Oriented inorganic films

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Since 1996 there have been over 500 literature citations for oriented inorganic films, although a majority of these papers are concerned with vapor phase processing routes such as chemical vapor deposition. Within the context of colloid and interface science there has been continued, incremental progress in so-called 'sol-gel' or 'solution chemical' processing of epitaxial ferroelectric and piezoelectric films for a variety of electronic and optical applications. A promising new approach that obviates the requirement of a single crystal substrate involves heterogenous nucleation and growth on preorganized organic and organically-modified surfaces. Such biomimetic schemes have also been used to form highly oriented porous films for use in separations, sensors, and catalysis. New hydrothermal routes have been devised to prepare oriented zeolite films as well as ferroelectric films. It is anticipated that the combination of self-assembly processes with innovative patterning strategies should lead to future advances in this field.

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Abbreviations

MMS	mesoporous molecular sieves
OIF	oriented inorganic films
PZT	lead zirconate titanate

Introduction

Oriented inorganic films can range from polycrystalline, microporous zeolitic membranes for use in molecular separations to dense, single crystal, lead zirconate titanate (PZT) films designed for optical data storage. Film orientation is often intended to exploit asymmetry in crystalline or composite structures, thereby enhancing transport, mechanical, magnetic, optical, or electronic properties.

This review discusses the recent progress in the synthesis and processing of oriented inorganic films (OIF), emphasizing recently published papers. I have defined 'oriented' to include any structure which exhibits a specific direction with respect to a substrate or surface. Epitaxial films, which show precise crystallographic orientation with respect to the substrate, are a subset of oriented films. For completeness, the review covers films (defined as continuous supported or free-standing layers) as well as *deposits* (consisting of supported, discontinuous assemblages of oriented structures). The scope of this review, however, is limited to oriented films prepared from molecular or colloidal precursors in liquid media, excluding the myriad of vapor phase routes to OIF such as chemical vapor deposition and molecular beam epitaxy.

The preponderance of research on OIF falls within three categories: dense, optimally epitaxial, ceramic films for electronic and optical applications; oriented microporous or mesoporous films for applications in molecular separation, sensing, and catalysis; and multilayered films for mechanical/tribological, sensing, and electronic applications. Two general synthetic approaches have been utilized to form these OIFs: those involving molecular or oligomeric precursors and those utilizing colloidal sols (sequential deposition schemes combine these two approaches). Much of the recent research on OIF has benefited from adaptation of biomineralization principles, namely the use of organized organic interfaces to regulate nucleation, growth, morphology, and orientation of inorganic crystals [1–3,4•,5•].

Epitaxial ceramic films

Epitaxial ceramic films are important for ferroelectric and opto-electronic devices, where one can optimize the anisotropic properties of perovskite materials such as $BaTiO_3$ and PZT. Chemical solution routes to formation of epitaxial or highly oriented ceramic films are well known (see for example [6–9]) and reviews of this topic were recently published by Lange [10•] and Schwartz [11•]. Most commonly, a homogeneous sol, prepared from metal alkoxide, carboxylate, or β-diketonate precursors, is used to deposit a continuous, amorphous film of the requisite stoichiometry onto a single crystal substrate. A low temperature heat treatment is used to decompose or pyrolyze the precursors, often inducing spontaneous nucleation of a polycrystalline film at the substrate surface. Epitaxy then occurs at higher temperatures by the conversion of this polycrystalline film into a single crystal. When the film and substrate have identical structures (despite different chemistries) and small lattice mismatches (5% or less), this conversion occurs simply by the growth of epitaxial grains located at the film/substrate interface [10•]. With regard to chemical considerations, it is well established that the choice of precursors and their extent of reaction prior to deposition ultimately govern solution homogeneity, pyrolysis temperature, onset of crystallization and densification behavior [11•]. The relationship, however, between this precursor chemistry and the epitaxy that takes place is less well defined because of the high temperatures (>700°C) required to grow the epitaxial grains to reach the surface. A consistent finding [11•] is that prereaction of the precursors, for example by hydrolysis, to form oxo oligomers or polymers diminishes film orientation [6,12]. It is argued that oxo species serve to preferentially nucleate randomly oriented crystals within the film, and that these sites compete with nucleation sites at the film/substrate interface, leading to growth of randomly oriented grains [6]. Prehydrolysis, however, also promotes low temperature nucleation, impeding densification, and thus may contribute to frustration of the epitaxial conversion process [10•].

