Biomimetic Pathways for Assembling Inorganic Thin Films


Living organisms construct various forms of laminated nanocomposites through directed nucleation and growth of inorganics at self-assembled organic templates at temperatures below 100°C and in aqueous solutions. Recent research has focused on the use of functionalized organosilane surfaces to form continuous thin films of single-phase ceramics. Continuous thin films of mesostructured silicates have also been formed on hydrophobic and hydrophilic surfaces through a two-step mechanism. First, under acidic conditions, surfactant micellar structures are self-assembled at the solid/liquid interface, and second, inorganic precursors condense to form an inorganic-organic nanocomposite. Epitaxial coordination of adsorbed surfactant tubules is observed on mica and graphite substrates, whereas a random arrangement is observed on amorphous silica. The ability to process ceramic-organic nanocomposite films by these methods provides new technological opportunities.

Biologically produced inorganic-organic composites such as bone, teeth, diatoms, and sea shells are fabricated through highly coupled (and often concurrent) synthesis and assembly. These structures are formed through template-assisted self-assembly, in which self-assembled organic material (such as proteins, or lipids, or both) form the structural scaffolding for the deposition of inorganic material (1). They are hierarchically structured composites in which soft organic materials are organized on length scales of 1 to 100 nm and used as frameworks for specifically oriented and shaped inorganic crystals (that is, ceramics such as hydroxyapatite, CaCO₃, SiO₂, and Fe₂O₃) (1–3). In some cases, structurally organized organic surfaces catalytically or epitaxially induce growth of specifically oriented inorganic thin films. Most importantly, however, nature’s way of mineralization uses environmentally balanced aqueous solution chemistries at temperatures below 100°C. This approach provides an alternative to the processing of inorganic thin films, especially in applications where substrates cannot be exposed to high temperatures, or more generally in the pursuit of increased energy efficiency.

A classic and a widely studied example of a biocomposite is the nacre of abalone shell, in which thin films of organic (<10 nm) and inorganic (<0.5 μm) phases are coupled together to produce a laminated structure with improved mechanical properties (4–6). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of this material are shown in Fig. 1. Because of this special architecture, composites such as nacre are simultaneously hard, strong, and tough (4–6). The core of the organic template is composed of a layer of β-chitin layered between “silk-like” glycine- and alanine-rich proteins (7). The outer surfaces of the template are coated with hydrophilic acidic macromolecules rich in aspartic and glutamic acids (8). Recent studies suggest that these acidic macromolecules alone are responsible for control of the polymorphic form and the morphology of the CaCO₃ (calcite versus aragonite) crystals (9), although the role of the β-chitin-supported matrix on the lamellar morphology of the CaCO₃ layers over macroscopic dimensions still remains to be determined. Morphological and crystallographic analyses of the aragonitic thin layers of nacre by electron microdiffraction show that c-axis-oriented aragonite platelets form a hierarchical tiling of a twin-related dense film with twin domains extending over three length scales (4, 10). Superposition of the aragonite lattices on all three possible sets of twins generates a new superlattice structure, which suggests that...
that the organic template adopts a single-
crystalline pseudohexagonal structure (10).
Although cellular activities leading to the
self-assembly of the organic template re-
main to be understood, the presence of an
organized organic template is essential to
the assembly of the inorganic layer.

Nature's way of processing such hier-
archically structured composite materials
with designed architecture is an invaluable
guide to developing new synthetic processes
that can produce useful materials with simi-
lar designs. Toward this goal, several key
aspects of the biomimORIZATION scheme
need to be understood. The first key aspect
is the mechanism leading to the self-assembly
of an organized organic template and
choice of organics to form a desired inor-
ganic. Second, the orienting and shaping
action of the assembled organic scaffolding
on the growing inorganic phase needs to be
elucidated, as does the oriented assembly of
organics on the deposited inorganic sub-
strates. Third, the controlled nucleation
and growth of inorganic material in specific sit-
es, and finally, the assembly of higher
order hierarchical structures and the role of
hierarchical architecture on property opti-
mization require explanation. Given the de-
mand for ceramic coatings with enhanced
optical, magnetic, electronic, mechanical,
and "intelligent" functions (11), a detailed
study of biomimetic film formation will not
only have important technological impact
but will also shed light on the fundamental
processes listed above.

