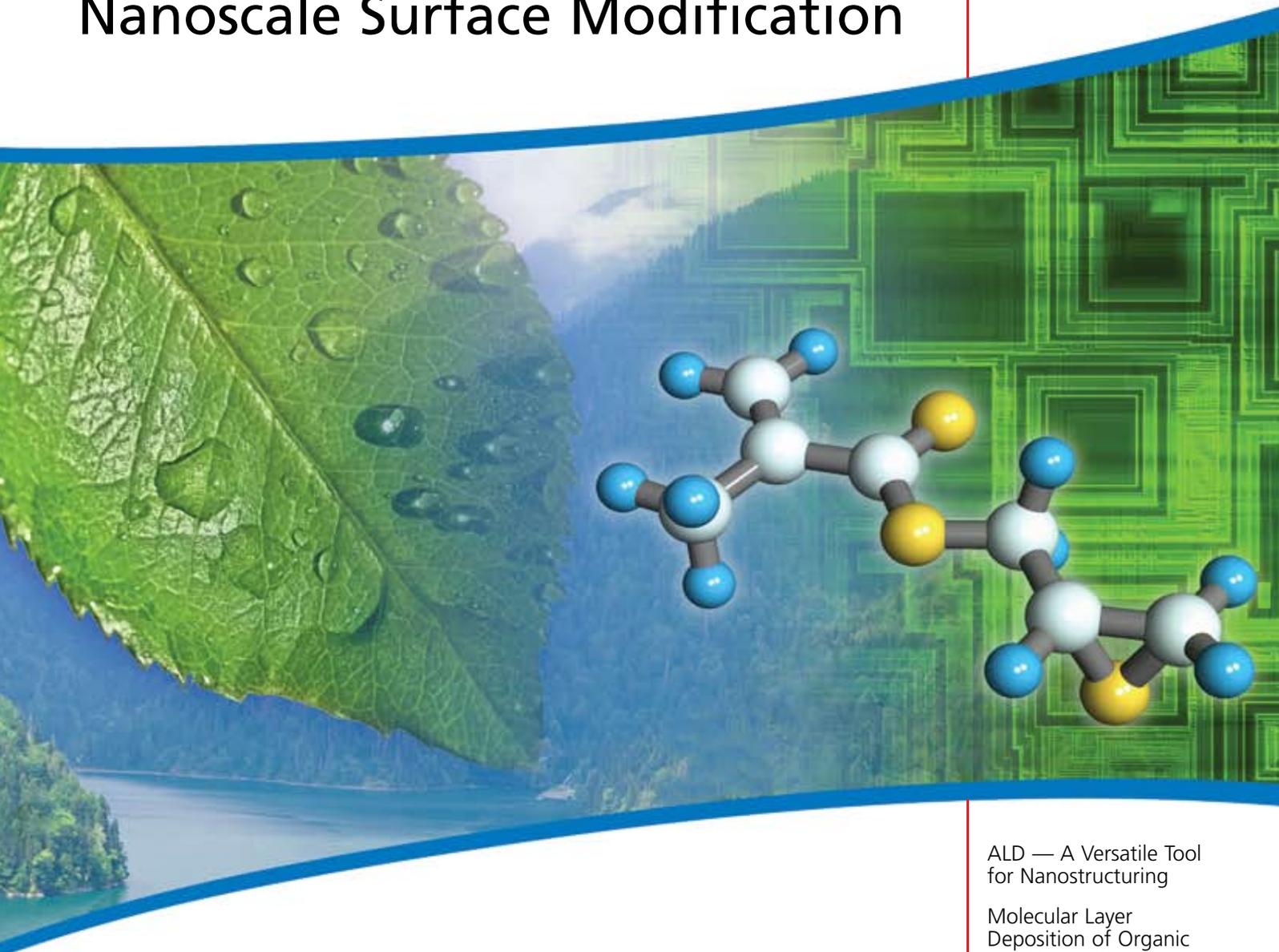


Material Matters™

Vol. 3, No. 2

ALDRICH
Chemistry

Nanoscale Surface Modification



*Nano-engineered surfaces —
learn from Nature*

ALD — A Versatile Tool
for Nanostructuring

Molecular Layer
Deposition of Organic
and Hybrid Organic-
Inorganic Polymers

Molecular Monolayers
on Silicon Surfaces

Universal Platform for
Surface Modification

SIGMA-ALDRICH®



Viktor Balema, PhD.
Aldrich Materials Science
Sigma-Aldrich® Corporation

Introduction

Welcome to the second issue of *Material Matters*™ in 2008 focused on the techniques used for nano-functionalization and nano-structuring materials' surfaces, and applications of modified materials in electronics, lithography and other relevant fields.

