Chem. Mater. **2007,** *19,* 839−843

Biomimetic Approaches for Fabricating High-Density Nanopatterned Arrays

Jennifer N. Cha,*,† Yuan Zhang,‡ H.-S. Philip Wong,‡ Simone Raoux,† Charles Rettner,†
Leslie Krupp,† and Vaughn Deline†

IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120, and Department of Electrical Engineering and Center for Integrated Systems, Stanford University, Stanford, California 94305

Received October 18, 2006. Revised Manuscript Received December 6, 2006

A variety of alternative approaches to lithography have been investigated to address the many challenges currently associated with scaling of feature sizes. One of the more cost-effective techniques has been to use the intrinsic self-assemblying properties of AB diblock copolymers to make polymer thin films as nanometer etch masks. A more etch-resistant film can be fabricated through enrichment of domains within the block copolymer thin films with metals such as silicon. In contrast to previous methods for mineralizing polymer thin films, we demonstrate here a biomimetic approach for synthesizing two-dimensional silica nanopatterns at neutral pH and mild temperatures within polystyrene-*b*-poly-4-vinylpyridine thin films. We further show that one can employ these benign synthetic conditions to fabricate sub-20 nm features of phase change materials (PCM) while keeping the PCM film in its amorphous state in order to study the effect that scaling these materials has on their crystallization temperatures.

Introduction

With the continual shrinkage of dimensions in microelectronics, there have been numerous efforts to discover novel cost-effective methods for fabrication in the sub-50 nm regime. One approach has been to use the self-assemblying properties of block copolymers because of their natural ability to phase separate.[1−4] Thin film morphologies of polystyrene containing AB diblock copolymers, including polystyrene-*b*-polymethylmethacrylate (PS-*b*-PMMA),[5,6] polystyrene-*b*-polyethyleneoxide (PS-*b*-PEO),[7] and polystyrene-*b*-polyvinylpyridine (PS-*b*-PVP),[8] have been studied in detail in recent years. All three families of block copolymers have furthermore been used as templates to seed silicon and transition metal oxide growth selectively within the PMMA, PEO, or PVP domains. The oxide chemistries employed in the PS-*b*-PMMA and PS-*b*-PEO systems often use highly reactive metal halides ($SiCl_4$, $TiCl_4$) as precursors, which are difficult to handle and control.[9−10] When more stable silicon precursors, such as tetraethylorthosilicate (TEOS), are used, acid or base catalysts are used in conjunction with the polymer templates and these are either sequestered within one of the polymer block domains or introduced in the vapor phase.[11−19] Because the presence of acids or bases may affect the properties of the underlying substrates, their exclusion from the self-assembly process would greatly facilitate the use of block copolymer thin films as etch masks. Furthermore, because of the difficulties in confining a catalyst to only one of the block domains without diffusion into the other, development of a method that does not require a catalyst would enable reproducibility and improve manufacturing.

Some of the difficulties of using either highly reactive precursors or acidic or basic environments can be precluded by using a biomimetic approach. In nature, biosilicification has been demonstrated to occur through enzymatic catalysis, a process that transpires at neutral pH and ambient conditions

---

* To whom correspondence should be addressed. E-mail: chaj@us.ibm.com. Phone: (408) 927-1585. Fax: (408) 927-3310.

† IBM Almaden Research Center.

‡ Stanford University.