**Synthetic Pathways**

All mineralization processes involve the
precipitation of inorganic material from so-
lution. A key requirement for successful
film formation is to promote the formation
of the inorganic phase on the substrate
directly (that is, heterogeneous nucleation)
and prevent the homogeneous nucleation
of particles in the solution (11). According
to classical nucleation theory (12), the free
energy change (∆F) associated with the
precipitation of an inorganic cluster from
solution onto a surface is given by:

\[
\Delta F = -n k_B T \ln S + \gamma_{p} A_{p} + (\gamma_{n} - \gamma_{p}) A_{n}
\]

where \( S \) represents the degree of supersatu-
ration in the fluid; \( n \) is the aggregation
number; \( k_B \) is Boltzmann's constant; \( T \)
is temperature; \( \gamma_{p} \), \( \gamma_{n} \), and \( \gamma_{p} \)
represent the inorganic/liquid, inorganic/substrate,
and substrate/liquid interfacial tension, respec-
tively; and \( A_{p} \) and \( A_{n} \) represent the corre-
sponding interfacial areas. When the inter-
action between the growing nucleus and sub-
strate surface represents a lower net interfa-
cial energy than the inorganic/solution
interfacial energy [that is, \( (\gamma_{n} - \gamma_{p}) A_{n} < \gamma_{p} A_{p} \)]
heterogeneous nucleation is favored
over homogeneous nucleation. This is the
case for the majority of precipitating inor-
ganic systems, and hence heterogeneous nu-
cleation is the dominant precipitation mech-
anism for thermodynamically controlled sys-
tems. Homogeneous nucleation will only
 dominate at relatively high levels of super-
saturation where the precipitation process
becomes kinetically controlled. Precipitation
times for homogeneous nucleation vary
enormously, from months to milliseconds,
depending sensitively on the value of \( S \) (13).
Thus, an important requirement for the bio-
imetic processing of thin inorganic films is
to maintain relatively low levels of supersat-
uration during the precipitation process in
order to minimize the amount of particle
formation in bulk solution.

In recent years, a substantial number of
researchers have demonstrated the viability
of this approach for the preferential growth
of inorganic crystals at the solid/liquid (11,
14) and liquid/air interfaces (15). Further-
more, through chemical modification of
these interfaces, by adsorbing surfactants or
other reactive moieties, the crystal phase,
morphology, growth habit, and even chirali-
ty of heterogeneously deposited inorganics
can be controlled. Innovative examples of
this approach include the work of Mann et
al. (16), where phase-specific, oriented cal-
cite crystals are grown underneath a com-
pressed surfactant monolayer at the air/wa-
ter interface. Changing surfactant type or
degree of monolayer compression results in
different crystal phases and orientations.
Another innovative approach is that of the
Pacific Northwest National Laboratories
(PNNL) (11). By chemically modifying sol-
idity, metal, plastic, and oxide surfaces, these
researchers have demonstrated selection of
phase and orientation of the depositing
crystalline inorganic at a variety of solid/
liquid interfaces. A particularly attractive
strategy is the use of the self-assembled
monolayer (SAM) approach to coat metal
and oxide substrates with surfactant mono-
layers of tailored hydrophilicity. This is ac-
complished by prepetrating the substrates
with a solution of functionalized surfac-
tants, such as sulfonic acid-terminated oc-
tadecyl trichlorosilane, before precipitation
of the inorganic phase. The choice of the
terminating moieties on the surfactant tail
determines surface charge and relative hy-
drophobicity of the chemisorbed surfactant
monolayer. In this way, oxide and metal
(17) substrates can be modified convenient-
ly to have the required surface properties
to promote inorganic film growth.

Potential applications for dense, poly-
crystalline inorganic films span a broad
range of industries. These include the pos-
sibility of applying hard optical coatings
to plastics in order to replace glass, abrasion-
resistant coatings for plastic and metal com-
ponents subject to wear, and the deposition
of oriented films of iron oxide phases for use
as magnetic storage media. For many of the
above applications, conventional ceramic
processing methods, which require high-
temperature sintering, cannot be used be-
cause of problems with substrate degrada-
tion. A significant advantage of the bio-
imetic processing methods described above
is the relatively low processing temperatures
involved (typically <100°C) and the use of
water rather than organic solvents (11).
Both of these factors render such methods
relatively environmentally benign.

