Rapid Test for ALD in High Aspect Ratio Spaces Utilizing Thermally Bonded Chips and Hydrazine with Titanium Tetrachloride for TiN Deposition

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The increasing demand for high-bandwidth memory necessitates the development of devices with 3D structures, such as DRAM. These devices rely on the deposition of conformal, particle-free films with complete coverage in high-aspect-ratio (HAR) spaces. Transmission electron microscopy (TEM) is the standard technique for verifying these parameters, but it is costly, time-intensive, and only inspects a very small area of the surface of interest. This study demonstrates a rapid and non-destructive alternative involving thermally bonded chips that provide HAR spaces for deposition. The chips can be debonded and analyzed using scanning electron microscopy (SEM) and atomic force microscopy (AFM). ALD titanium nitride (TiN), typically utilized as a 2 nm diffusion barrier between tungsten (or copper) and SiO_2 (or SiCOH) in HAR spaces, was employed using $TiCl_4$ and N_2H_4 precursors, to deposit a 20 nm layer in a thermally bonded chip with a 2000:1 aspect ratio (fig. 1). This is 10x the normal thickness of diffusion barriers which increase sensitivity to particle formation.

A control test was conducted on a clean, thermally bonded sample with no TiN deposition (fig 2). The debonded dies were analyzed as planar samples using AFM, SEM, and energy-dispersive spectroscopy (EDS), confirming no detectable titanium (0% atomic percent) in any region (edge, middle, center). The AFM RMS was measured at 2.06 nm. For TiN deposition, increasing precursor doses 1×, 2×, and 3× normal exposure (1x = 500 ms $TiCl_4$, 2750 ms N_2H_4, 30 sec purge, substrate temperature 475°C) were employed to evaluate penetration depth and particle formation. The RMS roughness values for the top die remained low at 1.92 nm, 1.77 nm, and 1.64 nm, respectively. This indicates no particle formation. Atomic Ti percentages from EDS decreased as the effective aspect ratio increased from 475:1 to 2000:1 aligning with predictions from the Gordon Model [1]. Additionally, the 3x smaller %Ti decreases at the center between the 3× and 2× dose sample further support the model's estimation of precursor penetration. Temperature variations across the sample may have prevented complete surface saturation. The low RMS roughness and absence of large features suggest that CVD particle formation did not occur in the HAR space, consistent with the $TiCl_4 + N_2H_4$ chemistry avoiding $NH_4Cl(s)$ formation [2].

AFM was used to analyze an area of over 111 μm^2, revealing no defects or CVD particles. In comparison, a typical TEM survey covers only 0.004 μm^2. This means SEM/AFM in debonded chiplets examined a region ~30,000x larger than TEM allowing large area determination of particles formation in HAR.

[1] Gordon, R.G., et al. (2003) 9: 73-78. https://doi.org/10.1002/cvde.200390005

[2] Fammels, Jannick et al. "Atomic Layer Deposition of TiN in Horizontal Vias Using Hydrazine as Nitrogen Precursor." *2024 IEEE International Interconnect Technology Conference (IITC)* (2024): 1-3.

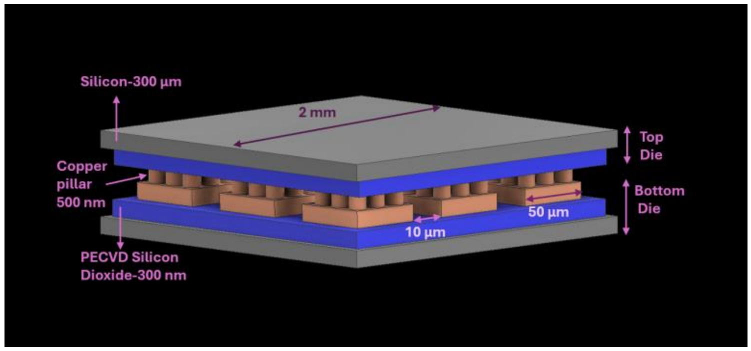


Figure 1: Schematic of the thermally bonded HAR space. Two chips are separated by 500 nm of copper. The gas flows in the 500 nm space created by the copper pillars into the center of the top die (1 mm to the center). This effectively creates a 2000:1 HAR space. The top die was evaluated for TiN penetration depth and the presence of particles.

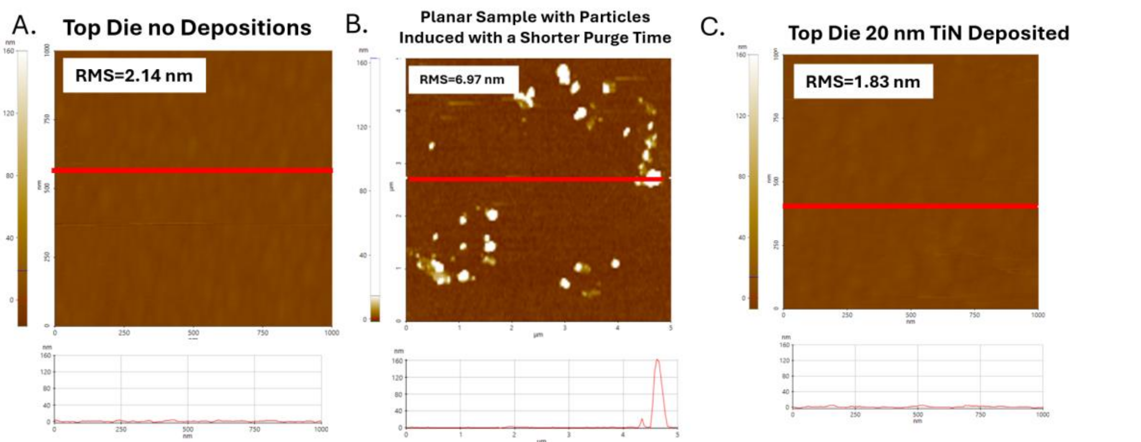
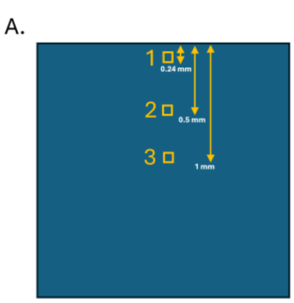


Figure 2:AFM analysis of particles on a clean HAR, particle induced planar, and HAR with TiN deposited. (A) Edge of clean top die has an RMS roughness of 2.14 nm with a maximum feature size of 7.5 nm. (B) Particle induced planar sample has an RMS roughness of 6.97 nm with a maximum feature size of 160 nm. (C) Edge of top die post 20 nm TiN ALD deposition has an RMS roughness of 1.83 nm with a maximum feature size of 7.5 nm and shows no sign of large particles



B.

Location	3x Dose (%Ti at location /edge %Ti)	2x Dose (%Ti at location /edge %Ti)	1x Dose (%Ti at location /edge %Ti)
475:1	1.0	1.0	1.0
1000:1	1.6	1.6	2.8
2000:1	2.5	6.8	17.8

Figure 3: Atomic Percentage Analysis of Titanium from SEM EDX at effective aspect ratios of 475:1 1000:1 and 2000:1 All EDX data was normalized to the percent Ti at the near edge region (475:1) for the specific sample. **(**A) Schematic of the top die. Distance from edge of top die is indicated **(**B) Ratio of %Ti at specified location to %Ti on the edge of the sample. Data shows a 2.5x decrease in Ti% from the edge to the center for triple dose. This is a 7x improvement from the single dose.