(1) Park, M.; Harrison, C.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. *Science* **1997**, *276*, 1401−1404.
(2) Black, C. T.; Guarini, K. W.; Milkove, K. R.; Baker, S. M.; Russell, T. P.; Tuominen, M. T. *Appl. Phys. Lett.* **2001**, *79*, 409−411.
(3) Cheng, J. Y.; Ross, C. A.; Smith, H. I.; Thomas, E. L. *Adv. Mater.* **2006**, *18*, 2505−2521.
(4) Hawker, C. J.; Russell, T. P. *Mater. Res. Soc. Bull.* **2005**, *30*, 952−966.
(5) Stoykovich, M. P.; Mueller, M.; Kim, S. O.; Solak, H. H.; Edwards, E. W.; de Pablo, J. J.; Nealey, P. F. *Science* **2005**, *308*, 1442−1446.
(6) Ryu, D. Y.; Shin, K.; Drockenmuller, E.; Hawker, C. J.; Russell, T. P. *Science* **2005**, *308*, 236−239.
(7) Kim, S. H.; Misner, M. J.; Xu, T.; Kimura, M.; Russell, T. P. *Adv. Mater.* **2004**, *16*, 226−231.
(8) Segalman, R. A.; Yokoyama, H.; Kramer, E. J. *Adv. Mater.* **2001**, *13*, 1152−1155.
(9) Kim, H.-C.; Jia, X.; Stafford, C. M.; Kim, D. H.; McCarthy, T. J.; Tuominen, M.; Hawker, C. J.; Russell, T. P. *Adv. Mater.* **2001**, *13*, 795−797.
(10) Kim, D. H.; Kim, S. H.; Lavery, K.; Russell, T. P. *Nano Lett.* **2004**, *4*, 1841−1844.
(11) Hayward, R. C.; Chmelka, B. F.; Kramer, E. J. *Adv. Mater.* **2005**, *17*, 2591−2595.
(12) Melde, B. J.; Burkett, S. L.; Xu, T.; Goldbach, J. T.; Russell, T. P.; Hawker, C. J. *Chem. Mater.* **2005**, *17*, 4743−4749.
(13) Pai, R. A.; Humayun, R.; Schulberg, M. T.; Sengupta, A.; Sun, J.-N.; Watkins, J. J. *Science* **2004**, *303*, 507−510.
(14) Cho, G.; Jang, J.; Jung, S.; Moon, I.-S.; Lee, J.-S.; Cho, Y.-S.; Fung, B. M.; Yuan, W.-L.; O'Rear, E. A. *Langmuir* **2002**, *18*, 3430−3433.
(15) Fujita, N.; Asai, M.; Yamashita, T.; Shinkai, S. *J. Mater. Chem.* **2004**, *14*, 2106−2114.
(16) Pai, R. A.; Watkins, J. J. *Adv. Mater.* **2006**, *18*, 241−245.
(17) Brinker, C. J.; Dunphy, D. R. *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 126−132.
(18) Nicole, L.; Boissière, C.; Grosso, D.; Quach, A.; Sanchez, C. *J. Mater. Chem.* **2005**, *15*, 3598−3617.
(19) Zhao, D.; Yang, P.; Huo, Q.; Chmelka, B. F.; Stucky, G. D. *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 111−121.

10.1021/cm062495i CCC: $37.00

starting with stable silicon precursors such as TEOS.[20] On this basis, researchers used block copolypeptides containing nucleophilic groups in one of the blocks to both catalyze silica sol−gel reactions at neutral pH and act as direct templating agents to produce well-defined silica structures.[21]

We demonstrate here that these biomimetic schemes can also be applied to block copolymer thin films where silicon alkoxide precursors such as TEOS are delivered to catalytic sites within the polymer films. Specifically, two-dimensional silica nanopatterns were synthesized using thin films of polystyrene-*b*-poly-4-vinylpyridine (PS-*b*-P4VP) as nanopatterned catalytic templates to synthesize silica from TEOS both at neutral pH and selectively within the pyridine domains. We furthermore show that all of the reactants can be delivered to the polymer film in the vapor phase, thereby removing any potential negative effect bulk solvent might cause, such as polymer delamination from the substrate and side sol−gel reactions. In contrast to published literature, we also found that the 4-vinylpyridine units are sufficiently nucleophilic to catalyze TEOS hydrolysis and condensation in less than 4 h.[15] Finally, we demonstrate that the mineralized silica−polymer films can also be used as patterned inorganic−organic bilayer resists for reactive ion etching (RIE) or ion milling into underlying substrates.

Experimental Section

Chemicals and Materials. All PS-*b*-P4VP copolymers were purchased from Polymer Source. TEOS (Sigma-Aldrich) was used as received.

