Atomic Layer Etching
Room Samda Hall - Session ALE1-TuM
Thermal Gas Phase ALE

Moderators: Steven M. George, University of Colorado at Boulder, **Chanmin Lee**, Samsung Electronics

8:00am **ALE1-TuM-1 Thermal Atomic Layer Etching in Next Generation 3D Devices*, Younghee Lee,*** Lam Research Corporation **INVITED**

Thermal atomic layer etching (ALE) enables precise material removal with atomic-level precision through sequential, self-limiting surface reactions. This study explores the use of ALE and atomic layer deposition (ALD) in 3D devices, focusing on applications in full release, partial recess, and etch-back processes. Key challenges such as selectivity, surface roughness, and potential damage or contamination are addressed with new chemistries, processes, and hardware. We discuss the mechanisms behind selectivity, efforts to control roughness, and methods to minimize damage and contamination using non-metal reactants and novel chemistries.

8:30am **ALE1-TuM-3 Isotropic Atomic Layer Etching of HfO_{-2} using Plasma Fluorination with NF_3 and Ligand Exchange with BCl_3*, Hyeongwu Lee,*** *Heeju Ha, Daeun Hong, Heeyeop Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Isotropic atomic layer etching (ALE) for HfO_2 was developed with plasma fluorination using NF_3 plasma followed by ligand-exchange using BCl_3.Hf-O-F bond was observed by X-ray photoelectron spectroscopy (XPS) after the plasma fluorination. The fluorinated layer of HfO_2 was selectively removed by ligand-exchange using BCl_3 without affecting the underlying HfO_2 layer. No etching was observed below 80°C, and 0.3 ~ 3.5 Å/cycle of etch per cycle (EPC) was observed in the range of 100 ~ 220°C. Self-limiting characteristic was confirmed after BCl_3 dose time of 15 seconds at a fixed fluorination time at the temperature of 200 °C. The surface roughness of amorphous HfO_2 film slightly decreased from 0.372 to 0.322 nm, but the surface roughness of crystalline HfO_2 film was increased from 0.375 to 0.675 nm after the 30 ALE cycles. The monoclinic phase of crystalline HfO_2 film was confirmed by X-ray diffraction (XRD), and the different facets have different etch rates after the ALE process.The maximum intensity of (-111), (111), (020), and (200) facets decreased by 58 %, 36 %, 37 %, and 25 %, respectively, after 30 ALE cycles, and this result attributed a rougher crystalline HfO_2 surface afterthe ALE. The similar EPC was confirmed in amorphous HfO_2 film on Si-trench patterns having aspect ratio of 6.8 by scanning electron microscope (SEM) analysis after the ALE process.

8:45am **ALE1-TuM-4 Thermal Atomic Layer Etching of Mo with $NbCl_5$ and O_2*, Juha Ojala*,** *Mykhailo Chundak, Anton Vihervaara, Marko Vehkamäki, Mikko Ritala,* University of Helsinki, Finland

With the constant demand to decrease component sizes in integrated circuits, the lowest level metal interconnects are approaching the performance limits of copper as a conductor. Molybdenum has been considered as an alternative material due to its lower resistivity at the nano scale and its potential for barrierless interconnects. In manufacturing future interconnects, highly controlled and selective etching processes such as atomic layer etching (ALE) will be beneficial, especially as 3D integration becomes more common. ALE can be used to pattern metal thin films, fine tune interconnect dimensions, and as a corrective step in area-selective deposition.

We present a new thermal ALE process for etching of Mo, where the surface of Mo is oxidized with O_2 and the resulting oxide etched with $NbCl_5$. The ALE process was studied using XRR thickness measurements and *in vacuo* XPS studies. The films were characterized before and after etching using XRD, EDS, SEM, AFM, and four-point probe.

Etching temperatures of 225–400 °C were studied and etching was seen at temperatures as low as 250 °C. Maximum etch per cycle (EPC) of around 5 Å was seen at 400 °C. Saturation with O_2 pulses is slow, but the increase of EPC slows down with longer pulses, indicating diffusion limited oxidation. The saturation of $NbCl_5$ is faster, taking only 2 s at 300 °C. *In vacuo* XPS studies revealed that $NbCl_5$ etches Mo^{6+} very quickly. The lower oxidation states of molybdenum are not completely etched at 300 °C, but the intensity of the peaks diminishes significantly. Oxidation of the surface to Mo^{6+} is also slow with O_2, which in part explains the slow saturation.

Effect of the etching on film properties is minimal. The crystal structure of the film is unchanged after partial etching, and no increase in resistivity was observed that could not be attributed to the decreasing film thickness. AFM and XRR showed that during etching the roughness of the film R_q increases slightly from around 3 nm to at most 4 nm. This is accompanied by the grain structure becoming clearer in AFM and SEM. XPS showed that after partial etching small amounts of Nb and Cl are left on the surface, but these are below the detection limit of EDS. After complete etching of the film no Mo, Nb, or Cl could be detected on the substrate with XPS.

