

Oriented Mesoscopic Silicate Patterns Through Guided Growth

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Oriented surfactant-silicate nanotubule structures have been prepared on solid substrates by infiltrating a reaction fluid into the capillaries of an elastomeric stamp with patterned, micron-scaled relief features in contact with the substrate. Application of an electric field (0.1-1 kV mm⁻¹) directed tangentially to the surface within these capillaries causes electro-osmotic fluid motion and enhanced rates of fossilization by localized Joule heating. After fossilization and removal of the mold, patterned bundles of oriented nanotubules remain on the surface. This technique provides a new method for fabricating nanostructured materials with designed microscopic patterns.

The development of low-cost lithographic techniques having the ability to pattern “designed” structural features on the nanometer size scale is important for the future manufacture of electronic, opto-electronic and magnetic devices with nanometer scaled dimensions. Technologies involving scanning electron beam^{1,2}, x-ray lithography^{3,4} and scanning proximal probe^{5,6} are currently under development, but the practicality of these techniques remains uncertain. A method for the formation of continuous mesoscopic silicate films at the interface between liquids and various substrates has recently been reported⁷. This method involves the supramolecular assembly of surfactant molecules at a solid/liquid interface to form “nanotubules” with dimensions of ~ 3 nm. Polymerization of the inorganic matrix around these tubules leads to a hexagonally packed array of surfactant channels. Although continuous films of these silicate materials can be formed, the orientation of the tubules depends primarily on the nature of the substrate-surfactant interaction and is difficult to control. Once films grow away from the ordering influence

of the interface, chaotic, hierarchical structures arise (see for example Fig. 1). Although these continuous films hold much promise for a multitude of technological applications (e.g., oriented nanowires⁸, sensor/actuator arrays⁹⁻¹¹, and optoelectronic devices¹²), a method of orienting the nanotubules into designed arrangements is clearly required for this approach to become viable as a nanolithographic tool. In this report we describe a method that allows the direction of growth of these tubules to be guided to form highly aligned, designed nanostructures. This method is independent of the substrate-surfactant interaction and thus allows oriented structures to be formed on any (non-conducting) substrate.

In order to achieve such patterning, we formed the ordered silicate structure within a highly confined space, using the Micromolding in Capillaries (MIMIC) technique described previously¹³. First, a network of patterned capillaries is formed by placing an elastomeric stamp (typically made of polydimethyl siloxane, PDMS) possessing designed relief features on its surface in contact with a flat substrate (see Fig. 2). Second, an acidified aqueous reacting solution of tetraethoxysilane (TEOS) and cetyltrimethylammonium chloride (CTAC) is placed in contact with the edge of the mold and wicked into the networked channels by capillary action. Typical molar ratios for the reacting solution are 1 TEOS : 1.2 CTAC : 9.2 HCl : 1000 H₂O. As has been shown previously⁷, the formation of a mesoscopic silica film begins to occur immediately upon contact of this solution with any interface onto which the surfactant can adsorb. A dilute solution of the TEOS silica source is specifically used to prevent homogeneous nucleation of inorganic material in bulk solution, and to promote heterogeneous nucleation and growth of a mesoscopic film at the substrate/solution interface.

Within the capillaries, because the reacting solution is dilute, reactants are quickly depleted, and film growth ceases. Moreover, the growth of mesoscopic film at the edges of the mold seals the capillaries and prevents diffusion of reacting species to the interior of the mold. To maintain a uniform concentration of reactants within the capillaries during the growth process, an electric field is applied parallel to the substrate in the manner illustrated in Fig. 2. Application of an electric field in this geometry has three effects: it induces electro-osmotic fluid flow; it aligns surfactant tubules; and it causes

localized Joule heating of the solution. These effects are synergistic in guiding and fossilizing the silicate mesostructures within the microcapillary reaction chambers. For applied fields $> 0.1 \text{ kV mm}^{-1}$, electro-osmotic fluid flow is observed within the capillaries, as a result of the interaction of the field with the ionic double layer charge near the capillary wall¹⁴. In our case, surface charge on the capillary walls arises from adsorption of the positively charged CTAC surfactant¹⁵. Maintaining a steady fluid flow through the capillaries during the entire growth process ensures that the reactant concentration within each micro reaction chamber remains constant with time - this constancy allows uniform films to be grown.

