Atomic Layer Etching
Room Samda Hall - Session ALE2-TuA

ALE Applications II

Moderators: Harm C.M. Knoops, Oxford Instruments Plasma Technology, Netherlands, **Jaewon Lee**, SK hynix

4:00pm **ALE2-TuA-11 Development of an Atomic Layer Etching Process Dedicated to Diamond Material***, **Marine Régnier**,* Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel; Institute of Applied Physics, University of Tsukuba; Japanese-French Laboratory for Semiconductor Physics and Technology J-FAST, CNRS, Univ. Grenoble Alpes, University of Tsukuba, France*; Aboulaye Traoré,* LSPM, CNRS, Université Sorbonne Paris Nord, France*; Marceline Bonvalot,* Univ. Grenoble Alpes, CNRS, Grenoble INP, LTM; Japanese-French Laboratory for Semiconductor Physics and Technology J-FAST, CNRS, Univ. Grenoble Alpes, University of Tsukuba, France*; Etienne Gheeraert,* Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel; Institute of Applied Physics, University of Tsukuba; Japanese-French Laboratory for Semiconductor Physics and Technology J-FAST, CNRS, Univ. Grenoble Alpes, University of Tsukuba, France

Diamond power devices, such as Schottky diodes and MOSFETs are currently being intensively investigated for possible application in power electronics and require dedicated fabrication processes to achieve adequate operating performances. Conventional etching techniques often lead to defects, surface roughness and sub-surface damages, which can significantly degrade carrier mobility and breakdown voltage of power devices. Thus, it becomes essential to develop diamond etching processes minimizing induced defects. Atomic layer etching (ALE) is then the perfect candidate allowing a very soft etching leading to defect-free etched surfaces and sub-surfaces. The first report of ALE of diamond dates back to 1988 with a patent describing a sequential process involving a surface modification upon NO_2 exposure, followed by a sputtering with a mixture of noble and hydrogen gasses [1]. However, since then, no further studies have been reported.

In this work, the ALE process optimization of (100) diamond is presented. The ALE process is achieved by first modifying the surface and then using a soft plasma to induce the selective removal of this modified surface. Experiments have been performed in a standard inductively coupled plasma reactive ion etching equipment with in-situ plasma monitoring by optical emission spectroscopy. They have been characterized as a function of the etching rate per cycle (EPC) estimated from diamond etched depth after 100 ALE cycles. The impact of the incident ionic bombardment kinetic energy during the 2nd ALE reaction has been evaluated from the dc self-bias voltage (V_{DC}). Results show a clear plateau of approximatively 5 V (Fig. 1), called ALE window, demonstrating the self-limiting effect of the etching process within one ALE cycle. The etching is of 6.7 Å per cycle, corresponding to the removal of two diamond (100) monolayers per cycle. Finally, synergy factor has been calculated. Synergy measures the effect of combining the two ALE steps. Separately, 100 cycles of step 1 then 100 cycles of step 2 leads to an etching rate of 3.8 Å per cycle. But 100 cycles of (1+2) steps lead to 6.7 Å per cycle, *i.e.* a synergy of 43%. This again demonstrate the effectiveness of the ALE process.

Reference

[1] M.N. Yoder, Atomic Layer Etching, US4756794A, 1988.

4:15pm **ALE2-TuA-12 Atomic Layer Etching of MgO-doped Lithium Niobate Using Sequential Plasma Exposures***, Austin Minnich,* ***Ivy Chen****, Jennifer Solgaard, Ryoto Sekine, Azmain Hossain, Anthony Ardizzi, David Catherall, Alireza Marandi,* Caltech*; James Renzas,* University of Nevada, Reno*; Frank Greer,* Jet Propulsion Laboratory (NASA/JPL)

Lithium niobate (LiNbO3, LN) is a ferroelectric crystal of interest for integrated photonics owing to its large second-order optical nonlinearity and the ability to impart periodic poling via an external electric field. However, on-chip device performance based on thin-film lithium niobate (TFLN) is presently limited by propagation losses arising from surface roughness and corrugations. Atomic layer etching (ALE) could potentially smooth these features and thereby increase photonic performance. Here, we report an isotropic ALE process for x-cut MgO-doped LN using sequential exposures of H2 and SF6/Ar plasmas. We observe an etch rate of 1.59 ± 0.02 nm/cycle with a synergy of 96.9%. The process is found to decrease the sidewall surface roughness of TFLN waveguides etched by physical Ar+ milling by 30% without additional wet processing. We also discuss alternate ALE chemistries using chlorine or bromine, as well as results for a directional etch. Our ALE process could be used to smooth sidewall surfaces of TFLN waveguides as a post-processing treatment, thereby increasing the performance of TFLN nanophotonic devices and enabling new integrated photonic device capabilities.

