

Area-Selective Atomic Layer Deposition: New Recipe Development

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Abstract:

Atomic layer deposition (ALD) allows thin films to be deposited layer-by-layer onto a substrate by a sequential flow of gaseous chemical precursors. These precursors interact with the substrate surface via self-limiting reactions and then the cycle can be repeated until the thin film reaches a desired thickness. Area-selective ALD deposits material onto one substrate while leaving another substrate unaffected. This is applicable in device manufacturing. The focus of this project is to develop a recipe to selectively deposit tantalum nitride (TaN_x) on one surface (SiO_2), while limiting the growth on another surface (Cu). We are interested in the thermal TaN_x ALD system, using pentakis(dimethylamino)tantalum (PDMAT) and ammonia (NH_3) as precursors. From previous studies, we know that PDMAT forms strong bonds with the SiO_2 substrate surface in the first half-reaction of the ALD cycle. We decided to add an 'etchant' — dimethylamine, $(\text{CH}_3)_2\text{NH}$ (DMA) — to the TaN_x ALD recipe to drive the reaction backwards, selectively favoring deposition on SiO_2 . We investigated the effect of DMA concentrations, DMA step placement, DMA dose times, and sub-saturation of PDMAT doses.

Introduction:

Tantalum nitride (TaN_x) is used as a diffusion barrier layer [1] in integrated circuits and devices to prevent copper (Cu) diffusion into the surrounding dielectric. It can be deposited via atomic layer deposition (ALD) onto a substrate via sequential flow of gaseous chemical precursors as seen in Figure 1.

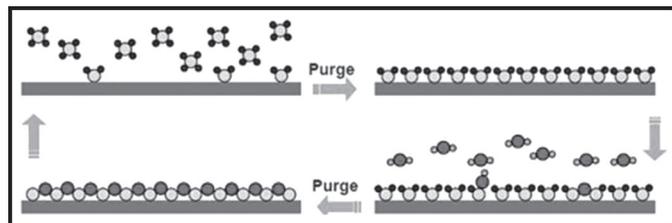


Figure 1: Schematic illustration of the ALD process. Photo Credit: http://gcep.stanford.edu/research/factsheets/atomic_layer_deposition.html

Area-selective ALD deposits material onto one substrate while leaving another substrate unaffected. This has many applications in industrial device manufacturing because it eliminates the need for patterning steps and is potentially more efficient and cost-effective.

Because the Ta precursor used, PDMAT, contains five diethylamido-groups, we have decided to use dimethylamine (DMA) to attempt the reversal of the first half-cycle reaction on Cu.

Experimental Procedure:

In order to develop a selective TaN_x ALD process with the addition of DMA, we decided to test three DMA dose parameters: 1) DMA dose time, 2) DMA dose step-placement, and 3) DMA partial pressure. For each parameter, we deposited 20 cycles of TaN_x on silicon dioxide, SiO_2 (native oxide), and Cu. The nominal sample temperature was 225°C for all depositions. The resulting thin-films were then analyzed using spectroscopic ellipsometry (SE) and wavelength-dispersive x-ray spectroscopy (WDX).

Results and Conclusions:

From spectroscopic ellipsometry (SE), we determined the average growth rate of TaN_x using SiO_2 substrates. SE is model-dependent so results vary depending on which model is used [Ta_2O_5 (because thin films oxidize in air) and Cauchy].

Growth rates of $0.43 \text{ \AA}/\text{cycle}$ (Ta_2O_5 model) and $0.39 \text{ \AA}/\text{cycle}$ (Cauchy model) were obtained, giving an average at approximately $0.4 \text{ \AA}/\text{cycle}$. This agreed with our expected growth rate of TaN_x on SiO_2 . From previous studies, we have found that the Cu substrate is rough and does not form an abrupt interface with the TaN_x layer, preventing reliable SE measurements [2].

