Investigation of Area Selective Atomic Layer Deposition with Microreactor and *in situ* Surface Analysis

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Primary CNF Tools Used: Acid hood, atomic layer deposition (ALD)

Abstract:

Atomic layer deposition (ALD) is a technique capable of precise control of film thickness and conformal film growth due to self-limiting nature of the precursors. Engstrom research group (ERG) has built a microreactor through which reactants of ALD are delivered and confined in a small region for deposition. This microreactor is coupled to an ultra high vacuum (UHV) chamber for surface characterization such that the deposited film is transferred *in vacuo*, without an air break, to the analysis chamber. In addition to the two reactants used in conventional ALD:ALD precursor and co-reactant, a third species called "co-adsorbate" is introduced for possible area selective deposition to act as a site-blocking layer.

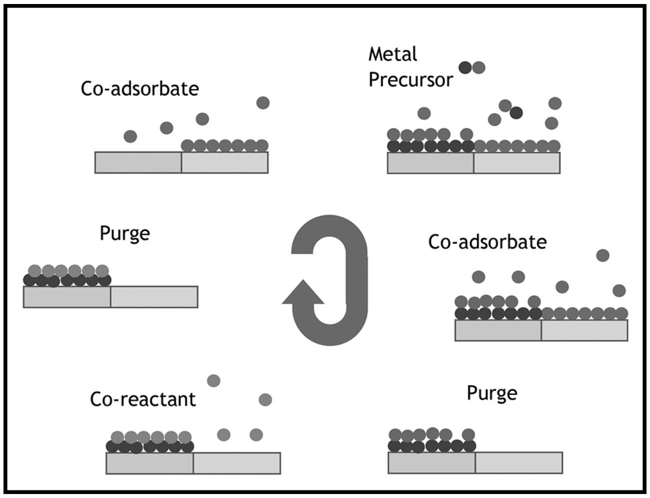

Figure 1: Schematic of an ALD cycle with co-adsorbate molecules.

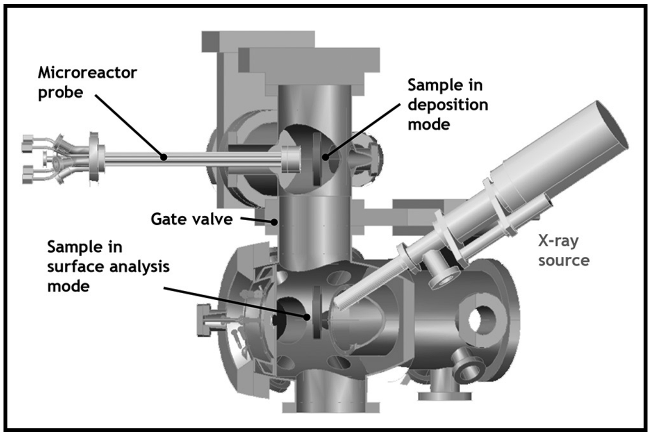

Figure 2: CAD rendering of the microreactor and UHV surface analysis chamber.

Summary of Research:

In continuous downscaling of semiconductor devices, ALD has emerged as a potential approach capable of meeting required criteria of next generation technologies. The self-limiting nature of ALD precursors brings about two major advantages unique to the technique: precise control of thickness of deposited film and conformal growth [1]. ALD is sequential binary gas-phase reaction separated by purge steps to prevent any unwanted parasitic reactions between the precursor and co-reactant. ERG takes this deposition technique a step further to study fundamental mechanisms involved in potential area-selective ALD. Co-adsorbate molecules are introduced within a conventional cycle of ALD: before, during, and after precursor pulse as in Figure 1, to investigate how this third species potentially allows for area selective deposition. The deposited film is transferred *in vacuo* to and characterized in a UHV chamber coupled with the microreactor using XPS.

The thickness of deposited film (~ a few nm) is often in the range that is most effectively probed with surface-sensitive characterization techniques that require UHV, $p < 10^{-9}$ Torr. Conventional ALD is typically conducted at low to medium vacuum conditions ($p \sim 10^{-3}$-10^{-2} Torr), thus in most cases UHV based analysis of the deposited thin films occurs in a separate chamber, requiring an air break that may significantly alter the surface composition, oxidation state, structure of the deposited film, and/or underlying substrate. Avoiding this air break is critical for fundamental studies of the growth of ultrathin films, particularly in the early stages. Figure 2 describes how a sample is exposed to precursors at the upper stage and transferred down to the lower stage of the chamber without exposure to air for post-deposition characterization.

