Atomic Layer Etching
Room Baekeland - Session ALE2-MoA
Plasma and/or Anisotropic ALE I

Moderators: Rémi Dussart, GREMI CNRS/Université d'Orléans, Geun Young Yeom, Sungkyunkwan University

4:00pm **ALE2-MoA-11 From Barrel to ALE: A Lifetime in Etch/A Material and System Design Perspective**, ***Mike Cooke,*** Oxford Instruments , UK **INVITED**

Plasma etching has accompanied advances in lithography for decades, both necessary to enable higher component density in semiconductor device manufacture. A low-pressure glow discharge can provide both chemically active radicals and directional energetic ion bombardment to a surface, driving chemistry which would otherwise require high temperatures. We will describe the principal formats of plasma etch tool, and their merits for delivering atomic layer etching.

Plasma etching equipment of all formats share some common concerns: avoiding etching the chamber or contaminating the wafer; suppression of unwanted parasitic plasmas; maintaining cleanliness; delivering a uniform process across the substrate and reliably from substrate to substrate; and safe operation. The talk will comment on lessons learned in working with plasma tools for more than 40 years, and on the prospects for evolution of the techniques.

4:30pm **ALE2-MoA-13 Understanding the Self-limiting Behavior in Atomic Layer Etched HfO_2,** ***Souvik Kundu,*** *T. Schram, F. Lazzarino, J. de Marneffe, P. Bezard, S. Decoster, I. Asselberghs,* IMEC, Belgium

For future generation transistor applications, two-dimensional (2D) channel materials have received significant research attention due to their favorable electronic properties. In aggressively scaled devices, selectively removing the top high-k layer from the 2D channel material is not possible by the conventional continuous plasma etching (CE) mainly due to poor etch selectivity between 2D and high-k materials, which leads to unwanted roughness and snap the channel layer below. In this regard, an alternative etching technique is required where the process variability can be controlled precisely, and the preferred layer can be removed using self-limiting reactions without punching through the layer below. The atomic layer etching (ALE) of HfO_2 with BCl_3/Cl_2 radical adsorption followed by low energy Ar+ desorption was investigated to soft-land on its underneath 2D material for Source/Drain *top contacts* formation. Since low ion energies are indispensable to minimize the plasma damage on 2D material, synchronously pulsed (SP) ALE was adopted where the plasma and bias powers were varied synchronously with a 30% duty cycle. The adsorption and desorption times were identified and an ALE window with 0.16 nm etch rate per cycle (EPC), low surface roughness (post-etch), and more than 90% synergy were obtained. Efforts were consecrated to understand the ALE mechanism and the effects of plasma power, bias power, and gas ratio on EPC, and synergy were further studied to understand their roles on ALE window. X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM), and atomic force microscope (AFM) were employed to characterize the post-etch HfO_2 surface and interfaces. To realize the efficacy of SP ALE, 10nm HfO_2 was etched from the *10 nm HfO_2/capped seed layer/3mono-layers WS_2/2 µm SiO_2/Si* stacks, where the WS_2 layer is exposed and the signature of non-etched WS_2 layer was confirmed by the results obtained from Raman spectroscopy, XPS, and AFM. In contrast to SP ALE, when a CE process is concerned, it was ascertained that the WS_2 layer is completely ruptured during the HfO_2 etch and eventually lands on the SiO_2 layer below. The challenges of SP ALE and transferring the process on patterned wafers will also be discussed.

4:45pm **ALE2-MoA-14 Area-Selective Atomic Layer Etching of SiO_2 Using Silane Coupling Agent**, *A. Osonio,* ***Takayoshi Tsutsumi,*** Nagoya University, Japan; *B. Mukherjee, R. Borude,* ASM International, Netherlands; *N. Kobayashi, M. Hori,* Nagoya University, Japan

An inherently area-selective atomic layer etching (ALE) process for silicon dioxide (SiO_2) over silicon nitride (SiN) is demonstrated in this study with the use of 1H, 1H, 2H, 2H perfluorooctyltrichlorosilane (POCS), a silane coupling agent. The area-selective adsorption of the chosen silane precursor is leveraged to achieve a substrate-dependent selectivity without the need for surface inhibitors at low substrate temperature (50ºC). A 100 MHz CCP plasma was used for the PE-ALE process. POCS was introduced in gas phase to the vacuum chamber, where the substrate and blanket samples were heated to 50ºC. Low energy Ar^+ bombardment without a bias power followed to remove the modified layer. The changes on the samples' thickness were monitored real-time using *in-situ* spectroscopic ellipsometry (SE) while the changes in the surface functional groups were investigated using *in-situ* FTIR spectroscopy.

