Atomic Layer Etching
Room Grand Ballroom A-C - Session ALE2-TuA

Low-Temperature and SiN ALE

Moderator: Dr. Kazunori Shinoda, Hitachi, Ltd.

4:00pm **ALE2-TuA-11 Atomic Layer Etching at Cryogenic Temperature***,* ***Thomas Tillocher****, G. Antoun, J. Nos,* GREMI CNRS/Orleans University, France*; C. Cardinaud, A. Girard,* IMN CNRS/Nantes University, France*; P. Lefaucheux, R. Dussart,* GREMI CNRS/Orleans University, France **INVITED**

Atomic Layer Etching (ALE) has been extensively studied for various materials these last years for microelectronic processes where high precision is required. Since cryogenic etching processes show interesting features, such as reduced reactor wall contamination, damage-free etching, enhanced surface residence time, ALE can benefit from cooling the substrate to cryogenic temperature (“Cryo-ALE”). Two approaches for Cryo-ALE have been developed and studied at GREMI for SiO_2, Si and Si_3N_4 and are presented in this paper.

Typically, ALE of SiO_2 is performed at room temperature and involves a C_4F_8 plasma in the modification step, which leads to some fluorocarbon deposition on the reactor walls, and eventually to process drifts. This can be addressed by flowing C_4F_8 in gas phase above the SiO_2 substrate cooled at cryogenic temperature. Under such conditions, species are physisorbed only at the cooled surface and therefore, wall pollution is suppressed. It is shown that repeating cycles of a C_4F_8 physisorption step followed by an Ar plasma with low energy ion bombardment, each separated by a purge step, makes it possible to sequentially etch SiO_2. Cryo-ALE of SiO_2 using C_4F_8 has proved successful results at -120°C and 3 Pa. However, no etching is observed at -110°C, since C_4F_8 does not significantly physisorb at such a temperature. In this paper, the role of the surface temperature on physisorption and the surface residence time is discussed by means of quasi in-situ XPS, mass spectrometry and in-situ ellipsometry.

In the second process presented in this paper, C_4F_8 physisorption is replaced by a SiF_4/O_2 plasma, with the substrate still cooled at low temperature. A SiO_xF_y layer is deposited at each cycle and acts as a fluorine reservoir used to etch the substrate when exposed to a low energy ion bombardment in an Ar plasma. It is shown that the process switches from a deposition regime at room temperature to an etching regime at low temperature. The threshold temperature, which is material dependent (-65°C for Si_3N_4 and -100°C for Si), is related to the deposition of a much thicker and more fluorinated SiO_xF_y layer. Therefore, there is a narrow temperature window in which it is possible to etch Si_3N_4 selectively to Si by ALE. This will be further discussed with in-situ ellipsometry measurements and quasi in-situ XPS analyses.

Acknowledgments: The authors thank K. Maekawa, K. Yamazaki, N. Sato, S. Tahara from TEL for financial support and helpful discussions. This work was also supported by CERTeM platform, which provides most of the equipment, and the CNRS-Réseau des Plasmas Froids for giving access to the Optimist platform.

4:30pm **ALE2-TuA-13 SiO_2 ALE based on High Boiling Point Fluorocarbon Physisorption***,* ***Dain Sung****, G. Yeom, H. Tak, D. Kim,* Sungkyunkwan University, Republic of Korea

