Atomic Layer Deposition Process Optimization and Characterization of Amorphous Metal-Oxide Films

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Abstract:

Atomic layer deposition (ALD) is used to create conformal thin films that have many applications due to the wide range of available materials and precisely-controlled thicknesses. Amorphous metal-oxide thin films are good candidate materials for dielectric gates, diffusion barriers and biocompatible coatings, among many other applications. ALD processes that have not been fully optimized and characterized result in wasted precursor, longer fabrication times and incomplete understandings of the films themselves. In this work, the processes for hafnium dioxide (HfO_2) and zirconium dioxide (ZrO_2) films were optimized for uniformity by varying precursor pulse and carrier gas purge times to create the most uniform films. The temperature dependence of film characteristics and differences between thermal and plasma-enhanced processes was explored for titanium dioxide (TiO_2) films. Uniformity was determined by comparing thicknesses measured by an ellipsometer at different positions in the reaction chamber. This project yielded ALD metal-oxide processes optimized for uniformity and a better understanding of film characteristics. All data is available on the Stanford Nanofabrication Facility's website.

Introduction:

ALD is a nanofabrication process consisting of a cyclic self-limiting chemical reaction with vapor-phase precursors, but only surface-phase reactions. A cycle of ALD consists of four steps; 1) surface saturation by precursor A, 2) purge of excess precursor A from the reaction chamber, 3) surface saturation by precursor B, and 4) purge of excess precursor B. For metal-oxide films, precursor A is the base metal with ligands attached and precursor B is water (for thermal processes) or oxygen plasma (for plasma processes). Steps 1 and 3 are quantified by the "pulse time," which is how long the valve on the cylinder containing the precursor stays open and is thus related to the amount of precursor in the reaction chamber. Steps 2 and 4 are quantified by the "purge time," which is how long the background carrier gas (Ar or N_2) flows through the reaction chamber without carrying any new precursor.

We sought to maximize film uniformity, minimize precursor waste, and minimize process runtime by varying only Steps 1 and 2. Thus, "pulse time" and "purge time" specifically refer to the precursor A pulse time and the purge time immediately after that, respectively. Other parameters varied were temperature, background carrier gas flow rate, type of deposition tool and water or oxygen plasma as precursor B. We also determined deposition rates.

Experimental Procedure:

Depositions were performed on two simultaneously-run 4-inch silicon wafers (placed side-by-side in the reaction chamber) after a standard RCA clean. The film thickness was measured at nine points per wafer, resulting in 18 thicknesses per deposition. These were used to compute the average thickness and non-uniformity, which was the standard deviation divided by the average thickness. We ran 100 cycles of ALD for all depositions (except those used to determine the deposition rate) on one of two Cambridge Nanotech ALD systems: Fiji or Savannah.

Results and Conclusions:

The ZrO_2 processes on both the Savannah and Fiji systems were wasting precursor A. We were able to determine the threshold for surface saturation by decreasing the pulse time for the Savannah process. A lack of surface saturation was indicated by a significant decrease in average thickness (Figure 1) as well as high non-uniformity. The standard recipe was adjusted from having a pulse time of 0.40s to 0.15s, saving a significant amount of precursor A. Increasing the purge time decreased the non-uniformity of the film (Figure 2), indicating that vapor-phase reactions took place at shorter purge times. This was also why the Fiji process had a non-uniformity of over 10% until the purge time was increased from 20s to 50s.

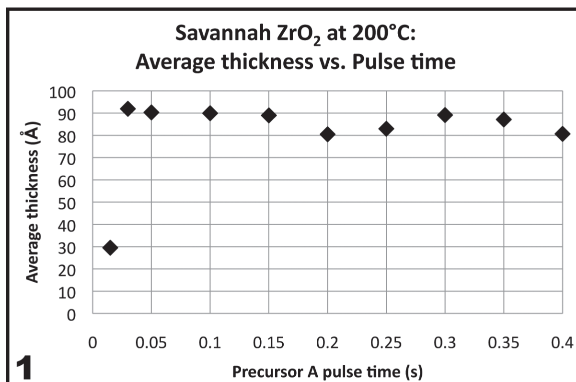

Figure 1: The thickness dropped off at a pulse time of 0.015s. The pulse time must be at least 0.03s to reach surface saturation.

