Ultrahigh Aspect Ratio Silicon Microstructures Coated Using ALD with Nucleation and Growth Enhancement for Energy Storage and Other Applications

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Ultrahigh aspect ratio microstructures are important for a wide variety of applications including energy storage, x-ray optics, sensors, catalysts, and drug delivery. Incorporating a hierarchical architecture with nanostructuring further increases the applications. For energy storage, there is interest in integrating energy storage onto silicon with sensors and energy harvesting. Efforts to integrate energy storage on a silicon die however have been limited.

Ultrahigh aspect-ratio nanoporous silicon microstructures etched using metal assisted chemical etching (MACE) [1] were prepared with aspect ratios of up to over 500:1, an order of magnitude higher than that achieved using deep reactive ion etching. The coating of such structures presents unique challenges because of the deep narrow paths that species need to diffuse into to coat the high aspect ratio microstructures. This is further exacerbated by poor nucleation and growth rates associated with ALD due to a lack of chemisorption sites and poor wettability. In this study, the nucleation and growth of ALD Pt during deposition is improved by initially functionalizing the surface with a single monolayer of organometallic molecules [2, 3] prior to Pt deposition (see Fig. 1). Also, the penetration of Pt into the ultra-high aspect ratios is facilitated by increasing the residency time of the precursors inside the microstructures using extended exposure times which also improves the nucleation and growth rates of the Pt films.

Electrochemical capacitors suitable for integrated energy storage were etched using MACE and then coated using the extended exposure ALD process with nucleation enhancement. The ultrahigh aspect ratio nanoporous Si microstructures were functionalized with trimethylaluminum (TMA) and then coated with Pt. Cross-sectional SEM images show that ALD films penetrates deep into the structures (see Fig. 2). These devices have significantly enhanced energy density as compared to prior studies [4] and have the potential to provide integrated on-chip energy storage.

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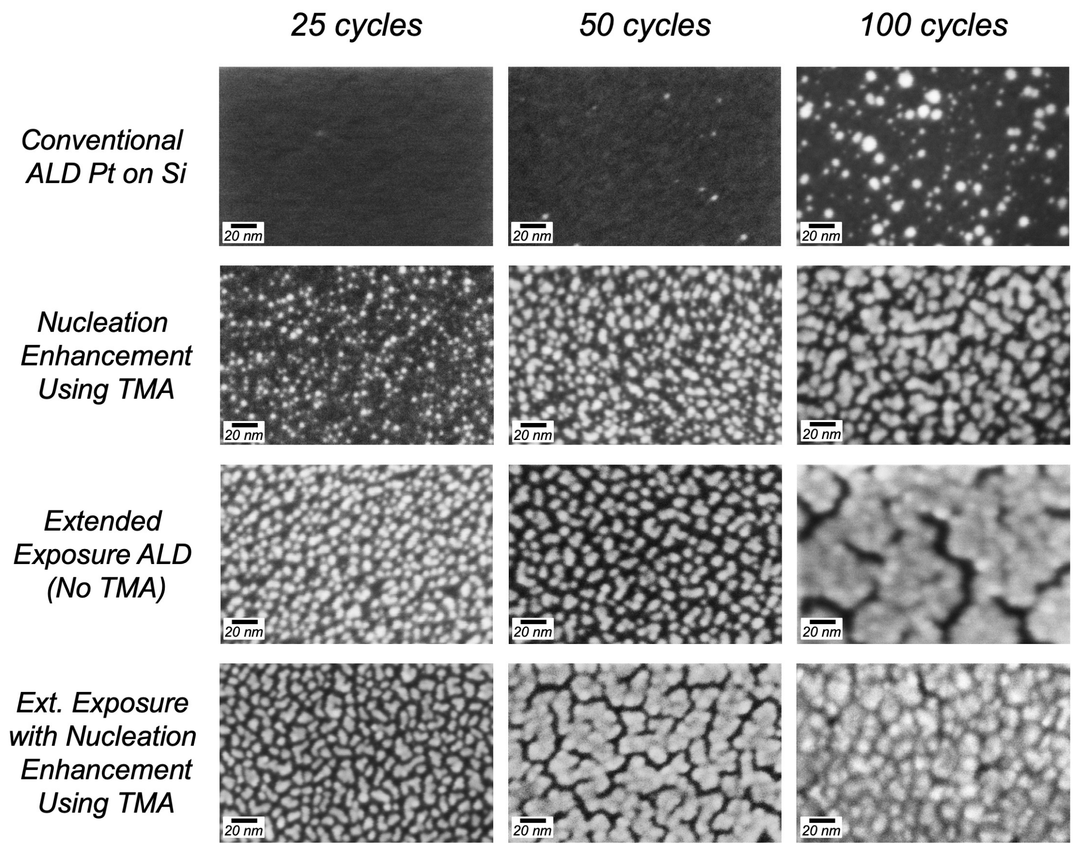
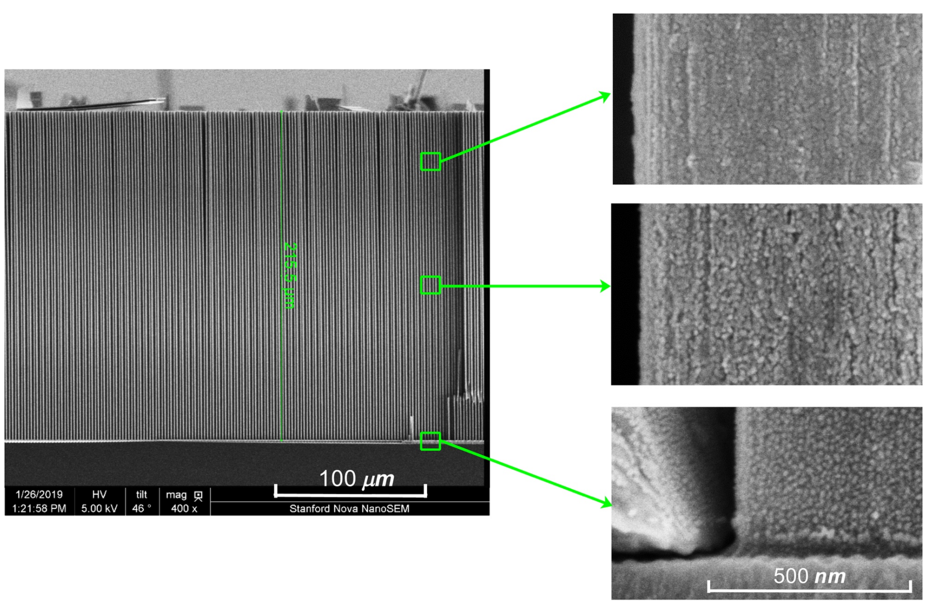


Fig. 1. ALD of Pt on planar Si surfaces vs. number of ALD cycles. Nucleation enhancement using TMA improved the coatings. Extended exposure times of 20 sec also improve the nucleation and aids in the diffusion of Pt into the structures. Estimated Pt thickness measurements using ellipsometry are beneath the images.



Fig, 2. SEM image of ultrahigh aspect ratio Si structures. ALD Pt covers the sidewalls of the patterned 215 micron deep nanoporous microstructures.