4:30pm **ALE2-TuA-13 Comparison of Gas-Pulsing Atomic Layer Etching (ALE) Characteristics Between Low-GWP Alternative Gases C_4F_6, $C_4H_2F_6$ and a Conventional Gas C_4F_8***, Shinjae You,* Department of Physics, Chungnam National University and Institute of Quantum Systems (IQS), Chungnam National University, Republic of Korea*;* ***Dongki Lee****, Inho Seong,* Department of Physics, Chungnam National University, Republic of Korea*; Young-seok Lee,* Tokyo Electron Korea Ltd., Republic of Korea*; Sijun Kim,* Laboratoire de Physique des Plasmas (LPP), CNRS, Sorbonne Université, École Polytechnique, Institut Polytechnique de Paris, Republic of Korea*; Chul_Hee Cho, Wonnyoung Jeong,* Department of Physics, Chungnam National University, Republic of Korea*; Ehsanul Haque Jami,* Department of Physics, Chungnam National University, Bangladesh*; Min-su Choi, Byeongyeop Choi, Seonghyun Seo, Isak Lee, Woobeen Lee, Won-gyun Park, Jinhyeok Jang,* Department of Physics, Chungnam National University, Republic of Korea

The conventional gases used in the semiconductor industry, such as C_4F_8, have a high Global Warming Potential (GWP), driving research efforts to find environmentally sustainable alternatives. Additionally, in 3D NAND structures, Self-Aligned Contact (SAC) etching is required, and Atomic Layer Etching (ALE) can be effectively utilized, particularly when uniformity and selectivity are critical. This study evaluates the performance of low-GWP alternative gases in ALE processes. In-situ ellipsometry was employed to monitor the self-limiting behavior of these processes in real time. Furthermore, diagnostic tools were used to analyze the key mechanisms that determine the etching characteristics of different materials. By measuring the gas species generated during the process and analyzing the surface composition after etching, this study aims to identify the key factors influencing the differences in the etch rates of SiO_2 and Si_3N_4 for each gas. Through this analysis, the impact of variations in chemical reactivity, Plasma-surface interaction, and byproduct formation on etch rates will be investigated.

4:45pm **ALE2-TuA-14 The Influence of Laminate Doping of Atomic Layer Etching of Zinc Oxide***,* ***Sabir Hussain****, Emily Duggan, Lynette Keeney, Jun Lin, Ian Povey,* Advanced Materials and Surfaces Group, Tyndall National Institute, University College Cork, Lee Maltings Complex, Dyke Parade, Ireland*; Mark Sowa, Laurent Lecordier,* Veeco Instruments

The challenging feat of both uniformly depositing and then conformally etching thin film materials can be overcome by the methods of both atomic layer deposition (ALD) and atomic layer etching (ALE) with Ångström-level control. This study examines the etching of ALD Zinc oxide (ZnO) and doped variants incorporating Hf and Al, (19:1 - Zn: metal ratio) at the full 200 mm wafer scale. Thin films were grown at 180 °C by using diethyl zinc and H_2O as precursors in a VEECO Fiji ALD system. All growth was performed on 200 mm silicon wafers with a 85 nm SiO_2 insulation layer to enable electrical characterization. The subsequent etching sequence was also performed in the same VEECO Fiji system, employing alternating acetylacetone (acac) and O_2 plasma pulses [1].

ZnO ALD produced polycrystalline Wurtzite material with a (100) preferred orientation. The growth rate was measured to be 1.86 Å per cycle, with a uniformity (after 500 cycles) of ~ 2% over a full 200 mm wafer. The measured resistivity (~8.5 X 10^{-3} Ω cm), mobility (~30 $cm^2 \cdot V^{-1} \cdot s^{-1}$) and carrier concentration (~2 x 10^{19} cm^3) are typical of ALD grown nominally undoped ZnO. The ALE of nominally undoped ZnO proceeds at a linear etch rate (~0.29 Å) for 400 cycles albeit at a lower etch rate as compared to Mameli et al. [1]. Etch uniformity is shown to be ~ 5 % across the full 200 mm wafer. The electrical properties were unchanged by the etching process beyond a small degradation of resistivity (8.5 x10^{-3} to 1.5 x 10^{-2} Ω cm) after 400 cycles.

