Selective Atomic Layer Deposition

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Abstract:

Atomic layer deposition (ALD) of tantalum nitride (TaN_x) has been performed on copper (Cu) and silicon dioxide (SiO_2) substrates with the goal of selective area deposition using self-assembled monolayers (SAMs) as an ALD blocking layer. The films have been analyzed using spectroscopic ellipsometry (SE), contact angle, x-ray photoelectron spectroscopy (XPS), and low energy ion scattering spectroscopy (LEISS). The molecules (heptadecafluro -1,1,2,2-tetrahydrodecyl) triethoxysilane (HDFTEOS) and 1H,1H,2H,2H-perfluoro-octyltrichlorosilane (FOTS) were deposited onto both substrates before ALD. We found that both molecules impeded growth on SiO_2 for the first 20 ALD cycles, shown with SE as well as XPS. After the initial growth impedance, TaN_x appears to grow on itself with a growth rate similar to the surfaces without SAMs.

Introduction:

Atomic layer deposition (ALD) is a method for depositing thin films characterized by precision thickness control through a series of self-terminating reactions. The technique is similar to chemical vapor deposition (CVD), except that ALD breaks the reaction down into half cycles. In addition to the ability to lay thin films accurately by varying the number of cycles, the gas phase and self-limiting nature of ALD makes it ideal for high aspect ratio depositions. The goal of this project was to study methods for selectively depositing the desired material, tantalum nitride, only onto one substrate and not another.

The ability to deposit material only where it is wanted would be a powerful tool. One place where selective ALD could be beneficial is in the semiconductor industry. Currently copper (Cu) is used as the interconnect metal in devices. However, copper has been shown to diffuse into the dielectric layers creating shorts and heat dissipation problems, limiting the effectiveness of the device [1]. One fix would be to use a thin layer of TaN_x between the Cu and dielectric as a diffusion barrier layer [2]. Depositing the film would require a method of selectively depositing TaN_x on different areas.

Experimental Procedure:

Two different substrates were studied: copper and chemical oxide (silicon dioxide, or chem ox). Three different scenarios were examined: 1) plain substrates (no SAMs), 2) with HDFTEOS, or 3) with FOTS. The SAMs were deposited onto both surfaces using a molecular vapor deposition method before the ALD depositions. The large number of fluorine atoms on the SAM molecules could create an unreactive surface that would stop ALD growth. ALD of TaN_x at a heater temperature of 300°C was subsequently performed on the samples. The ALD precursors used for this procedure were pentakis(dimethlyamino) tantalum (PDMAT) and ammonia (NH_3).

After depositions, the surfaces were then analyzed using contact angle, spectroscopic elipsometry, XPS, and LEISS.

Results:

From contact angle measurements, information was determined about the samples. Figure 1 shows that changes in contact angle occurred after depositing HDFTEOS and after heating the sample to an ALD temperature of 300°C. This seems to indicate that HDFTEOS was deposited onto the surface, but was not thermally stable on Cu. The change in angle after heating was not observed on chem ox. From spectroscopic ellipsometry, we saw that the long term growth rate of TaN_x is 0.4Å per cycle with no SAMs and 0.38Å per cycle with HDFTEOS. This corroborated theoretical TaN_x growth rates as well. Figure 2 is a close up of ultrathin film thickness from spectroscopic ellipsometry. Here we saw that for low ALD cycles, the HDFTEOS made a significant difference in the film thickness. Figure 3 shows XPS areas of the tantalum ($4d_{5/2}$) peak corroborating the difference in tantalum deposition for low TaN_x ALD cycles on chem ox. There did not appear to be a difference in the amount of Ta on Cu, as shown in Figure 4. FOTS results were also included in the XPS data, which followed a similar trend as the HDTFEOS surfaces.