Hydrothermal techniques are commonly used to prepare zeolitic films and membranes (discussed below), but it is only recently that they have been explored as a low temperature route to production of epitaxial ceramic films [13,14•]. Using anatase TiO_2, $Pb(NO_3)_2$, and ZrOCl as precursors under alkaline aqueous conditions where $Pb(Zr_xTi_{1-x})O_3$ is the thermodynamically favored phase, Chien *et al.* [14•] demonstrated epitaxial growth of PZT on (001) $SrTiO_3$ and $LaAlO_3$ single crystal substrates at 90–150°C. X-ray diffraction of films on $SrTiO_3$ showed alignment of (*h*00) and (00*l*) planes of PZT with (00*l*) planes of $SrTiO_3$. Epitaxial growth initiates by formation of {100} faceted islands. Growth and coalescence of the islands can lead to smooth, continuous films with only occasional porosity. This appears to be a promising new approach to making epitaxial ceramic films. Electronic applications, however, may be limited because of the likely incorporation of hydroxyl groups during the hydrothermal process.

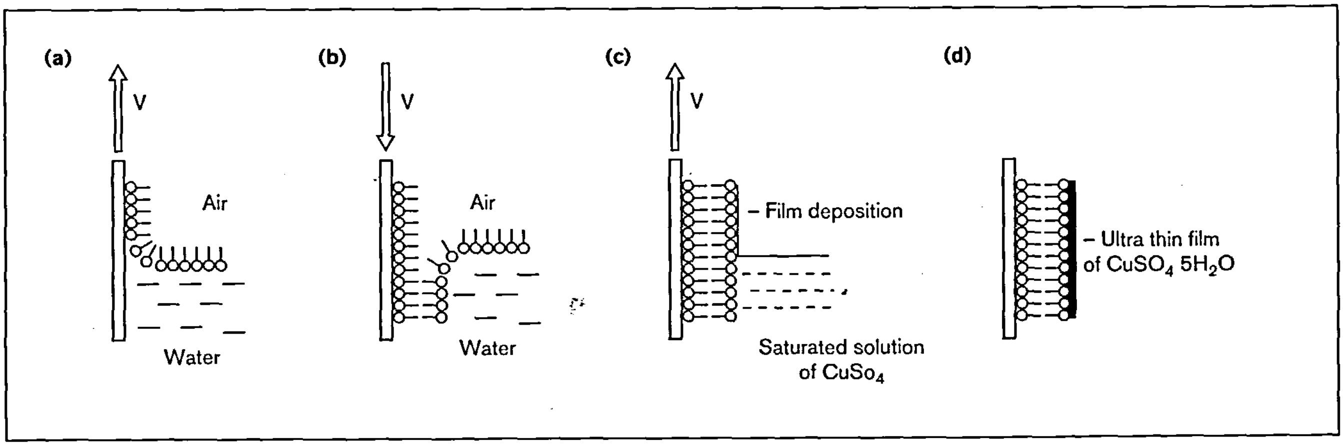
Ceramic films prepared on organic surfaces

Another recently discovered route to the production of oriented ceramic films is the deposition onto functionalized organic surfaces [15,16,17••]. This approach mimics biomineralization, where preorganized organic surfaces serve to template the heterogeneous nucleation and growth of oriented inorganic crystals in aqueous media. Studies of biomineralization and adaptation of biomineralization schemes to inorganic materials processing have focused on establishing the structural and stereochemical relationships between the organic template and the precipitating inorganic phase. The most comprehensive studies are those of crystallization under Langmuir monolayers (for reviews see [18,19]). Recently, Litvin *et al.* [20•] demonstrated the crystallization of [010]-oriented aragonite ($CaCO_3$) under a monolayer of 5-hexadecylcyloxyisophthalic acid. On the basis of molecular modeling results, they concluded that close structural correspondence between the *ac* face of aragonite and the periodic hydrogen-bonded network of the self-assembled Langmuir monolayer was responsible for interfacial molecular recognition and specificity of the oriented crystallization.

