

High-Selectivity Ar/CF₄ Reactive Ion Etching of Colloidally Patterned Sapphire Nanostructures

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Sapphire nanostructures have emerged as a platform to engineer optical and surface properties for high-transmittance materials in applications such as anti-glare, anti-dust, anti-fogging, or scratch-resistant surfaces¹. Due to the chemical inertness of sapphire, these nanostructures can be used in extreme environments such as very high temperature, underwater, and aerospace conditions. However, current state-of-the-art processing for nanopatterned sapphire relies on complex, multi-step fabrication processes that combine multiple material deposition, lithography, laser processing, and etching steps that limit scalability and lead to high processing cost for large area substrates¹⁻³. This work addresses that limitation by developing a low-cost, scalable nanopatterning route for sapphire based on colloidal templates and simplified Reactive Ion Etching (RIE).

This work explores an alternative nanopatterning route for c-plane sapphire. The process is based on colloidal self-assembly of silica or polystyrene nanospheres, which defines the lateral feature size and fill factor. It is followed by e-beam deposition of nickel into the colloidal interstices to form a hard mask. A subsequent one-step Ar/CF₄ plasma sapphire etching is performed using RIE. The process concludes with piranha etching to remove the metallic mask, as shown in Figure 1. In this enhanced Ar/CF₄ plasma, CF₄ chemically attacks the Al-O bonds in sapphire, forming an AlF₃ passivation layer on the surface⁴, while Ar ions physically sputter away the AlF₃ without significantly eroding the nickel mask, thereby increasing etch selectivity. By eliminating conventional SiO₂ hard masks and photoresist-based lithography¹, as well as PMMA or resist layers for Ni mask fabrication², and instead leveraging bottom-up colloidal templates with a single metallic hard-mask deposition, the method simplifies processing while enabling tunable nanostructure dimensions over wafer-scale areas at low cost.

The initial RIE etching results presented here demonstrate 300 nm-high sapphire structures with local periodic patterns, as shown in Figure 2 and Figure 3a. Obtained etch rates were on the order of nanometers per minute, as seen in Figure 3b. The maximum resulting sapphire-to-nickel etch selectivity was 3.3, which is higher than the maximum reported in the literature for photoresist (1.4)⁵ or SiO₂ masks (2.1),^{1,3} but less than the etch selectivity of sapphire and a multilayer of SiO₂/Si/SiN (7),³ that requires multistep etching. These findings validate the feasibility of the colloidal assembly and nickel mask approach for sapphire nanopatterning. Also, the preliminary results highlight clear pathways, through optimization of mask chemistry, thickness, colloidal crystallinity, and plasma conditions, to further enhance etch selectivity and enable higher-aspect-ratio nanostructures with expanded optical design space, while preserving scalability and low processing cost for the applications mentioned above.

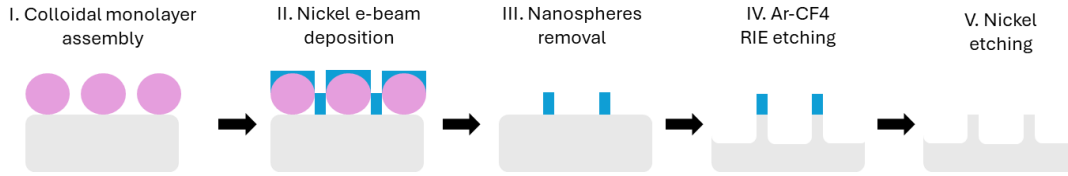


Figure 1. Fabrication process of nano-structures.

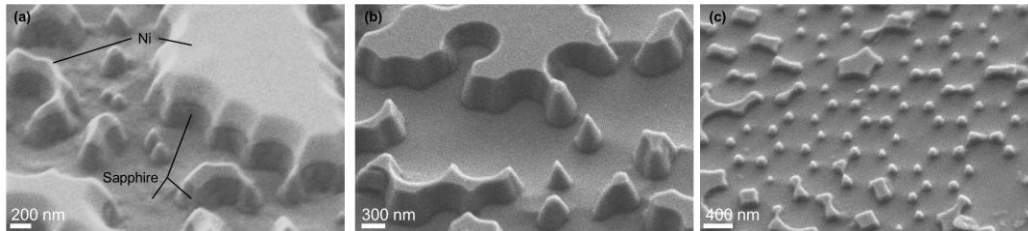


Figure 2. (a) SEM image of etched sapphire before nickel hard mask etching. (b) Etched sapphire structures with approximately 300 nm height without nickel mask. (c) Local periodicity of sapphire nanostructures without nickel mask.

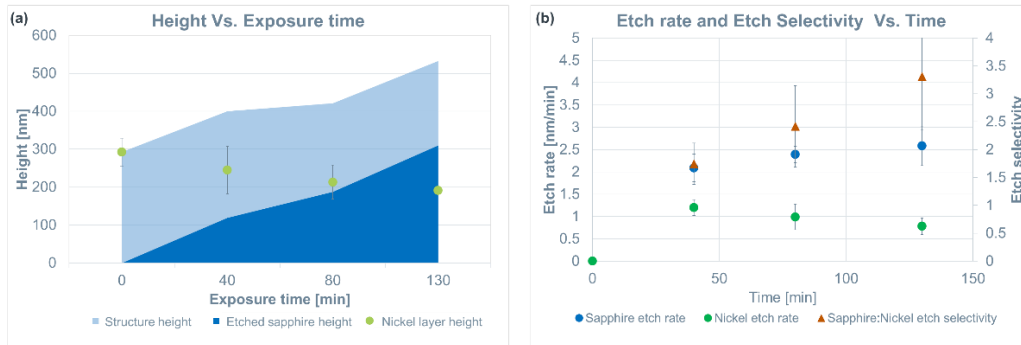


Figure 3. (a) Evolution of the nanostructures height over Ar/CF₄ exposure time. (b) Etch rate and sapphire:nickel etch selectivity over Ar/CF₄ exposure time.

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