Modifying materials by coating them with nano-scale organic, ceramic or hybrid layers is a versatile way to add new value, advanced features and unique properties to otherwise conventional materials. Creating a nano-film on a material's surface can significantly improve or even completely change its optical, electrical and electronic properties, the wettability and biocompatibility as well as introduce new unique properties such as exceptional hardness or corrosion resistance. Frequently, the modification method determines properties of the surface created. As modification techniques improve, increases also the variety of materials that can be altered and customized.

The current issue features four different methods for accomplishing surface modification on the nano-scale by thought leaders. Dr. Mato Knez from Max-Planck-Institute of Microstructure Physics, Halle, Germany, provides an introduction to vapor deposition approaches to surface modification and thin film fabrication. Professor Steven George and Dr. Byunghoon Yoon from the University of Colorado, Boulder, discuss molecular layer deposition of organic and hybrid organic-inorganic polymers. Dr. Greg P. Lopinski and Professor Daniel D. M. Wayner, Steacie Institute for Molecular Sciences, Ontario, Canada, review the enhancement of the functionality of silicon based materials and devices by controlled formation of organic molecular monolayers on silicon surfaces. Finally, the article from the Clemson University group lead by Professor Luzinov focuses on synthesis and characterization of nano-thick, chemically grafted polymer films (polymer brushes) on various inorganic and polymeric substrates. The article is accompanied by a description of the surface modification kit developed at Sigma-Aldrich based on Luzinov's technique.

Products that accelerate your research in the fundamental science of nanoscale surface modification are highlighted. Please visit Aldrich Materials Science at sigma-aldrich.com/matsci for product information. We invite you to send comments, questions and suggestions about *Material Matters* and materials of interest to matsci@sial.com.

About Our Cover

Nature offers numerous examples of achieving big objectives with tiny tools. Design of natural materials often serves as a model for many technical innovations. Nanoscale modification of various surfaces to make them hydrophilic, hydrophobic or resistant to external hazards is widespread in Nature and highly desired in modern technology. In many cases, long-chain organic molecules or polymers attached to natural materials are responsible for their remarkable properties. The molecule of glycidyl methacrylate shown on the cover allows modification of dimethylsiloxane-based surfaces. Such surfaces find broad use as stamps for micro-lithography and other patterning applications related to advanced electronic materials. Glycidyl methacrylate-based polymers linked to polydimethylsiloxane serve as anchor layers for other molecules and polymers offering a broad range of highly desired properties as discussed on p. 44–48 of this issue.

Material Matters™

Vol. 3 No. 2

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Joe Porwoll

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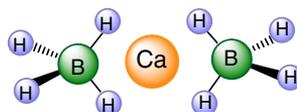
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Calcium borohydride—New Material for Hydrogen Storage

Dr. Grigorii L. Soloveichik of General Electric Global Research kindly suggested that we introduce the solvent-free calcium borohydride, $\text{Ca}(\text{BH}_4)_2$, as a material for advanced fuel cell applications.¹ Unsolvated $\text{Ca}(\text{BH}_4)_2$ is a base-material for novel hydrogen storage systems.² In the crystal, the Ca^{2+} ion is surrounded by six tetrahedral BH_4 -units and each BH_4 -unit contacts with three Ca^{2+} ions. Hydrogen release from $\text{Ca}(\text{BH}_4)_2$ begins at 360 °C and is complete at 500 °C; the amount of hydrogen released is 9.6% by weight of the hydride. The material is a reversible hydrogen source. It can be regenerated by reaction with hydrogen gas at 700bar/400–440 °C.² The regeneration pressure and temperature can be significantly reduced³ by doping $\text{Ca}(\text{BH}_4)_2$ with TiCl_3 (**Aldrich Prod. No. 695254**).

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Calcium borohydride

695254-1G

1 g

Advanced Materials for Surface Modification Featured in This Issue

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ALD — A Versatile Tool for Nanostructuring



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Introduction

The acronym ALD stands for atomic layer deposition. Although the process was developed during the 1970s, ALD remained more of a niche process, since initially most applications of this technique were bound to electronics. In recent years considerable interest in ALD has emerged, mainly due to its ability to controllably coat even very small structures, e.g. nano- or microstructures. Using various strategies and modifications, a number of groups worldwide have produced novel structures or functionalized materials. Some of the most innovative and promising strategies include template-directed synthesis of novel structures, area-selective deposition of materials, low-temperature ALD deposition temperature-sensitive substrates, and also the development of new processes to increase the versatility of ALD.