To date, crystallization under Langmuir monolayers has resulted exclusively in deposits of isolated crystals [19]; although these can be transferred to a substrate, they are of limited technological significance. Tang and Tai [21••] used Langmuir–Blodgett films of 9-(hexadecylimino)-4,5-diazafluorene, prepared over a range of area pressures, as templates for the deposition of $CuSO_4{\cdot}5H_2O$ by dip-coating from aqueous solution (Figure 1). It is noteworthy that at a pressure where the lattice parameters of the Langmuir–Blodgett layer matched that of (010) $CuSO_4{\cdot}5H_2O$, a continuous [010]-oriented film resulted.

Although the above results support the central tenet of biomineralization (that template functionalization and supramolecular organization play a key synergistic role in oriented crystallization), there exists counter examples [22–25] where, for example, the extent of compression of the Langmuir monolayer had little effect on the resulting crystal structure or monolayers of similar headgroup spacings resulted in different crystallographic orientations

Figure 1



Formation of ultrathin oriented crystals on Langmuir–Blodgett bilayer templates. Steps **(a)** and **(b)**: deposition of Langmuir–Blodgett bilayer template with ordered hydrophilic surface. (Arrows refer to the direction of motion and velocity, V, of substrate). Step **(c)**: dip-coating in aqueous $CuSO_4$ solution to form oriented $CuSO_4{\cdot}5H_2O$ film with [010]-orientation. Step **(d)**: finished product. Adapted with permission from [21••].

of the crystalline deposit. Based on biomineralization studies of calcite and aragonite ($CaCO_3$), where only polyanionic proteins are needed to provide stereospecific control of nucleation, orientation and phase, it has been concluded [26,27•] that periodic, preorganized organic arrays are not necessarily needed for regulation and orientation of crystal growth [26,27•]. Tarasevich *et al.* [28••] reached the same conclusion in a comprehensive study of goethite (FeOOH) crystallization from aqueous media. They observed the formation of continuous [020]-oriented FeOOH films on sulfonated polystyrene and sulfonated self-assembled monolayers (vinyl terminated alkyl (C_{17}) silanes reacted with sulfur trioxide vapor). Because sulfonate sites are disordered on polystyrene, they proved that ordered organic lattices are not necessary to obtain oriented inorganic structures. As the (020) or *ab* planes of FeOOH have the greatest iron density, perhaps orientation results in this case from maximization of iron–sulfonate interactions rather than complementary periodicity of template and crystal.

Zeolitic films and membranes

Zeolites are microporous crystalline solids characterized by one-, two-, or three -dimensional pore channel systems with unimodal pore size distributions. Because of their precisely defined pore sizes, zeolite films are of interest for molecular separation membranes, sensors, and optical hosts [29•]. Recent research has emphasized the synthesis of thin, oriented zeolite films in order to enhance transmembrane flux, improve sensor response, and achieve ordered, transparent optical hosts [30,31,32•]. The most common strategy to prepare oriented zeolitic films is hydrothermal deposition from clear solutions. Orientation appears to originate from a conformal gel layer formed on the substrate surface [29•,32•,33]. For example, if an MFI-type zeolite (ZSM-5) is grown on a flat substrate under appropriate conditions, the crystals will grow within the gel layer with their long axes parallel to the substrate surface; this is beneficial for membrane applications [34]. This orientation is not epitaxial and is rather insensitive to the substrate composition.

The ability to obtain a thin, continuous, oriented zeolite film appears to depend on maintaining a continuous thin gel layer throughout the synthesis process as oriented crystallites, nucleated at the gel/liquid interface, grow and coalesce [32•]. Zeolite orientation is affected by substrate roughness and porosity [29•,32•,33]. Although often detrimental to the orientation of the film, this orientational influence was exploited by Wu and co-workers [35•,36] who prepared a vertically oriented AFI-type zeolite ($AlPO_4$-5) on a porous anodic alumina support, characterized by periodic 200 nm diameter pores oriented perpendicular to the support surface. The AFI zeolite deposits were highly oriented, with their [001] axes perpendicular to the support surface (i.e. parallel to the support pore channels). It is thought [35•,36] that this orientation results from oriented nucleation occurring within the substrate pore channels — again a conformal gel layer (created within the pores) may be influential in defining orientation.

