ALD Applications
Room Tamna Hall A - Session AA2-TuM
EUV and Patterning Applications

Moderators: Jiyoung Kim, University of Texas at Dallas, **Hanjin Lim**, Samsung Electronics Co., Inc.

10:45am **AA2-TuM-12 Defect-free Carbon based EUV Pellicle by using Bi-layer Capping with Atomic Layer Deposition***, **Park Jihoon**, Yoon Hwi,* Yonsei University, Korea*; Wi Seong Ju, Lee Yunhan, Lee Byunghoon, Bae Sukjong, Choi Jin,* Samsung Electronics, Republic of Korea*; Kim Hyungjun,* Yonsei University, Korea

For several decades, semiconductor device scaling down has been steadily progressing. Therefore, lithography technology has also been developed to engrave smaller patterns into circuits. Extreme ultraviolet lithography (EUVL) technology which uses a wavelength of 13.5 nm, which is significantly shorter than conventional lithography, has emerged as a solution. However, the increased light source power of EUV causes the chamber to become harsher and high temperature. These conditions accelerate mask damage and require frequent mask replacement. So, as EUV equipment advances, demand for pellicle increases.

Carbon-based pellicles are considered as EUV pellicle materials because they have high transmittance, good thermal stability, high emissivity, and good mechanical properties. However, they have low durability against hydrogen plasma in EUV equipment, so a capping layer is essential. Therefore, in this study, we attempted to deposit a very thin and uniform film of MoN with low EUV absorption coefficient and H_2 plasma durability through ALD. However, plasma pre-treatment or PEALD was required to perform ALD on graphite with an inert surface, which caused graphite damage.

In this study, we greatly improved the adsorption using physisorption on the graphite surface at high precursor vapor pressure. An oxide thin film less than 2 nm was deposited as the first layer, and the coverage was confirmed by comparing the I_d/I_g peak ratio of Raman spectrum before and after H_2 plasma treatment. After full coverage of the oxide thin film, a defect-free graphite capping layer was successfully deposited by depositing a MoN film less than 5 nm. Next, we conducted a characteristic evaluation as an EUV pellicle. Our research will be a basic experiment for a carbon-based pellicle capping layer.

11:00am **AA2-TuM-13 Three-Step Plasma-Enhanced ALD of Ultra-Thin SiNx with Enhanced Etch Resistance for EUV Pellicle Applications***, **Hye-Young Kim**, Hyun-Mi Kim, Yoonjeong Shin, Jonghyuk Yoon,* Korea Electronics Technology Institute, Republic of Korea*; Ji-Beom Yoo,* Sungkyunkwan University (SKKU), Republic of Korea*; Seul-Gi Kim, Hyeongkeun Kim,* Korea Electronics Technology Institute, Republic of Korea

Silicon nitride (SiN_x) thin films are widely recognized for their hardness, chemical inertness, and exceptional barrier properties, making them indispensable as passivation layers and gate insulators in semiconductor devices. Recent studies have shown that enhancing film density through optimized deposition parameters can significantly reduce the etch rate in hydrofluoric acid (HF). To build on this concept, an optimized ALD process was developed, using SiN_x as a capping material to protect the base materials of extreme ultraviolet (EUV) pellicles. A three-step ALD process, consisting of Si_2Cl_6 (precursor) - NH_3 plasma (reactant 1) - N_2 plasma (reactant 2), was developed to enhance resistance to potassium hydroxide (KOH), which is crucial for pellicle capping, and to protect the base material from hydrogen plasma generated in the EUVL chamber. A detailed investigation was conducted by comparing SiN_x films deposited using NH_3 plasma alone, N_2 plasma alone, and their sequential combination. The NH_3 plasma–N_2 plasma sequence resulted in the highest film density of 3.10 g/cm^3, compared to 2.85 g/cm^3 for films deposited using NH_3 plasma alone. This increase in density correlated well with the improved etch resistance in KOH, as the etch rate was significantly reduced from 3.3 Å/h (NH_3 plasma alone) to 1.8 Å/h in the three-step ALD process. Additionally, the formation of Si etch pits was nearly eliminated, further confirming the enhancement in etch resistance. Further analysis was conducted to investigate how the additional N_2 plasma in the three-step process influenced film density, composition, and hydrogen bonding. To this end, XPS and FT-IR analyses were performed to examine changes in these properties. Additionally, to determine whether ion bombardment played a primary role in densification, a modified three-step process incorporating Ar plasma instead of N_2 plasma was implemented for comparison. Furthermore, in situ Optical Emission Spectroscopy (OES) was conducted during the plasma exposure step and resultant emission signals were matched with dissociated reaction products to investigate the reactive species generated in each process and their impact on the final film properties.

11:15am **AA2-TuM-14 Mo_2C-Coated CNT with Hydrogen Radical Resistance for EUVL Pellicles***, Hyeongkeun Kim, **Su Min Lee**, Yongkyung Kim Kim, Jonghyuk Yoon, Kihun Seong, Heongyu Lee, Sun Gil Kim, Hyun-Mi Kim,* Korea Electronics Technology Institute (KETI), Republic of Korea*; Gu Young Cho,* Dankook University, Republic of Korea*; Seul-Gi Kim,* Korea Electronics Technology Institute (KETI), Republic of Korea

Extreme ultraviolet lithography (EUVL) is a key technology in advanced semiconductor manufacturing, enabling precise patterning at the nanoscale. However, mask contamination poses a major challenge, necessitating the use of EUV pellicles to protect the mask while ensuring high transmission of EUV light. To meet performance requirements, EUV pellicles must achieve over 90% transmission and maintain mechanical stability at thicknesses of just a few nanometers. [1]

Single-walled carbon nanotube (SWCNT) membranes are promising for EUV pellicles due to their high transmittance, thermal stability, and mechanical strength. However, their vulnerability to hydrogen radical etching at higher EUV source powers limits their durability. [2] To address this, we developed a molybdenum carbide (Mo_2C)-coated CNT membrane with enhanced resistance to hydrogen plasma. [3]

The Mo_2C capping layer was synthesized using atomic layer deposition (ALD) of molybdenum carbide (MoC_x) with molybdenum pentachloride ($MoCl_5$), followed by carbidization in a methane (CH_4) atmosphere. This process enabled uniform Mo_2C capping while preserving the CNTs' intrinsic properties.