Using *in-situ* SE, the area-selective chemisorption of the POCS on SiO_2 over SiN was confirmed from the increase in thickness after dosing which, at the same time, exhibits self-limiting characteristics. *In-situ* FTIR studies confirmed the functionalization of SiO_2 with the CF_2 and CF_3 functional groups and the simultaneous removal of the free OH on the surface during the modification step. After the Ar plasma exposure for the etching step, the removal of the CF_x bonds and the increase in the absorbance of the free -OH peak were found, related to the consumption of the modified layer. Overall, the work shows an alternative course to realize an ideal ALE process that has both self-limiting modification and etching steps. It attempts to address the challenges of stringent parametric control on existing area-selective ALE processes for SiO_2 using other fluorocarbon chemistries.

5:00pm **ALE2-MoA-15 Improving SiO_2 toSiN_x ALE Selectivity with Surface Pre-functionalization for SiO_2/SiN_x Stacks**, ***Xue Wang,*** Colorado School of MInes; *R. Gasvoda, P. Kumar, E. Hudson,* Lam Research Corporation; *S. Agarwal,* Colorado School of Mines

The downscaling of semiconductor devices to sub-7nm generation will require increasingly high etching selectivity with atomic-scale control over the etch profiles in high aspect ratio device structures. Plasma-assisted atomic layer etching (ALE) is a promising technique to tackle these challenges. We previously demonstrated that in ALE, selectivity for SiO_2 over SiN_x can be achieved through the selective pre-functionalization of the SiN_x surface with aldehydes prior to etching. Etching was performed using a cyclic C_4F_6/Ar and Ar plasma ALE process. We used *in situ* attenuated total reflection Fourier transform infrared spectroscopy to monitor the changes in the surface chemical composition on SiN_x and SiO_2. Pre-functionalization of a pristine, plasma-deposited SiN_x surface with benzaldehyde accelerated the formation of a graphitic hydrofluorocarbon layer, which in turn lowered the initial loss of SiN_x prior to an etch stop. However, in technological applications, both SiN_x and SiO_2 surfaces are either exposed to atmosphere or are used as stacks where the underlying SiN_x surface is already exposed to an etching plasma before it can be dosed with the hydrocarbon (see Fig.1a). An atmosphere-exposed SiN_x surface forms a skin layer of SiO_xN_y, and an SiN_x surface exposed to an etching plasma has a layer of residual CF_x. In each case, we discovered that the surface $–NH_x$ groups present after plasma deposition are partially to largely removed. While benzaldehyde does not react with SiO_xN_y and SiO_2 surfaces, it readily reacts with the CF_x reside on the plasma etched SiN_x and SiO_2 surfaces, which prevents selective reaction of aldehydes with the SiN_x surface.

In this presentation, we will also show that on partially etched SiN_x and SiO_2 surfaces, benzaldehyde can be attached selectively to the SiN_x surface after one ALE cycle by minimizing the CF_x residue on the SiO_2 surface. Thus, on the SiN_x surface, we utilize the reactivity of the surface $–NH_x$ groups and the residual CF_x layer to obtain selectivity for reaction to benzaldehyde (see Fig.1b). Our results also show that the selectivity of benzaldehyde attachment reduced with the slow accumulation of carbon-rich residue on both surfaces during ALE process. For SiN_x and SiO_2 surfaces that were pre-etched for one ALE cycle, using 4-wavelength *in situ* ellipsometry, we show that benzaldehyde dosing reduced the amount of SiN_x etched and increased the etch selectivity from 1.7 to 2.1 for 20 ALE cycles (see Figure 2). If we introduced a second dose for benzaldehyde after the 5th ALE cycle, which is prior to significant CF_x accumulation on SiO_2, the selectivity could be further improved from 2.1 to 3.4.

