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Enabling Low-Resistivity, Halogen-Free TiN Films in Advanced Nodes with BRUTE® Hydrazine

April 2025

Low-resistivity, conformal TiN is critical for modern semiconductor applications including DRAM, 3D NAND, and logic. With reduced thermal budgets, conventional ALD methods using $TiCl_4$ and NH_3 suffer from high impurity levels, limited step coverage, and Cl-induced substrate damage. While plasma based processes can address some of these issues, they may not be compatible with complex geometries.

RASIRC has partnered with the Kummel Lab at UC San Diego to evaluate anhydrous BRUTE® Hydrazine as a reactant to enable low-temperature, thermal TiN ALD. The study compared metalorganic Ti precursors (TDMAT, TDEAT, TEMATi) with $TiCl_4$, and investigated how precursor thermal stability and BRUTE® Hydrazine exposure influence film resistivity, conformality, and contamination.

BRUTE® Hydrazine Enables Low-Resistivity Films

TiN thin films were deposited by thermal ALD using $TiCl_4$ or organic Ti precursors with BRUTE® Hydrazine at various temperatures. Films grown with TEMATi at 425°C achieved a record low resistivity of ~220 μ Ω·cm, outperforming other halogen free routes. Beyond 425°C, the precursor begins to thermally decompose, increasing carbon incorporation and degrading film quality.

As a baseline process, $TiCl_4$ and BRUTE® Hydrazine were used to deposit TiN at 500°C, achieving resistivity below 90 μ Ω·cm.[1]

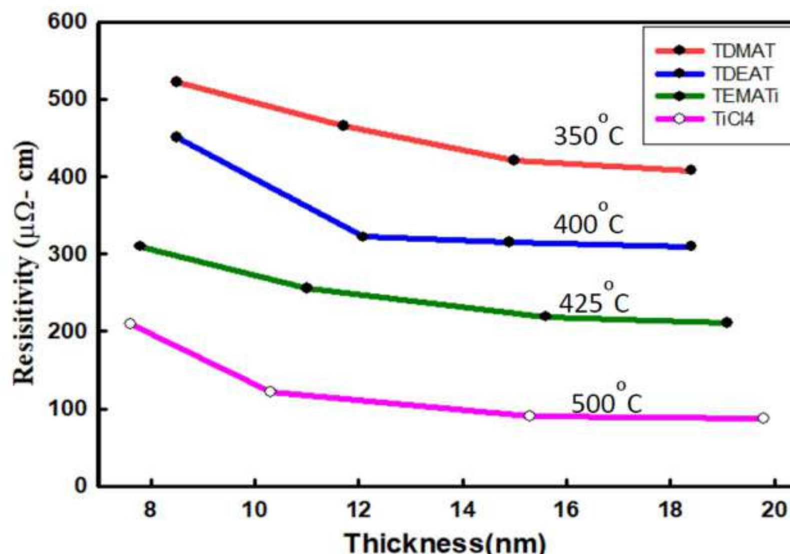

Figure 1. Resistivity vs TiN film thickness using various Ti precursors and BRUTE® Hydrazine.

High Conformality in Horizontal Vias

The conformality of TiN grown using BRUTE® Hydrazine was validated in horizontal vias with 5:1 aspect ratios (100nm x 20nm fins). TEM images confirm the sub-4nm films were deposited uniformly throughout the structures using $TiCl_4$ and TEMAi at 425°C. EDX mapping was used to confirm the film composition. [1]

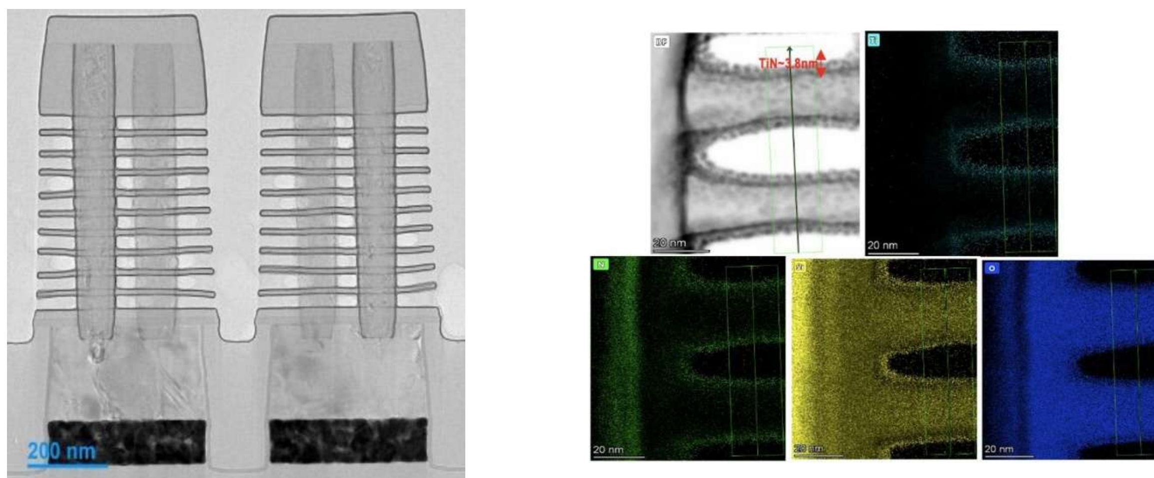

Figure 2. Imaging of the (left) 3D lamella challenge structure and (right) TiN film and EDX mapping. Conformal TiN thin films are deposited via thermal ALD using $TiCl_4$ and TEMATi at 425°C. In addition to high conformality, record low published resistivity values were achieved. *Reproduced from Kuo et al. (2024).*

Summary and Outlook

BRUTE® Hydrazine enables:

- Plasma-free, halogen-free ALD of TiN suitable for advanced 3D structures
- Lower resistivity films through impurity suppression
- High conformality using both traditional and metal-organic precursors
- Process flexibility across multiple deposition temperatures

These results demonstrate that BRUTE® hydrazine is a powerful and scalable alternative to NH_3 for thermal TiN ALD and offers unique advantages in advanced node integration. Readers seeking additional technical depth are encouraged to consult Kuo et al.[1] for comprehensive process details and characterization results.

About RASIRC

RASIRC innovations convert low vapor-pressure liquid chemistries into safe and reliable gas flow for most processes. RASIRC technology delivers hydrazine gas and hydrogen peroxide gas in controlled, repeatable concentrations. RASIRC products include BRUTE® Peroxide, BRUTE® Hydrazine, Peroxidizer®, and RainMaker® Humidification System. These products incorporate proprietary and patented technology that enables them to deliver gas to process with precision. BRUTE® Peroxide generates ultra-dry hydrogen peroxide gas and can be used with or without a carrier gas. The Peroxidizer® is the first commercial vaporizer capable of delivering concentrations greater than 5% H_2O_2 gas by volume from 30% H_2O_2 liquid source.

Reference

[1] **Kuo, C.-H., Mcleod, A. J., Lee, P.-C., Huang, J., Kashyap, H., Wang, V., Yun, S., Zhang, Z., Spiegelman, J., Kanjolia, R., Moinpour, M., & Kummel, A. C.** (2024). *Low-Resistivity Titanium Nitride Thin Films Fabricated by Atomic Layer Deposition with $TiCl_4$ and Metal–Organic Precursors in Horizontal Vias*. **ACS Applied Electronic Materials**, **5**(9), 4422–4432. https://doi.org/10.1021/acsaelm.3c00245

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