Area Selective ALD
Room Baekeland - Session AS-WeM

Selective ALD I

Moderators: Dennis Hausmann, Lam Research, Hanjin Lim, Samsung Electronics Co., Inc.

10:45am **AS-WeM-1 Promixity Effect of Selective Co ALD on the Nanoscale***, **Michael Breeden**, S Wolf, A Anurag, V Wang,* University of California San Diego*; D Moser, R Kanjolia, M Moinpour, J Woodruff,* EMD Performance Materials*; A Kummel,* University of California San Diego*; M Li, M Bakir,* Georgia Institute of Technology

The use of selective-area Co ALD is desired both for bottom-up fill of Co in interconnect and vias, as well as in forming connections between stacked dies in packaging. The cobalt ALD process using Co(DAD)$_2$ and formic acid (HCOOH) or tertiary-butyl amine (TBA) is known to have nearly infinite selectivity (>1000 cycles) on metal vs. insulator (SiO$_2$ or low-k SiCOH) planar surfaces [1,2]. However, when the spacing between the metal and insulator regions is less than 100 nm, there can be a reduction in selectivity under identical ALD conditions, due to the diffusion of molecularly-adsorbed metal precursor from reactive to non-reactive surfaces [3].

In this report, Co ALD was performed using Co(DAD)$_2$ + TBA at 180°C on 85 nm wide Cu stripes on SiO$_2$, as well as on suspended Cu stripes with a 200 nm spacing between the Cu growth surfaces. The planar structure of these stripes enables top-down scanning electron microscopy (SEM) imagery and x-ray photoelectron spectroscopy (XPS) quantification to be used to monitor the presence of unwanted Co nuclei on insulator (SEM) and the growth rate on Co (XPS). To control precursor dose, multiple precursor pulses were employed in each cycle to limit the maximum pressure when dosed through a turbomolecular pump to minimize background contamination. XPS is performed without breaking vacuum to prevent oxidation of Co. The Cu stripes were tested for open- or short-circuit connection between surfaces due to Co ALD growth. Finally, cross-sectional transmission electron microscopy of the alternating strips was performed.

Four strategies have been found to improve Co ALD selectivity: adding a passivant to remove insulator defect sites, increasing the purge time, decreasing the precursor dose, and periodic annealing at 260°C in vacuum. SEM of the striped pattern with a longer purge time shows decreased unwanted nucleation; while the periodically annealed stripe pattern shows a removal of all unwanted nuclei on SiO$_2$, along with a densified film and edge buildup of Co. This is consistent with reabsorption of the Co nuclei from the insulator surface to the growth surface in a low-temperature nanoscale reflow process. It is possible the low temperature nanoscale reflow process would enable further scaling of the diffusion barriers to SiCOH. For packaging, this low temperature ALD process has the potential to induced selective Cu bump bonding as shown by the results on the suspended Cu stripes.

1. M. Kerrigan, et al. J. Chem. Phys, 2017 **146**, pp. 052813.

2. S. Wolf, et al. Appl. Surf. Sci., 2019, **510**, pp. 144804

3. F. Grillo, et. al. ALD Conference Proceeding, Seattle, WA 2019

11:00am **AS-WeM-2 Cobalt Electron-Enhanced Atomic Layer Deposition (EE-ALD) Using High Electron Flux Hollow Cathode Plasma Electron Source (HC-PES): Rapid Growth and Bottom-Up Fill***, **Zachary Sobell**, A Cavanagh,* University of Colorado - Boulder*; S George,* University of Colorado - Boulder

Electron-enhanced atomic layer deposition (EE-ALD) facilitates low temperature ALD using an electron beam that can remove surface species by electron stimulated desorption. Previous work has demonstrated BN [1] and Co [2] EE-ALD using an electron gun. Higher electron fluxes by a factor of > 3000 can be produced by a hollow cathode plasma electron source (HC-PES). In addition, the HC-PES is more resistant to chemicals and has significantly faster ON/OFF times. This HC-PES has been used to grow Co films with area selectivity using cobalt tricarbonyl nitrosyl [CTN, Co(CO)$_3$NO] exposures together with electron exposures.

Rapid Co EE-ALD is observed with cycles times of ~40 s/cycle. In situ ellipsometry measurements reveal that nucleation is rapid on the native oxide of silicon wafers (Figure 1). Co EE-ALD displays growth rates of ~2.5 Å/cycle over an area of > 4 cm^2. The uniform film thickness over this area also argues that the electron exposures are able to obtain saturation behavior by desorbing all the ligands from the adsorbed CTN species. The high electron fluxes have also led to new growth phenomena. At small electron exposures <0.05 C/cm^2, normal "ALD like" Co growth is observed versus sequential CTN and electron exposures. At higher electron fluxes >0.1 C/cm^2, the Co growth enters a new regime where the growth can continue for many precursor doses following only one electron exposure. Co film thickness as large as 1000 Å have been grown using multiple CTN exposures following only one electron exposure.

