Published in final edited form as:

J Colloid Interface Sci. 2011 December 15; 364(2): 546–554. doi:10.1016/j.jcis.2011.08.076.

Sub-Minute Formation of Supported Nanoporous Mesoscale Patterns Programmed by Surface Energy

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Abstract

We demonstrate an original and powerful concept for elaborating spontaneous, high fidelity patterns of nanoporosity from nanoscale building blocks using patterned surface chemistry (i.e., “surface energy gating”) to corral the growth of colloidal structures at a solid surface. Composite films consisting of polymethylsilsesquioxane nanoparticles uniformly dispersed in polypropylene glycol polymer were examined at temperatures beyond the decomposition of the polymer as a function of the substrate surface energy to clarify nanoparticulate ensemble behavior. The principle behind this colloidal assembly can be understood by taking into consideration the entropy and enthalpy dictating the mutual interactions between substrate surface, polymeric solvent, and dispersed colloids in the decomposition regime. The relevance of this research is shown by demonstrating how the principle of surface energy gating can be utilized to achieve spontaneous and controllable spatial patterns of nanoporous, high surface area thin films in a cost-effective and energy-efficient manner via brief thermal exposure. The simplicity and general nature of this methodology are further exemplified by showing the facility with which high-contrast fluorescent bioconjugate arrays can be prepared from nanoporous organosilicate patterns.

Keywords

Patterning; Surface energy; Nanoporous films; Nanoparticle-polymer systems; Entropy; Enthalpy

INTRODUCTION

Spontaneously self-assembled systems that are formed through thermodynamic interactions between individual components is a rapidly growing area of research as it offers facile means to fabricate uniquely tailored nanostructures. Approaches involving the use of nanoparticles as individual building blocks for realization of such systems are especially

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Supporting Information Available: Optical micrograph images of large area NPO patterns used for ellipsometer characterization and the real time video of the spontaneous pattern formation are available in the supplementary information provided online (<http://www.sciencedirect.com>).

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relevant. Such “bottom-up” fabrication methodologies offer unprecedented control on fine tuning the optical, mechanical and electrical properties of the resultant material. Towards this, self organization of nanoparticles dispersed in polymers is by far the most rigorously studied areas of research.[1–13] In such systems, nanoparticle distribution within the polymer is primarily determined by the interplay between entropic and enthalpic effects between the dispersed nanoparticles and the polymer chains.[5, 8, 10] Such an interplay has been efficiently exploited to fabricate novel nanoparticle multilayered films to coatings that can self heal upon damage.[8, 14] In these studies, the role of the surface chemical functionality over the bulk film morphology is often overlooked as the substrate interface effects are effectively shielded from the bulk through the formation of a wetting polymer layer or a layer of segregated nanoparticles at the interface.

Three dimensional bulk control of nanostructure in thin films through the use of chemically patterned substrates was however demonstrated for block copolymer systems.[2, 15] It was reported both theoretically and experimentally that through the use of appropriate surface gratings and boundary conditions, block copolymer orientation may be accurately controlled. Preferential wetting behavior of the individual blocks of the copolymer with the chemically patterned surfaces was the key to achieving this nanoscale orientation provided commensurability of the stripe pattern and the block copolymer period was satisfied. This concept has been further expanded to achieve precisely placed nanoparticle arrays over chemically patterned substrates[2].

All the reported systems were however restricted to temperatures at or below the glass transition temperature of the polymers. We have recently shown that when systems bearing crosslinkable and temperature stable nanoparticles dispersed in polymers are subjected to temperature above the decomposition temperature of the polymer, it was possible to rapidly fabricate highly porous nanoparticulate thin films with exquisite control on their nanostructure.[16] Here, both the magnitude of the thermal input provided and the surface chemical functionality of the substrate determined the equilibrium state of the system following the curing/calcination process. The role of the substrate surface chemical functionality becomes dominant in such a scenario as preferential wetting of either of the phases (polymer/dispersed nanoparticles) at the interface leads to a profound morphology change across the entire bulk of the film upon reaching equilibrium. Here, we demonstrate that through the use of chemically patterned substrates, this system behavior may be exploited to achieve spontaneously patterned nanostructured thin films whose properties are dictated by the underlying substrate surface. This is the first time surface chemical functionality, with no imposed boundary conditions are utilized to precisely control the bulk nanostructure within nanoparticle based films as thick as 400 nm.

