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

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Primary CNF Tools Used: ALD, acid hoods

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.

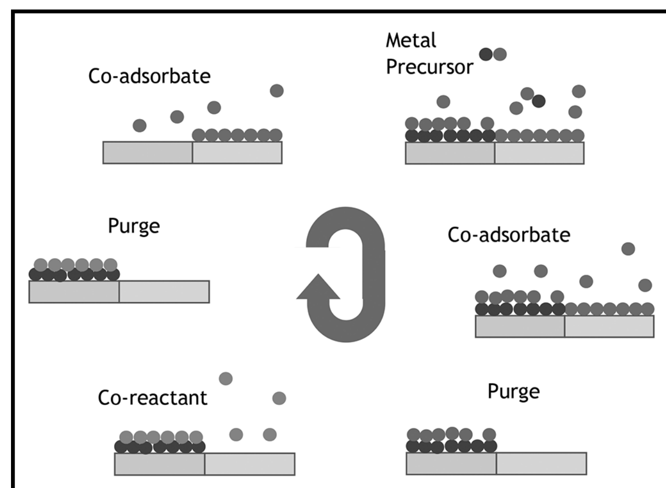

Figure 1: Schematic representation of an ALD cycle with co-adsorbate molecules.

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 reaction separated by purge steps to prevent any unwanted parasitic reactions between the precursor and co-reactant in gas phase. 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 x-ray photoelectron spectroscopy (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 assess the feasibility of achieving 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 which 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 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 as shown in Figure 3. This sample holder 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 is introduced to surfaces to form site-blocking layer to prevent incoming ALD precursor from adsorbing on undesired surfaces. The co-adsorbate molecules are present at relatively high ratio compared to ALD precursor during and after the precursor pulse to ensure area selective deposition. After purge of the precursor and co-adsorbate, pulse and purge of co-reactant occurs, just like in conventional ALD cycle. Deposited metal oxide films are characterized with *in situ* 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].

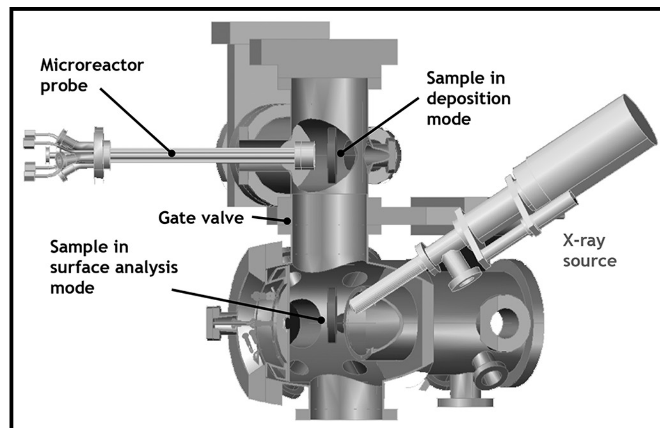

Figure 2: CAD rendering of the microreactor and UHV surface analysis chamber.

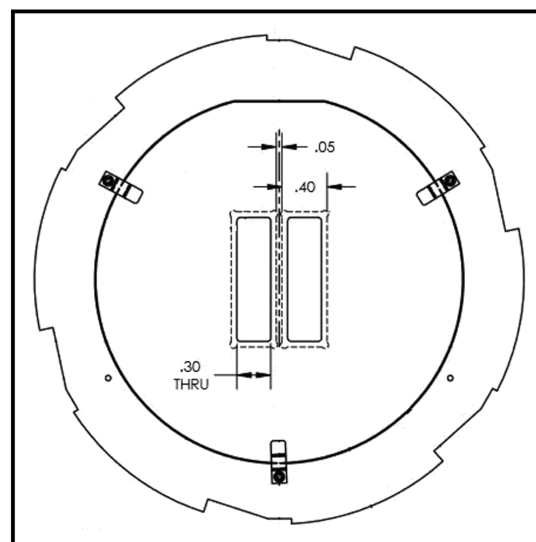

Figure 3: Sample holder capable of holding two copper samples.

Chemistry

References:

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