Atomic Layer Etching
Room Hall 3F - Session ALE1-TuM
ALE Applications and Methodologies

Moderators: Hannah Margavio, North Carolina State University, Prof. Dr. Fred Roozeboom, University of Twente and Carbyon B.V., The Netherlands

8:00am **ALE1-TuM-1 Current Status of ALE in Semiconductor Processes***, **Keun Hee Bai**,* Samsung Electronics Co., Republic of Korea **INVITED**

ALE process has been studied and used in the semiconductor processing for years.

There are a few benefits with the ALE, not only higher selectivity but also fine etch amount control or less loading.

In this presentation, we review the status of the ALE in the Fab for semiconductor manufacturing. What kinds of ALE and how much has it been adapted in the fab till now.

Considering the merits of the ALE, it has not been adapted widely. We will review the issues of the process in the line and what is necessary for more wide spread of the ALE.

8:30am **ALE1-TuM-3 ALE Preparation of Diamond Surfaces for Materials and Device Applications***, **Jeffrey Daulton**, M. Geis, M. Polking,* MIT Lincoln Laboratory

The expected high performance of ultrawide-bandgap semiconductors, resulting from the superior critical field, mobility, and thermal conductivity, has created substantial interest for their use electronics. Polishing of such substrates, however, has generally proven problematic, as the high bond energy that results in their wide bandgap also makes these materials relatively chemically-inert, limiting the effectiveness of CMP. Diamond, in particular, tends to form significant defects during the polishing process. As a consequence of the diamond sp^3 phase being metastable under standard conditions, these defects generally exhibit graphitic sp^2 bond character, making them readily etched in hydrogen plasmas. This results in even short exposures to hydrogen plasmas forming deep, crystallographically-etched pits in the polished surface. This has the effect of significantly limiting the quality of epitaxial growth on such surfaces, as diamond CVD growth inherently relies on initiation of the growth process with a hydrogen plasma. Such highlighting of defects also has negative implications for the mobility of diamond surface FETs, where the such a hydrogen plasma exposure is used to terminate the diamond surface and form a high-density 2-dimensional hole gas (2DHG) channel on the surface.

Smoothing by ALE has been demonstrated across a wide range of materials, suggesting the possibility for its use in pre-epitaxy surface preparation, provided near-surface plasma damage can be reduced sufficiently. Here, we use a Cl_2/Ar ALE cycle to prepare very smooth (Ra = 0.058 nm) diamond surfaces. Because of the tendency of damaged diamond to exhibit graphitic sp^2 bond hybridization, we use Raman spectroscopy, which is capable of differentiating between the diamond sp^3 peak and the graphitic sp^2 phase. This allows for observation of any reduction of near-surface damage with ICP etching or with ALE. Raman spectroscopy shows a clear reduction in sp^2 bonding with ALE from the ICP-etched surface, suggesting that this process removes the lattice damage induced by the ICP etching process. The remaining shallow, uniform sp^2 surface layer can then be easily removed during initiation of CVD growth to yield a high-quality growth interface.

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8:45am **ALE1-TuM-4 Comparison of Different PEALE Modes on AlGaN/GaN Heterostructures***, C. Miersch, **Sarah Seidel**,* Fraunhofer Institute for Integrated Systems and Device Technology IISB, Germany*; A. Schmid, J. Heitmann,* Department of Applied Physics, Technical University of Freiberg, Germany*; F. Beyer,* Fraunhofer Institute for Integrated Systems and Device Technology IISB, Germany

