Monday Morning, June 27, 2022

Atomic Layer Etching
Room Baekeland - Session ALE-MoM2
Thermal and/or Isotropic ALE I

Moderators: Steven M. George, University of Colorado at Boulder, Anil Mane, Argonne National Laboratory

10:45am **ALE-MoM2-1 Photon-Activated Metal Ale***, X. Yang, B. Coffey,* ***John Ekerdt,*** University of Texas at Austin **INVITED**

Long nucleation delays during area selective ALD of metals can lead to unwanted growth outside the patterned regions.Unwanted nucleation also results when a passivating film begins to breakdown.In the event non-selective nucleation occurs on passivated regions, we describe a low temperature ALE route to etch clusters/islands on the passivated regions faster than the desired film.This low temperature route exploits the general finding by others that metal oxides can be etched by a variety of vapor phase etchants – the issue is controlled oxidation while minimizing damage to adjacent surfaces.We present a low temperature route that involves vacuum ultraviolet (VUV) activation of O_2 to produce atomic oxygen and ozone, with atomic oxygen being the dominant species that oxidizes the near surface region of Pd and Ru.Oxidation extents differ between continuous films and discontinuous films enabling the removal of metal islands without significantly etching the film.Pd and Ru can be etched at temperatures ranging from 50 °C – 200 °C by co-exposing the zero-valent metal to 1 Torr of O_2 and VUV photons (6.5 < hv < 11.3 eV) from a D_2 lamp.Density functional theory and nudged elastic bandcalculations are used to understand the diffusion of oxygen into the metal and the kinetic barriers that limit oxidation to the first and second layers.Metal oxidation proceeds because the flux of atomic oxygen is sufficient to compensate for competing recombinative desorption of molecular oxygen.The oxides of Pd and Ru are etched in an ALE half cycle with 0.50 Torr HCOOH vapor exposure for 30 sec.Metal islands/nuclei are completely oxidized in an exposure cycle while oxidation of a film is limited to approximately one atomic layer.

Photon activation of O_2 in the gas phase above the surface to atomic oxygen leads to an inherently isotropic process since the atomic oxygen can diffuse to any exposed surface before the atomic oxygen is lost through gas-phase loss reactions.This talk will also discuss the use of halogenated hydrocarbons that can possibly adsorb at the process temperature and be activated in the adsorbed state to restrict metal oxidation to those surfaces exposed to the photons.

11:15am **ALE-MoM2-3 Plasma-Assisted Thermal-Cyclic Etching of Silicon Germanium Selective to Germanium***,* ***Kazunori Shinoda,*** Hitachi , Japan*; H. Hamamura,* Hitachi, Japan*; K. Maeda, M. Izawa,* Hitachi High-Tech, Japan*; T. Nguyen, K. Ishikawa, M. Hori,* Nagoya University, Japan

Silicon germanium (SiGe) and germanium (Ge) may play an important role in future generations of semiconductor devices. For example, one candidate of future logic devices will be a Ge-channel gate-all-around field-effect transistor (GAA FET), which may require lateral selective etching of the SiGe sacrifice layer with respect to the Ge-channel layer. Isotropic, self-limiting cyclic etching of SiGe selective to Ge will thus be attractive in developing future generations of logic devices. This paper addresses plasma-assisted, thermal-cyclic etching of SiGe, which is selective to Ge. Experiments were conducted with several SiGe and Ge samples with different Ge content. Radical-exposed surfaces of the samples were produced in plasmas excided with hydrofluorocarbon-based gas mixtures that contain nitrogen. Nitrogen was added to the gas mixture because it is essential for forming ammonium-salt-based modified surfaces. Photoelectron-emission measurements were conducted after transferring the samples in vacuum into an x-ray photoelectron spectroscopy (XPS) system under ultra-high vacuum. The XPS spectra obtained after radical exposure consisted of a nitrogen 1s peak at 402 eV, which was likely ascribed to the N-H bond. One explanation of this observation is that a modified surface that consists of ammonium salt formed on the surface of the samples after radical exposure. The intensity of the N-H peak decreased as the Ge composition in the samples increased. The nitrogen 1s peak at 402 eV disappeared when the samples were heated at 100°C. This suggests that the ammonium-salt-based modified surface decomposes and desorbs from the film during heating. We conducted cyclic etching of SiGe and Ge samples with an etching tool developed for 300-mm wafers. Radical exposure and infrared heating were repeated multiple times with this tool. The etching depths of the samples were evaluated using in-situ ellipsometry. The thickness of the SiGe decreased as the number of cycles increased. The etched amount of SiGe in one cycle ranged from 3 to 7 nm. The etched amount of the Ge in one cycle was smaller than that of the SiGe. A maximum SiGe selectivity of 5 was obtained with respect to Ge at optimum stage temperature during radical-exposure steps. The selectivity was due to the selective formation of the ammonium-salt-based modified surface on SiGe compared with that on Ge. The etched amount for one cycle of SiGe and Ge exhibited saturation behavior as the radical-exposure time increased. Self-limiting thermal-cyclic etching of SiGe selective to Ge was thus successfully demonstrated.