9:00am **ALE1-TuM-5 Film and Surface Stress During Thermal Atomic Layer Etching of Al_2O_3 and Tungsten*, Ryan B. Vanfleet,*** *Steven M. George,* University of Colorado at Boulder

Film and surface stress were measured during thermal atomic layer etching (ALE) using in situ wafer curvature techniques in a custom reactor. Aluminum oxide (Al_2O_3) thermal ALE using hydrogen fluoride (HF) and trimethylaluminum (TMA) as the reactants was employed as a model system. Al_2O_3 ALE was explored at different temperatures ranging from 225 to 285°C using initial Al_2O_3 ALD films. The initial Al_2O_3 ALD film was under tensile stress of 400 MPa. Therefore, Al_2O_3 ALE led to an apparent compressive film stress resulting from the removal of the Al_2O_3 ALD film. Additionally, the initial fluorination of the Al_2O_3 surface resulted in a pronounced compressive stress.

The surface stress from the individual TMA and HF surface reactions was also measured by the high sensitivity wafer curvature measurements. The TMA exposure resulted in a compressive surface stress of -0.5 N/m. This compressive stress can be attributed to repulsion between the methyl species left on surface after the TMA ligand-exchange reaction. The HF fluorination reaction then removed the surface methyl species and released the compressive stress. The surface stress changes resulting from the TMA and HF reactions were large compared with the apparent compressive stress resulting from one Al_2O_3 ALE cycle during the removal of the Al_2O_3 ALD film.

Thermal tungsten (W) ALE using O_3/O_2 and tungsten hexafluoride (WF_6) as the reactants was explored at 285°C by additional in situ measurements. The initial W ALD film was under tensile stress of 1000 MPa. Consequently, W ALE led to an apparent compressive film stress resulting from the removal of the W ALD film. The surface stress was also measured resulting from the individual O_3/O_2 and WF_6 surface reactions. The O_3/O_2 exposure resulted in a compressive surface stress of -6.0 N/m. This compressive stress can be attributed to volume expansion resulting from W oxidation. The WF_6 exposure then released the compressive stress. These in situ wafer curvature measurements of film and surface stress during Al_2O_3 ALE and W ALE are providing new insight into the details of thermal ALE.

9:15am **ALE1-TuM-6 The Invention of Atomic Layer Etching: on the Conception of Cycled Exposures of Silicon to Halogens and Pulses of Heat, Ions, and More, by Seiichi Iwamatsu*, Fred Roozeboom,*** University of Twente, Netherlands*; Dmitry Suyatin, Jonas Sundqvist,* AlixLabs A.B., Sweden*; Kuniyuki Kakushima,* Tokyo Institute of Technology, Japan

While the history of Atomic Layer Deposition (ALD) has been reported in excellent reports on the VPHA-project (www.vph-ald.com/) initiated in 2013 by Puurunen (1), and in articles by Malygin(2) and Parsons *et al*. (3), the "reverse" process, Atomic Layer Etching has lagged behind. For long (4,5) the first patent published on ALE was thought to have been initiated by Max Yoder (6), who in 1987 conceived the idea on etching diamond by "flooding" its surface with intermittent pulses of NO_2 and noble gas ions mixed with H_2 gas. This date of conception still holds for plasma-assisted ALE of diamond. However, from extensive AI-assisted patent searches we found that thermal ALE of silicon was conceived by **Seiichi Iwamatsu** (Fig. 1) of Seiko Epson, Japan. In 1981 he filed an application on Si-etching by repeated exposure to iodine (I_2) vapor at moderate temperatures (20-100 °C), followed by a light or heat pulse up to ~300 °C (7); see Fig. 2. Several other patents on ALE in his name followed (8). One of them disclosed plasma-assisted quasi-ALE, named "digital etching" (9) via Si-surface modification by “lamination” with a single Cl-atomic layer from exposure to Cl_2 gas, followed by a removal step carried out by Ar^+-ion bombardment to etch off "one atomic layer or at most three atomic layers by controlling the kinetic energy". Soon after, other researchers in Japan published on the digital etching of GaAs, with similar two-step physico-chemistry recipes(10). Today, ALE has come to maturity, fueled by early-leading groups, who worked on thermal and plasma ALE of metals, metal oxides, metal nitrides, semiconductors, and their oxides; see the reviews in refs. (11,12).

This presentation will highlight the groundbreaking work and background of the Japanese inventor Seiichi Iwamatsu. Born in 1939 in Kyoto to a family of physicians, he grew up and studied in Osaka, after which he spent many years as a "master inventor" (over 1200 patents filed in his name) for Seiko Epson (~1970-1990) and others afterwards. He played key innovative roles in thin-film technology and e-beam lithography, and contributed also this way to the success story of Seiko's quartz watch (13), a masterpiece in micromachining and heterogeneous integration with electronics. We conclude that Dr. Iwamatsu, now 86 years old, can be recognized as the original inventor of Atomic Layer Etching of silicon.

Acknowledgement

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