Tsapatsis and co-workers [37,38••,39] have developed a very promising two-step approach to forming oriented zeolite films by utilizing particulate zeolite nanocrystals as 'seeds'. In the first step, a colloidal nanosol is used to prepare a supported or unsupported film. The second hydrothermal step is used to grow the zeolite seeds with little additional zeolite nucleation. In the case of silicalite [38••], the initial seed layer was randomly oriented but the secondary growth conditions were such that the crystallographic *b* axes were oriented parallel to the film surface. Greater orientation was achieved in zeolite A systems by growing the initial seeds to a size of 200–300 nm at which size they acquired a cubic shape [39]. In this case the initial seed layer exhibited a high degree of two-dimensional order. Secondary growth using oriented seeds resulted in continuous films exhibiting (*h*00) orientation parallel (and perpendicular) to the substrate. Gas separation membranes prepared by this approach exhibit excellent selectivity and flux [38••].

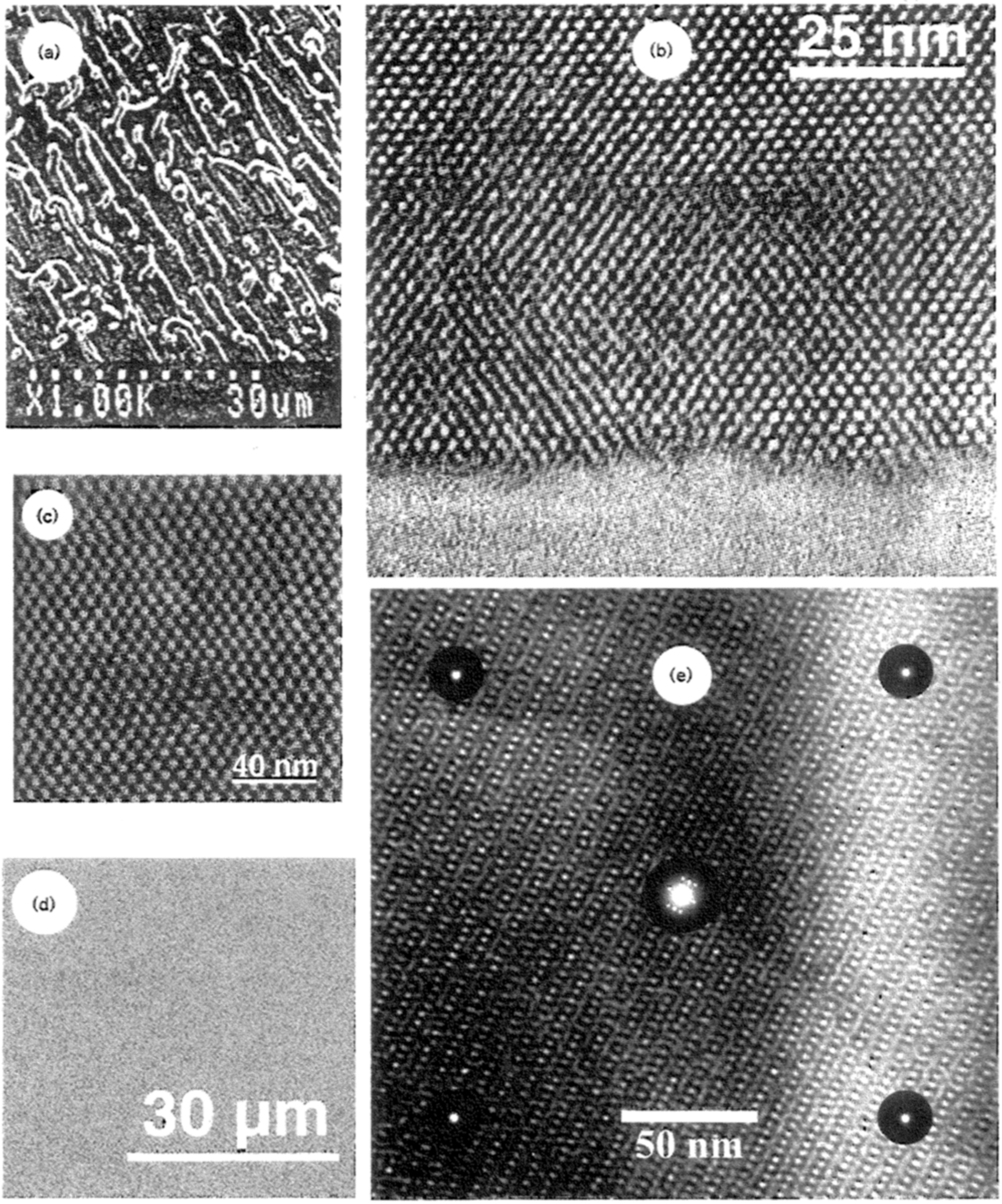
Bein and Feng [29•,40,41] pioneered the use of functionalized organic surfaces to induce nucleation and growth of oriented molecular sieve deposits. Recently Mintova *et al.* [42] used organic surfaces to orient zeolite seed crystals on piezoelectric quartz crystalline microbalances. Adsorption of silicalite-1 crystals of 60 nm diameter onto a siloxane surface derived from a cationic polymer resulted in a *b*-axis-oriented seed layer. Secondary hydrothermal growth resulted in a continuous, [010]-oriented silicalite film with the straight pore channels of the silicalite oriented perpendicular to the quartz crystlline microbalances substrate.