All of these applications of ALD show the power of this deposition method and its impact on advanced materials research. Particularly simple yet effective processes together with the increasing number of commercially available ALD reactors have attracted the interest of scientists worldwide as reflected in the increasing number of scientific publications in the field of “nano-ALD.”

In this manuscript a few examples of recent work, including the above-mentioned areas, will be shown. This is, however, only a glimpse of current developments. A more comprehensive review can be found elsewhere.¹

The ALD Process

The ALD process is a vapor phase thin film deposition method chemically very similar to Chemical Vapor Deposition (CVD). The similarity can be seen from the fact that ALD precursor materials can be used for CVD, however, not necessarily vice-versa. Physically, there are significant differences. Using the example of Al_2O_3 -deposition from trimethylaluminum (TMA, Aldrich Prod. No. 663301) and water. The major difference between CVD and ALD will be explained.

While in the CVD process two precursor materials, TMA and H_2O , are jointly introduced into a reaction chamber to produce Al_2O_3 which deposits on a substrate, in the ALD process the chemical reaction is split into two half-reactions. Initially the substrate is exposed to TMA forming a chemisorbed (sub) monolayer (Figure 1a). After adsorption the excess TMA in the gas phase is removed by purging. Successively the substrate is exposed to H_2O to react with the (sub)monolayer of TMA forming a layer of Al_2O_3 (Figure 1b). Removal of the reaction products (here: methane) and excess of H_2O finishes one cycle

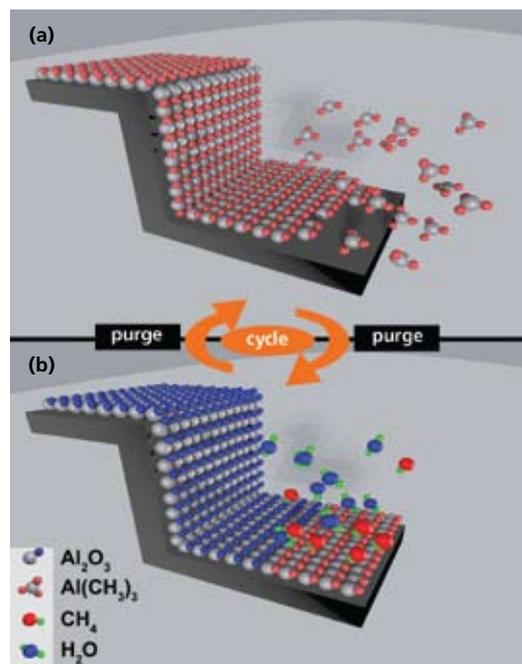


Figure 1. Schematic of one cycle of an ALD process. The schematic illustrates a simplified model for the deposition of Al_2O_3 using TMA and water as precursors.

of growth, which can be repeated until the desired thickness of the layer is obtained. If the process is performed in a precursor-specific temperature range, the so-called “ALD-window,” the growth of the film is linear and the thickness can be controlled on the Å-scale.

The big advantage of ALD is that the process is driven by the chemical saturation of surfaces with the precursor (e.g., TMA) rather than a directed deposition, as is the case with CVD. Therefore the ALD process allows for conformally coatings of surfaces of nanopores even with very high aspect ratios² or very complex materials such as aerogels.³

Template-Directed Synthesis of Nanostructures

Template-directed synthesis of nanostructures is the fastest growing area in ALD. Various templates can be used for conformal coating and replication or functionalization of nanostructures. These include nano- and microporous substrates, arrangements of nanospheres, nanowires, nanotubes or even single nanoparticles.