Whitesides' group at Harvard University
(18) has developed a microcontact printing
method by which complex, designed SAM
patterns may be transferred onto substrates
with an elastomic stamp. This approach
sets up lateral variations in the \( \gamma_{n} - \gamma_{p} \) value
along the substrate and may be used to se-
lectively nucleate and grow inorganic phase
on the functionalized regions. The PNNL
(19) group has demonstrated the spatially
resolved deposition of FeOOH mineral
through an analogous SAM approach by us-
ing electron and ion beam lithography to
pattern the SAM layer. This technique al-
lows micrometer-scaled patterning of inor-
ganic materials on a variety of substrates
through confined nucleation and growth of
inorganic films. Similar work has recently
been reported by the Case Western Reserve
University group (20, 21), where photoli-

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**Fig. 2.** SEM images of mesoscopic silica films grown at (A) mica/water, (B) graphite/water, and (C) silica/water interface for 24 hours, respectively. Oriented tapes are observed on mica and graphite. The films grown at the silica/water interface are uniform initially (dark background) but spiral-like structures (light features) form later.
thography was used to pattern the SAM layer prior to area-selective mineralization of TiO₂, ZrO₂, SiO₂, or Y₂O₃ films. An alternative to the SAM approach is the method of micromolding in capillaries (MICM) developed by Kim et al. (22). In this case, submicrometer-scale patterning of inorganic films is achieved by placing an elastomeric stamp, containing relief features on its surface, into contact with a substrate. Contact between the elastomeric stamp and the substrate forms a network of interconnected channels that may be filled with an inorganic precursor fluid [such as poly(ethoxymethylsiloxane)] through capillary action. After the material in the fluid is cross-linked, crystallized, or deposited onto the substrate, the elastomeric stamp is removed to leave behind a patterned inorganic film with microstructures complementary to those present in the mold.

The above techniques represent advances in the selective nucleation and growth of inorganic crystals with specific phase, orientation, and micropatterns. However, once the inorganic layer begins to grow away from the substrate/solution interface, there is no facility for organic material to adsorb onto or to become incorporated within the growing inorganic structure or to do both, as in the case of nacre. The deliberate and designed fabrication of hierarchically structured materials built by multilayering of self-assembled nanocomposite films has not been explored. In learning from nature, our goal is to build exactly these types of composite materials rather than single-phase inorganics.

**Template-Assisted Thin Films Through Surfactant Self-Assembly**

The synthesis of silica-based mesostructured materials (23) by using supramolecular assemblies of surfactant molecules to template the condensation of inorganic species has attracted considerable interest as a biomimetic approach to the fabrication of organic/inorganic nanocomposites. This synthesis scheme has now been extended to include a wide variety of transition metal oxides (24) and, recently, to cadmium sulfide and selenide semiconductors (25). Although the exact mechanism for this type of mineralization is still controversial (26), this technique holds great promise as a synthetic scheme to produce nanstructured materials with novel properties. For any of these applications to be realized, however, what is required is a method by which these nanostructures can be formed into controlled shapes and patterns rather than the microscopic particularizes that have been previously reported.

One approach has been to start with a well-defined interface such as mica, as recently illustrated by Yang et al. (27). Under acidic conditions, reactive SiOH anchoring sites on mica are assumed to provide binding sites for the silica-surfactant micellar precursor species and orient a hexagonal phase of mesostructured silica as a continuous thin film. Our work has shown that this approach is not just limited to the hydrophilic surface of mica but can be generalized to form continuous mesostructured silicate films onto a wide variety of substrates, including hydrophobic surfaces such as graphite. The mechanism of film formation is also revealed through atomic force microscope (AFM) analysis of the growing films. Of primary concern here is the structure of the first layer of adsorbed surfactant at each of these interfaces. Although the molecular organization and self-assembly of surfactants at interfaces is a widely studied area, little is still known about the precise structure of adsorbed surfactant layers. Recent work (28) has shown that three-dimensional surfactant structures such as cylindrical tubes and spheres can be formed at solid/liquid interfaces. Adsorbed hemimicellar arrangements are observed on poorly orienting amorphous substrates, such as silica, and aligned tubular structures are observed on more strongly orienting crystalline substrates such as mica and graphite. The latter substrates orient adsorbed surfactants through anisotropic attraction (either van der Waals or electrostatic) between the crystalline substrate and the surfactant molecule. The amorphous silica substrate has no preferential orientation for surfactant adsorption.

