Atomic Scale Processing Mini-Symposium
Room 116 - Session AP1+EM+PS+TF-TuM

Atomic Layer Etching I: Thermal Processes

Moderators: Steven M. George, University of Colorado at Boulder, **Austin Minnich**, California Institute of Technology

8:00am **AP1+EM+PS+TF-TuM-1 Highly Selective and Isotropic Atomic Layer Etching using Dry Chemical Removal**, ***Nobuya Miyoshi,*** Hitachi High-Tech America, Inc. **INVITED**

As semiconductor devices shrink to sub-10 nm dimensions, the introduction of new device structures, integration schemes, and materials brings many challenges to device manufacturing processes. A new structure with gate-all-around (GAA) nanosheets has been introduced to reduce the power consumption of transistors and achieve higher transistor integration density. For advanced semiconductor memory devices, 3D NAND flash has been introduced to achieve higher bit densities. Fabricating these three-dimensional (3D) devices requires isotropic etching of thin films with atomic layer control, high selectivity to underlying materials, and high uniformity over high-aspect-ratio 3D structures. Thermal atomic layer etching (ALE) is a promising method for isotropic etching with atomic-level precision and high conformality over three-dimensional structures. We developed a dry chemical removal (DCR) tool with an infrared (IR) wafer annealing and quick cooling system to perform highly selective thermal ALE for various materials. Thermal ALE was demonstrated for Si_3N_4 and SiO_2 films using the formation and desorption of $(NH_4)_2SiF_6$-based surface-modified layers. Thermal ALE processes for W and TiN films were also demonstrated by the formation and desorption of halogenated surface-modified layers. These ALE processes show a self-limiting formation of modified layers, enabling conformal and precisely controlled etching. In addition, spontaneous and highly selective etching of SiO_2 was demonstrated on the DCR tools using HF/CH_3OH vapor. SiO_2 films can be etched spontaneously with high selectivity to SiN films when the temperature of the substrate is lower than −20ºC.

8:30am **AP1+EM+PS+TF-TuM-3 Selective Si or Ge Dry, Thermal Spontaneous Etching Using HF Vapor**, ***Marcel Junige***, *T. Colleran, S. George,* University of Colorado Boulder

Advanced 3D structures in microelectronics require novel self-aligned techniques. For example, selective etching may remove one specific material while leaving intact others in proximity. This multi-color challenge gets particularly difficult for selectivity between Si-based materials, as well as between Si and Ge. Instead of plasma activation, this work focused on developing gas-phase spontaneous etch pathways based on thermal chemistry using anhydrous hydrogen fluoride (HF) vapor.

In situ spectroscopic ellipsometry experiments discovered substantial spontaneous etching of Si by HF at 275℃. The Si etch rate was 12.2 Å/min at an HF pressure of 3 Torr. The Si etch rate increased further with higher HF pressures. In addition, Si etched selectively with an exceptionally high selectivity factor of >1,000:1 versus the retention of SiO_2 and stoichiometric Si_3N_4.

Temperature-programmed quadrupole mass spectrometry (QMS) experiments confirmed the spontaneous etching of crystalline Si nano-powder by HF. SiF_4 and H_2 were observed as the main volatile etch products. QMS detected the SiF_4 product with a gradual onset above ~175℃. This temperature dependency indicated that the etch reaction may be limited by SiF_4 desorption from the Si surface. SiF_4 desorption from fluorinated Si surfaces has been reported to occur at >125℃.

Additional QMS experiments also observed the spontaneous etching of Ge nano-powder by HF. GeF_4 and H_2 were revealed as the main volatile etch products. QMS detected GeF_4 already at 25℃. The GeF_3^+ signal intensity increased with elevating temperature and exhibited a maximum at ~80-85℃. Subsequently, the GeF_3^+ signal decreased below the noise level above ~125℃.

These results suggest that Si etching could be achieved selectively over Ge retention at >175℃. Likewise, Ge etching could be accomplished selectively over Si retention at <125℃. This reciprocal selectivity between Si and Ge etching will depend on the influence of proximity effects resulting from the volatile etch products when Si and Ge are both present in the reactor.

