Atomic Layer Etching
Room Baekeland - Session ALE1-TuM

ALE Selectivity and Anisotropy

Moderators: Ankur Agarwal, KLA-Tencor, Sumit Agarwal, Colorado School of Mines

9:00am **ALE1-TuM-3 Highly Selective Atomic Layer Etching for Semiconductor Application***, **Akiko Hirata**,* Sony Semiconductor Solutions Corp., Japan **INVITED**

The self-limiting process is one of the most important features of atomic layer etching (ALE). The self-limiting process refers to the highly selective etching of a modified layer over a pristine substrate. One ALE cycle consists 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 reduced so that it is easier to remove than the bulk. For the generation of a reactive layer, chemical adsorption and chemical/physical modification are generally employed. In this study, we investigate tin-doped indium oxide (ITO) and SiN ALE, and their mechanisms, to achieve the high selectivity.

ITO is a difficult-to-etch material, since the boiling points of indium halides are very high (>700 °C). Surface modification through chemical adsorption of reactive species is difficult. Thus, surface modification by energetic hydrogen ions followed by Ar desorption was proposed. The ITO was reduced by hydrogen injection, and generated an In-rich layer on the surface. The In-rich layer of ITO could be selectively etched by controlling the incident ion energy. Thus, the self-limited etching of ITO was demonstrated.

The etch rate selectivity of ITO over a mask material is indispensable for device fabrication. We intentionally controlled the amount/incubation time of Si generated from the upper electrode, and demonstrated the highly selective cyclic etching of ITO/SiO_2. The cyclic etching by area-selective surface adsorption of Si could precisely control the etch rates of ITO and SiO_2, which resulted in an almost infinite selectivity for ITO over SiO_2.

In the case of SiN ALE, the chemical adsorption of a reactive species (CH_xF_y polymer) was employed to obtain high selectivity with SiO_2 and Si. However, the SiN ALE was easily etch-stopped, owing to the excess adsorption of polymer during cyclic etching. Thus, a sequential 3-step ALE (adsorption, desorption, and O_2 ash) was proposed. After this 3-step ALE, the SiN surface was oxidized, which resulted in a fluctuation of the etched amount. To overcome these issues, plasma-enhanced conversion ALE was proposed. First, 3-step ALE was performed for SiN ALE, and the surface SiO_2 (converted from SiN by oxidation) was generated. Subsequently, highly selective SiO_2 ALE over SiN was performed. By combining highly selective SiN and SiO_2 ALE, a stable ALE process was realized.

When we use the differences in precursor incubation time among different materials effectively, highly selective etching is expected. Thus, a database of the surface adsorption of many kinds of precursors is strongly required for future highly selective ALE processes.

9:30am **ALE1-TuM-5 Aspect-Ratio Dependence of Isotropic Thermal ALE and Mitigation Thereof***, **Andreas Fischer**, A Routzahn, T Lill,* Lam Research Corp.

Advanced memory chip manufacturing is increasingly pushing the boundary toward high aspect ratio (HAR) designs in which many layers of memory cross points are stacked on top of each other. Especially in 3D-NAND memory structures, the ability to perform isotropic etches to recess high-k oxides made of hafnia or alumina or to remove excess material beneath shaded overhangs will be a critical addition to the established suite of etch and deposition processes in chip design.

In this work, we have focused on the dependence of isotropic atomic layer etching on the aspect ratio of the structures that are being etched. Utilizing the well characterized vapor-based DMAC ligand exchange mechanism, we have investigated the dependence of lateral etch rate of this process as a function of depth in nanometer-size holes of hafnium oxide. Inside these holes, we measured the horizontal etch rates and found that it slowed to a rate of 85% at the bottom of 50:1 aspect ratio holes compared to the rate at the very top of the structures for our standard ALE process.

To overcome this issue, we established that this aspect ratio dependence could be significantly suppressed by operating the process closer to saturation in the modification as well as removal step by expanding the process step time for each of the steps.

In additional experiments we found that the use of low level, zero-bias plasma can boost the etch rate in deep structures thereby reducing the aspect ratio dependence further.

We propose a simple mechanism for explaining the dependence on step time and use of plasma.

9:45am **ALE1-TuM-6 Precise Ion Energy Control with Tailored Waveform Biasing for Atomic Layer Etching***, **Tahsin Faraz**, Y Verstappen, M Verheijen,* Eindhoven University of Technology, Netherlands*; J Lopez, E Heijdra, W van Gennip,* Prodrive Technologies B.V., Netherlands*; E Kessels, A Mackus,* Eindhoven University of Technology, Netherlands

Anisotropic plasma ALE utilizes energetic and directional ions to remove any given material in a selective and self-limiting fashion.[1] However, high selectivity and etch control requires well-defined ion energies lying below the sputter etch threshold of the material, which serves as the upper limit of the so-called ion energy window of an anisotropic plasma ALE process.[2,3] In this contribution, we report on precise ion energy control – independent of the ion flux – using low-frequency (100 kHz) tailored bias voltage waveforms applied to a substrate in a commercial remote plasma reactor. Ion energies in such reactors are typically controlled by applying a radio-frequency (RF: 13.56 MHz) sinusoidal bias voltage waveform to the substrate undergoing plasma exposure. However, this yields ions with a broad energy distribution that leads to non-selective and continuous etching. Furthermore, the use of high frequency RF bias voltages entails electron heating mechanisms that do not allow for controlling the ion energy independent of the ion flux.[4] Precise ion energy control by applying a tailored bias voltage waveform[5,6] to a substrate undergoing plasma exposure is currently not employed in the field of ALE.

In this work, a prototype low-frequency bias voltage generator has been used to apply tailored bias waveforms consisting of a voltage pulse and a ramp. Such waveforms yielded ions having narrow energy distributions for energies upto 200 eV (measured using a retarding field energy analyzer, RFEA) in collisionless Ar plasmas. The energetic ions were used to sputter etch thin films of different materials (e.g. Si, SiO_2). Such investigations provide reliable experimental data on sputter etch thresholds of different materials that are typically determined by extrapolation of sputter yields measured at ion energies >> 100 eV to the low energy range,[7] which does not give accurate values. These thresholds serve as essential input (i.e. upper limits of ion energy windows) for designing novel anisotropic plasma ALE chemistries. To demonstrate the feasibility of this technique in performing anisotropic plasma ALE, a conformal SiO_2 layer on a 3D trench nanostructure was etched using directional ions whose energies were enhanced to 100 eV with tailored waveform biasing.

[1] Faraz et al., *ECS J. Solid State Sci. Technol*. 4, N5023 (2015)

[2] Kanarik et al., *J. Phys. Chem. Lett.* 9, 4814 (2018)

[3] Berry et al., *J. Vac. Sci. Technol. A* 36, 01B105 (2018)

[4] Sobolewski et al., *J. Appl. Phys.* 102, (2007)

[5] S.-B. Wang and A.E. Wendt, *J. Appl. Phys.* 88, 643 (2000)

[6] Kudlacek et al., *J. Appl. Phys.* 106, (2009)

[7] *Sputtering by particle bombardment* (Behrisch & Eckstein), Springer 2007

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