In order to promote growth of a mesostructured inorganic on these substrates, an aqueous recipe that includes an excess of adsorbing cetyltrimethyl ammonium chloride (CTAC) surfactant and a dilute acidic solution of tetraethoxy silane (TEOS) inorganic precursor is used. Inorganic solute concentrations are purposefully kept dilute in order to decrease the rate of homogeneous nucleation to such an extent that the more thermodynamically favored heterogeneous nucleation route is dominant (29).

![Fig. 3. In situ AFM images of mesostructured films growing on mica, graphite, and amorphous silica substrates, respectively. AFM images of the mica, graphite, and silica substrates used to grow mesoscopic silica films are shown in the insets. (A) and (B) illustrate the periodic mica and graphite atomic lattices, respectively, onto which CTAC adsorbs and orients. (C) reveals a smooth, amorphous silica substrate. Images of the films were obtained in "noncontact" mode, utilizing the electrical double layer force described in (28, 31).](image-url)
Figure 2 shows SEM images of mesoscopic films grown for a period of 24 hours at the mica, graphite, and silica/water interfaces (30). All of the films are continuous and display distinctly different textures at length scales between 0.5 and 10 μm. Figure 3 shows in situ AFM images of the atomic lattice of each substrate as well as the structure of the mesoscopic silica overlayer growing on each surface (31, 32).

In the case of mica, Fig. 3A reveals meandering stripes with a spacing of 6.2 to 6.8 nm. These are observed at every stage of the reaction (33). As discussed below, x-ray diffraction (XRD) analysis of these films reveals a distorted hexagonal stacking of surfactant tubules (5.6 nm nearest-neighbor spacing) that lie parallel to the surface and are axially aligned along the next-nearest-neighbor direction of the hexagonal oxygen lattice on the mica surface. Figure 4 shows TEM images of a mesostructured film on mica, cut in two different transverse directions. All three methods reveal a consistent structure of the mesostructured film on mica. AFM images similar to those in Fig. 3A were obtained without TEOS present, but these interfacial surfactant films are limited to one or two layers of cylindrical tubules (34). The self-assembly of micellar layers without the presence of the inorganic agent suggests a sequential growth and polymerization for the silicate films (Fig. 5A). First, the surfactant self-assembles on the mica substrate to form meandering tubules, and second, silicon hydroxide monomers (or multimers) polymerize at the micellar surface. As polymerization continues, more surfactant is adsorbed to the freshly formed inorganic surface and allows the templated mesoscopic structure to replicate itself and grow in to the bulk solution. After growth periods of 24 hours, the mesoscopic composite films begin to develop larger scale structural features such as those shown in Fig. 2A. At this stage, aligned “tapes” and steps appear with macroscopic grain boundary angles of 60° and 120°. These macroscopic angles clearly result from atomic level registry of the surfactant tubules with the underlying mica lattice.

For graphite substrates (Figs. 2B and 3B), the surfactant tubules are also aligned parallel to the surface, but in this case they are rigid, parallel stripes without the meandering curvature observed on mica. Measured nearest-neighbor spacings similar to that seen on mica and microscopic grain boundaries can be clearly imaged, which again suggests a preferential axial orientation of the surfactant tubules with the hexagonal graphite lattice. The graphite surface is distinct from mica in that it is hydrophobic and does not contain ionizable moieties to engender surface charge. Attractive interactions (hydrophobic and van der Waals) between the graphite surface and surfactant tails cause them to adsorb horizontally (Fig. 5B), and the resulting large interaction area...
per molecule gives rise to a strong orientation effect between molecule and substrate (28) that is preserved in the cylindrical aggregates. Mica interacts only with the head group (28) and orients the adsorbed molecules vertically; the smaller interaction area gives rise to a correspondingly smaller orientation effect. At long reaction times, macroscopic features grow out of the oriented, uniform film similar to those seen on mica. As with mica, edges with macroscopic angles of 60° and 120° are also observed.