Oriented mesoporous films

Mesoporous molecular sieves (MMS), often referred to in the literature as MCM (Mobil Composition of Matter)-type materials, are formed by a supramolecular templating process involving amphiphilic surfactant molecules [43,44]. According to several possible reaction pathways, inorganic oligomers and surfactant molecules co-organize or sequentially organize in aqueous media to form composite structures resembling lyotropic liquid crystalline mesophases with inorganic constituents located adjacent to the hydrophilic head groups of the surfactant. Removal of the surfactant templates creates ordered mesoporous solids, usually in the form of precipitates.

Some of the most promising applications of MMS would be in the form of films for use as membranes, sensors, and optical hosts. Two approaches to the formation of MMS films have been developed. Yang *et al.* [45••,46•] and Aksay *et al.* [47•] showed that exceeding the critical micelle concentration of a bulk silica–surfactant solution results in formation of hexagonal mesophases by interfacial self-as-

Figure 2

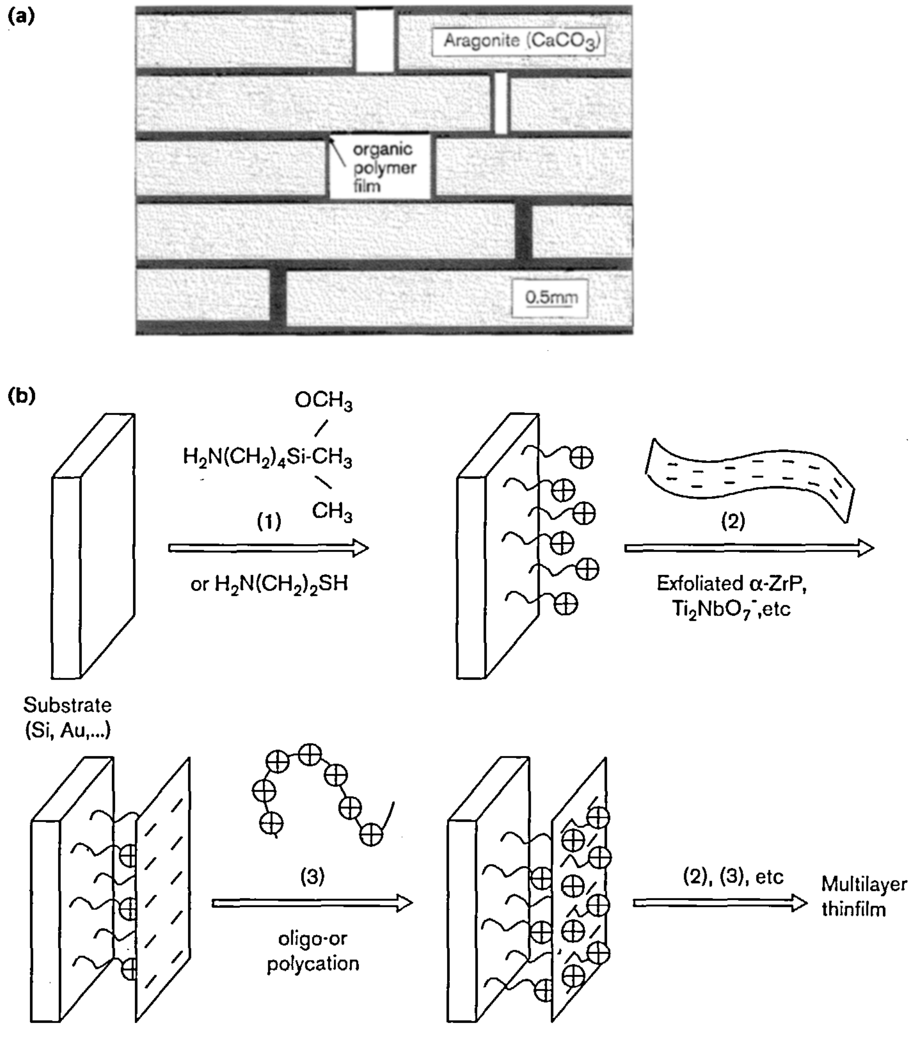


Oriented mesoporous thin film microstructures. **(a)** Initial nucleation and growth of isolated oriented crystallites of hexagonal mesoporous silica on mica [45••]. **(b)** Cross-section of mesoporous silica film grown on mica showing hexagonal arrangement of one-dimensional pore channels oriented parallel to the substrate surface [45••]. The bottom edge of the mesoporous structure represents the original film–liquid interface. **(c)** Atomic force microscopy image of pure 18-3-1 surfactant (consisting of an 18-carbon aliphatic chain attached to a dimethylquaternary ammonium connected by a three-carbon link to a trimethylquaternary ammonium) adsorbed on