Preparation of PS-*b*-P4VP Thin Films. Dilute solutions (0.5−1 wt %) of PS-*b*-P4VP were solubilized in either filtered toluene or cyclohexanone and spun-coat onto 1 in. silicon wafers. The polymer films were annealed under toluene vapor at 60 °C for 12 h. To image in height mode by AFM, we either immersed some of the films in filtered methanol overnight or exposed them to water vapor (60 °C) overnight.

Preparation of Silica−Polymer Composite Films. After characterization by AFM, the films were next exposed for variable lengths of time (5−16 h) to TEOS and water vapors. The vapors were created by placing two 1 mL glass vials with TEOS and water, respectively, inside a larger glass jar. The films were then placed in between the TEOS and water vials and the glass jar was then sealed and placed in a 60 °C oven for 5−16 h. After mineralization using the sphere-forming PS-*b*-P4VP polymer, the polystyrene domains were selectively removed by CO_2 reactive ion etching. In the cylindrical PS-*b*-P4VP systems, the polymers were removed after exposure to TEOS and water by heating the samples at 450 °C under nitrogen for 2 h.

Fabricating Sub-20 nm Features in PCM Films. Ten nanometer films of diamondlike carbon were first deposited on 10−20 nm sputtered films of amorphous GeSb. Thin films of PS$_{35.5\mathrm{K}}$-*b*-P4VP$_{3.6\mathrm{K}}$ were next spun directly onto the dlc films and toluene-annealed for 12 h at 60 °C. The films were then exposed to TEOS and water vapor at 60 °C for 12 h. The polystyrene domains and dlc between the silica nanospheres were removed by a 50 s CO_2 RIE treatment. Using the nanopatterned dlc as a mask, we ion-milled the PCM filmsfor 70 s to reveal a nanopatterned GeSb film whose dimensions were on the order of 12 nm.

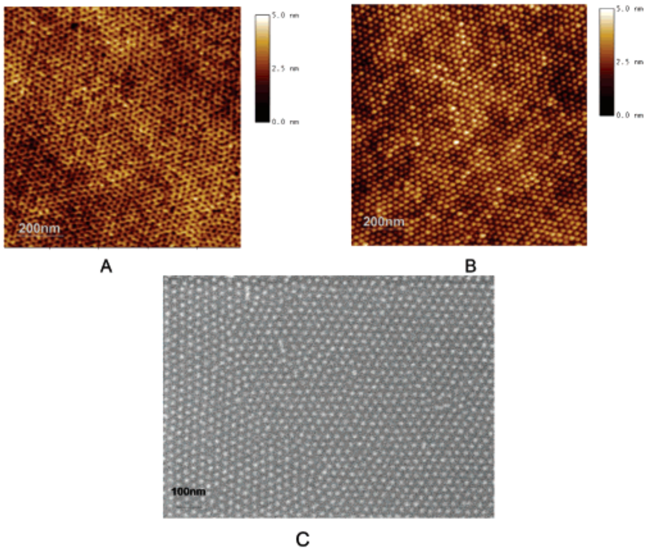

Figure 1. (A) Height-mode AFM image of a PS$_{35.5\mathrm{K}}$-*b*-P4VP$_{3.6\mathrm{K}}$ after exposure to toluene vapor for 12 h followed by an overnight immersion in methanol. (B) Height-mode AFM image of a PS$_{35.5\mathrm{K}}$-*b*-P4VP$_{3.6\mathrm{K}}$ thin film after annealing under toluene vapor followed by exposure to TEOS and water vapors at 60 °C for 8 h. (C) SEM image of sample shown in Figure 1B.

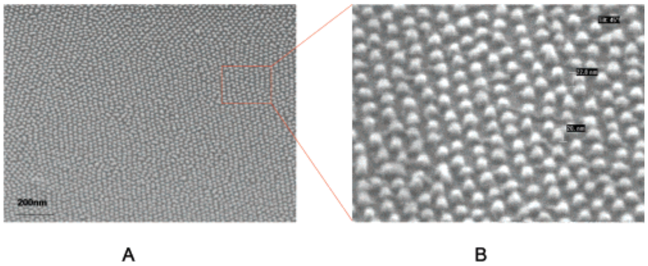

Figure 2. (A) SEM image of sample shown in Figure 1C after 50 s CO_2 RIE. (B) Higher-magnification image of sample shown in Figure 1A.