The implications of this research are many. It offers means to facile patterning of nanoporous films and fabrication of other exotic thin film nanostructures with spatially graded optical, mechanical and electrical characteristics simply by manipulating the substrate chemical functionality. Scheme 1 illustrates the process for surface-guided formation of nanoporous organosilicate (NPO) patterns. Polymethylsilsesquioxane (PMSSQ) nanoparticle-polypropylene glycol (PPG) films were used in this study, deposited on chemically patterned substrates and subjected to a high temperature curing/calcination step (Here, high temperature implies that the system was subjected to temperatures above the decomposition temperature of PPG (> 200 °C). The reported procedure therefore addresses the long standing problem inherent to nanoporous films, i.e., the challenge in obtaining patterned nanoporous thin films. Conventional photolithography often fails when patterning these structures due to their high surface areas, interconnected porosity and their fragile nature resulting in significant damage and loss of functionality. Thus, the process often necessitates a post-patterning repair step.[17, 18]

MATERIALS AND METHODS

Preparation of NPO Precursor Solution

Commercially available PMSSQ (GR650F, Tehneglas, Inc.) was used for the preparation of PMSSQ nanoparticles. Propylene glycol methyl ether acetate (PGMEA 98%, Sigma-Aldrich) and polypropylene glycol (PPG, average molecular weight (M_n) of 425, Sigma-Aldrich) were used as received. The preparation of precursor solutions follows closely the procedures used in a previous communication.[16] Briefly, 30% (w/w) solutions of PMSSQ and PPG in PGMEA were prepared separately and sonicated to ensure complete dissolution of the respective solutes. These individual stock solutions were then mixed together at a 1:1 (w/w) ratio and sonicated to achieve a homogenous mixture with a final PMSSQ:PPG:PGMEA composition of 3:3:14 (w/w/w). All films were deposited from this precursor solution. “NPO precursor solution” refers to the solution that was used to obtain the nanoporous organosilicate films. Any reference to “PMSSQ solution” in this work simply refers to a 1% (w/w) solution of PMSSQ in PGMEA.

Surface Energy Measurements

Surface energy values of the various surfaces used in this study were calculated from the static contact angle measurements of three probe liquids: diiodomethane, formamide and deionized water. A VCA Optima (AST products Inc) contact angle measurement system was used for this purpose and the in-built surface energy calculator software (SE2500) was used to arrive at the reported values, calculated using the geometric mean approach.[19]

Chemically-Patterned Substrates

Scheme 2 shows the process flow diagram for achieving a chemically patterned surface on a silicon substrate. In this process, high surface energy regions were defined by plasma activated thin PMSSQ films whereas the low surface energy regions were defined by hydrogen terminated silicon surface. First, a thin film (~ 14 nm) of PMSSQ was deposited on silicon substrates by spin coating a 1% (w/w) PMSSQ solution in PGMEA at 3000 rpm/30 s followed by a curing step of 450 °C/2 min. The films were then exposed to low power carbon dioxide plasma using a customized capacitively-coupled plasma enhanced chemical vapor deposition (PECVD) to increase its surface energy through the formation of Si-COO⁻ and Si-O⁻ moieties[20, 21], conducive towards pore collapse. The following conditions were used for the plasma treatment: base pressure, 20 mTorr; working pressure, 550 mTorr; CO₂ flow rate, 50 sccm; power: 6 W; and treatment time, 4 min. This effectively resulted in highly hydrophilic surfaces with a measured surface energy values of ~60 mJ cm⁻². Defining distinct surface energy regions (as required to control porosity) on the silicon substrate was accomplished through photolithography and subsequent etching of the exposed PMSSQ film patterns by a brief hydrofluoric acid (HF) dip (1:10 HF:water). After the complete removal of the exposed PMSSQ patterns, the HF etchant solution also passivates the now exposed silicon surface through the formation of Si-H surface moieties (conducive towards porous film formation with a measured surface energy value of ~46 mJ cm⁻²). A typical etch was completed within 30 seconds, as evidenced by the displacement of the aqueous etchant solution from the etched regions due to increased hydrophobicity of the resultant Si-H terminated surfaces.

