Mesoporous Thin Film Quantum Materials via Block Copolymer Self-Assembly Patterned by Photolithography

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Primary CNF Tools Used: Oxford 81 etcher, VersaLaser engraver/cutter tool, ABM contact aligner

Abstract:

The use of block copolymers (BCPs) as structure directing or templating agents, offers facile pathways toward quantum metamaterials with highly tunable mesostructures via scalable solution processing. Here, we report the preparation of mesoporous niobium carbonitride-type thin film superconductors through spin-coating of a hybrid solution containing an amphiphilic BCP swollen by niobia sol precursors and subsequent thermal processing in combination with photolithography. Spin-coated as-made BCP-niobia hybrid thin films on silicon substrates after photolithographic definition are heated in air to produce a porous oxide, and subsequently converted to carbonitrides via high temperature treatment in reactive gases including ammonia. Electrical transport measurements show initial exponential rise in resistance before dropping to zero into a superconducting state. Such cost-effective and scalable solution-based quantum materials fabrication approaches may be integrated into existing microelectronics processing, combining the capabilities of soft matter self-assembly with quantum materials.

Summary of Research:

The general solution-based fabrication route toward NbCN-type thin films on silicon substrates is depicted in Figure 1, based upon past efforts to synthesize similar materials in the bulk [1]. The structure-directing BCP in the study is an amphiphilic triblock terpolymer poly(isoprene-*b*-styrene-*b*-ethylene oxide) (PI-*b*-PS-*b*-PEO, referred to as ISO hereafter), synthesized by sequential anionic polymerization. The inorganic niobia sol precursor is prepared from the hydrolytic condensation of niobium (V) ethoxide. Upon mixing the sol with ISO in tetrahydrofuran (THF) and subsequent spin-coating and self-assembly (Figure 1a,b), the niobia sol particles selectively mix with the hydrophilic PEO block of the ISO to form a nanostructured composite thin film.

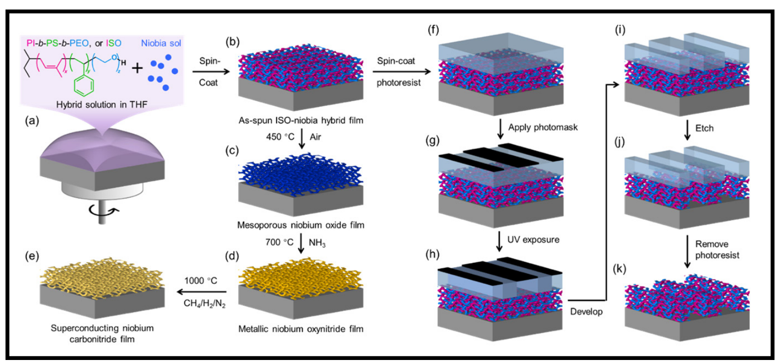

Figure 1: Schematic of solution-based fabrication processes. (a) ISO and niobia sol hybrid solution in THF is spin-coated on a silicon substrate. (b) As-spun ISO-niobia hybrid thin film. (c) Mesoporous niobium oxide thin film after heating in air at 450°C. (d) Metallic niobium nitride thin film after treatment in ammonia at 700°C. (e) Superconducting niobium carbonitride-type thin film after final treatment in carburizing gas at 1000°C. (f) – (k) Photolithography route to patterned thin films that can be further processed along (c) to (e).

Without post-deposition annealing such as solvent vapor annealing, the hybrid films are treated in air at 450°C to further condense the niobia and remove the structure directing ISO. The resulting niobium oxide thin films (Figure 1c) show locally ordered mesoporous structures,

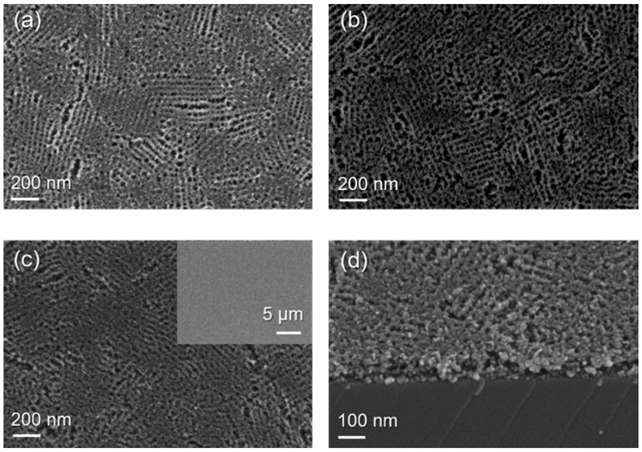

Figure 2: SEM images of thin films at different processing stages. Plan views of (a) the niobium oxide film; (b) the niobium nitride film; (c) the niobium carbonitride film (inset at low magnification). (d) 45-degree cross-sectional view of the niobium carbonitride film displaying the film edge on the cleaved silicon substrate.