Fig. 3 shows SEM images of square and lined patterns of mesoscopic silica grown on a silica substrate after 5 h of reaction time. A DC field of 0.15 kV mm^{-1} was applied during the entire reaction process, and fresh reacting fluid was continuously dripped on one side of the mold to replenish the volume removed by the electro-osmotic flow. In each case, the patterns formed replicate the structures of the mold. Within the capillaries, films begin to grow on all exposed surfaces, i.e., at both the PDMS mold and the substrate/aqueous solution interface. As the reaction progresses, the capillaries narrow in the center and eventually seal completely. The high conductivity of the acidic reaction solution gives rise to significant Joule heating at these applied voltages. Positioning the electrodes in an excess reservoir of reacting solution outside the microcapillary volume (Fig. 2) allows high fields to be applied across the aqueous solution confined within the capillaries. In such a scheme, rapid electrolysis ($\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$) ensues, however bubble formation is confined to the fluid reservoir near each electrode and does not disturb the formation of silica mesostructures within the capillaries. At voltages of 1 kV mm^{-1} , sparks are occasionally observed within the fluid confined in the microcapillary as a result of intense localized heating. At lower fields, sparks are not observed and the Joule heating accelerates the fossilization rate of the mesoscopic silica by increasing the rate of polymerization of the TEOS precursor to silica. The dependence of silica polymerization rates on temperature is a well studied phenomenon¹⁶. With no applied field, $0.5 \text{ }\mu\text{m}$ thick films are typically grown in a period of 24 h; with an applied field of 0.1 kV mm^{-1} , similar thicknesses are achieved in 1-5 h. Localized heating of the reacting solu-

tion in this manner thus provides a useful method of rapidly rigidifying the aligned surfactant tubular structures formed within the microcapillaries.

In order to determine the orientation of the surfactant nanotubules within these structures, cross-sectional samples were prepared using a Leica ultramicrotome and analyzed by high resolution transmission electron microscopy (TEM). Fig. 4 shows a typical example of the resulting TEM images as well as a typical selected area electron diffraction pattern (SAED). These reveal a hexagonally packed arrangement of tubules with a nearest neighbor spacing of 3.0 nm. Detailed examination of diffraction pattern reveals a slightly distorted packing arrangement, with a deviation of 4% from perfect hexagonal. This distortion may be a result of the accelerated fossilization process described above: with no applied field, no distortion is observed. Multiple cross-sections taken of the 1 μm line structures shown in Fig. 3 all appear identical to the image shown in Fig. 4. This indicates that all tubules within the capillaries are aligned parallel to the substrate, the long axis of the capillary, and the direction of the applied field. This result is a dramatic contrast to the “unconfined” mesoscopic silica film synthesis⁷, which always results in a chaotic and non-aligned arrangement of tubules (Fig. 1). In our case, rather than taking on a random configuration, growing tubules are guided within the confined space of the capillary and remain parallel to the walls. This orientation occurs either as a result of the action of the external field, i.e., alignment of tubules resulting from polarization body forces that operate in regions of dielectric constant gradient ($\sim \nabla \epsilon E^2$)^{14,17,18} or by virtue of the confined space within which the reaction is performed. In both cases, the tubules would be aligned parallel to the capillary walls. For field-induced alignment, such configurations minimize the overall electrostatic energy - provided a difference in dielectric constant exists between the inner and outer volume of the tubule. It is also known that the formation of end-caps in self-assembled surfactant cylinders is not favored, given their high free energy of formation¹⁹. Thus, within a highly confined region, surfactant cylinders will take on configurations which minimize the number of end-caps. Consequently, they will tend to elongate along the long axis of the capillary rather than truncating at capillary walls.