Spontaneous Patterning of NPO Films

Spontaneously patterned nanoporous organosilicate films were achieved by depositing the NPO precursor solution on the chemically patterned surfaces followed by high-temperature curing/calcination. Film deposition was performed by spin coating at 3000 rpm/30 s followed by immediate subjection to high temperature by placing the substrates on a pre-

heated hotplate. This led to spontaneously patterned regions of thin films with distinct degree of porosities as determined by the surface chemical functionality of the underlying substrate. Temperatures of 250 °C, 350 °C, 450 °C, and 550 °C were used in this study. All films were cured for 5 min unless otherwise specified. For time dependant studies of the nanostructure evolution, films were cured at 540 °C for different times ranging from 5 s to 120 s.

Characterization of the NPO patterns

Optical characterization of the porous and nonporous films was performed using variable angle spectroscopic ellipsometry (VASE™, J.A Wollam, Inc.) to obtain thickness, refractive indices and a depth profile of the refractive indices using Cauchy and modified Cauchy model with graded layers.[22] Measurements were taken at 60° and 70° incident angles between 300 to 1200 nm incident wavelengths. All refractive index values reported correspond to values measured at 630 nm wavelength unless otherwise specified. Large-area patterns $1 \times 1 \text{ cm}^2$ were generated to facilitate taking ellipsometer data for distinct patterns of thin films from the same substrate (Supporting Information, Figure S1a).

Bioconjugation of Protein A-FITC on Patterned NPO Films

Protein A conjugated with fluorescein isothiocyanate (Protein A-FITC) was purchased from Sigma-Aldrich and used as received without further purification. Buffers used were 2-(*N*-morpholino)ethanesulfonic acid (MES, Sigma-Aldrich) and Dulbecco's phosphate buffered saline (PBS, Sigma-Aldrich). EDC (1-Ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride) and sulfo-NHS (*N*-hydroxysulfosuccinimide) were purchased from Pierce Biotechnology and used for the conjugation of Protein A-FITC to NPO surfaces. Immediately prior to bioconjugation, patterned films were subjected to a mild CO₂ plasma treatment to functionalize the surfaces with oxygen-containing (e.g., hydroxyl, carboxyl) groups. Plasma treatment was conducted using conditions described above.

A two-step coupling protocol with EDC and sulfo-NHS was used to convert carboxyl-functionalized films into amine-reactive surfaces.[23] Briefly, for every 1 ml of activation buffer (0.1 M MES, 0.5 M NaCl, pH 6.0), 0.4 mg EDC and 1.1 mg of sulfo-NHS were added. The films were then immersed in this solution for 15 min at room temperature. Following this incubation period, the films were subsequently washed with PBS. Protein A-FITC was diluted to a final concentration of 10 µg/ml in PBS buffer (pH 7.1) and enough protein solution was added to cover the entire film surface (~2 ml) and incubated for at least 2 hours at room temperature (22 °C) and stored overnight at 4 °C. Following the incubation period, loosely bound protein molecules were removed by gently washing the substrates 3× with fresh PBS (pH 7.1). The bioconjugated substrates were stored in PBS prior to fluorescence imaging. Imaging was performed using an Olympus BX51W1 fluorescence microscope with a 150 W Hg lamp and a FITC-3540B filter set to "zero pixel shift" (Exciter 482 ± 17 nm, Emitter 536 ± 20 nm, Dichroic 446–500 nm center wavelength with a bandwidth of 513–725 nm, Semrock, Rochester, NY). The samples were observed and imaged using a 4× objective lens (Olympus).