8:45am **AP1+EM+PS+TF-TuM-4 Theoretically Designed Thermal Atomic Layer Etching Processes for Interconnect Metals**, ***Miso Kim****, H. Cho,* Hongik University, Republic of Korea*; D. Lee, J. Lee, J. Kim, W. Kim,* Hanyang University, Republic of Korea*; B. Shong,* Hongik University, Republic of Korea

Atomic layer etching (ALE) is emerging as a key technology for the precise and selective removal of materials at the atomic level, especially for manufacturing of nanoscale three-dimensional semiconductor devices. Previously known thermal ALE processes often involve two-step sequence of surface chemical reactions: surface modification of the substrate such as halogenation, followed by volatilization using another etchant. For example, a recent study reported a thermal ALE process for Ni, employing SO_2Cl_2 for halogenation and $P(CH_3)_3$ for volatilization via ligand addition [1]. Since ALE process is based on self-limiting surface chemical reactions, it is desirable to design ALE processes by understanding their surface reactions. However, the mechanistic aspects of such thermal ALE reactions remain significantly underexplored. In this work, we employed neural network potential (NNP) calculations to screen for suitable process conditions for thermal ALE process of metals, especially those considered as materials for nanoscale interconnects. Our findings demonstrate that several metals are capable of forming energetically stable volatile compounds via halogenation and ligand addition of thermal molecular etchants. Several novel thermal ALE processes that were theoretically predicted are experimentally demonstrated with varying etch rates and selectivity between the substrates. Overall our study show the applicability of theoretical analysis of the surface chemical reactions toward design of novel ALE processes.

References. (1) Murdzek, J. A.; Lii-Rosales, A.; George, S. M. Chem. Mater. 2021, 33 (23), 9174–9183.

Acknowledgments. This work was supported by Samsung Electronics.

9:00am **AP1+EM+PS+TF-TuM-5 X-ray Photoelectron Studies of Removal of Sputter Damage from InGaP Surfaces Using Thermal Atomic Layer Etching**, ***Ross Edel,*** University of Colorado Boulder*; E. Alexander,* MIT*; A. Cavanagh,* University of Colorado Boulder*; T. Nam,* Soonchunhyang University, Republic of Korea*; T. Van Voorhis,* MIT*; S. George,* University of Colorado Boulder

InGaP is widely used for red LED devices. Surface defects on LED devices can lead to non-radiative electron/hole pair recombination that reduces their light output. This light quenching effect is more severe for smaller µLEDs that have high surface-to-volume ratios. The surface defects are believed to be formed by energetic ion species during plasma processing that forms the µLEDs. Thermal ALE may provide a method to remove these defects.

To quantify the removal of surface damage, x-ray photoelectron (XPS) studies employed InGaP samples sputtered with argon as a model system. These InGaP samples simulate the µLED sidewalls that are exposed to energetic species during plasma processing. Thermal InGaP ALE was then performed using static, sequential HF and dimethylaluminum chloride (DMAC) exposures. This procedure yielded etch rates of 0.5–1.0 Å/cycle at temperatures from 300–330 °C, respectively. This work was conducted using a new apparatus that combines a hot wall ALD/ALE reactor with *in vacuo* Auger spectroscopy to allow sample characterization without exposure to air.

InGaP samples damaged by Ar^+ ion sputtering were analyzed using *ex situ* X-ray photoelectron spectroscopy (XPS) before and after thermal ALE by tracking the shifted components in the P 2p XPS region that correspond to sputter damage. An *ex situ* XPS scan of a sputtered InGaP sample displayed two shifted doublets (Figure 1a) while an unsputtered sample showed only a bulk doublet (similar to Figure 1b). DFT simulations identified the higher energy doublet as phosphorus directly bound to three-coordinate indium or gallium and the lower energy doublet as three-coordinate phosphorus (Figure 2a). In contrast, the DFT simulations showed only a bulk doublet for InGaP without under-coordinated surface atoms (Figure 2b).

InGaP ALE can then remove the XPS features associated with the damaged lattice. A bulk-like XPS spectrum showing minimal damage was recovered after 50 ALE cycles for a sample initially exposed to 500 eV sputtering (Figure 1b). By contrast, annealing for 72 hours at 300 C without etching was not sufficient to eliminate the damage. AES analysis similarly showed that the argon implanted in the sample by sputtering was removed after etching but not annealing. Increasing the sputtering ion energy to 2 keV required more extensive etching to remove the sputter damage. In this case, 100 ALE cycles were able to largely remove the surface defects. The corresponding AES data showed a linear decrease in implanted argon and reached zero after 100 ALE cycles. The etch depth consistent with 100 ALE cycles indicates a damaged material depth of ~4 nm.