Results demonstrated that Mo_2C-coated CNT membranes exhibit superior resistance to hydrogen plasma etching compared to uncoated CNTs. This study highlights the potential of Mo-$_2$C-coated CNTs as high-performance EUV pellicles, paving the way for improved lithography processes in semiconductor fabrication.

References

1. Raymond Lafarre and Raymond Maas, *Proc. SPIE 11609, Extreme Ultraviolet (EUV) Lithography XII*, 1160912 (2021)
2. Ivan Pollentier, Marina Y. Timmermans, Cedric Huyghebaert, Steven Brems and Emily E. Gallagher, *Proc. SPIE 11323, Extreme Ultraviolet (EUV) Lithography XI*, 1132347 (2020)
3. Yongkyung Kim, Kihun Seong, Jonghyuk Yoon, Donggi Lee, Seungchan Moon, Sung Kyu JangHyun-Mi Kim, Seul-Gi Kim, Jinho Ahn and Hyeongkeun Kim, *Proc. SPIE 12750, Proceedings Volume International Conference on Extreme Ultraviolet Lithography*, 127500L (2023)

11:30am **AA2-TuM-15 ALD Outstanding Presentation Award Finalist: Vapor-Phase Infiltration of Hafnium in Poly(Methyl Methacrylate) Thin Films for Extreme Ultraviolet Lithography Applications***, Md Istiaque Chowdhury, Xinpei Wu,* Brookhaven National Laboratory*; Won-Il Lee, Mueed Ahmad,* Stony Brook University*; J. Anibal Boscoboinik, Kim Kisslinger, Aaron Stein, Nikhil Tiwale,* Brookhaven National Laboratory*; Jiyoung Kim,* University of Texas at Dallas*; **Chang-Yong Nam**,* Brookhaven National Laboratory

Vapor-phase infiltration (VPI), an organic-inorganic hybridization technique derived from atomic layer deposition (ALD), has demonstrated the ability to generate novel hybrid photoresists for extreme ultraviolet EUV lithography applications. In this study, we investigated hafnium (Hf) infiltration in poly(methyl methacrylate) (PMMA) via VPI using tetrakis(dimethylamido)hafnium (TDMA-Hf) as a precursor. Unlike typical metal oxide VPI, we employed a metal precursor-only VPI approach, capped by a short water pulse at the end of the procedure, under various VPI temperatures ranging from 85 °C to 150 °C.

Using in-situ mass gain measurement by quartz crystal microbalance (QCM) and a suite of ex-situ characterizations including polarization-modulated infrared reflection-absorption spectroscopy (PM-IRRAS), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS), we discovered that: (a) TDMA-Hf could infiltrate PMMA uniformly over the tested thickness of approximately 30 nm despite its relatively large molecular size; (b) the carbonyl (C=O) group in PMMA primarily interacted with infiltrating TDMA-Hf, most likely forming weak coordination bonds; however, at temperatures above 120 °C, a new unidentified bond was formed, likely resulting from stronger covalent interactions; and (c) VPI protocols needed optimization to minimize the inadvertent introduction of oxidants (e.g., water, oxygen) and subsequent formation of undesired Hf oxides within PMMA.

The synthesized Hf-PMMA thin films were subjected to a lithographic patterning study using 100 kV electron-beam lithography (EBL), revealing that VPI temperature directly influenced EBL sensitivity. By employing an appropriate developer, Hf-PMMA infiltrated below 100 °C demonstrated up to a ~60% improvement in EBL sensitivity compared to the un-infiltrated PMMA control. However, at higher infiltration temperatures, sensitivity decreased, which we attribute to the stronger chemical binding between the infiltrated Hf precursor and PMMA. These results highlight the critical importance of understanding and controlling precursor-polymer interactions during VPI to generate organic-inorganic hybrid thin films for advanced lithography applications, including EUV lithography.

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11:45am **AA2-TuM-16 Atomic Layer Deposition and Atomic Layer Etch cycles to minimize "Mushroom Growth" effect in Area Selective Atomic Layer Deposition***, **Birol Kuyel**, Joe Alex,* NANO-MASTER

Area-Selective Atomic Layer Deposition (AS-ALD) is a bottom-up thin-film deposition technique that enables selective growth on targeted regions while preventing deposition on adjacent areas. This method has gained significant interest due to its self-aligning and self-inhibiting properties, which help mitigate edge placement errors inherent in traditional top-down fabrication processes. However, the isotropic nature of Atomic Layer Deposition (ALD) can lead to undesirable lateral growth, commonly referred to as the "mushroom growth" effect. In this study, we aim to experimentally develop an integrated ALD and ALE cycle to mitigate this effect in the area-selective deposition of SiO_2 and Si_3N_4. To achieve this, we utilize the NANO-MASTER NLE-4000 hybrid system, which enables both Plasma-Enhanced ALD (PEALD) and Plasma-Assisted ALE (PAALE) within the same chamber.

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