RESULTS AND DISCUSSION

Temperature-Dependent Surface Energy Gated Nanostructures

Nanoparticle-polymer systems subjected to temperatures above the decomposition temperature of the polymer serve as interesting model systems where ensemble behavior of the nanoparticles may be studied relatively easily employing non-invasive optical characterization techniques. For systems comprising chemically homogenous nanoparticles, the index of refraction of the film is governed by the inherent refractive index (*n*) of the

nanoparticles as well and the volume fraction of voids introduced into the film during film formation. Therefore, a study of the refractive index profile across the thin film may be used as an indirect measure of the density distribution of the nanoparticles across the film.

Using nanoparticles (3–7 nm) of PMSSQ dispersed in PPG, we have demonstrated that the increased entropy of the nanoparticles upon PPG decomposition translated to its random Brownian motion, with the inter-particle crosslinking finally driving the system to a new equilibrium. While curing/calcination temperature largely determined the final pore volume fraction and film thickness, substrate surface energy played a critical role in determining whether the final state of the system was driven towards forming porous or dense films. Nanoporous film formation occurred when the surface energy of the substrate lay between 28 mJ cm^{-2} and 50 mJ cm^{-2} . Substrates with surface energies $<28 \text{ mJ cm}^{-2}$ led to discontinuous films due to excessive de-wetting of the film, while substrate surface energies exceeding 56 mJ cm^{-2} gave rise to pore collapse resulting in formation of a dense film upon curing/calcination.

In this paper, chemically patterned surfaces were defined by photolithographically patterned regions of hydrogen terminated silicon (Si-H) and plasma oxidized PMSSQ thin film surfaces. Scheme 2 provides more details on surface patterning employed in this study. Hydrogen terminated silicon surfaces with a measured surface energy of $\sim 46 \text{ mJ cm}^{-2}$ are the regions conducive to porous film formation. Plasma oxidized PMSSQ film surfaces, with a measured surface energy of $\sim 60 \text{ mJ cm}^{-2}$ were used as surfaces to induce pore-collapse.

Figure 1(b–e) shows the substrate surface energy directed nanostructured film patterns obtained at various curing/calcinations temperatures. The contrast between the films present on the two distinct surface energy regions (Si-H terminated silicon surface and plasma modified PMSSQ thin films) are easily distinguished by the difference in reflectivity arising from changes in both thickness and refractive index (n) of the regions. Figures 1f and g show the plot of n and thicknesses of the obtained film patterns as a function of curing/calcination temperature respectively. As a reference, n and the thickness for non-porous PMSSQ films are also plotted.

The obtained films indicate an interesting trend in their nanostructure evolution. The magnitude of the thermal input determines the pore volume fraction within the films in both surface energy regions; albeit following divergent trends. For the films on Si-H terminated silicon surfaces, n progressively decreases as a function of increasing temperature indicating the pore volume fraction within the films increases. This was accompanied by a slight increase in thicknesses of the obtained films from 250°C to 350°C , indicating no mass loss of the nanoparticles from the film occur at these curing/calcination temperatures. However, temperatures above 350°C results in a remarkable drop in film thicknesses. We attribute this thickness drop at high temperatures to the increased kinetic energy of the nanoparticles at those temperatures being great enough for the nanoparticles to completely escape the system.[16]

On the other hand, nanoparticulate films obtained over the high surface energy, plasma oxidized PMSSQ films displayed opposite trend. The n of these films was significantly higher, indicating a lower pore volume fraction within these films. The films progressively densified with increasing temperatures with a consequential drop in thickness. Comparing the n of these films with that of non-porous PMSSQ films, it can be further inferred that complete pore collapse occurred at temperatures $>500^\circ\text{C}$. It is noteworthy that the density of the films increased beyond that of the non-porous PMSSQ films when the curing/calcination temperatures were greater than 500°C .