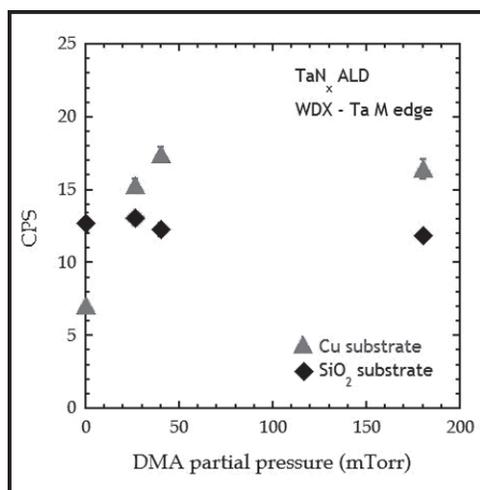


Figure 2: WDX intensities for Ta M edge for TaN_x films deposited on Cu (filled triangles) and SiO₂ (filled diamonds) substrates, plotted against amount of DMA introduced to the system.

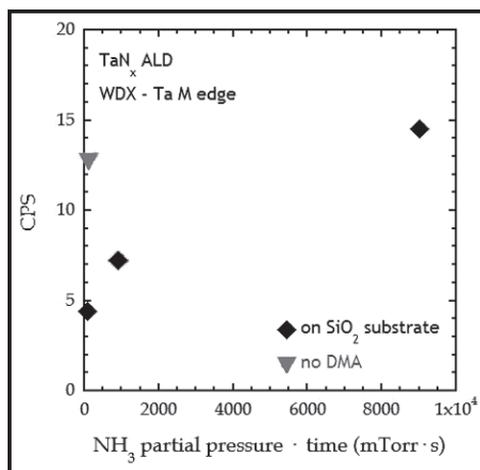


Figure 3: WDX intensities for Ta M edge for TaN_x films deposited on SiO₂ (filled diamonds) substrates, plotted against amount of NH₃ introduced to the system.

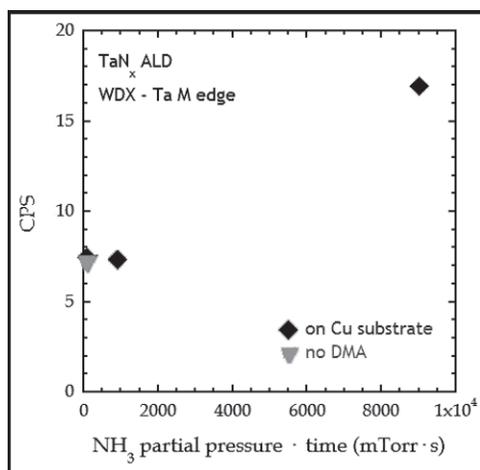


Figure 4: WDX intensities for Ta M edge for TaN_x films deposited on Cu (filled triangles) substrates, plotted against amount of NH₃ introduced to the system.

In Figure 2, we show that DMA partial pressure does not affect TaN_x film growth on SiO₂. On the Cu substrates however, a clear increase in Ta signal is observed with increasing DMA concentration.

We also introduced DMA in the NH₃ dose step (an NH₃/DMA co-exposure) in the hope that the NH₃ would react with the PDMAT on the surface where we wanted it to deposit (SiO₂) while the DMA would act to remove the adsorbed PDMAT from the surface where we did not want TaN_x deposition (Cu). From Figure 3, we see that NH₃/DMA co-exposure exhibited a typical saturation curve as expected. The upside down triangle shows the typical TaN_x recipe, which agrees with the saturated dose of NH₃.

However on the Cu substrates (Figure 4), we see that the TaN_x does not exhibit an expected saturation curve. From this result, we infer that DMA doses do not affect TaN_x on SiO₂ yet increases growth on Cu.

Future Work:

Although manipulating DMA dose placement, step time, and concentration to inhibit TaN_x on Cu — but not SiO₂ — did not affect growth as intended, there are still additional avenues where TaN_x on Cu can be suppressed (ALD temperature, DMA dosage in conjunction with PDMAT sub-saturation doses etc.). Additionally, the stoichiometry of our TaN_x films on SiO₂ and Cu has yet to be determined. We may be depositing more Ta on Cu, but it is likely that many of the ligands from PDMAT were not removed. Future x-ray photoelectron spectroscopy (XPS) measurements will shed some light on this subject.

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References:

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- [2] W. Zhang, R.K. Nahm, P.F. Ma, J.R. Engstrom, J. Vac. Sci. Technol. A 31, 061101 (2013).