The laminate doping of ZnO at a 19:1 ratio introduce complexity in doping process, Under the same etching conditions Al doped ZnO did not appear to etch even after 400 cycles, whereas the Hf doped ZnO appeared to undergo etching that terminated after an initial number of cycles due to the formation of an etch barrier or poisoned layer. Here we present physical (XRD, XPS, AFM, SKPFM) and electrical data to elucidate the mechanism of etch retardation

[1] A. Mameli, M. A. Verheijen, A. J. M. Mackus, W. M. M. Kessels, and F. Roozeboom. ACS Applied Materials & Interfaces 2018 10 (44), 38588-38595

5:00pm **ALE2-TuA-15 Ale of Tin Using Sf$_6$:H$_2$ Plasma: The Role of H, F, and Hf in Defining the Ale Window***, **Guillaume Krieger**, Silke Peeters, Erwin Kessels,* Eindhoven University of Technology, The Netherlands*; Harm Knoops,* Oxford Instruments Plasma Technology, UK, Eindhoven University of Technology, Netherlands

Recently, etching processes relying on in-situ HF formation in plasmas have proven to tackle several challenges in the semiconductor industry such as etching high aspect ratio (HAR), enabling atomic scale control, and achieving high selectivity.[1] The selectivity between a nitride and its oxide counterparts is an important research field in the development of HF-based atomic layer etching (ALE) processes, with a strong focus on the selective etching between SiN and SiO_2.[2] Beyond Si-based materials, good selectivity between metal oxides and metal nitrides is also of interest. SF_6:H_2 mixtures have been used to selectively etch the oxidized top-layer of TiN over the bulk of the film, enabling an ALE process of TiN by alternating the oxidation and plasma etch step.[3] This selectivity is suggested to be driven by the formation of HF in the plasma. However, the roles of the various plasma species in defining the SF_6:H_2 upper and lower boundaries of the ALE window remains unclear.

In our work, we experimentally confirm that the formation of HF is driving the aforementioned ALE processes. Additionally, we demonstrate that the presence of HF cannot, by itself, explain the ALE window as a function of the $SF_6/(SF_6 + H_2)$ gas ratio of the etch step. We have correlated this window with various species measured in the plasma including H and F atoms by optical emission spectroscopy (OES) and HF, H_2S, and SF_6 by quadrupole mass spectroscopy (QMS). These measurements demonstrate that the upper bound, in terms of the $SF_6/(SF_6 + H_2)$ ratio, is determined by the presence of F atoms in the plasma leading to spontaneous TiN etching. For establishing the lower bound, an ABC-type recipe with an H_2 plasma between the oxidation step and the SF_6:H_2 plasma has been used to highlight the role of the H radicals in the ALE process. The H_2 plasma quenches the etching of the SF_6:H_2 plasma, suggesting prominent role of H in reducing TiO_2 top-surface, which prevents the etching by HF. These results suggest a strong interplay between H, F, and HF in the selective etching mechanism. This understanding can act as a stepping stone to expand this ALE process to other conductive nitrides.

References:

1. Kihara, Y., et al., *IEEE Symposium on VLSI Technology and Circuits,* 1–2 (IEEE, Kyoto, Japan, 2023).
1. Hsiao, S. N. *et al., Vacuum* **210**, 111863 (2023).
1. Hossain, A. A. *et al., Journal of Vacuum Science & Technology A* **41**, 062601 (2023).

5:15pm **ALE2-TuA-16 Atomic Layer Etching of Ruthenium Using Surface Oxidation with O$_2$ Plasma and Chelation with Formic Acid***, **Hojin Kang**, Eunsu Lee, Minsung Jeon, Heeyeop Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Atomic layer etching (ALE) was developed via oxidizing the Ru surface with O_2 plasma, followed by removing the oxidized surface with a chelation reaction using formic acid (HCOOH). Surface oxidation reactions were performed up to 300 °C, and the RuO_2 layer after oxidation was identified using X-ray photoelectron spectroscopy (XPS). The Ru^{2+} oxidation state and Ru to O atomic ratio of 1:2 suggest that the oxidation layer formed is RuO_2. In the removal step, the RuO_2 layer is removed via a chelation reaction with HCOOH at process temperatures above 150 °C. The etch per cycle (EPC) of Ru is about 3 Å/cycle at a process temperature of 150 ~ 200 °C, and the EPC gradually decreases at temperatures above 200 °C, possibly due to the decomposition reaction of HCOOH. The EPC of Ru increases with increasing O_2 plasma exposure time without any saturation. The EPC of Ru was saturated at 3 Å/cycle with an HCOOH injection time of 100 sec. The surface roughness increases from 0.57 to 1.68 nm after ALE cycles, which can be attributed to etch rate differences according to facets. Ru has a hexagonal polycrystalline structure of (1,0,0), (0,0,-2), (1,0,1), (1,0,2), (1,1,0), (1,0,3), (1,1,2), and (2,0,1), which was confirmed by X-ray diffraction (XRD). No crystal structure changes after 100 cycles of ALE, and the maximum strength decreases by 97, 66, 74, 68, 89, 63, 52, and 75%, respectively. The surface oxide residue is less than 4% after ALE, which is similar to the pristine Ru. The Ru to SiO_2, HfO_2, and Si_3N_4 selectivity is infinity, and 56 for TiN and 77 for TaN.

Author Index

Bold page numbers indicate presenter