9:15am **AP1+EM+PS+TF-TuM-6 Chemical Vapor Etching or Atomic Layer Etching of ZnO? in Situ Ellipsometry and Mass Spectrometric Studies***, **Terrick McNealy-James**, S. Berriel, B. Butkus, P. Banerjee,* University of Central Florida

"Atomic layer etching (ALE) stands out as a remarkable technique for precise Angstrom-level control for material removal. With a growing demand in the semiconductor and nanotechnology sectors, ALE becomes a promising solution to address evolving challenges in patterning and in the shrinking of device dimensions. For ideal ALE, processes must demonstrate self-limiting, dose independent etch behavior with well-defined temperature windows. These set of criteria are a challenge for many recently demonstrated metal oxide films.[1]

Here we present the etching characteristics of zinc oxide (ZnO) films, using Hacac and O2 plasma[2]. We comprehensively map the etch rates using *in situ* spectroscopic ellipsometry. The chemistry of the etching process is verified using mass spectrometry. Etch rate per cycle (EPC) is optimized within a temperature window of 220 – 280 ^{o}C. However, it is found that the etch rates are dose dependent and are not only governed by the Hacac pulse times but also by a subsequent “hold” step which continues to etch the ZnO film with no signs of self-limiting behavior. In this context, the Hacac + O2 plasma process appears to be a controllable chemical vapor etch process.

The impact of inserting etch stop layers in ZnO is explored. While a single monolayer of Al2O3 slows the EPC, 3 monolayers of Al2O3 are sufficient to completely block further etching. These results point to the non self-limiting behavior of Hacac etching of ZnO and strategies which may provide EPC control and selectivity with ZnO composition tuning.

References:

(1) Jonathan L. Partridge, Jessica A. Murdzek, Virginia L. Johnson, Andrew S. Cavanagh, Andreas Fischer, Thorsten Lill, Sandeep Sharma, and Steven M. George
Chemistry of Materials 2023 35 (5), 2058-2068

(2) A. Mameli, M. A. Verheijen, A. J. M. Mackus, W. M. M.Kessels, and F. Roozeboom, ACS Appl. Mater. Interfaces, vol. 10, 38588, (2018).

9:30am **AP1+EM+PS+TF-TuM-7 Examination of Atomic Layer Etch Mechanisms by Nuclear Magnetic Resonance Spectroscopy***, **Taylor G. Smith**, J. Chang,* University of California, Los Angeles **INVITED**

As atomic layer etching (ALE) becomes more widespread, there is a need to better understand the underlying mechanisms by which it operates. Of particular interest is the removal half-cycle of thermal ALE wherein a vapor-solid reaction leads to the formation of a volatile etch product. Solid state magic angle spinning nuclear magnetic resonance (MAS-NMR) can provide a wealth of structural and chemical information, but it has not yet been used to examine ALE reaction mechanisms. In this work, MAS-NMR of CuO etched in solution phase formic acid (FA) is demonstrated and compared with prior density functional theory results[1]. Although it may seem a simple system, the paramagnetic nature of CuO and the formation of many products with slightly different structures both lead to complicated NMR spectra. The issue of significant peak broadening by paramagnetic relaxation can be alleviated in part by spinning at very fast speeds (>30kHz). From the resulting spectra, confirmation of $Cu(HCOO)_2 \cdot 4H_2O$ as a product is possible by comparison to a commercial reference powder. However, assignment of other peaks requires correlation spectroscopy showing ^{13}C-^{13}C and ^{1}H-^{13}C correlations to deduce the structures of the various products, illuminating the reaction landscape of CuO with FA. To extend these findings to the vapor-solid interactions present in ALE, a special heterogeneous NMR rotor can be used that was originally designed for use with high pressure gases. To adapt this rotor use with lower pressure FA vapor, a novel rotor packing method that separates the FA from the CuO prior to vaporization is presented.

Author Index

Bold page numbers indicate presenter