The directionality of the electrons is also useful for area selective EE-ALD. Because the electron flux is normal to the surface, the horizontal surfaces are exposed to higher electron fluxes than the vertical surfaces. Consequently, EE-ALD on vias should occur primarily from the bottom up. Co EE-ALD films were grown on high aspect vias and then examined using transmission electron microscopy (TEM). Co EE-ALD was performed using 45 CTN/electron cycles with electron energy at 140 eV and electron exposure at 10 mA for 10 s. For the vias with an aspect ratio of ~4, the TEM images revealed a film thickness of ~5 nm on the sidewall (Figure 2) and ~30 nm on the bottom (Figure 3). The six times larger deposition on the bottom could facilitate bottom-up fill of the via.

[1] J.K. Sprenger et al., "Electron-Enhanced Atomic Layer Deposition (EE-ALD) of Boron Nitride Thin Films at Room Temperature and 100°C", *J. Phys. Chem. C***122**, 9455 (2018).

[2] Z.C. Sobell et al., "Growth of Cobalt Films at Room Temperature Using Sequential Exposures of Cobalt Tricarbonyl Nitrosyl and Low Energy Electrons", *J. Vac. Sci. Technol. A***37**, 060906 (2019).

11:15am **AS-WeM-3 Probing the Selectivity of Area-Selective Spatial ALD + Etch-Back Supercycles for SiO$_2$ by Low Energy Ion Scattering***, **Alfredo Mameli**,* TNO/Holst Center, Netherlands*; P Brüner,* IONTOF GmbH, Germany*; F Roozeboom,* TNO/Holst Center, Netherlands*; T Grehl,* IONTOF GmbH, Germany*; P Poodt,* TNO/Holst Center, Netherlands

Area-selective ALD interleaved with etch-back steps in a supercycle fashion has recently been reported as very effective in achieving high selectivity. Such supercycles can result in lower defectivity on the non-growth area and thicker layers on the growth area, as compared to solely area-selective ALD.[1, 2] The complementarity of deposition and etching techniques can therefore offer great potential for reaching the ultimate requirements in advanced device manufacturing.

Here we use low energy ion scattering (LEIS) to probe the selectivity of the first supercycle, consisting of plasma-enhanced selective spatial-ALD of SiO$_2$ and conventional CF$_4$-based reactive ion etching (RIE). Given its extreme sensitivity to the top monolayer(s) of a thin film, LEIS can reliably quantify the selectivity and defectivity on the non-growth areas in terms of surface coverage and derived thickness.

For the selective spatial ALD a three-step approach was adopted,[3] consisting of successive inhibitor, silicon precursor (BDEAS) and O$_2$ plasma exposures. Silicon wafers (growth area) with large ZnO patterns (non-growth area) were used as substrates. After 20 spatial ALD cycles, no silicon was detected on the non-growth area by LEIS (detection limit 2 % SiO$_2$ surface coverage), implying excellent process selectivity. The selectivity is however gradually lost by increasing the number of ALD cycles up to 110. On the non-growth area, the SiO$_2$ layers now had an averaged thickness of 3.5 nm as measured by spectroscopic ellipsometry (SE) and corroborated by LEIS measurements (86% Si surface coverage). At the same time on the growth area, a SiO$_2$ thickness of 11 nm was measured. In order to correct for the selectivity loss, a 3 seconds RIE step was applied, which restored the Si coverage and reduced the SiO$_2$ thickness on top of the non-growth area back to zero, as demonstrated by LEIS. Concurrently, 8 nm thick SiO$_2$ was left on the growth area.

The data presented in this work demonstrate the effectiveness of combining selective spatial ALD + etch-back corrections to achieve extreme SiO$_2$ selectivity while retaining high deposition rates. Furthermore, we will discuss how LEIS can provide useful information on selectivity as well as defect formation on the non-growth area. Finally, we have extended the plasma-enhanced selective spatial ALD of SiO$_2$ to other non-growth areas.

[1] R. Vallat et al., *JVSTA*, 35, 01B104 (2017).

[2] S. K. Song et al., *Chem. Mater*. 31 4793-4804 (2019).

[3] A. Mameli et al., *ACS Nano*, 11, 9303-9311 (2017).

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