Growth of these films at the silica/water interface gives rise to silica films with macro- and microstructures dramatically different from the ones described above. Figure 3C shows an in situ AFM image of the reacting film grown from a silica substrate. Rather than the parallel stripes observed on the previous substrates, this image shows periodic arrays of dimples suggesting an orientation of surfactant tubules out of the plane of the interface. An XRD analysis confirms a distorted hexagonal packing of the tubules. The dimpled pattern suggests a twisting arrangement of hexagonally packed tubules attached to the interface at one end and spiraling into the solution. Similar dimpled structures were also observed with neat CTAC solution, which suggests the formation of roughly spherical surfactant aggregates that act as starting points on the surface for growth of cylindrical tubules into the solution. Micellar structures of quaternary ammonium surfactants on silica have been previously postulated and observed by other workers (28, 35).

As in the case of mica and graphite, the structure formed in the silica substrate films is a direct consequence of the arrangement of the first layer of adsorbed surfactant on the surface. It appears that the ordering ability of the silica interface, which is dramatically different from that of mica and graphite, is not great enough to confine the surfactant tubules to lie straight on planar surfaces. Indeed, having nucleated one end of the tubules at the interface, the long axes of the tubules appear to wander over a wide range of slowly curving configurations in three dimensions, suggesting that it takes very little energy to bend the tubules along their long axes. This effect may simply be understood in terms of a Helfrich (36) bending energy model of the tubule surfactant layer:

$$E = k_2/2 \left( R_1^{-1} - R_2^{-1} \right) + k_3 R_1 R_2$$

where $E$ is the free energy per unit area (effectively, an energy per surfactant molecule); $k_2$ and $k_3$ are the rigidity and Gaussian curvature constants, respectively, and $R_1$, $R_2$, and $R_3$ are the principal radii and the spontaneous radius of curvature, respectively. Although this form was derived for the thin-film limit in which the radii are large compared to the thickness of the surfactant layer, it also appears to describe reasonably well certain cases in which the surfactant layer thickness is comparable to $R_1$ and $R_2$ (37). $R_3$, the small radius of the tube, is strongly constrained by the length of the surfactant molecules. Insofar as $R_3$ is fixed by the surfactant composition and is small (≈5 nm), as is typically the case for single-chain surfactants, and if $R_2 \gg R_1$ as is the case for long, thin tubes, then Eq. 2 is well approximated by:

$$E = k_3/2 \left( R_1^{-1} - R_2^{-1} \right)^2$$

In other words, the energy of bending along the long axis of a tubule does not figure prominently into the bending energy. Unless order is imposed on the tubules by external forces, such as adsorption forces, the tubules will sample a wide range of slowly varying configurations. This prediction is also consistent with observed macroscopic structures of mesoscopic silica films formed after long growth times at the silica/water interface (Fig. 6). These films begin growing as very uniform structures but soon become increasingly textured and chaotic as the film thickness increases. Rather than the oriented tapes observed in the cases of mica and graphite substrates, the silica substrate films display chaotic, spiral-like structures wrapped in a hierarchical fashion around each other.
within these films through the growth of tubule bundles away from the oriented film is a common feature of all of these films. For mica and graphite, these bundles form wormlike structures, and for silica, tapes and spirals are formed that wrap around each other in a hierarchical manner. The hierarchical structures formed in thick films thus appear to result from the release of accumulated strain energy associated with the epitaxial mismatch between the first layer of adsorbed surfactant and the periodic atomic lattice of the substrate. In all cases, this is observed to occur only for relatively thick films ($\geq 0.5 \mu m$) where the ordering influence of the substrate no longer exists.

Summary

The understanding of biominalization processes can lead to innovative approaches to materials synthesis. The strategy of manipulating macroscopic material properties through hierarchical control of composite microstructure is an important lesson for the materials engineer from biology. In order to create hierarchical composite structures, novel synthetic pathways are required. One of these pathways is the lamination of organic and inorganic thin films to create structures similar to those observed in nature. We have surveyed a variety of techniques that attempt to control the phase, orientation, and microstructure of inorganic films precipitated at interfaces. Although the future of biomimetic processing encompasses the fabrication of bulk composites as well as thin films, we have focused our attention on film processing primarily to enable a fundamental understanding of the templating interactions that occur at the organic/inorganic interface. Another reason to concentrate on thin films is their numerous technological applications.