11:30am **ALE-MoM2-4 Thermal Atomic Layer Etching of Cobalt with Chlorine Plasma and Hexafluoroacetylacetone (Hhfac)***,* ***Yongjae Kim****, H. Ha, H. Chae,* Sungkyunkwan University (SKKU), Korea (Republic of)

Copper is widely adopted for interconnect lines in semiconductor devices, but the resistance increases of copper is rapidly increasing due to surface scattering of electrons. [1] Cobalt is considered as an alternative metal because cobalt does not require a barrier/liner and has less resistance than copper below 10nm in dimension. [2] Chemical-mechanical polishing (CMP) processes are used for planarization in interconnect, but they leave interlayer dielectric (ILD) defects due to slurry particles and mechanical forces. Atomic layer etching (ALE) process can be an alternative to reducing the defects in cobalt removal. In this work, ALE process was performed for cobalt in an inductively coupled plasma (ICP) reactor. The ALE process consists of two steps: surface modification with chlorine plasma and ligand volatilization with hexafluoroacetylacetone (Hhfac). In the first step, the surface of cobalt is chlorinated to $CoCl_2$ using chlorine plasma. In the second step, the $CoCl_2$ layer was removed by ligand volatilization with Hhfac. Cobalt ALE process was conducted with changing process temperature at 100~250 degree, and the ALE window was confirmed. Etch rate of cobalt was self-limited at the Hhfac injection time of 90 second. The thickness of the cobalt film before and after the ALE process was confirmed by cross-sectional SEM imaging. The etch rate of cobalt could be controlled below 1 nm/cycle. Surface roughness was compared according to process temperature and chlorine plasma power.

References

[1] D. Bobb-Semple, K. L. Nardi, N. Draeger, D. M. Hausmann, and S. F. Bent, Chem. Mater 31, 1635 (2019)

[2] N. Bekiaris, Z. Wu, H. Ren, M. Naik, J. H. Park, M. Lee, T. H. Ha, W. Hou, J. R. Bakke, M. Gage, Y. Wang, and J. Tang, In 2017 IEEE International Interconnect Technology Conference (IITC), IEEE, 1 (2017)

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11:45am **ALE-MoM2-5 Thermal-Cyclic Atomic Layer Etching of Cobalt by Plasma Oxidation and Organometallization***,* ***Sumiko Fujisaki,*** Hitachi Ltd,. R&D group, Japan*; Y. Yamaguchi,* Hitachi, Ltd., R&D group, Japan*; H. Kobayashi,* Hitachi High-Tech, Japan*; K. Shinoda, M. Yamada, H. Hamamura,* Hitachi, Ltd., R&D group, Japan*; K. Kawamura, M. Izawa,* Hitachi High-Tech, Japan **INVITED**

The technology node has been scaled down to below 10 nm, and gate-all-around (GAA) FET and C-FET are expected to be utilized in logic devices in the near future.

Isotropic atomic-layer etching (ALE), which can perform atomically precise removal, plays an important role in semiconductor manufacturing under these circumstances. Highly selective ALE is required to process new materials for miniatulized 3D devices. Over the past several years, isotropic ALE of various materials has been reported, including thermal ALE for metal oxides and thermal-cyclic ALE for nitride films [1]. To meet the requirements concerning the variety of materials to be etched, isotropic ALE of cobalt must be developed—for example, for advanced interconnect metallization. Thermal ALE of cobalt by using formic acid and ligands has been reported [2]. Also, the authors have successfully demonstrated isotropic ALE of cobalt film with smoothly etched surfaces by introducing a two-temperature process [3].

The experimental apparatus used in this study is a 300-mm ALE tool equipped with an inductively coupled plasma source and infrared (IR) lamps. One cycle of the thermal-cyclic ALE process is divided into two major steps: oxidation and organometallization. In the first step, the surface of cobalt film is oxidized by oxygen plasma at low temperature, and in the second step, it is converted into an organo-cobalt complex by diketone at high temperature. The organo-cobalt complex then desorbs from the film surface due to its higher volatility. This two-temperature

process is crutial because it enables well-controlled etching that leads to a smoothly etched surface. Our ALE tool exhibits a short processing time thanks to its IR lamps for rapid heating. It is desirable that the cobalt oxide formed in the first step be completely removed in the second step (i.e., within one cycle), so the etched amount is controlled by the oxidation thickness of cobalt and the number of cyclic repetitions.

The mechanism of the cobalt ALE reaction was examined by x-ray photoelectron spectroscopy (XPS). Several oxygen 1s peaks were detected in the range of 525 to 535 eV after plasma oxidation at various temperatures. A peak at 530 eV, which preferentially decreased after being exposed to diketone, is the dominant oxidation state for organometallization, and is presumably ascribed to divalent cobalt oxide. It also implies that some other oxidation states of cobalt are removed after converting to the oxide with a 530-eV oxygen 1s XPS peak.

[1] K. Shinoda et al., J. Phys. D: Appl. Phys. **50**, 194001 (2017).

[2] C. Winter, AVS 65th, PS+EM+TF-ThM5 (2018).

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