Results and Discussion

Thin films of PS-*b*-P4VP were spun cast from dilute solutions (0.5−2% w/v) onto UV−ozone-treated 1 in. silicon wafers and solvent-annealed at temperatures ranging from 25 to 65 °C to promote phase separation and long-range order.[7] Spherical PS-*b*-P4VP morphologies (PS$_{35.5\mathrm{K}}$-*b*-P4VP$_{3.6\mathrm{K}}$) were annealed under toluene vapor for 12 h and immersed in filtered methanol for another 12 h to promote chain rearrangement of the poly-4-vinylpyridine chains; this also allowed characterization by height-mode atomic force microscopy (AFM) (Figure 1A). The imaged films were then exposed to TEOS and water vapors at 60 °C for variable lengths of time (4−16 h).

Similar to the earlier biomimetic silica work using nucleophilic block copolypeptides,[21] it was reasoned that the 4-vinylpyridine moieties of PS-*b*-P4VP would be sufficiently catalytic to facilitate the hydrolysis of TEOS at neutral pH. Because the introduction of solvents can either swell or cause delamination of thin polymer films from substrates, both TEOS and water were delivered to the polymer surfaces in the vapor phase. Because polystyrene is highly hydrophobic and TEOS hydrolysis and condensation can occur only in

---

(20) Cha, J. N.; Shimizu, K.; Zhou, Y.; Christiansen, S. C.; Chmelka, B. F.; Stucky, G. D.; Morse, D. E. *Proc. Natl. Acad. Sci., U.S.A.* **1999**, *96*, 361−365.

(21) Cha, J. N.; Stucky, G. D.; Morse, D. E.; Deming, T. J. *Nature* **2000**, *403*, 289−292.