mica. The hexagonally close-packed micelles probably serve as nucleation sites for *c*-axis-oriented $P6_3/mmc$ mesoporous silica films [50••]. **(d)** Scanning electron microscopy plan view image of oriented hexagonal mesoporous silica film prepared by dip-coating, showing macroscopic homogeneity (compare to [a]) [51••]. **(e)** Plan view image of [210]- or [01-10]-oriented cubic or three-dimensional hexagonal film prepared by transformation from a lamellar mesophase. Central electron diffraction is of the mesophase and the square arrangement of satellite spots is from the underlying [100]-oriented silicon substrate, confirming the orientation of the film with respect to substrate. Adapted from [51••].

sembly. These mesophases, which have one-dimensional pore channels, form at substrate/liquid and liquid/vapor interfaces. Atomic force microscopy investigations [47•,48] indicated that, on mica and graphite, oriented crystallites are nucleated by adsorbed cylindrical or hemicylindrical micelles [49]. Continuous films form by growth and coalescence of isolated crystallites (Figure 2a) [45••,47•], resulting in pores oriented rigorously parallel to the substrate surface (Figure 2b). Using a novel two-headed surfactant, Tolbert *et al.* [50••] used the same approach to prepare films with space group $P6_3/mmc$ both on mica and at the air/water interface. These films, which can be considered to consist of hexagonally close-packed spheres, ellipsoids, or interconnected ellipsoids, were shown by atomic force microscopy to be nucleated on mica by interfacially assembled hexagonally close-packed spherical micelles (Figure 2c). Orientation of the *c*-axis of the mesophase should thus guarantee transport normal to the substrate surface, which is necessary for membrane and sensor applications.