In the absence of an ordering field, a wide range of slowly curving configurations of tubules is formed in three-dimensions (Fig. 1). As described previously^{7,20}, such a configuration can be understood in terms of a simplified Helfrich²¹ bending energy model of the surfactant tubule, $E = k_c/2(1/R_1 - 1/R_0)^2$, where E is the free energy per unit area (effectively, an energy per surfactant molecule in the tubule), k_c is a rigidity constant, and R_1 and R_0 are respectively the principal and spontaneous radius of curvature of the tubule. In so far as R_0 is fixed by the surfactant composition and is small (~ 5 nm), as is typically the case for single chain surfactants, the above equation shows complete insensitivity to R_1 for values $\gg R_0$. This analysis implies that the energy of bending along the long axis of a tubule does not figure prominently in the bending energy. Thus, unless order is imposed on the tubules by external forces, such as adsorption forces, or an electric or flow field, the tubules will sample a wide range of slowly varying configurations. This concurs during “unconfined” film growth⁷, where it was shown that orientation and alignment of tubules can be controlled in the initial stages of film growth by manipulating the strength and nature of the specific surfactant-substrate interactions. Although this growth scheme gives some control over the film structure, once the film grows away from the interface, the orientation that existed in the first layers begins to be lost as the ordering influence on the interface diminishes. In our case, the combined influence of confining geometry and applied field allows the synthesis of mesoscopic silicate nanostructures with precisely controlled geometries. In this way, the tubule geometry is controlled in all regions of the film and the synthesis can be performed on any required substrate, regardless of the nature of the surfactant-substrate interaction. An enormous variety of patterns can be formed using the MIMIC approach, with nanotubules aligned parallel to capillary walls. Capillary thicknesses of 1 μm , corresponding to roughly 300 nanotubules, are easily achieved by this method and thinner structures can also be formed using molds formed from masters prepared by electron beam lithography¹³.

As a viable method for the production of thin films with complex nanometer and micron-scaled hierarchical architectures, the guided growth of mesoscopic silicates within confined geometries provides a convenient method for fabrication of nanostructured

materials in a variety of applications ranging from sensors and actuators to optoelectronic devices.

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Figure Captions:

Figure 1:

Scanning electron microscope (SEM) image of an “unconfined” mesoscopic silica film grown on an amorphous silica substrate. Once the film becomes thicker than $\sim 0.5 \mu\text{m}$, a chaotic, hierarchical structure of winding tubules is formed.

Figure 2:

Schematic illustration of the technique used to induce guided growth of mesoscopic silicate structures.

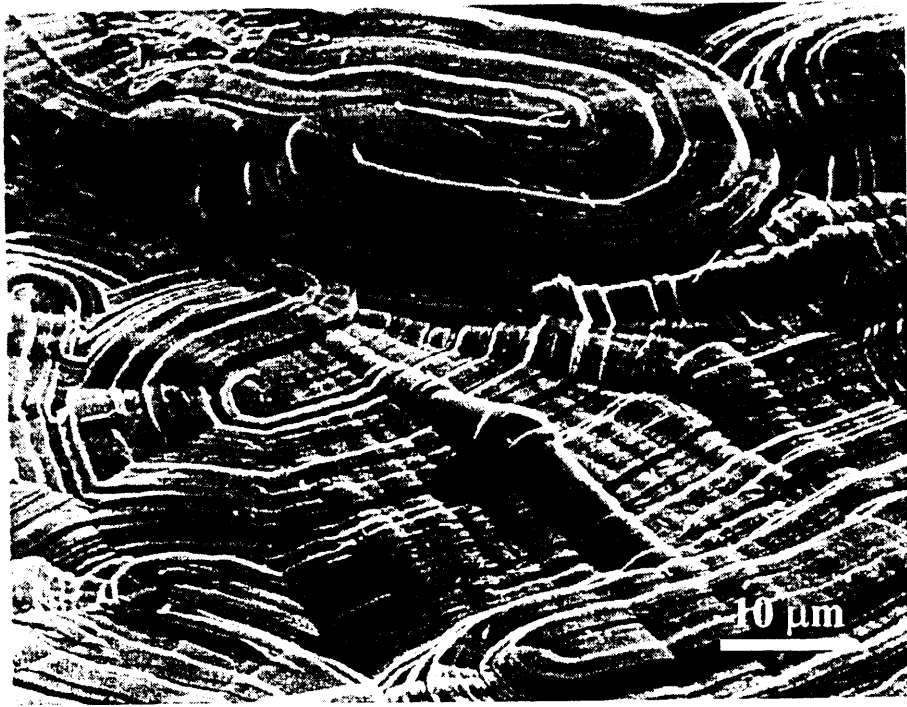
Figure 3:

(a) and (b) SEM images of $1 \mu\text{m}$ line and square mesoscopic silicate patterns formed by guided growth within microcapillaries. Electro-osmotic flow is used to transport reacting fluid through the capillaries, and localized Joule heating triggers rapid polymerization of the inorganic around aligned surfactant tubules.