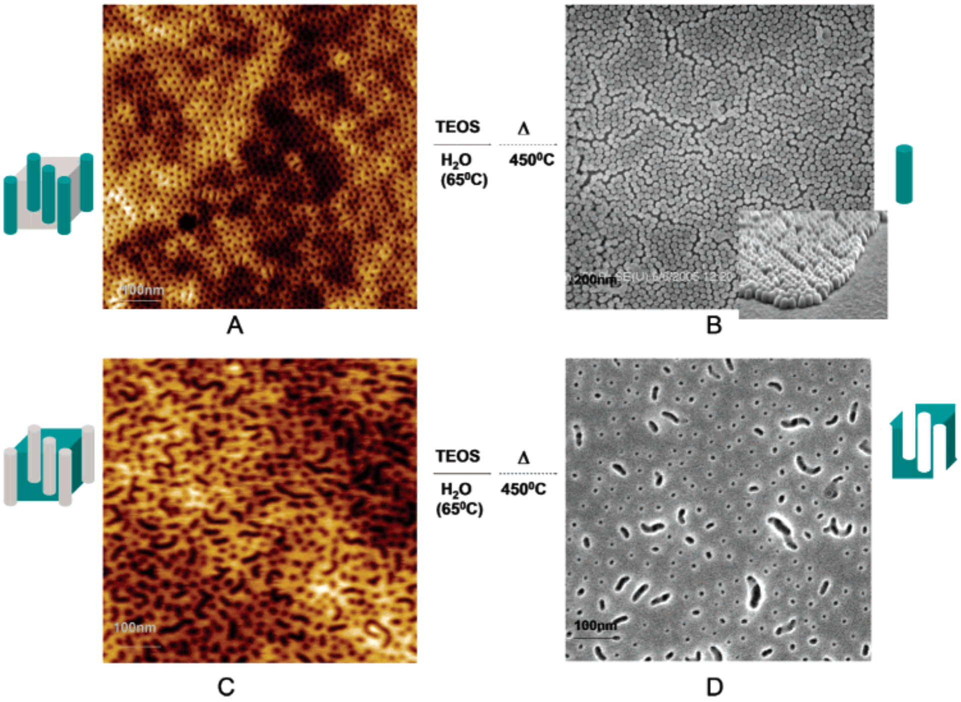

Figure 3. (A) Height-mode AFM image of a PS$_{31.9K}$-*b*-P4VP$_{13.2K}$ film after annealing in toluene and water. (B) SEM image of the silica pattern obtained after exposing the PS$_{31.9K}$-*b*-P4VP$_{13.2K}$ film to TEOS followed by calcination at 450 °C. (C) Height-mode AFM image of a PS$_{20.5K}$-*b*-P4VP$_{36K}$ film after annealing in toluene and water. (D) SEM image of the silica pattern obtained after exposing the PS$_{20.5K}$-*b*-P4VP$_{36K}$ film to TEOS followed by calcination at 450 °C.

the presence of a catalyst such as 4-vinylpyridine, the sol–gel reactions should occur exclusively within the pyridine domains. As is demonstrated in panels B and C of Figure 1, after exposure of the PS-*b*-P4VP films to TEOS and water vapors for 4 h, silica polymerization was clearly visualized by both AFM (Figure 1B) and scanning electron microscopy (SEM; Figure 1C). Auger electron spectroscopy quantified the atomic concentration of silicon in the films to be 22%. Height-mode AFM analyses revealed that the spherical P4VP domains had become filled with silica and that the reaction conditions did not appear to alter the original order or nanostructure of the polymer thin film (Figure 1B). Interestingly, leaving the films under TEOS and water vapor for as long as 24 h did not appear to cause major changes to the overall film quality as well as block copolymer nanopattern. However, leaving the films under TEOS and water vapor for extended periods of time up to 96 h visually showed a significant amount of silica overgrowth on the film. Because the synthesis conditions here seem mainly dependent on the reaction temperatures and the time exposed to TEOS and water vapors, it may be possible to quantifiably control the silica synthesis by varying these parameters.

As will be discussed later in more detail, cross-sectional transmission electron microscopy (TEM) of these films showed a monolayer of ∼10 nm silica spheres embedded within the PS-*b*-P4VP micelles; the silicon enrichment of the PVP micelles afforded visualization of the PVP domains without the need to prestain the polymer film (Figure 4B). After exposing the sphere-forming PS$_{35.5K}$-*b*-P4VP$_{3.6K}$ thin films to TEOS and water vapor, we selectively removed the polystyrene domains by RIE, producing hexagonal arrays of silica dots approximately 10–15 nm in size. To use such sphere-forming organic–inorganic nanopatterns as etch masks, a single layer of silica nanospheres is desired; this was achieved by systematically tuning the film thicknesses such that only a single layer of PS-*b*-P4VP spherical micelles is obtained on the substrate. It is furthermore well-understood for PS-*b*-PVP block copolymers that a brush layer of PS-*b*-PVP assembles first at the silicon substrate because of PVP's affinity for the native oxide surface. Because of the presence of this PVP brush layer at the polymer–substrate interface, it is likely that exposing the PS-*b*-P4VP films to TEOS and water vapor also caused a uniform layer of silica to form at the polymer–substrate interface. Although this was not clearly observed by cross-sectional TEM analysis, the presence of a thin silica layer at the polymer–substrate interface may explain the longer lengths of time needed to both RIE and ion mill into the underlying substrates, as will be shown later.

As with the sphere-forming polymer, thin films of cylindrical (PS$_{31.9K}$-*b*-P4VP$_{13.2K}$) and inverse cylindrical (PS$_{20.5K}$-*b*-P4VP$_{36K}$) morphologies of PS-*b*-P4VP block copolymers were spin-cast onto silicon substrates, solvent-annealed under toluene and water, and characterized by AFM (images A and C of Figure 3). The thin films of the cylindrical and inverse cylindrical forming PS-*b*-P4VP block copolymers were next exposed to TEOS and water vapors for 5 to 16 h, followed by calcination of the samples at 450 °C for 2 h under nitrogen. As opposed to the spherical PS-*b*-P4VP system, because the silica growth in the cylindrical and inverse cylindrical films occurred throughout the entire thickness of the PS-*b*-P4VP film, all of the polymers could be removed by calcination, leaving behind silica nanopatterns that directly reflected the P4VP morphologies (images B and D of Figure 3). In the cylindrical PS-*b*-P4VP thin films, hexagonally packed 50 nm silica posts remained

