Atomic Layer Etching
Room On Demand - Session ALE2
Gas-phase and/or Thermal ALE

ALE2-1 Anomalous Etch Behavior of NHC-Containing Gold Precursor, ***Eden Goodwin,*** Carleton University, Canada*; M. Griffiths,* Wayne State University, Canada*; A. Kadri,* McMaster University, Canada*; S. Barry,* Carleton University, Canada

N-Heterocyclic carbenes (NHCs) have been shown to reconstruct gold surfaces by dislocation and displacement of individual atoms on the surface (Amirjalayer, Bakker, Freitag, Glorius, & Fuchs, 2020). When NHCs are used as ligands for gold precursors, the role of NHC could be two-fold; they saturate surface sites and promote self limiting growth like phosphines (Van Daele et al., 2020) or they could abstract gold atoms and reorganize or etch the film.

In this work we analyze the surface behaviour of a newly reported NHC-containing gold precursor – 1,3-diisopropylimidazol-2-ylidene)methylgold(I) – on a gold coated quartz crystal microbalance (QCM). For a 100-cycle pulse sequence (60s pulse, 20s N_2 purge). In situ QCM data demonstrates frequency growth that begins at a rate of 19.6Hz/cycle, gradually decreases to 2.0Hz/cycle, and has an overall rate of 3.9 Hz/cycle (Figure 1). This figure demonstrates the stepwise etch, where the frequency increases during the precursor pulse and plateaus during the purge. Based on the QCM crystals intrinsic mass to frequency ratio of 17.7ng/cm$^{-2}\cdot$Hz, we observe an initial etch rate of 8.9 Au atoms/nm$^{2}\cdot$cycle, a final rate of 1.1 Au atoms/nm$^{2}\cdot$cycle, and an overall rate of 2.1 Au atoms/nm$^{2}\cdot$cycle (compared to 13 atoms/nm^2 in a gold closest packed layer).

Etched QCM crystals were analyzed by atomic force microscopy (AFM) and compared against a standard. The QCM standard had a root mean square roughness of 1.42 nm, while an etched crystal had an enhanced roughness of 2.04 nm. The presence of NHCs on the surface was confirmed by energy dispersive X-Ray analysis (EDX). Changes in surface morphology were also apparent by scanning electron microscopy.

The magnitude of mass loss and its dependence on the presence of the NHC-containing gold precursor, combined with the increased roughness of the surface suggests that surface NHCs induce gold mobility leading to surface reorganization and mass loss of newly-formed gold-containing species. The precursor-surface interaction will be discussed, and in situ mass spectrometry will be shown to support potential surface mechanisms of this precursor.

ALE2-2 Thermal Cyclic Etching of Non-Volatile Material by Self-Stabilizing Organometallic Complex Formation, ***Yoshihide Yamaguchi,*** *S. Fujisaki, K. Shinoda,* Hitachi, Japan*; K. Sato, M. Izawa,* Hitachi High Technologies, Japan

Remarkable progress on the thermal cyclic etching of non-volatile materials has been made in recent years. The typical procedure for thermal cyclic etching of non-volatile materials such as HfO_2 is cyclic repetitions of formation and desorption of the organometallic complex at a constant temperature [1]. The key steps in thermal cyclic etching is the formation and the desorption of the volatile organometallic complex layer on the surface. The organometallic layer will prevent the diffusion of etching species into the deep at the formation step and it must be easily removed at the desorption step. Our previous study on the thermal cyclic etching of La_2O_3 reported that thermal instability of the corresponding organo-lanthanum complexes must be suppressed in the essential presence of a stabilizer material [2]. In the current study, we present a novel thermal cyclic etching of non-volatile material via a self-stabilizing organometallic complex formation without any additional stabilizer.

The experimental apparatus we used is a tool for thermal gas phase cyclic etching equipped with a single liquid source vaporizer. A La_2O_3 thin film sputtering deposited on a SiO_2/Si wafer was used as a sample. In the first step, the La_2O_3 film was exposed to the vapor of a non-diketonate ligand liquid as the etchant that had a self-stabilizing moiety in the molecule. The sample was then annealed up to 350°C to remove the corresponding organo-lanthanum complex layer from the surface. After consecutive processes of complex formation and its desorption, the La_2O_3 film thickness remaining on the sample surface was evaluated using ellipsometric measurements.

The results showed that the cumulative etched thickness of La_2O_3 film increased linearly in proportion to the number of cycles and that no additional stabilizer was needed. The etching selectivity of La_2O_3 to some other oxides was also confirmed.

From these findings, we conclude that a novel thermal cyclic etching of La_2O_3 by self-stabilizing organometallic complex formation without an additional stabilizer has been successfully demonstrated.

[1] Y. Lee et al., Journal of Vacuum Science & Technology A 36, 061504 (2018).

[2] Y. Yamaguchi et al., ALE workshop AP+PS+TF-ThM1 (2019).

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