A second approach, developed by Lu *et al.* [51••], begins with an alcohol–water–silica sol prepared with an initial surfactant concentration much less than the critical micelle concentration. Alcohol/water evaporation during sol-gel dip-coating progressively increases the concentrations of

Figure 3



(a) Schematic of aragonitic portion of abalone nacre showing oriented nano-laminate construction. **(b)** Schematic representation of 'molecular beaker epitaxy via sequential adsorption of inorganic two-dimensional anions and oligomeric or polymeric cations. Adapted with permission from [52].

silica and surfactant, thus inducing mesophase development in the depositing film. Macroscopically homogeneous films (Figure 2d) rapidly form in a continuous coating process. Through variation of the initial surfactant concentration a variety of film structures are attainable, including hexagonal mesophases with one-dimensional pore channels oriented parallel to the substrate, cubic and hexagonal mesophases with three-dimensional pore channels, and lamellar phases comprising alternating sheets of silica and surfactant oriented parallel to the substrate surface. Lu *et al.* [51••] demonstrated that lamellar films could transform to highly oriented cubic or hexagonal films during aging or heating (Figure 2e). It is believed [51••] that the perfection and order of transformed films are derived from those of the lamellar precursor films. Mesophase development, therefore, via phase transformation may represent an excellent general route to highly oriented thin film microstructures.

Nanolaminated films

Laminated films composed of alternating organic/inorganic, metal/inorganic, or semiconductor/inorganic layers oriented parallel to the substrate surface are of interest for a variety of tribological, electronic, and optical applications A classic example is that of seashells [4•,47•], where the laminated polymer–aragonite composite (Figure 3a) is twice as hard and one thousand times as tough as the parent $CaCO_3$. In addition to the supramolecular templating approach described above, various sequential or multistep procedures have recently been developed to achieve well-defined nanolaminates. Mallouk and co-workers [52] and Kleinfeld and Ferguson [53,54] have developed a process (referred to as 'molecular beaker epitaxy' [52]) involving sequential layering of sheet-like colloidal polyanions (e.g. exfoliated clay) with a variety of oligomeric or polymeric cations (Figure 3b). The interspacing of structurally well-defined sheets eliminates interlayer penetration and ensures a constant interlayer thickness. Although this route requires many successive deposition (adsorption) steps to achieve practical film thicknesses, it results in predictable heterostructures and, as recently demonstrated by Kleinfeld and Ferguson [54], is self-healing (i.e. defects are not propagated from layer to layer). Even more important is its potential for the preparation of heterosuperlattices composed of custom-designed sequences of a diverse combination of materials.

Kunitake and co-workers [55,56,57•] have developed an elegant synthetic approach to the preparation of organic–inorganic nanolaminates based on intercalation of ions or clusters into multibilayer cast films. Multibilayer films are formed by casting aqueous solutions of bilayer membranes and provide ordered architectures at both the molecular and macroscopic scale. The geometric packing of the hydrophilic head groups, the surface charge, and the surface density may be accurately controlled through appropriate design of the amphiphile to provide a tailored intercalation host. Rather recently Kimizuka *et al.* [56] demonstrated the formation of a periodically spaced, cyano-bridged, bimetallic complex $[Ni(CN)_4\text{-}Cu]$ via sequential intercalation of a multibilayer with $[Ni(CN)_4]^{2-}$ and aqueous copper nitrate. Maoz *et al.* [58] used a preorganized, hydrogen-bonded bilayer structure as both a host micro-reactor and template for its own replication. Octadecyltrichlorosilane bilayers were intercalated into pre-existing bilayers, followed by hydrolysis. After n successive treatments, $2n-1$ siloxane bilayers were created periodically ordered on the substrate surface.

Conclusions and perspectives

The emerging trend in OIF formation is the use of organics to control the phase, orientation, periodicity, pore connectivity, and so on of the deposited inorganic film. It is anticipated that this trend will continue, with even greater emphasis on the use of self-assembly/self-orgainzation processes to directly form the desired microstructure in a robust, reliable process with a minimum of steps. We may envision that multifunctional organics will begin to be utilized. For example, polymerizable amphiphiles could serve both as supramolecular templates and as polymerizable monomers, and therefore enable efficient formation of organic–inorganic polymer laminates that mimic organic shell. Self-assembled monolayers could be designed to both induce epitaxial crystal growth and provide a means of patterning the oriented film deposition process. In this regard, several groups have recently demonstrated patterned film deposition on organic functionalized surfaces [59–62], but to date there seem to be few examples of patterned oriented films [17••].

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- •• of outstanding interest

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