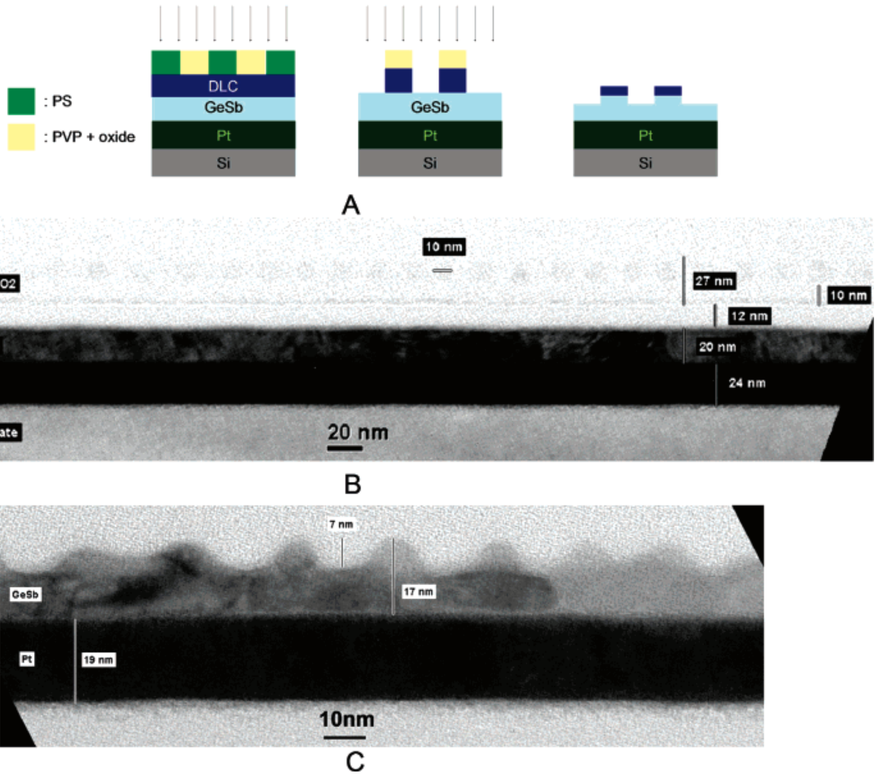

Figure 4. (A) Schematic diagram of the process flow used to fabricate 20 nm features in PCM films. Ten nanometer films of diamondlike carbon (dlc) are first deposited on thin, sputtered films of GeSb. Thin films of $PS_{35.5K}$-*b*-$P4VP_{3.6K}$ are next spin-coated onto the dlc layer, and silica was selectively mineralized in the poly-4-vinylpyridine domains from TEOS and water vapors. The polystyrene domains and the dlc between the silica spheres was then etched for 60 s using a highly directional CO_2 reactive ion etch (RIE) tool (Unaxis), leaving behind nanopillars consisting of oxide and dlc on top of the GeSb layer. The pattern was next transferred into the PCM film by ion milling with Ar ions (300 eV, VEECO) at 10 degrees for 90 s while the sample was rotated. (B) Cross-sectional TEM image of a 20 nm $PS_{35.5K}$-*b*-$P4VP_{3.6K}$ film on dlc on GeSb after exposure to TEOS. (C) Cross-sectional TEM image of the nanostructured GeSb layer after ion milling.

after calcination of the polymer (Figure 3B); in the inverse cylindrical film, a porous silica template containing approximately 20 nm pores was observed (Figure 3D).

