Atomic layer etching of nickel aluminide binary intermetallic using a super-cycle sequence based on Hhfac and $Al(CH_3)_3$

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Nickel aluminide (NiAl, Ni_3Al) binary intermetallics have garnered significant interest as potential materials for next-generation barrier-less interconnects and extreme ultraviolet (EUV) mask absorbers, owing to their lower resistivity compared to conventional metals[1] and superior optical properties[2]. However, their high chemical stability and low gas-phase volatility present substantial challenges in developing a precise and controllable etching process. In this work, we introduce a super-cycle atomic layer etching (ALE) approach tailored for the selective and compositionally stable etching of NiAl-based intermetallics. The ALE process consists of two alternating sub-cycles: (1) a nitrogen/hydrogen (N_2/H_2) plasma exposure step, which modifies the Ni surface, followed by hexafluoroacetylacetone (Hhfac) vapor exposure to facilitate the removal of Ni, and (2) an SF_6 plasma activation step coupled with trimethyl-aluminum (TMA) exposure to selectively etch Al. By optimizing the exposure duration for each sub-cycle, we achieve precise control over the etching of different nickel aluminide phases, including NiAl and Ni_3Al.

A comprehensive characterization of the ALE process was performed using in-situ spectroscopic ellipsometry to monitor thickness variations and self-limiting behavior. X-ray reflectivity measurements confirmed tunable etch rates ranging from 0.5 ± 0.10 Å/super-cycle at 250°C to 3.3 ± 0.23 Å/super-cycle at 350°C. Additionally, atomic force microscopy (AFM) analysis demonstrated that the surface remains smooth throughout the etching process, with only minor roughness observed after extended cycles. X-ray photoelectron spectroscopy (XPS) further confirmed that the elemental composition of the Ni aluminide alloys is preserved after etching.

This work presents a novel ALE strategy for Ni aluminides, offering a promising pathway for the precise patterning of these intermetallics in advanced semiconductor fabrication. The ability to maintain composition control and surface smoothness makes this process a strong candidate for future applications in high-performance interconnects and EUV lithography mask technology.

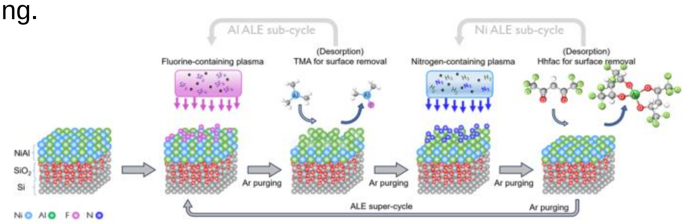

Figure 1. General reaction scheme of one complete super-cycle isotropic plasma atomic layer etching of nickel aluminide binary intermetallic.

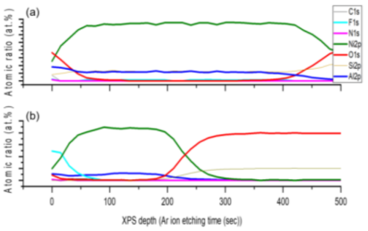

Figure 2. XPS depth profile of NiAl films (a) pristine sample (b) after etching by 20 super-cycles.

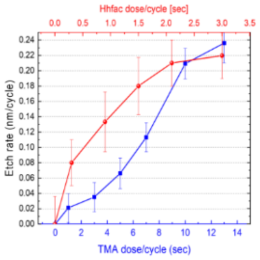

Figure 3. Dependency of etch rate of pure Ni and Al on Hhfac and TMA exposure time/cycle, respectively.

References

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