Probably, the easiest method for templated nanostructure synthesis involves the use of porous materials. During the past few years a number of manuscripts have been published, showing the synthesis of nanotubes from a variety of materials or even arrays of nanotubes.² More recently, the focus of nanotube synthesis has shifted from the deposition of basic materials towards functional materials. Recently, for example, the ability to produce magnetic nanotubes from nanoporous anodic alumina templates by ALD deposition of iron oxide (see Figure 2) or nickel has been shown.^{4,5}

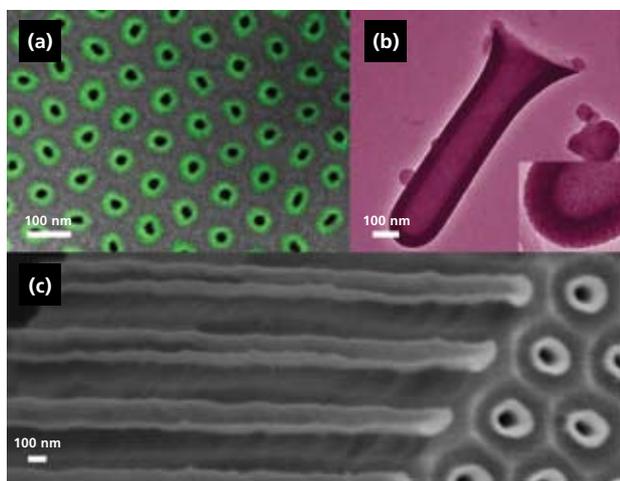


Figure 2. Electron micrographs (scanning, SEM; transmission, TEM) of iron oxide tubes. Scale bars: 100 nm. (a) SEM of an array of narrow tubes (11 ± 4 nm Fe_2O_3 , green circles) embedded in the alumina template; contrast enhanced by colorization. (b) TEM of a single thick and short tube (42 ± 4 nm Fe_2O_3) isolated by dissolution of the template; the inset zooms in on the very smooth wall. (c) SEM of an array of thick $\text{ZrO}_2/\text{Fe}_2\text{O}_3/\text{ZrO}_2$ tubes ($12\pm 2/26\pm 4/12\pm 2$ nm) embedded in the template: edge view at a crack, with tubes broken in their length and emerging on the top side of the membrane. Image reprinted with permission from *J. Am. Chem. Soc.* **2007**, *129*, 9554–9555, Copyright 2007 American Chemical Society.

Similar to nanoporous materials, nanowires can also be used as templates for ALD deposition on and successive removal of the initial nanowire. Inducing a solid-state diffusion reaction also produces nanotubes in specific circumstances.^{6,7}

A trend towards the synthesis of functional nanostructures has been observed. Recently, a combination of ALD deposition, reduction and initiation of the Rayleigh instability led to the synthesis of TiO_2 -nanotubes with incorporated Cu-nanoparticles in a regular nanochain arrangement (**Figure 3**).⁸ After optimization such nanostructures may find future application in nanooptics or plasmonics.

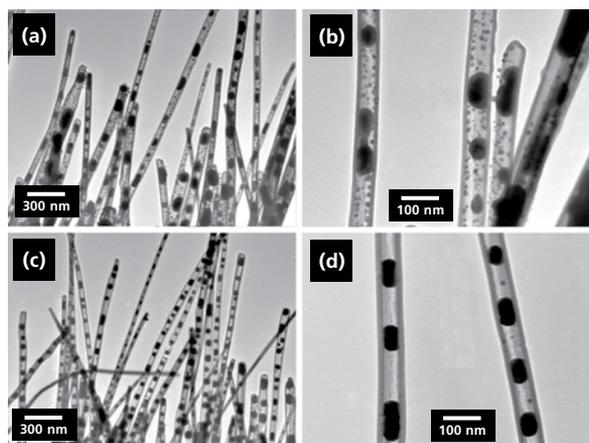


Figure 3. TEM images of Cu nanoparticle chains prepared by reduction of CuO nanowires with 20 nm Al_2O_3 shells with H_2 for 1 h at different temperatures: (a,b) sample prepared at 600 °C; (c,d) sample prepared at 750 °C. Panels (b) and (d) are TEM images corresponding to panels (a) and (c) at higher magnification. Image reprinted with permission from *Nano Lett.* **2008**, *8*, 114–118. Copyright 2008 American Chemical Society.

Advanced optical nanostructures produced by ALD already exist. Due to the benefits of this deposition method the production of inverse opal structures from a variety of materials by replicating highly ordered arrangements of nanospheres became possible. Research groups at Georgia Institute of Technology and Harvard University have been very active in this field. A number of various inverse opals were synthesized by ALD and characterized. The materials deposited include WN, TiO_2 , Ta_3N_5 , ZnO, GaAs or even TiO_2/ZnS multilayers.^{9–12} Such structures show enormous potential, for example, as photonic crystals. Thanks to this simple synthesis method such structures can and surely will be further developed in the coming years.