In this report, we investigate a mechanism that can possibly achieve area-selective deposition with ALD by employing co-adsorbate molecules. Two substrates of different composition are used as initial surfaces: chemical oxide and metallic copper. Substrate preparation for the dielectric is conducted in the acid hood of CNF at Cornell University. This wet chemical etch includes submerging Si <100> wafer in buffered oxide etch (BOE) (6:1) for two minutes that produces hydrogen-terminated Si, confirmed by hydrophobicity of the surface. The substrate is then immersed in nanostrip for 15 minutes, which generates hydroxyl group termination with a known density of ~ 5×10^{-14} OH/cm^{-2} [2]. This cycle of removing native oxide and generating chemical oxide is repeated twice. OH-terminated SiO_2 and copper substrates are loaded into the vacuum chamber within a sample holder which allows simultaneous exposure of substrates to reactants such that gas-surface reactions will occur under identical+ experimental conditions.

In area-selective ALD experiments, substrates are annealed to substrate temperature of 180°C for an hour prior to exposure. Then co-adsorbate species, unsaturated hydrocarbon in this report, is introduced to surfaces to form site-blocking layer to prevent incoming ALD precursor from adsorbing on non-growth surfaces. The co-adsorbate molecules are present at relatively high ratio compared to ALD precursor before, during, and after the precursor pulse to ensure excess co-adsorbate molecules are present for competitive adsorption. After purge of the precursor and co-adsorbate, pulse and purge of co-reactant occurs, just like the second half cycle in conventional ALD. Deposited metal oxide films are characterized with *in situ* x-ray photoelectron spectroscopy (XPS) using several parameters: photoionization cross section, inelastic mean free path, and kinetic energy, etc. [3]. The absolute atomic density of metal atom is calculated using calibration of semi-infinite Au film and methods described elsewhere [4].

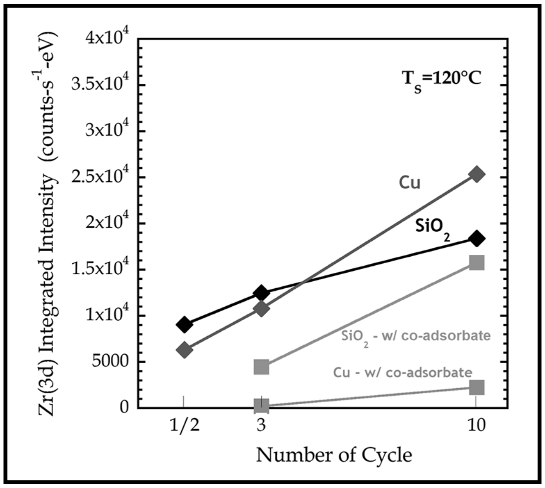

Figure 3: Sample holder capable of holding two coupon samples.

Results from preliminary AS-ALD experiments with an unsaturated hydrocarbon as the co-adsorbate species are summarized in Figure 3. The top two curves represent the integrated intensity of Zr(3d) detected in ½, 3, and 10 ALD cycles of Zr-containing precursor with an oxidant. As expected for an ALD process, the amount of transition metal within the deposited thin film is linearly proportional to the number of cycles. Density functional theory (DFT) calculations demonstrate that the co-adsorbate species has stronger affinity towards Cu than SiO_2. Experimental results show good correlation with the theoretical calculations; in Figure 3, the two bottom curves represent the amount of Zr(3d) detected on SiO_2 and Cu from 3 and 10 ALD cycles in presence of the co-adsorbate.

In the three-cycle experiment with the co-adsorbate, complete inhibition of Zr adsorption is obtained, most likely due to competitive adsorption between the co-adsorbate and ALD precursor for surface active sites. In the ten-cycle experiment, some Zr(3d) is detected, but the amount of Zr on SiO_2 compared to Zr on Cu is greater by approximately a factor of 10.

References:

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