As a viable method for the production of thin composite films with designed nanoscale architecture, we have presented a technique that uses the supramolecular assembly of surfactant molecules at interfaces to template the condensation of an inorganic silica lattice. In this manner, continuous mesostructured silica films can be grown on many substrates, with the corresponding porous nanostructure determined by the specifics of the substrate surfactant interaction. XRD analysis has revealed epitaxial alignment of the adsorbed surfactant layer with crystalline mica and graphite substrates, and significant strain in the mesophasic silica overlayer has also been measured. As films grow thicker, accumulated strain is released resulting in the growth of hierarchical structures from the ordered film. This scheme of mesostructured film synthesis with control of structural features over several length scales is a novel general approach to the synthesis of inorganic composites with designed architecture at the nanometer-scale size. We envision that this technique will become a useful synthetic tool for the convenient and economic manufacture of biomimetic thin films for a wide variety of applications, especially when the method is extended to compositions other than silica and also to form patterns and complex shapes.

REFERENCES AND NOTES


14. The SAM approach for metal substrates involves the use of organoammonium rather than chlorosilane surfactants.


Synthesis of Novel Thin-Film Materials by Pulsed Laser Deposition


Pulsed laser deposition (PLD) is a conceptually and experimentally simple yet highly versatile tool for thin-film and multilayer research. Its advantages for the film growth of oxides and other chemically complex materials include stoichiometric transfer, growth from an energetic beam, reactive deposition, and inherent simplicity for the growth of multilayered structures. With the use of PLD, artificially layered materials and metastable phases have been created and their properties varied by control of the layer thicknesses. In situ monitoring techniques have provided information about the role of energetic species in the formation of ultrahard phases and in the doping of semiconductors. Cluster-assembled nanocrystalline and composite films offer opportunities to control and produce new combinations of properties with PLD.

The first PLD experiment was carried out more than 30 years ago, shortly after the invention of the pulsed ruby laser (1). However, it was only during the past decade that PLD received extensive experimental development and came into widespread use for film-growth research. The impetus was the discovery that high-quality high-temperature (high-Tc) superconductor (HTS) films can be grown in a low-pressure oxygen environment by PLD without the need for further processing (2). This discovery opened the field of oxide ceramic film growth and research to PLD; in turn, PLD has invigorated and enriched the oxide field. During the past 9 years, PLD's advantages for the deposition of oxides and other complex materials have been used to grow films with an enormous variety of properties, including ferroelectrics, ferrites, amorphous diamond and other ultrahard phases, biocompatible and tribological coatings, polymers, compound semiconductors, and nanocrystalline materials (3).

This article describes the ablation process and its characteristic advantages and limitations for film deposition. Three themes in contemporary PLD research then are examined: (i) the creation of artificial structures and metastable phases and the systematic variation of their properties, (ii) information about the role of energetic ablated species in the formation of ultrahard phases and in the doping of semiconductors, and (iii) emerging opportunities in the synthesis of nanocrystalline and composite thin-film materials with PLD.

Pulsed Laser Ablation

Although the underlying ablation process is complex, PLD is conceptually and experimentally simple. An ultraviolet (UV) pulsed laser beam (pulse duration, 10 to 50 ns) is focused with an energy density Eo of 1 to 5 J/cm² onto a rotating polycrystalline target (Fig. 1). Several events occur during the laser pulse: rapid heating and vaporization of the target; increasing absorption by the vapor until breakdown occurs to form a dense plasma; and absorption of the remainder of the laser pulse to heat and accelerate the plasma, which contains neutral atoms, molecules, and ions, in both ground and excited states, as well as energetic electrons. These atoms and ions undergo collisions in the high-density region near the target (the Knudsen layer, which is a few hundred micrometers thick) to create a highly directional expansion perpendicular to the target surface with initial velocities ≳10⁶ cm/s. If ablation is carried out in a low-pressure reactive gas such as oxygen, simple oxide molecules are also formed in the expanding ablation beam. In an ambient gas, a shock front results from collisions between the expanding plasma and the gas molecules (Fig. 2). This front propagates with gradu-