Technical Brief

Effective Silicon and Metal Nitride Deposition at Reduced Temperature

RASIRC BRUTE Hydrazine for Low Temperature ALD for Emerging Device Applications

Silicon and metal nitrides are extensively used in the semiconductor industry in logic and memory chip manufacturing. These nitride films (e.g., SiN_x, TiN_x, TaN_x, WN_x) are found in all smartphones, laptops, PCs, internet servers and IoT devices.

	Silicon nitride	Metal nitrides
Gate dielectric layers	✓	
Side wall spacers	✓	
Etch stops	✓	
Charge storage layer	✓	
Passivation layer	✓	
DRAM electrodes		✓
High-k metal gate electrodes		✓
Metal diffusion barriers		✓†
Liners	✓	✓
Hard masks	✓	✓
Multiple patterning hard masks	✓	✓

† *TiN_x in particular is an efficient diffusion barrier to tungsten fluoride during tungsten metal fill. TaN_x is also used as a diffusion barrier to copper (Cu) on low-k insulators, improving device reliability.*

Plasma Enhanced Atomic Layer Deposition (PEALD) approaches have found success in this area. However, they carry significant risk of poor step coverage and surface damage in 3-Dimensional and High-Aspect-Ratio (HAR) structures. In most cases, non-line-of-sight deposition is required, leaving thermal ALD as the preferred solution. This has forced the semiconductor industry to develop more effective co-reactants to deposit high quality films at temperatures below 430°C.

BRUTE® Hydrazine Technology

Anhydrous hydrazine is the favored solution as a precursor in low temperature thermal ALD. Advantages of this chemistry over PEALD include:

- Better step coverage in HAR structures and dense high surface area arrays
- Little to no surface damage or interfacial layer growth

BRUTE Hydrazine provides a stable, reliable flow of anhydrous hydrazine gas from a liquid source in a sealed vaporizer. The liquid source combines hydrazine and a proprietary solvent for stability. Hydrazine gas is swept to process via the pressure gradient or by an optional carrier gas (Figure 1).

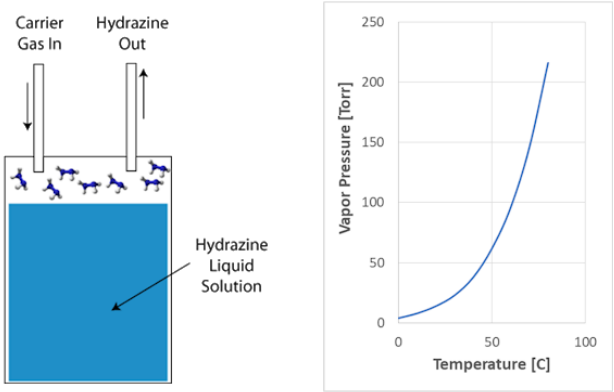

Figure 1. Novel delivery system for ultra-dry hydrazine vapor (left).
Vapor pressure of BRUTE Hydrazine (right).

Performance in Low Temperature Silicon Nitride Deposition

RASIRC in collaboration with The University of Texas, Dallas developed a low temperature thermal ALD process using Hexachlorodisilane (HCDS) and BRUTE Hydrazine. The process recipe delivers ultra-pure hydrazine gas (less than 800ppb water) into carrier gas flow at 12-14 Torr (at R.T.) for thermal ALD at 250°C to 400°C.

Silicon nitride films generated using BRUTE Hydrazine exhibit a high refractive index (~1.8) and strong growth rate (0.4-0.5 Å/cycle). In addition, the refractive index increases (to above 1.9) with further densification using a novel treatment (Figure 2).

XPS analysis showed low contamination levels for chlorine (~1%) and oxygen (3-6%). The films were also N-rich in stoichiometry. Wet etch rate in diluted HF was as low as 0.3-0.5 nm/min and lower than PEALD SiN reference samples, indicating denser higher quality films.

