# Wednesday Morning, June 25, 2025

## Atomic Layer Etching Room Samda Hall - Session ALE2-WeM

#### **ALE Applications III**

Moderators: Keun Hee Bai, Samsung Electronics Co., Younghee Lee, Lam Research Corporation

#### 10:45am ALE2-WeM-12 In-Situ Observation of Surface Reaction and Advanced Process for Damage-Less Atomic Layer Etching, *Takayoshi Tsutsumi*, Nagoya University, Japan INVITED

The atomic layer deposition (ALD) process has been widely adopted as one of the manufacturing processes for advanced semiconductor devices, but there are few applications of the atomic layer etching (ALE) process. On the other hand, the ALE process is expected to be one of the processes that can perform damage-less uniform processing on the entire wafer or inside the high aspect hole. Although ALD is an effective process for forming thin films, film growth with high crystallinity is difficult. Therefore, the ALE process will be important for etching while maintaining the crystal structure of the surface. In the case of plasma enhanced ALE, it has been reported by simulation [1-4] and experimental analysis [5-8] that the change in crystal structure after ion bombardment extends to several layers. *In-situ* observation of the damage layer formation mechanism and radical adsorption on the layer is essential to understand the surface reaction of atomic layer processes.

We have developed a surface analysis system with atomic spatial resolution without exposing the chemically active surface required for observation of the damage formation mechanism to air. In this paper, we introduce our research about *in-situ* observation of surface reactions, and also introduce advanced processes using light active species, electrons and photons, toward the realization of damage-free ALE.

References

[1]H. Ohta and S. Hamaguchi, J. Vac. Sci. Technol. A 19, 2373 (2001).

[2]D. B. Graves and D. Humbird, Appl. Surf. Sci. 192, 72 (2002).

[3]S. Rauf, T. Sparks, and P. L. G. Ventzek, J. Appl. Phys. 101, 033308 (2007).

[4]A. Agarwal and M. Kushner, J. Vac. Sci. Technol. A 27, 37 (2009).

[5]K. Nakane, R.H.J. Vervuurt, T. Tsutsumi, N. Kobayashi, and M. Hori, ACS Appl. Materials Interfaces 11, 37263 (2019).

[6]M. Hasegawa, T. Tsutsumi, A. Tanide, S. Nakamura, H. Kond, K. Ishikawa, M. Sekine, and M. Hori, J. Vac. Sci. Technol. A **38**, 042602 (2020).

[7]T Tsutsumi, A Asano, H Kondo, K Ishikawa, M Sekine, and M Hori, J. Vac. Sci. Technol. A **42**, 032603 (2024).

[8]S. Nunomura, T. Tsutsumi, N. Takada, M. Fukasawa, and M. Hori, Appl. Surf. Sci. **672**, 160764 (2024).

11:15am ALE2-WeM-14 Isotropic ALE of 2D Crystalline MoS<sub>2</sub> using SF<sub>6</sub>:H<sub>2</sub> Plasma and O<sub>2</sub> Plasma, Sanne Deijkers, Christian Palmer, Nick Chittock, Guillaume Krieger, Silke Peeters, Marcel Verheijen, Eindhoven University of Technology, The Netherlands; Harm Knoops, Oxford Instruments Plasma Technology, Netherlands; Erwin Kessels, Adrie Mackus, Eindhoven University of Technology, The Netherlands

Two-dimensional crystalline  $MoS_2$  is an emerging material for nanoelectronics, where it can be applied as a channel material in field effect transistors.  $MoS_2$  exhibits a high carrier mobility, even at the monolayer thickness of 6.5 Å, and therefore it is expected to replace Si in the future [1]. Application of  $MoS_2$  in nanoelectronics requires highly controlled deposition and etching processes. Currently available ALE processes either require an external step like a wet treatment [2], or are optimized for amorphous  $MoS_2$  [3]. Here, we present a plasma-enhanced ALE process, which can etch crystalline  $MoS_2$  in an isotropic manner.