This disparity in the bulk behavior of the system brought about by the substrate interface is intriguing and thus far unexplored. The role of the chemical functionality of the substrate surface becomes especially relevant for composite systems subjected to temperatures wherein decomposition of one component of the system becomes imminent. This is because, unlike low temperature processed systems where the substrate effects are effectively shielded from the bulk through the formation of a segregated monolayer of one of the phases at the interface, decomposition led depletion of the segregated labile phase for high temperature processed systems leads to profound morphological changes in the bulk film. For the system under study, the following key characteristics are worth noting:

- i. The amphiphilic nature of the PPG molecules ensures good miscibility with the PMSSQ nanoparticles and maintains a fairly uniform distribution of the nanoparticles across the bulk of the “as-deposited” film irrespective of the surface energy of the underlying substrate. This is evident from the identical attenuated total reflection (ATR)-infrared absorption spectra of the films obtained on the Si-H and the plasma oxidized PMSSQ films (Figure 2a). The region 2940–2800 cm^{-1} could be attributed to the CH_2 stretching vibrations from structures present in PPG. The absorbance peaks at 2970 cm^{-1} and 1270 cm^{-1} are attributed to the CH_3 groups from PMSSQ. The most intense absorption peaks seen at 1135 and 1035 cm^{-1} are attributed to Si–O stretching vibrations from the PMSSQ molecules with caged and bridging configurations, respectively.^[24, 25] Since ATR infrared absorption relies on the interaction of the evanescent field with the film at the air interface extending ~400 nm into the sample, substantial segregation of the nanoparticles to either of the interfaces should have led to preferential enrichment of one phase over the other at the air interface that would have manifested in the FTIR spectra.
- ii. The nanoparticle distribution within the films is profoundly influenced by the nature of the substrate interface as soon as the films are subjected to the temperature step. From the FTIR spectra of Figure 2b, differences are readily apparent in the relative concentrations of the PPG phases (region 2940–2800 cm^{-1}) for the films processed on different substrate surfaces. PPG concentrations at the air interface fell dramatically for the films processed on plasma oxidized PMSSQ surfaces compared to the films processed on Si-H surfaces although identical heating conditions were used for both the cases. This behavior is rationalized on preferential migration of the PPG phase to the substrate interface for films deposited on high surface energy surfaces (plasma-oxidized PMSSQ surfaces) to minimize the enthalpic contact between the hydrophobic PMSSQ nanoparticles and the highly hydrophilic substrate surface. Depletion of the PPG phase at the interface brought about by its decomposition serves as a continuous driving force for directional migration of the PPG molecules from the bulk of the film to the substrate interface during the temperature treatment step. The consequential reduction in the mean free path (and separation distances) between the nanoparticles due to this results in increased van der Waals forces between the nanoparticles in this region. For two identical spheres, it is always an adhesive force (F_{adh}) given by the expression:[26]

$F_{\text{adh}} = \frac{AR}{12D^2}$, where A is the Hamaker constant for the nanoparticles-air system, R the radius of the nanoparticles and D is the separation distance between the nanoparticles. This results in the eventual formation of the condensed (dense) phase of the nanoparticles. On the other hand, when no preferential segregation of the PPG phase occurs, as it does for films deposited on the Si-H surfaces, decomposition of the PPG phase leaves the initially confined nanoparticles in the rapidly expanding gaseous decomposition products of PPG. The

increased entropy of the nanoparticles, random interparticle collisions and crosslinking drives the system towards the equilibrium porous state with the degree of porosity determined by the magnitude of the thermal input provided.

Temporal Evolution of NPO Nanostructures

Figure 3a shows the temporal evolution of the film patterns obtained at a curing/calcination temperature of 540 °C. It may be observed that the patterns spontaneously emerge as soon as the coated film is brought in contact with the heated surface. The averaged n and thickness plots of Figure 3b further points to the fact that the equilibrium state of the system, i.e., whether the system is driven towards a porous or a condensed state, is determined by the nature of the underlying substrate surface the moment the films were subjected to the heat treatment step. Within 5 s of contacting the hot surface, the film present on the Si-H surface region acquired sufficient nanoporosity (with a relatively low n of 1.2). Porosity of the films further increased with curing/calcination time with a greater fraction of the nanoparticles escaping the system. On the other hand, films present on the oxidized PMSSQ region rapidly reached the final dense (equilibrium) state. There was less relative change in the thickness for the collapsed pore region compared to the porous region with no loss of mass occurring (from particles escaping the system) from this region.