Nitrogen based group III-V compound semiconductors have become an integral part of consumer electronics and are essential for high-power and high-frequency applications. The Baliga's figure shows especially for GaN and AlN offer theoretically a high break down voltage (GaN: 5 MV/cm [1] and AlN: 15 MV/cm [2]) at low specific on-resistance [3,4]. Transistors based upon nitride semiconductors are high electron mobility transistors (HEMTs) and it can be realized by a heterojunction of an AlGaN barrier to a GaN buffer layer is forming two-dimensional electron gas (2DEG) [5,6], due to spontaneous and piezoelectric polarization. This normally-on transistors are desirable normally-off, which increases the safety for power-switching applications and suits to the established MOSFET circuit design. One way to shift the threshold voltage V_{th} in positive direction is to bring the gate contact closer to the channel by a precious and damage free recess etch of the AlGaN barrier (Fig. 1) [7]. This requires increasing demands on the manufacturing processes like dry etching to achieve smaller and high controllable etching rates, low damage, and minimized surface roughness. For this challenge atomic layer etching (ALE) is ideal. A conventional ALE approach on a AlGaN/GaN heterostructure could be described as followed. In the first step, the so-called modification step, the surface is modified by chlorine etching chemistry, producing a thin layer, ideally on an atomic scale, of volatile $GaCl_x$ and $AlCl_x$ products. In the second step, the so-called removal step, this thin layer can be easier removed then the unmodified surface below, by a physical impact of accelerated low energy Argon-ions. Typically purging in between the steps is applied, which increases the cycle time and affects the processing costs. An optimization of the cycle times and the implementation of other ALE methods can be beneficial.

For the experiments, a plasma enhanced ALE is used for etching. In this study, we develop an ALE recipe for the $Al_{25}Ga_{75}N$ barrier layer and optimized it in respect to the cycle times and the plasma damage. Furthermore, we compare different ALE methods: with purging in between the steps, purge-free [7], continuous plasma and a bias-pulsed [8] option. The evaluation of the developed processes will be performed by morphological and electrical characterization (gate recessed HEMTs). The induced damage will be investigated by structural and defect spectroscopical analysis.

9:00am **ALE1-TuM-5 Quasi-ALE Process for GaN: High Etching Rate Without Compromising the Surface Roughness***, P. Mouriño-Miñambres, R. Resta-López, F. Martin-Romero, **Miguel Sinusia Lozano**, V. Gómez,* Nanophotonics Technology Center - Universitat Politècnica de València, Spain

The atomic layer etching (ALE) process allows, theoretically, the selective atomic layer etching of the selected compound. In this work a Cl-based ALE process is developed to etch Ga-polar GaN (0001). Several parameters of the etching process are evaluated for assessing their influence on the ALE process namely, the ratio of the cycle devoted either to chlorination or Ar-sputtering and the applied RF power. The developed etching process, carried out at 5 mTorr, provides EPC values as high as 4 nm per cycle. Furthermore, because of the low-energy Ar plasma sputtering step, the etching process does not degrade the surface properties as reflected by the atomic force microscopy (AFM) and photoluminescence (PL) measurements without degrading the surface roughness [1]. Similar to other ALE processes reported in the literature, the smoothness of the surface is improved [2,3]. However, in comparison the EPC cycles in this work are larger-without any purge step within the cycle- thus reducing the time needed when the ALE process is applied during the nanofabrication process.

1. Choi, K.J.; Jang, H.W.; Lee, J.-L. Observation of Inductively Coupled-Plasma-Induced Damage on n-Type GaN Using Deep-Level Transient Spectroscopy. *Applied Physics Letters***2003**, *82*, 1233–1235, doi:10.1063/1.1557316.
1. Mannequin, C.; Vallée, C.; Akimoto, K.; Chevolleau, T.; Durand, C.; Dussarrat, C.; Teramoto, T.; Gheeraert, E.; Mariette, H. Comparative Study of Two Atomic Layer Etching Processes for GaN. *Journal of Vacuum Science & Technology A***2020**, *38*, 032602, doi:10.1116/1.5134130.
1. Ruel, S.; Pimenta-Barros, P.; Le Roux, F.; Chauvet, N.; Massardier, M.; Thoueille, P.; Tan, S.; Shin, D.; Gaucher, F.; Posseme, N. Atomic Layer Etching of GaN Using Cl2 and He or Ar Plasma. *Journal of Vacuum Science & Technology A***2021**, *39*, 022601, doi:10.1116/6.0000830.