5:15pm **ALE2-MoA-16 Plasma-Assisted Atomic Layer Etching of Silicon Nitride with Unfragmented Fluorocarbons**, ***Chon Hei Lam,*** *M. Carruth,* University of Texas at Austin; *Z. Chen, J. Blakeney, P. Ventzek, S. Sridhar, A. Ranjan,* Tokyo Electron America Inc.,; *J. Ekerdt,* University of Texas at Austin

The self-limiting behavior in atomic layer etching (ALE) processes promise to deliver atomic scale fidelity for three-dimensional device fabrication. ALE processes typically alternate cycles of chemical modification to weaken the surface bonds followed by ion bombardment to remove material with limited amount. ALE may provide fine control over the etch rate and can limit physical damage to the substrate through the layer-by-layer etch process. Since silicon nitride films are a component used in self-aligned multiple patterning schemes, ALE of silicon nitride is an important consideration in process development. ALE using plasma fragmented

fluorocarbons can result in undesirable film growth. Ideally, the process should restrict fluorocarbon film build up to avoid taper profiling, clogging or etch stop. We explore ALE of silicon nitride by utilizing undissociated fluorocarbon (CF_4 and CHF_3) adsorption followed by gentle argon ion bombardment. The impact of gas precursors, energetic ion, temperature, and the nature of the surface chemical modification are discussed. We follow the surface chemistry and monitor structural damage during ALE.

Using CHF_3 we illustrate fluorocarbon surface modification and using energetic argon ion bombardment we illustrate changes to the adsorbed layer during bombardment. The ALE steps are performed at 24 °C and 100 °C (Figure 1). The films are characterized by *in situ* using X-ray photoelectron spectroscopy and spectral ellipsometry. The silicon nitride film is exposed to CHF_3 at 30 mTorr for 1 min as the fluorocarbon adsorption step followed by an argon ion bombardment. The F 1*s* peak appears after the (3 min, 100 eV) argon ion bombardment at 24 °C. The energetic argon ions fragment the fluorocarbon and activate the interaction between fluorine and silicon, and lead to the formation of SiF_x (Fig 2a). When the sample temperature is elevated to 100 °C, the SiF_x shoulder appears in the Si 2*p* spectra upon the CHF_3 adsorption step (Fig 2b) demonstrating the reaction between CHF_3 and silicon nitride is thermally activated. An SiF_x feature remains in the Si 2*p* spectra after the ion bombardment. The shoulder from SiF_x is more intense at 100 °C compared to the 24 °C. The ellipsometry result (Fig 1) shows a gradual change of etch rate over the first 5 ALE cycles as the starting surface is partially oxidized and transitions to silicon nitride. After the removal of the oxidized layer, the etch rate increases and corresponds to approximately 1 nm/cycle. The F 1*s* peak intensity remains at the same level after 5 and 10 ALE cycles indicating the residual fluorine on the surface after ion bombardment.

5:30pm **ALE2-MoA-17 Silicon Atomic Layer Etching with Surface Chlorination and Removal with Ar or He Plasma***, **Namgun Kim,*** Sungkyunkwan University, Korea (Republic of)*; D. Shin, J. Kim, C. Lee, K. Yoon,* Samsung Electronics, Korea (Republic of)*; Y. Kim, H. Chae,* Sungkyunkwan University, Korea (Republic of)

Si atomic layer etching (ALE) has attracted a lot of attention in the semiconductor manufacturing industry due to its excellent depth uniformity with precise control and damage-less compared to conventional reactive ion etching (RIE). [1] Si ALE is generally consisted of two steps, Cl2 adsorption and Ar desorption. The desorption step is the key process of transferring energy to the modified surface and is a major step that determines selectivity and uniformity. [2] Ar was mainly used as the sputtering gas for the desorption step, and there were few studies on other inert gases. In previous papers, the ALE window range was enlarged and the etch per cycle (EPC) was lowered when He was used as sputtering gas instead of Ar, but the recent GaN He ALE study showed different results. [3][4] In this work, Cl2 based Si ALE process was performed using He or Ar as sputtering gas in an 300mm inductively coupled plasma (ICP) reactor. The range of the ALE window did not change to 25V in either condition, the EPC increased from 5.96 Å/cycle to 7.02 Å/cycle, and a nonself-limited behavior was observed when He was used as the sputtering gas instead of Ar. The oxygen atomic fraction was increased in He ALE compared to Ar ALE when an x-ray photoelectron spectroscope (XPS) was observed by changing the number of cycles and bias power. Both ALE processes were compared with conventional RIE by measuring selectivity and roughness. In conclusion, Si quasi-ALE was successfully performed using Ar or He as sputtering gas with Cl2 plasma in the conventional plasma etching tool, and the difference in ALE performance according to the sputtering gas was also investigated.

References

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