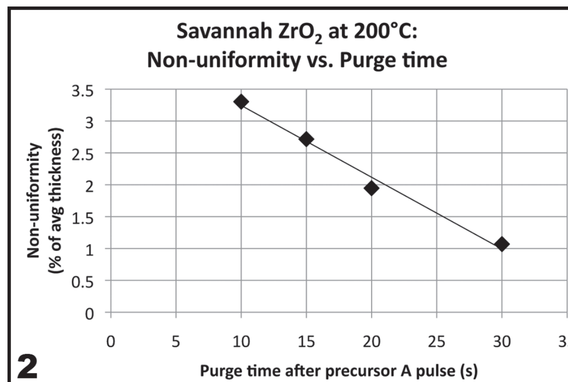

Figure 2: The non-uniformity of the film decreased as the purge time increased, indicating vapor-phase reactions occurred at shorter purge times.

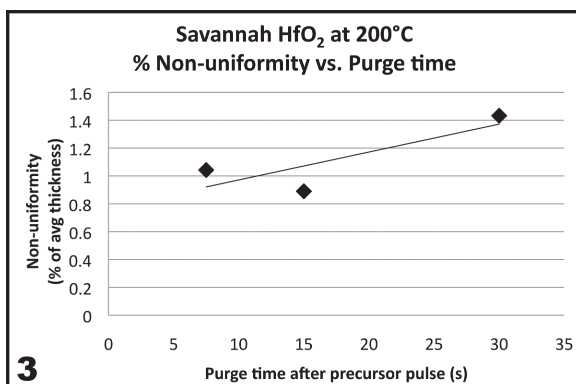

Figure 3: The non-uniformity of the film increased as the purge time increased, indicating desorption occurred at longer purge times.

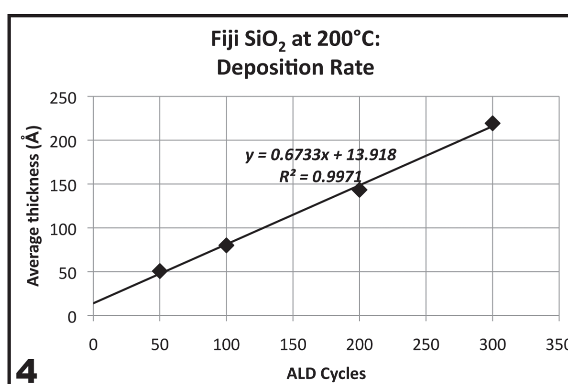

Figure 4: The Fiji SiO_2 deposition rate is 0.7Å/cycle.

The Savannah HfO_2 process was verified to be at optimal performance. Pulse time, purge time and background flow were varied to confirm that the standard recipe had the highest uniformity. However, it was found that desorption of precursor A occurred at longer purge times (Figure 3) due to excessive volatility. Despite this trend, the initial purge time of 15s had the lowest uniformity, indicating that it was a good balance between desorption and potential vapor-phase reactions.

The deposition rate of Fiji SiO_2 was 0.7Å/cycle with 14Å of native oxide (Figure 4), which is due to oxygen diffusing into the substrate at room temperature before deposition. The deposition rate of Savannah ZrO_2 was 0.8Å/cycle with 11Å of native oxide.

Thermal and plasma Fiji TiO_2 films were deposited at 100-300°C. The plasma films showed little change in average thickness over the temperature range. The thermal films were thicker at lower temperatures due to precursor condensation.

Future Work:

The Fiji ZrO_2 process should be further optimized to increase uniformity and reduce precursor waste. More process optimization should be done on the plasma Fiji TiO_2 process because most films had twice the non-uniformity of those from the thermal process for the explored temperature range. The Fiji TiO_2 deposition rate should also be determined. Capacitors can be made with the films to determine the electrical properties such as breakdown voltage and capacitance with respect to both high and low sweeping voltages. These properties could then be compared for films deposited at different temperatures, by different tools or through different processes (thermal vs. plasma).

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