The ensemble behavior of the nanoparticles, in terms of density distribution across the films as a function of the curing/calcination time was investigated by studying the n profiles across the film thicknesses. Ellipsometric modeling of transparent films using a Cauchy model with grading essentially works by dividing the thickness of the films into thin discrete layers and assigning optical constants to each layer from the substrate-film interface to film-air interface fitted to an exponential function.[22] Figures 4a–d show the depth profile of the refractive indices for the films processed on Si-H surfaces for various times of curing/calcination at 540 °C.

The refractive index profiles indicate that a gradient in the density of the nanoparticles across the film develops as soon as the substrate is placed on the hotplate. The density profile further goes from an initial linear gradient (at $t < 10$ s) to a more exponential distribution ($10 \text{ s} < t < 60$ s). Remarkably, the refractive index profile reverses for $t > 120$ s. A simple argument for these density profiles may be made taking into consideration the temperature gradient that develops across the film during the initial stages of heating. Therefore, the kinetic energy of the nanoparticles ($\approx kT$) across the film becomes a function of its spatial location with respect to the substrate interface; nanoparticles closer to the substrate interface having more energy than those at the air interface. Thus the nanoparticles experience a net drift towards the air interface where excess accumulation of the nanoparticles results in progressively increasing n at that interface, as exemplified by the n profiles (Figure 4a–c). It is noteworthy that a continuous mass loss in the form of nanoparticles escaping the system at the film-air interface is evident from the plots, manifested as a drop in the overall thickness of the films with the time of curing. The reversal of the n profile for longer heating times is particularly intriguing (>120 s). This may be rationalized by considering the fact that the interparticle crosslinking rate responsible for kinetically driving the system to the equilibrium state is also a function of temperature. Therefore, nanoparticles at the substrate interface are driven towards equilibrium at a faster rate compared to nanoparticles at the film-air interface. Therefore, mass loss at the film-air interface proceeds for a longer duration manifesting as higher porosities at the air interface than at the substrate interface.

The ensemble behavior of the nanoparticles for the films processed on plasma oxidized PMSSQ thin films essentially remained identical for various times of heating. A representative plot of the n profile for these films (treated at 540 °C) is shown in Figure 5.

This further shows that the films in this region were driven to equilibrium at a much faster rate than those present on the Si-H surfaces. A dense interface layer (~4 nm) with an n of 1.55 was observed at the substrate interface for all the films possibly due to the reaction of PMSSQ with silicon forming SiCO ceramic like structures. A graded refractive index profile was observed in the bulk of the film (Figure 5b) indicating that the rate of interparticle crosslinking and film densification follows the temperature distribution established across the film.

Fidelity of the NPO Patterns

Figure 1 clearly shows there is a lateral scaling in the obtained patterns of the nanoporous and collapsed pore regions from the original mask design. The width of the collapsed regions shrinks to approximately half of the width of the original mask design (from 400 μm wide to 220 μm for the 550 $^{\circ}\text{C}$ processed films). Table 1 summarizes the scaling of the collapsed regions on the various temperature processed films observed in this study. This lateral scaling arises due to the reduction in volume from densification of the film in this region. The ~50% scaling for films processed at temperatures $>350^{\circ}\text{C}$ is consistent with the values estimated for collapse of films consisting of 50% (w/w) PMSSQ nanoparticles in PPG.

Nevertheless, note that the feature sizes were highly reproducible for specific curing/calcination protocols. The generated features have remarkably straight edges considering that high temperature porous film generation is a spontaneous process. Hence by taking into account this predictable scaling behavior, any desired pattern can be generated with high reproducibility.

In addition to lateral scaling, differences in nanoparticle mobilities across the two distinct surface regions also lead to excess accumulation of the nanoparticles at the porous and collapsed pore interfaces. This is manifested through the formation of a wavelike surface patterns, especially when lower curing/calcination temperatures are used (see Figure 6, panels a and b). However, beyond the critical curing/calcination temperature (at which the nanoparticles have enough kinetic energy to escape the system), the transition between the porous and collapsed pore regions becomes progressively sharp, as can be seen from Figure 6b.