SiO_2 atomic layer etching (ALE) using fluorocarbon plasmas as adsorption process is currently investigated to etch silicon dioxide for self-aligned contact (SAC) etch process of logic devices due to various benefits such as high etch selectivity over silicon nitride, low aspect ratio dependent etching (ARDE), low surface damage, controlled etching, etc.However, for conventional SiO_2 ALE utilizing fluorocarbon plasmas, a drift in etch process through cycles could be induced by chamber contamination caused by dissociated fluorocarbon radicals during the plasma generation. To avoid chamber contamination by fluorocarbon radicals, adsorption of fluorocarbon gases instead of generation of fluorocarbon plasmas by using cryo etching technique is also currently investigated, however, it requires extremely low substrate temperature facilities, etc. To overcome these challenges, ALE based on high boiling point PFC physisorption in low substrate temperature as the fluorocarbon adsorption is proposed as an alternative process. In this study, 100nm Si_3N_4 line masked SiO_2 was etched in an ICP etch system and high boiling point (HBP) PFC was used as a precursor during the physisorption step. When the substrate was cooled at 0°C and -10°C, HBP PFC molecules were adsorbed on SiO_2 and Si_3N_4 because it has boiling point higher than room temperature. After purging step, the etching step is achieved by using Ar plasma with a low energy ion bombardment. After the ALE process, ellipsometry and field emission scanning electron microscopy (FE-SEM) were used to analyze the etch properties such as etch rate, etch selectivity, and etch profiles of SiO_2. Compared to C_4F_8 plasma ALE, physisorption ALE using HBP PFC exhibited higher SiO_2 etch selectivity over Si_3N_4 in addition to no contamination of chamber walls.

4:45pm **ALE2-TuA-14 Cryogenically Cooled, Saturating Quasi-ALE of Silicon Nitride***,* ***Frank Greer****, D. Shanks, R. Ahmed, J. Femi-Oyetoro, A. Beyer,* Jet Propulsion Laboratory (NASA/JPL)

Silicon Nitride is one of the most important materials used in photonic integrated circuits. Anisotropic Plasma Atomic Layer Etching (ALE) is well known for its inherent advantages of uniform, precise, and smooth etching of materials. These features may make the technique attractive for waveguide etching to reduce sidewall losses. However, there are some important limitations of a truly atomic layer-by-atomic layer etching approach. Waveguides can be ~800nm thick, making sub-nanometer etch rates per cycle (EPC) substantially slower than conventional ICP and RIE etching processes. Although there are reported approaches that enable higher EPC, the process conditions cited are difficult to repeat in a standard ICP etching chamber due to the high process pressures utilized.[1] Additionally, some materials, like silicon nitride, do not have plasma chemistry that naturally divides into saturating reaction and desorption steps with high ALE synergy.[2]

In this work, we have leveraged cryogenic substrate temperatures to dramatically enhance the ALE synergy of silicon nitride etching for films from two different LPCVD silicon nitride deposition recipes. Our cyclic Cryo-ALE process utilizes a simple gas chemistry involving H2, SF6, and Ar where a biased hydrogen implantation dose step creates a chemically modified damage layer, that is removed by a gentle SF6/Ar ICP etch step. ALE synergy dramatically improves as substrate temperature is reduced because cryogenic temperatures largely quench the spontaneous etching caused by fluorine radicals. At 10C, ALE synergy is ~30%, but increases to as high at 70% at -50C. As expected, saturating behavior for EPC is improved in the SF6 step at low temperature. Additionally, cryo-temperatures are accompanied by smoother etched surfaces. As with the previous report for quasi-ALE of silicon nitride, our cryo-ALE process EPC can be controlled precising by tuning the bias voltage of the hydrogen implantation step. Surprisingly, however, despite the high degree of ALE synergy and the nearly identical silicon to nitrogen ratio of the two LPCVD films, the etch profile was very different, showing that the hydrogen content of the as-deposited film and/or the density also plays a role.

These results suggest that the combination of creating a chemically modified damage layer with cryogenic etching temperatures may be a general approach to simultaneously increase EPC and ALE synergy for fluorine-based etching of materials. Opportunities to generalize this approach and silicon nitride device data will also be discussed.