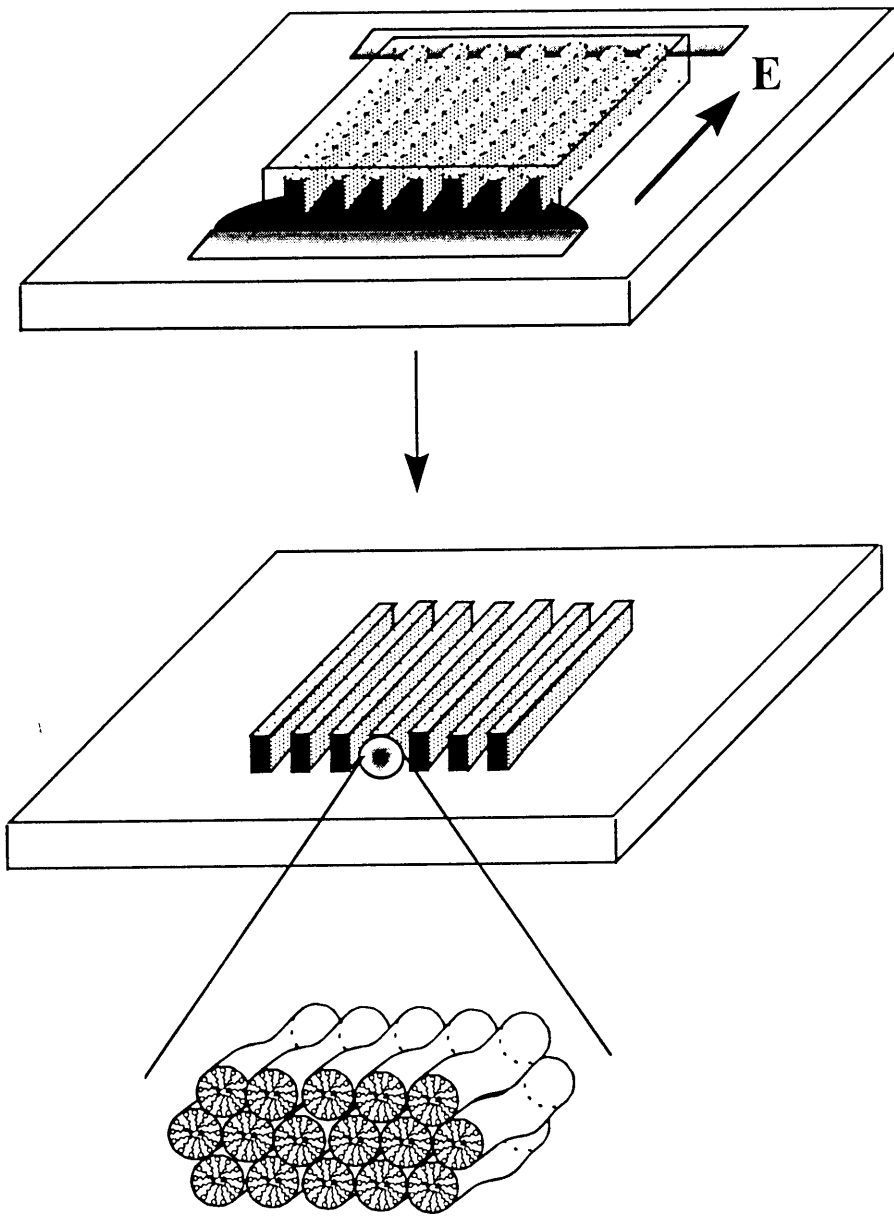
Figure 4:

(a) and (b) TEM images of a patterned mesoscopic silica structure grown on a Thermanox plastic substrate (Electron Microscopy Sciences). These display a hexagonally packed

