Synthesis of an Ordered Porous SiCN Ceramic Film by Self-Assembly of Inorganic-Organic Diblock Copolymer

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Introduction

Silicon carbide/silicon carbonitride (SiC/SiCN) as a typical non-oxide ceramic has been the most interested due to the unique physical and chemical properties such as high thermal conductivity, excellent thermal stability in air, high mechanical strength and chemical inertness. That make them attractive, for example, for high temperature catalysis supporters, separation and sensing, optical and electronic systems[1], as well as in the solid electrodes in a fuel cell need to be stable at a high operating temperature of between 600 and 1000°C [2]. Well-defined nanoporous SiCN materials are essential for a number of these applications.

Herein, we newly developed poly(vinyl)silazane-*block*-polystyrene (PVSZ-*b*-PS) *via* living free radical polymerization using 4-diethylthiocarbamoylsulfanulmethyl-benzoic acid as a reversible addition fragmentation chain transfer (RAFT) agent and 2,2'-azo-bis-isobutyrylnitrile as the initiating system. We also demonstrate a self-assembly approach to the preparation of large-scale, highly ordered nanoporous SiCN films. The SiCN precursor molecular are arranged into well-defined nanostructure by the self-assembly of poly(vinyl)silazane-*block*-polystyrene diblock copolymers. In addition, the pyrolysis of the ordered films to generate patterned arrays of ceramic nanostructures is described. The key to success of such a strategy is the survival of the original nanostructure through pyrolysis. This might appear extremely challenging, since a high ceramic yield requires heating the materials to temperature as high as 800°C and above.

Experimental

The synthesis of block copolymer was described elsewhere [3]. The thin film fabrication process is shown schematically in Figure 1. The process induces fours steps: (1) PVSZ-*b*-PS films were prepared by spin coating onto silicon wafers from dilute toluene solution. (2) Annealing the diblock copolymer film at 120°C for 24 hours under an applied electric field, causes the cylindrical microdomains to orient parallel to the field lines. The sample was subsequently increased up to 180°C for 1 hour for completely cross-linked PVSZ blocks, and then was cooled to room temperature. (3) The upper electrode was peeled away, and the PS domains were can be removed by rinsing with THF. (4) Finally, nanoporous PZSV film is pyrolyzed at 800°C under inert gas to form nanoporous SiCN ceramic film. The resulting nanoporous SiCN ceramic films were analyzed by atomic force microscopy (AFM) and field emission scanning electro microscopy (FE-SEM).

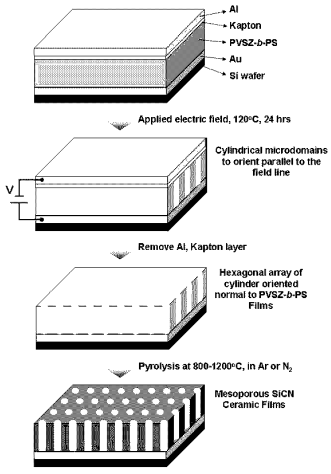

Figure 1. A schematic representation of the fabrication mesoporous SiCN ceramic films from PVSZ-*b*-PS diblock copolymer.

Results and discussion

The non-applied electric field film of the PVZS-b-PS shows the cylindrical nanodomains oriented normal to the surface, when thickness of film around 30-35 nm and after annealing at 180°C for 2 day in Ar. Figure 2 shows AFM images of a phase-separated film after removal of the PS block and pyrolysis at 900°C in Ar gas, illustrating that the cylinders are oriented perpendicular to the surface and showing short-range hexagonal ordering.

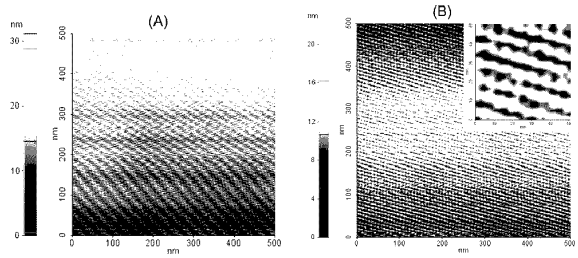

Figure 2. AFM images of PVSZ-*b*-PS thin film that were spin-coated on Si wafer then annealed at 180°C (A) and at 900°C (B) under an Ar atmosphere.

Following the procedure of Figure 1, we fabricated a film with thickness up to 500 nm. The morphology of film after applied electric field (250V/cm^2) at 120°C for 2 day is observed by AFM image, as shows in Figure 3.

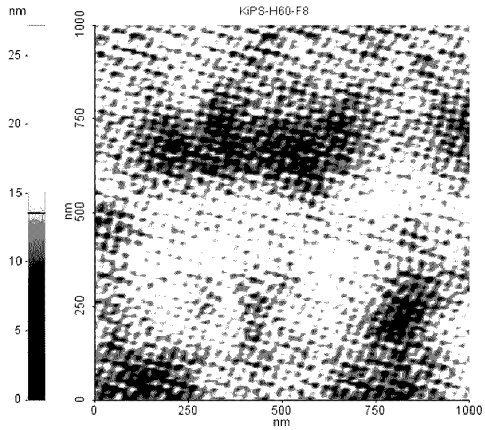

Figure 3. AFM image of PVSZ-*b*-PS film that was spin-coated on Si wafer then annealed at 120°C under an applied electric field in a vacuum.

The orientation-dependent polarization energy associated with the cylinders, dielectric bodies that are anisotropic in shape, are aligned the cylinders parallel to the electric field lines. Under strong enough fields, interfacial interactions can be overcome to produce cylindrical microdomains oriented normal to the substrate.

Conclusions

Finally, it was obviously demonstrated that polymer and ceramic nanostructures have been fabricated by using various organic-inorganic diblock copolymers from different pathway, which paved a variety of applications in the fields of tribological MEMS and chemical resistant microfluidics, in combination with new functional inorganic resins and different fabrication processes.

References

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