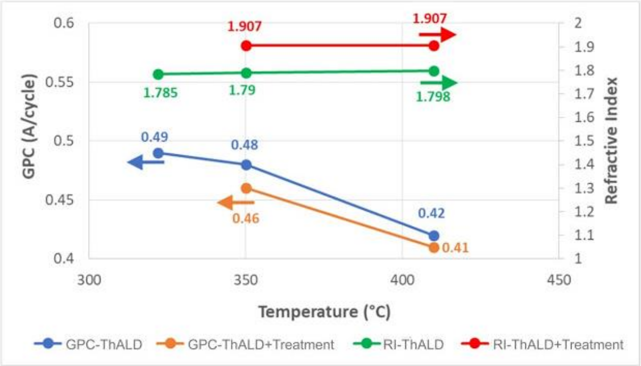

Figure 2. The ALD process window for thermal SiN ALD
using HCDS and hydrazine.

Performance in Low Temperature Metal Nitride Deposition

In collaboration with University of California, San Diego and Applied Materials, RASIRC investigated thermal ALD of TaN_x and TiN_x using hydrazine as a reactive N-containing source.

Films grown at low temperatures show lower resistivities and fewer impurities than those grown with NH_3:

- Nearly stoichiometric Ta_3N_5 films were deposited with less than 4% oxygen and 5% carbon incorporation at 100°C using tris(diethylamido)(tert-butylimido) tantalum (TBTDET) (Figure 3).
- Stoichiometric TiN films growth at 300°C with tetrakis(dimethylamido)titanium (TDMAT).

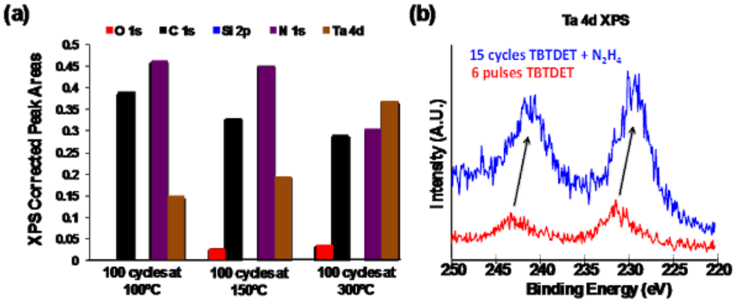

Figure 3. TaN_x deposition from TBTDET + N_2H_4. a) XPS of 100 cycles of TBTDET and N_2H_4 at 100°C, 150°C, and 300°C. b) Ta 4d XPS peaks after 6 pulses of TBTDET and after 15 TaN_x cycles. The initial 6 pulses confirmed interfacial Si-O-Ta bond formation, while after 15 cycles an ~2eV shift is seen consistent with formation of Ta-N bonds.

Uniform, highly conductive, nearly stoichiometric films of 0.44 nm RMS roughness using titanium tetrachloride ($TiCl_4$) at 300-400°C.Testing confirmed that films grown with N_2H_4 had fewer impurities (O, C and Cl) compared to NH_3-grown films. In addition, N_2H_4 produced comparable TiN film resistivity at dramatically lower temperature (300°C) than NH_3 (400°C) (Figure 4). These finding demonstrate that N_2H_4 serves as a reducing agent and is a good proton donor to Ta and Ti ligands.

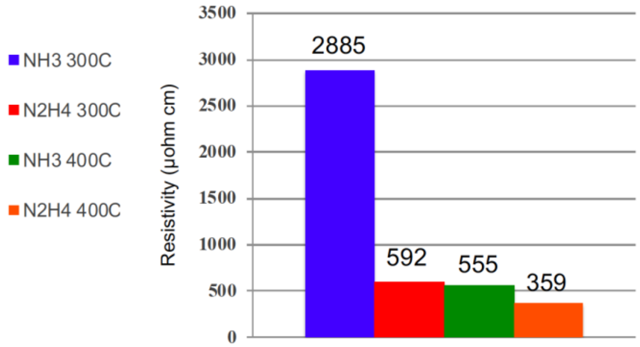

Figure 4. TiN_x grown with Brute Hydrazine at 300°C gives comparable resistivity to TiN_x grown with NH_3 at 400°C.

These studies show that BRUTE Hydrazine is a viable low temperature thermal ALD solution for Silicon and Metal Nitride films where thermal constraints limit the use of Ammonia.