In the ALE cycle, the crystalline ALD-grown MoS<sub>2</sub> film was first fluorinated and subsequently oxygenated to create volatile  $Mo_xO_yF_z$  species. The fluorination step employs a plasma mixture containing SF<sub>6</sub> and H<sub>2</sub>, which is believed to produce *in situ* HF, as suggested by previous studies on H<sub>2</sub>diluted fluorine plasmas [4,5]. F radicals, which are known to etch MoS<sub>2</sub> continuously [6,7], are scavenged by the hydrogen to form HF as observed in the plasma [8]. The SF<sub>6</sub>:H<sub>2</sub> ratio was tuned to ensure modification occurs without continuous etching. For the oxygenation half-cycle an O<sub>2</sub> plasma was used, whereas O<sub>2</sub> gas and H<sub>2</sub>O did not result in significant etching.

The resulting etch per cycle combining the SF<sub>6</sub>:H<sub>2</sub> plasma and O<sub>2</sub> plasma is 0.92  $\pm$  0.02 Å. Before ALE the crystallinity of the films was confirmed by

observation of the characteristic MoS<sub>2</sub> peaks in Raman spectroscopy, and after ALE a decrease in these peaks is seen, verifying etching of the crystalline material. Furthermore, no F contamination was observed after ALE by x-ray photoelectron spectroscopy (XPS). However, XPS showed the presence of some oxidation of Mo and S. The isotropic nature of the ALE process was confirmed using transmission electron microscopy in 3D trenches.

[1] Kim et al., Nat. Nanotechnol., 2024

[2] Lee et al., Applied Physics Express, 2017

[3] Soares et al., Chem. of Mater., 2023

[4] Jung et al., JVST A, 2020

[5] Kihara et al., 2023 IEEE Symposium on VLSI Technology and Circuits, 2023

[6] Jeon et al., Nanotechnology, 2015

[7] Xiao et al., Sci Rep, 2016

[8] Krieger et al., ALD/ALE 2024, 2024

11:30am ALE2-WeM-15 Enhanced Plasma Ignition and Sustaining of Transformer-Coupled Plasma Source with a Secondary Coil, Tae S Cho, Jae Hoon Choi, Hak Min Kim, Gi Won Shin, Soo Young Hwang, Ji Hyun Kim, Wonik IPS, Republic of Korea

The need for miniaturization in the semiconductor industry, characterized by sub-10 nm features, 3D stacked architectures, and complex gate-allaround structures, requires increasingly sophisticated plasma processing technologies. These advanced applications require plasma radical sources such as transformer-coupled plasma (TCP) that can operate over a wide pressure range while providing high fluxes of reactive species with minimizing ion-induced damage to delicate device structures. However, ignition with electronegative gases in TCP sources requires high breakdown voltages, often requiring initial plasma generation with an inert gas such as argon, which reduces process throughput. To overcome this limitation, a secondary coil was introduced to generate the high voltage for plasma ignition. The ignition and sustain ranges in argon-nitrogen mixtures were investigated using a TCP source incorporating several ferrite cores. One of the ferrite cores integrated both primary and secondary coils, with the secondary coil terminals connected to reactors on both sides of the core. The current induced in the secondary coil generated an additional electric field between the reactors, enhancing both plasma ignition and sustaining. Experiments were performed at pressures of 0.5-2 Torr and radio frequency (RF) powers up to 3000 W at frequencies of several hundred kHz using various argon-nitrogen gas mixing ratios. The secondary coil enabled stable plasma ignition across a wider range of argon-nitrogen mixtures, eliminating the need for initial plasma generation with inert gas, unlike conventional TCP discharges. This enhanced ignition and sustain ranges provide significant advantages for precise control of process gases and short plasma on/off times in advanced manufacturing processes such as atomic layer deposition (ALD) and atomic layer etching (ALE).

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