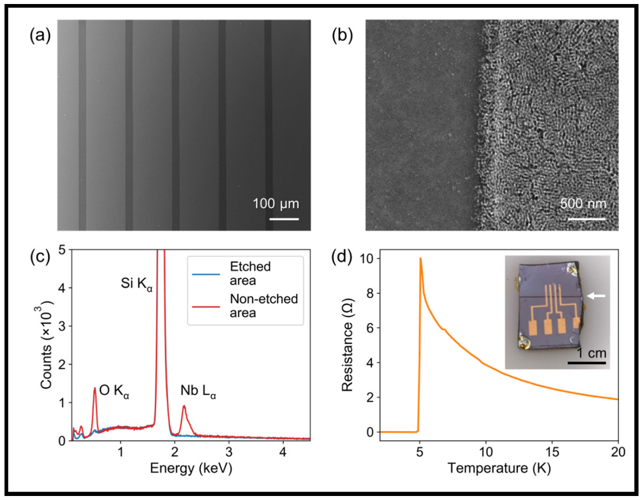

Figure 3: Lithographic patterning of spin-coated thin films. (a) Plan-view SEM image of niobium carbonitride thin film patterned through photolithography, with 25 µm wide strips etched away shown in dark. (b) Higher magnification SEM image of the patterned film showing the edge along with details of the self-assembled mesostructure. (c) EDS spectra of areas of plain film and etched film after 10-min CF_4 plasma etching. (d) Plot of resistance versus temperature from an individual patterned 400 µm wide strip thin film. Inset shows the single lithographically patterned niobium carbonitride strip (white arrow) with four co-linear metal contacts across the strip.

as evidenced by scanning electron microscopy (SEM, Figure 2a). X-ray scattering suggests the morphology is consistent with a deformed alternating gyroid structure, in which the niobia in the original hybrid film is retained as a single inorganic minority network replicating the PEO plus inorganic. To render the thin films electrically conducting, a nitridation step in ammonia (NH_3) at 700°C converts the mesoporous oxide into niobium nitride (NbN, Figure 1d), albeit with some oxygen (and vacancies) likely remaining. The mesostructure appears largely unchanged, with a slight coarsening of the nodes in the network (Figure 2b).

Finally, heating the NbN thin films to 1000°C in a mixture of methane (CH_4), hydrogen (H_2), and nitrogen (N_2), known as carburizing gas ($CH_4/H_2/N_2$), yields a superconducting niobium carbonitride (NbCN)-type material (Figure 1e) without substantial further growth in crystallite size. The overall mesoporous structure is retained, albeit with additional coalescence of struts (Figure 2c). With the simple spin-coating technique, a uniform thin film with arbitrary lateral dimensions can be fabricated without major macroscopic defects (inset of Figure 2c).

Photolithography was performed to illustrate compatibility of our solution-based synthesis approaches to mesoporous superconducting samples with typical semiconductor nanofabrication processing (Figure 1f-k).

First, a photoresist is applied on the ISO-niobia hybrid thin films pre-treated at 300°C to minimize swelling or dissolution by photoresist solution. After exposure using the ABM contact aligner and development, 25 μm wide strips of photoresist layers are removed. Pattern transfers are achieved by a combination of wet etching using buffered oxide etchant (BOE) and dry etching using oxygen plasma. The clear and sharp patterns demonstrate the viability for the superconducting thin films based on solution processing to be incorporated into standard microelectronic processing, with additional self-assembled 3D features at the mesoscale (Figure 3a,b).

A separate pattern was transferred from a shadow mask (fabricated using the VersaLaser engraver/cutter tool) through CF_4 plasma etching using the Oxford 81 Etcher. The CF_4 plasma etching can completely remove the ISO-niobia hybrid materials, as evidenced by the disappearance of the Nb La peak in energy-dispersive X-ray spectroscopy (EDS) spectra (Figure 3c). Films patterned via plasma etching (Figure 3d, inset, white arrow) have a superconducting transition temperature of 5 K (Figure 3d).

In summary, our work opens pathways toward solution-based thin film technologies at the intersection between soft matter self-assembly and quantum materials with tremendous academic as well as industrial potential.

References:

[1] Beaucage, P. A.; Van Dover, R. B.; DiSalvo, F. J.; Gruner, S. M.; Wiesner, U. B. Superconducting Quantum Metamaterials from Convergence of Soft and Hard Condensed Matter Science. Adv. Mater. 2021, 33, 2006975.

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