One traditional method for using block copolymer thin films as pattern-transfer masks has been to translate the nanometer features into underlying inorganic substrates, such as silicon dioxide or silicon nitride.[1] Another route recently demonstrated by Cheng et al. used the silicon-containing block copolymer, poly(styrene-*b*-ferrocenyldimethylsilane), where the latter block acted directly as an etch resist to produce magnetic nanopattern arrays.[22] We show here that selectively incorporating silica into the pyridine domains of PS-*b*-P4VP thin films also produces inorganic−organic bilayer resists that can be used to etch nanometer features into an underlying substrate.

To demonstrate this application, the silicon-enriched PS-*b*-P4VP films were used to pattern high-density sub-20 nm arrays of phase-change materials (PCM) for nonvolatile memory applications. One of the key fundamental questions regarding the use of phase-change materials for devices is their scaleability and in particular how the feature sizes affect the materials' amorphous to crystallization temperatures. To execute these X-ray diffraction studies, we require high-density nanopatterned arrays of phase-change material larger than a few millimeters; because obtaining long-range order is not a prerequisite, using such silica-enriched block copolymer films to produce sub-20 nm domains of PCM is very ideal.

To develop a pattern-transfer method for phase-change materials, thin films of the sphere-forming PS-*b*-P4VP were spin-cast onto 10 nm films of diamondlike carbon (dlc) that was deposited on 10−20 nm sputtered amorphous germanium antimony (GeSb) films. GeSb has been shown to be a promising phase-change material because of its high crystallization temperature of ∼250 °C with good scaling behavior for thin films.[23] As before, the polymer films were solvent-annealed in toluene and then exposed to TEOS and water vapors at 60 °C. The ability to induce order in the PS-*b*-P4VP thin films using solvent annealing was ideal here because the low temperatures used (<60 °C) prevented any crystallization of the as-sputtered amorphous GeSb thin films. In this way, any effects scaling the GeSb structures below 20 nm might have on the crystallization temperature could still be investigated.

The silicon-enriched micelles of the spherical PS-*b*-P4VP films provided enough etch resistance to RIE that the block copolymer patterns could be transferred into the dlc layer, which in turn could act as a further resist for ion milling into the underlying GeSb film. Cross-sectional TEM imaging of the films after TEOS exposure clearly shows the silicon-enriched domains within the two-dimensional PS-*b*-P4VP

---

(22) Cheng, J. Y.; Ross, C. A.; Chan, V. Z.-H.; Thomas, E. L.; Lammertink, R. G. H.; Vansco, G. J. *Adv. Mater.* **2001**, *13*, 1174−1178.

(23) Raoux, S.; Rettner, C. T.; Jordan-Sweet, J.; Deline, V. R.; Philipp, J. B.; Lung, H.-L. *Proceedings of the European Symposium on Phase Change and Ovonic Science*, 2006; pp 127−134.

micelle arrays (Figure 3A). After undergoing RIE for 50 s followed by ion milling for 70 s, a nanostructured GeSb film showing 10 nm features was clearly visible by cross-sectional TEM (Figures 3B). A more systematic study using various RIE and ion milling times is currently underway to ultimately produce well-separated high-density sub-20 nm arrays of phase-change materials. In summary, we have demonstrated here the feasibility of using nucleophilic block copolymer films as biomimetic templates to produce silica nanopatterns on solid supports under ambient conditions and at neutral pH. Because both the hydrolysis and condensation reactions of TEOS were confined to the catalytic 4-vinylypyridine sites, silica nanostructures having high fidelity to the original block copolymer morphology could be fabricated. Furthermore, because all of the reactants were delivered in the vapor phase, any negative effects bulk solvent might have on the block copolymer films were removed. Finally, we also demonstrated that selectively enriching the 4-vinylpyridine domains with silicon produced a composite inorganic–organic film that can be used as an alternative resist etch mask to produce sub-20 nm features in other materials, such as those used for memory applications.

Acknowledgment. This work was partially supported by the Semiconductor Research Corporation (Contracts 2006-OJ-1406 and 2006-VJ-1429). We thank H. C. Kim, R. D. Miller, J. Frommer, and P. Rice for experimental assistance and advice.

CM062495I