9:15am **ALE1-TuM-6 A New Challenge for Developing Novel Atomic Layer Etching: Applying the Leidenfrost Effect to Obtain Floating Nanomist-Assisted Vapor Etching***, **Thi-Thuy-Nga Nguyen**,* Nagoya University, Japan*; Y. Yamaguchi, K. Shinoda,* Hitachi, Ltd., Japan*; K. Sun,* Nagoya University, Japan*; K. Maeda, K. Yokogawa, M. Izawa,* Hitachi High-Tech Corp., Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Selective etching of three-dimensional nanostructures in semiconductor devices requires a high-performance etching technology. In our previous study, we developed a wet-dry etching or wet-like plasma etching that combines the advantages of wet etching (high isotropy and selectivity) and dry etching (high controllability) [1]. By using a high-density vapor plasma (wet-like plasma) at medium pressure, high-density reactive radicals are generated, significantly increasing the chemical reaction rate to the sample surface. This paves a new path for our development of the new dry atomic layer etching methods, named wet-like atomic layer etching (ALE).

Here we have proposed a new wet-like ALE method, named floating nanomist-assisted vapor ALE at relatively low temperature, that is aiming to minimize the damage from sputter effect in plasma ALE, high temperature treatment in thermal ALE during volatilization, and nanostructure damage in wet ALE. The phase with intermediate properties between mist liquid phase and vapor phase, named mist-vapor phase or nanomist phase that can maintain the wet properties of liquid phase at the minimal size less than 100 nm is proposed here for nanodevice applications. At the Leidenfrost point, the nanomist floats on its own stable vapor cushion film over the whole sample surface [2]. By using the Leidenfrost effect, the sample surface can be modified and/or etched by the floating nanomist-assisted vapor, this is an optimal condition to obtain an ultra-thin liquid-like layer in the shortest time. In the first step of cyclic process, the nanomist A is introduced and approaches the sample surface to form the floating nanomist A. Under the floating nanomist A, a stable vapor film A exists and reacts with the sample surface to form a modified layer. In the second step, the modified layer is removed by dissolving it in the highly volatile nanomist B flow, resulting in a clean surface and a controllable cyclic process.

An example of trying to apply the Leidenfrost effect to obtain floating nanomist-assisted vapor etching is demonstrated here for TiAlC film by using the H_2O_2 based mixtures at medium pressure. The nanomists of these liquid mixtures were generated by an originally developed atomizer that was controlled at room temperature. The highest etch rate of TiAlC film was obtained at the temperature of 175 ^{o}C that is considered as the Leidenfrost point of the nanomist produced from the aqueous liquid mixture, in which the TiAlC surface is supposed to be etched by the floating nanomist-assisted vapor.

[1] T.T.N. Nguyen *et al*., Sci. Rep. **12**, 20394 (2022).

[2] B.S. Gottfried *et al.*, Int. J. Heat Mass Transf. **9**, 1167-1187 (1966).

9:30am **ALE1-TuM-7 Electron-Enhanced Etching of Molybdenum Using Sequential O_2 and HCl Reactive Background Gases to Form Volatile Molybdenum Oxychlorides***, **Michael Collings**, S. George,* University of Colorado, Boulder

Molybdenum (Mo) is important for future back-end interconnects resulting from its favorable resistivity scaling as metal lines continue to shrink. Precision etching techniques are needed to fabricate these interconnects and clean the metal contacts. In this study, Mo etching was achieved utilizing O_2 and HCl reactive background gases (RBGs) in conjunction with low energy primary electrons at ~100 eV to create volatile Mo oxychloride products. The electrons can dissociate O_2 and HCl to generate ions or radicals. The electrons can also desorb surface species by electron stimulated desorption (ESD). In addition, the primary electrons at ~100 eV can form secondary electrons at lower energies. The primary electrons were obtained from a hollow cathode plasma electron source (HC-PES). The HC-PES is a chemically robust electron source that can deliver currents >200 mA over an area >10 cm^2.