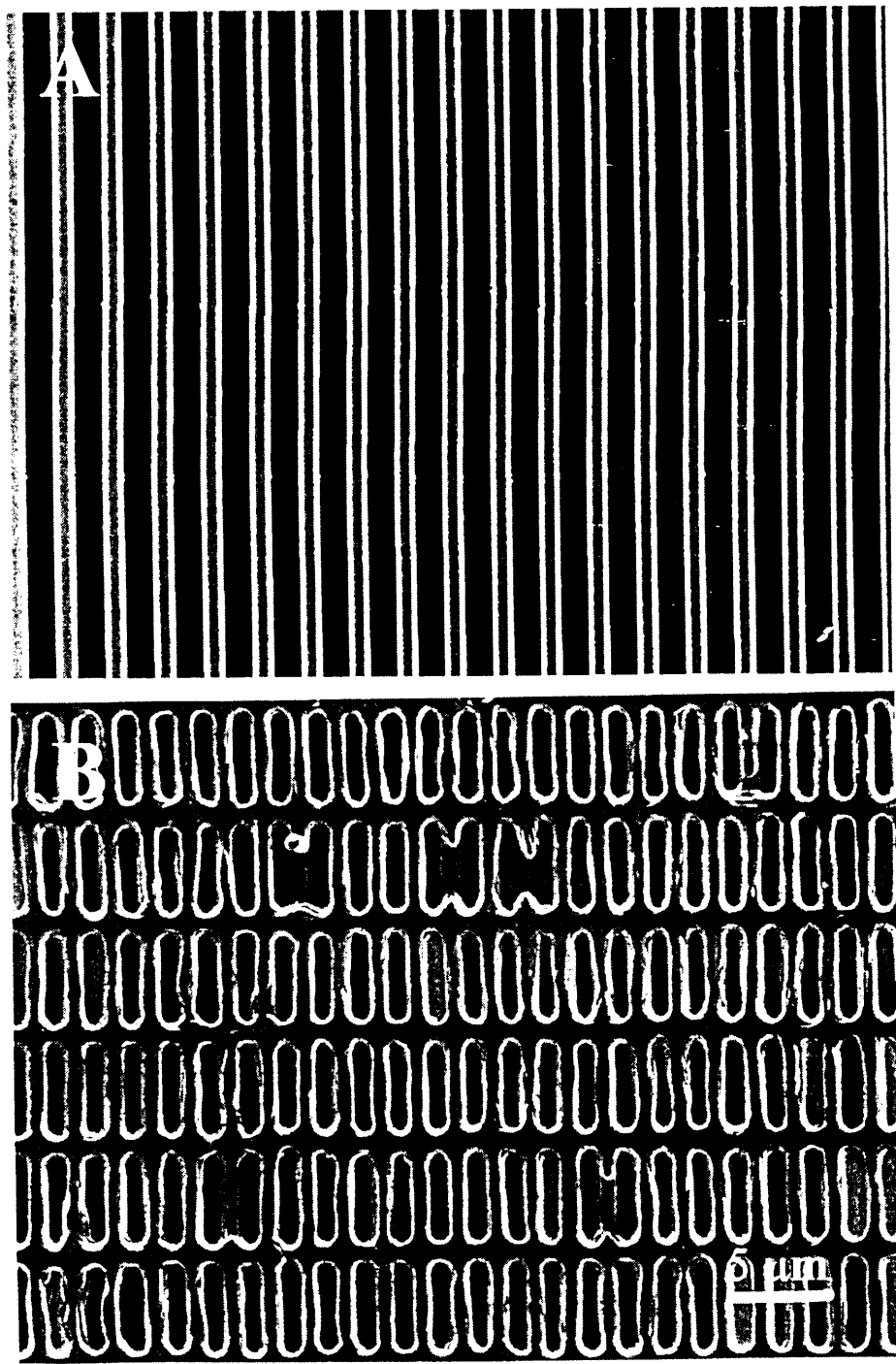
surfactant tubule structure within the micron-sized lines shown in Fig. 3. The cross-sectional view of each line reveals an identical hexagonally packed pattern of tubules, suggesting global alignment of tubules parallel to the substrate and capillary walls. Similar images have also been obtained for “confined” films grown on silica substrates. The insert displays the corresponding electron diffraction pattern obtained from (b), as well as a fourier transform filtered image. The diffraction pattern reveals a slightly distorted hexagonal lattice with 4 % strain. The strain appears to be caused by the rapid fossilization of the inorganic phase induced by localized Joule heating of the confined reacting fluid.



Trau *et al.* Figure 1



Trau *et al.* Figure 2



Trau *et al.* Figure 3

