; A Girard, C Cardinaud,* IMN Université de Nantes/CNRS, France*; K Yamazaki,* Tokyo Electron Limited, Japan*; J Faguet, K Maekawa,* TEL Technology Center, America, LLC

Cryogenic Atomic Layer Etching (Cryo-ALE) is a different approach for ALE, proposed in order to limit drifts due to reactor wall contamination during a process. The proof of principle has been performed on SiO_2 using a fluorocarbon gas and presented in [1].In this process, C_4F_8 is injected in gas phase, and physisorbs on the cooled surface of the substrate. Then Ar plasma is initiated in order to activate the etch. However, in [1], the authors demonstrated the possibility to achieve the etching only at -120°C in their experimental conditions. The aim of this paper is to better understand the mechanisms involved in Cryo-ALE in order to enhance the process and increase the operating temperature.

In order to achieve this work, an ICP reactor has been used. An in-situ ellipsometer as well as an Electrostatic Quadrupole Mass Spectrometer (QMS) are coupled to the reactor. The ellipsometer is used in kinetic mode in order to follow the thickness variation during the process. The QMS is used to follow some species in Multiple Ion Detection (MID) mode. Tests were all performed on SiO_2 coupons glued on SiO_2 6” carrier wafers.

In addition, for surface characterization, quasi in-situ X-Ray Photoelectron Spectroscopy (XPS) measurements were also performed. The ICP reactor used here is different and the substrate is moved from the reactor to the XPS chamber with a transfer rod while keeping the substrate at low temperature.

In order to understand the mechanisms involved in Cryo-ALE, QMS tests were first performed by injecting a C_4F_8 gas flow during one minute on a cooled surface. The substrate temperature and the pressure of C_4F_8 were then varied in order to determine their influence on the surface residence time of C_4F_8. Those tests were also followed by ellipsometry in order to monitor the thickness physisorbed on the substrate surface. XPS tests in same conditions were performed and correlated with QMS results. Indeed, it has been demonstrated that decreasing temperature increases the C_4F_8

surface residence time and hence increases the concentration of fluorine at the surface.

With those data, it was possible to perform new cryo-ALE cycles by increasing the temperature to -90°C. Hence, very regular 150 cryo-ALE cycles were achieved with an etching amount of 0.13 nm/cycle.

The authors would like to thank S.Tahara for all the discussions that helped contributing to those results.

[1] G. Antoun, P. Lefaucheux, T. Tillocher, R. Dussart, K. Yamazaki, K. Yatsuda, J. Faguet, and K. Maekawa, Appl. Phys. Lett. **115**, 153109 (2019).

2:30pm **ALE1-TuA-7 Interpretation of SiO_2 Atomic Layer Etching via a Simple Analytic Model***, **Youngseok Lee**, I Seong, J Lee, S Lee, C Cho,* Chungnam National University, Korea*; S Kim,* Nanotech, Korea*; S You,* Chungnam National University, Korea

We established a simple analytic model of SiO2 thickness changes during SiO_2 atomic layer etching (ALE) and analyzed our experimental data of sample thickness change trends at various ALE conditions via our model. SiO2 ALE experiments were conducted with C4F8/Ar inductively coupled plasma by admitting C4F8 gas into continuous Ar plasma for surface modification (reaction A) of the SiO_2 surface and turning the C4F8 gas off for removal of the modified surface (reaction B) by the Ar plasma ion bombardment. During that process, the thickness change of the SiO_2 samples was monitored using an in-situ multi-wavelength ellipsometer, which showed an increase of the total sample thickness including that of a fluorocarbon (CFx) film deposited on the SiO_2 surface during reaction A and a decrease during reaction B. Then, the ellipsometric results were fitted with our analytic model, which is based on the mechanism of conventional SiO_2 etching using CFx plasma that has previously been understood in detail. As a result, our model could explain several characteristic trends of the sample thickness change under different conditions, and the trends seemed to be mainly related to the deposition rate of CFx film on the SiO_2 surface. The higher CFx film deposition rate is expected to lead to more desirable ALE results. In addition to experimental data analysis, useful insights for advanced SiO_2 ALE could be achieved through the model, helping to decide the optimized ALE condition. In this presentation, physical validity of the model and SiO_2 ALE interpretation that was obtained by the model will be discussed.

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