1 Sonam D. Sherpa *and* Alok Ranjan JVST A **35**, 01A102 (2017)

2 Akiko Hirata *et al* 2022 *Jpn. J. Appl. Phys.***61** 066002

5:00pm **ALE2-TuA-15 High Throughput SiN ALE and Its Damage Control***,* ***Akiko Hirata,*** Sony Semiconductor Solutions Corporation, Japan **INVITED**

The miniaturization of semiconductor devices has almost come to an end, but the combination of 3D devices / 3D structures, miniaturization, and new materials continues to meet market demands. Dry etching technology using plasma is one of the most important processes in achieving this performance improvement. In particular, processing technology at the atomic/molecular level is required to realize device shrinkage and dimensional control of several nm is indispensable for manufacturing cutting-edge devices. Atomic Layer Etching (ALE) can realize high-precision etching, however, has the issue of long processing time. In the conventional ALE (conv.-ALE), the low ion energy is used to realize the self-limited reaction at the atomic level. Self-limiting process means the extremely high-selective etching of a modified layer over the pristine substrate. One ALE cycle consisted of a surface modification step and a removal step of the modified layer. In the modification step, the binding energy in the surface reactive layer is weakened so that it is easier to remove than the bulk. ALE was performed by irradiating Ar ion for a long time.

In this study, we focused on SiN ALE [1]. We verified the feasibility of high-throughput ALE (HT-ALE). To reduce the time, we performed HT-ALE with high ion energy and evaluated the amount of etched SiN. SiN HT-ALE for short time with high ion energy exhibited a quasi-self-limited reaction, which is a characteristic of ALE, and the processing time could be reduced by 1/5th. To further analyze HT-ALE with varying energy in the desorption step, the energy required to remove the reaction layer was calculated. The amount of etching in the reaction layer was determined by the number of Ar ions, incident energy considering IEDF, energy loss in the polymer, and process time. Next, the interface trap density values after conv.-ALE and HT-ALE were performed for damage evaluation. However, HT-ALE using CH_3F in the adsorption step exhibited signs of increased damage due to ion injection with high energy. The HT-ALE has a deeper H penetration depth and a deeper Si damage layer than the conv.-ALE from the surface analysis. Thus, C_4F_8 that does not contain H can significantly reduce the damage, even in HT-ALE conditions. Damage is generated by the knock-on effect of H, which has a small atomic weight. H-less HT-ALE achieves both damage-less and high throughput. To alleviate the issue of long ALE processes, it is important to precisely control the ion energy/flux, process time, and damages.

[1]Hirata, A., Fukasawa, M., Kugimiya, K., Karahashi, K., Hamaguchi, S., Hagimoto, Y., and Iwamoto, H.,*Japanese Journal of Applied Physics* **61**, SI1003 (2022).

5:30pm **ALE2-TuA-17 The Atomic Layer Etching Database: A Valuable Crowd-Sourced Platform for the Community**, *N. Chittock, A. Mackus, H. Knoops, B. Macco,* ***Erwin Kessels,*** Eindhoven University of Technology, The Netherlands

In this contribution, we will introduce the ALE database (DOI:10.6100/aledatabase [https://www.atomiclimits.com/aledatabase/]) which is free of charge available on the AtomicLimit.com blog site. It was established after launching the ALD database (DOI: 0.6100/alddatabase [https://www.atomiclimits.com/alddatabase/]) in 2019. The latter has become very popular in academia and in industry and it has appeared in many presentations and publications in recent years. It has also been used as a starting point in review papers, for example by applying data analytics. We hope that a similar thing will happen to the ALE database in order to serve the ALE community.

The ALE database displays all ALE process reported in the literature in the format of the periodic table. It distinguishes between anisotropic ALE processes and isotropic ALE processes. By clicking on an element in the periodic table, a list of materials containing that element is displayed as etched by an ALE process. The etchants species are listed per ALE process and there is also a direct link to the publications in the literature. The ALE database been compiled from the data in the literature and new processes can be added by visitors of the website. This means that it stays up to date by crowd-sourcing. Authors of ALE papers are stimulated to add their ALE processes to the database.

In the presentation, the features of the ALE database will be highlighted and also some scientific trends will be discussed as can be inferred from the data in the ALE database. Also the possibilities for data mining will be addressed and potential future extensions (relying on contributions from the community) will be discussed. The intention is to make the ALE database an even more valuable platform for the ALE community.

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