Lastly, an important consequence of this unique surface-guided patterning process is that the pristine surfaces and nanostructure of the porous regions are well preserved during the mesoscale nanoporosity development. Figure. 7 shows the patterned NPO film, plasma surface functionalized and bioconjugated with a fluorescent protein (fluorescein isothiocyanate (FITC)-labeled protein - A) across the entire surface. The high contrast in the binding densities for the labeled protein is readily apparent between the nanoporous and collapsed-pore regions due to the large surface area of the nanoporous films. These results are concordant with the patterns observed in Figure. 1e, indicating that surface functionality is retained during the patterning process.[27]

CONCLUSIONS

In closing, we report a unique phenomenon of self directed nanostructure evolution in thin films comprised of functionalized nanoparticles. Exquisite control of the film properties, including the degree of porosity, density gradient across the film thickness and the ability to achieve spontaneously patterned regions with distinct physical characteristics were demonstrated in this study through an interplay between the entropic and enthalpic terms across thermally labile polymers, thermally stable, functionalized nanoparticles and the substrate surface chemical functionality. We have demonstrated that the ensemble behavior

of nanoparticles in response to a given thermal input may be utilized to fabricate novel thin films with precisely graded density profiles. Under identical boundary conditions, the system behavior exclusively depends on the nature of the substrate; the system being driven towards a highly porous state or a collapse state depending on the surface energy of the substrate. Such a high degree of control was demonstrated for the first time on optically clear thin, high surface area nanoporous films. The immediate relevance of this study was shown by applying the reported techniques to solve the long standing problem concerning patterning of nanoporous thin films. We have successfully demonstrated spontaneous patterning of nanoporous thin films and demonstrated their utility as high density substrates for diagnostic microarray development.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The authors gratefully acknowledge the financial support from the National Institutes of Health (Award number 2-U42RR014821) and the Leonard Wood Institute (Award number: 291-001). The authors would also like to thank Dr. Luis Polo-Parada for providing access to his lab for bioconjugation and fluorescence imaging.

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Figure 1.

(a) Photoresist mask pattern that was used to pattern NPO films in this study, (b–e) obtained micropatterns at curing/calcination temperatures of 250 °C, 350 °C, 450 °C, and 550 °C, respectively. (f and g) Refractive indices (n) and thicknesses of the porous and the collapsed films as a function of curing temperature, for a 5 min curing period.

Figure 2. ATR-FTIR spectra of (a) as-deposited NPO films on different substrates and (b) porous and collapsed regions in NPO films subjected to a 250 °C heating step for different durations.

Figure 3.

(a) Evolution of the patterns as a function of curing time (from left to right, scale bar = 1 cm, see supplementary information for the corresponding real time video). The film was deposited on surface energy patterned silicon substrate and heat cured at 540 °C on a pre-heated hotplate. (b) The refractive index and (c) thickness of the porous and the nonporous regions as a function of curing/calcination time at 540 °C.

Figure 4.

Depth profiles of the refractive index (n) of porous films fabricated by treatment at 540 °C for (a) 5 s, (b) 20 s, (c) 60 s, and (d) 120 s.

Figure 5.
Depth profile of the refractive index of the collapsed film after a 20 s treatment at 540 °C.
(Inset shows the expanded plot to clarify the grading in the bulk of the film.)

Figure 6.
Atomic force microscope images of the transition between porous and collapsed-pore regions for patterns treated at (a) 250 °C and (b) 350 °C.

Figure 7. Fluorescence micrograph image of protein A-FITC immobilized onto a patterned NPO film. NPO patterns were attained by treatment at 540 °C for 5 min.

Scheme 1.

Illustration of surface energy gating to control proximal nanoporosity in supported NPO films.

Scheme 2.

Flow diagram summarizing the chief steps involved in developing controlled surface-guided NPO patterns.

TABLE 1

Lateral Scaling of NPO Features

Sample	Width of the porous region (μm)	Width of the collapsed region (μm)
Mask pattern	30 ± 3	400 ± 4
NPO film, 250 °C treatment	45 ± 3	385 ± 7
NPO film, 350 °C treatment	221 ± 5	216 ± 8
NPO film, 450 °C treatment	181 ± 26	254 ± 17
NPO film, 550 °C treatment	221 ± 9	223 ± 5