Electron-enhanced etching was demonstrated on Mo films using sequential O_2 and HCl RBGs. Oxygen was dissociated by the electron beam and oxidized the Mo surface to form MoO_x. The Mo oxidization was dependent on the voltage potential on the substrate. In situ spectroscopic ellipsometry (SE) measurements of the MoO_x film thickness showed that Mo oxidation with a +20 V stage voltage was >7X faster compared with oxidation using a 0 V or -20 V stage voltage (Figure 1). We believe that the positive stage voltage can activate a new process mechanism involving secondary electrons (Figure 2). The attachment of secondary electrons to O_2 produces O_2 dissociation. O_2 dissociation creates negative O^- ions that are then attracted to the positive stage voltage. This mechanism explains the greatly enhanced oxidation rates with positive stage voltage.

Subsequently, the HCl RBG was dissociated by the electron beam to form chlorine species. The reaction of chlorine species with the MoO_x surface produces volatile MoO_xCl_y compounds. In situ SE measurements of the MoO_x film thickness monitored the etching of MoO_x by HCl RBG (Figure 3). The MoO_x etching was also dependent on the stage voltage. Low etching rates were observed at stage voltages ≤ +20V.Greatly enhanced etch rates were observed at stage voltages ≥ +30V. This enhancement is also attributed to secondary electrons that create Cl^- from the HCl RBG after dissociative electron attachment. Secondary electron emission from samples followed by electron attachment to form negative ions provides a new class of reactive species for etching. Positive stage voltages can be used to pull the negative ions to the substrate to enhance the etch rates.

9:45am **ALE1-TuM-8 Impact of Activation Strategies for Sio_2 Atomic Layer Etching Applied to Contact Patterning***, **Antoine Ronco**, F. Boulard, S. Lecré,* Univ. Grenoble Alpes, CEA, Leti, France*; N. Possème,* ST Microelectronics, France

The etching of SiO_2 for contact etching is classically carried out using continuous reactive ion etching (RIE). However, the development of novel architectures for advanced devices and applications often uncover new problematics. This motivates the refinement of etching techniques and processes, in order to etch high aspect ratio (HAR) features while maintaining very high values of selectivity to the underlying layer [1]. For this reason, Atomic Layer Etching (ALE) is receiving attention as it promises to enable a higher control of the process than RIE. In the case of SiO_2, to maintain throughput and etch HAR patterns, the contact etching process is carried out in a Capacitively Coupled Plasma (CCP) reactor. In these conditions, reaching ideal ALE is challenging for two reasons: the non-self-limited nature of the modification step, and the difficulty of obtaining an ideal activation step [2]. This way, developing processes that are free from variability such as aspect ratio dependent etching (ARDE) or intra-wafer non-uniformity is needed.

This work presents developments of Quasi ALE processes of SiO_2 and focuses on different strategies for the optimization of the activation step in order to increase the robustness of these processes.

Blanket and patterned samples are studied. Blanket samples consists of SiO_2 on Si wafers. Patterned samples consists of SiO_2 on SiN on Si wafers. These experiments are performed in a 300 mm FLEX FL CCP reactor from Lam Research. The modification step is carried out with a C_4F_6 / Ar plasma using the high frequency power generator. The activation step consists of an Ar plasma using the high and low frequency generators. The reactor is cleaned using an O_2 plasma before and after etching each wafer. Etch rates of SiO_2 and SiN are determined by ellipsometry and cross-section SEM.

The sputtering threshold of SiO_2 in low-pressure Ar plasma is investigated depending on the RF power used on the low and high frequency power generators. Conditions of ideal ALE activation in CCP and the implications on throughput are reported.

To limit ARDE and etch stop, alternative activation strategies are investigated through the addition of O_2 to the Ar activation plasma. The impact on pattern shape and SiO_2:SiN selectivity at the bottom of the contact is studied.

Finally, the implementation of a three-step cycle, with a deposition, activation and cleaning step, is investigated. The use of the cleaning step during each cycle or punctually after a certain amount of cycles is discussed, along with the development of said cleaning step.

[1] T. Bédécarrats et al., IEEE (IEDM), (2021).

[2] K. J. Kanarik et al., JVSTA **33**, no 2, 020802, 2015

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