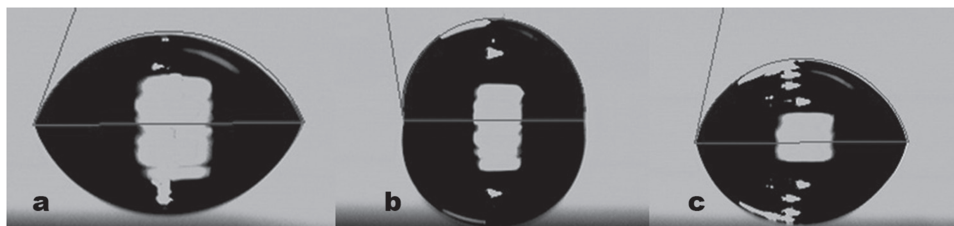
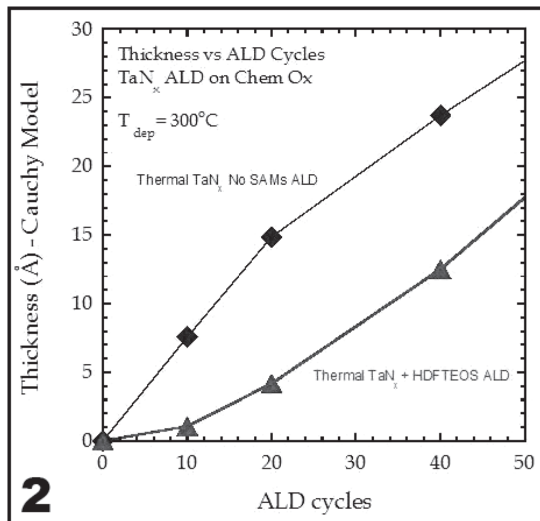
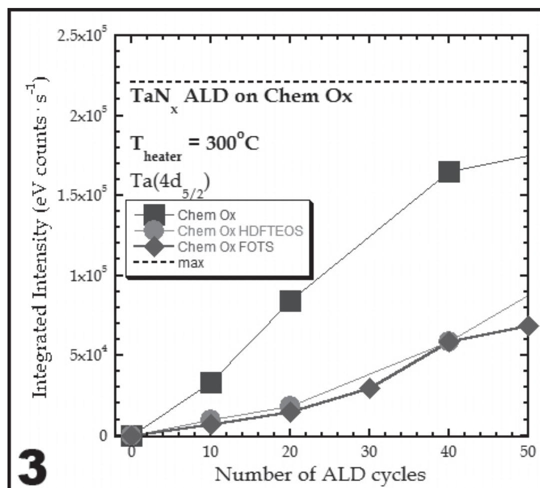
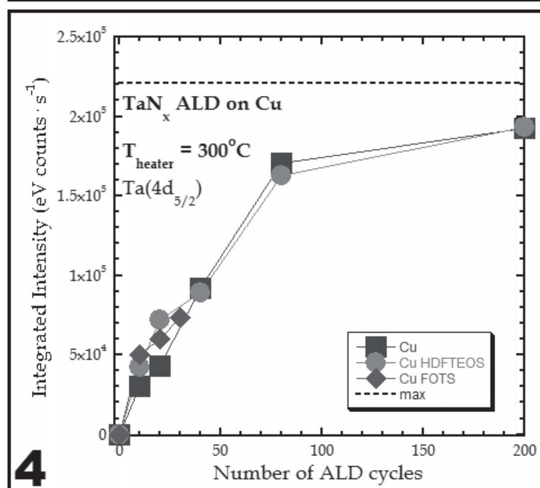


Figure 1: a] No SAMs (69.3°), b] HDFTEOS (98.7°), c] HDFTEOS (77.6°) after 0 ALD cy at 300°C.







LEISS is a surface sensitive technique and is helpful in obtaining information in regards to what is on the topmost layer of our films. Although we predicted that the SAMs formed a uniform monolayer right above the substrate, fluorine was observed with LEISS after as many as 80 TaN_x ALD cycles on copper with HDFTEOS.

Conclusions and Future Work:

The SAMs HDFTEOS and FOTS have been demonstrated to act as a blocking layer for ultrathin films. Both impeded growth on SiO_2, but on copper, the HDFTEOS was not thermally stable and FOTS did not significantly affect TaN_x growth. As the number of cycles increased, the blocking layer was less effective because the film began to grow on itself.

The first molecules on the surface likely bound to defects in the SAMs and grew upwards from those points. A more uniform SAM layer could increase the effectiveness of the blocking layer. If tantalum nitride was binding to defects, it would mean that some FOTS or HDFTEOS should still be on the surface until the TaN_x completely covered it. This hypothesis was supported by the fact that fluorine was observed with LEISS after 80 ALD cycles. Another possible explanation is that fluorine atoms diffused through the film and were being observed on the surface. In the future, we will conduct angle resolved XPS to determine where in the film the fluorine is.

A similar method of applying SAMs to different surfaces and testing the effectiveness as blocking layer could be applied to other films and substrates.

Acknowledgements:

I would like to thank the National Nanotechnology Infrastructure Network Research Experience for Undergraduates (NNIN REU) Program and the National Science Foundation for the sponsoring this research. I also appreciate the guidance and support from Wenyu Zhang, James Engstrom, Melanie-Claire Mallison, and the CNF staff.

References:

[1] H. Chung, et al. (2006), US Patent 7,049,226.

[2] Ma, P. et al Interconnect Technology Conference, 2009. IITC 2009. IEEE International, vol., no., pp.38-40, 1-3 June (2009).

Figure 2: Spectroscopic ellipsometry model dependent film thickness.

Figure 3: XPS Ta ($4d_{5/2}$) peak area as a function of TaN_x ALD cycles.

Figure 4: XPS Ta ($4d_{5/2}$) peak area as a function of TaN_x ALD cycles.