A comparatively difficult area is the use of carbon nanotubes (CNTs) as templates. As the surface of carbon nanotubes is rather inert, it becomes very difficult to coat CNTs by ALD. Nevertheless, due to their shape and stability CNTs remain very interesting as templates. Therefore strategies were developed in order to achieve uniform coatings. Various reports showed that after functionalization of CNT with, for example, NO_2 , a coating with Al_2O_3 , HfO_2 or Ru-oxide indeed becomes possible.^{13–16} These coatings could be beneficial for the improvement of the physical and/or chemical properties of the CNT. However, technological use will still require further research and development.

Probably the most difficult nanoscale template for ALD is a single nanoparticle. Although it might be easily coated, difficulties in handling such materials appear frequently. If one wants to obtain a continuous conformal coating, one has to prevent any contact of the nanoparticles with each other and/or with the walls of the reactor. Nevertheless, here too some progress has been achieved. A group in Boulder, Colorado, showed that there are at least two ways to handle nanoparticles during ALD deposition in order to obtain conformality.¹⁷

Area-Selective Deposition of Materials

A highly interesting field of development in ALD is area-selective deposition. Although the most powerful application of ALD is the conformal coating of all accessible surfaces, there is the possibility to direct the deposition to discrete areas by chemically tuning them. Patterns of lithographically produced structures can be selectively switched to hydrophilic or hydrophobic (e.g., by various silanes) in order to direct or prevent the adsorption of precursor molecules.¹⁸ This route is a very elegant way to obtain nanoscale patterns of materials needed for certain applications. The principle itself is simple as well as effective. Most likely this strategy will be broadly applied to deposit a variety of materials in a structured manner in order to obtain electronically or optically active materials.

Low-Temperature ALD Deposition

Low-temperature ALD (LT-ALD) is playing an increasingly important role. In thin film deposition the ability to coat materials that are temperature-sensitive and cannot be coated with other methods (e.g. CVD); substrates include polymers or biological templates.

Initial experiments on LT-ALD were performed in 1994, involving deposition of SiO_2 at room temperature.¹⁹ Since then a number of (LT-ALD) processes were successfully developed for materials like CdS, Al_2O_3 , TiO_2 , B_2O_3 , V_2O_5 , HfO_2 , ZrO_2 , ZnO and even metallic Pd.^{1, 20, 21} Although this list of materials is already impressive, undoubtedly a larger number of available processes, particularly for the deposition of metals would be of high interest. If one considers the possibility to deposit metallic electrodes on polymer structures in order to obtain

flexible electrodes, the significance of LT-ALD becomes obvious. Development in this area is at the very beginning and one can expect that more materials will be deposited by LT-ALD technique in the near future.

A particularly interesting application of LT-ALD is the possibility to coat or functionalize biological nanostructures. Nature has already applied nanotechnology for millions of years. If one considers the hydrophobicity of lotus leaves, which is related to micro- and nanostructures, it becomes obvious that mankind can still learn from nature. In some cases nature provides perfect nanostructures, which could easily be replicated thus avoiding more complex growth and fabrication with nanometer precision. However, one of the limiting factors here is the technology involved; for example, in the case of ALD the vacuum process and the deposition temperature. As the vacuum process cannot be avoided, for structures that are vacuum resistant, the deposition temperature is of significance. A few attempts have already been reported to coat biological nano- and microstructures by ALD. Initial experiments of this kind involved the coating of plant viruses and ferritin spheres with metal oxides, which lead to tiny metal oxide nanotubes and freestanding films with embedded ferritin molecules (Figure 4).

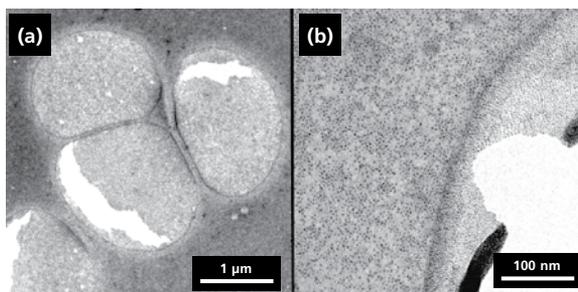


Figure 4. TEM (200 kV) images of ferritin molecules treated with Al_2O_3 (a) and TiO_2 (b) by ALD. The images show ferritin molecules embedded in amorphous freestanding Al_2O_3 and TiO_2 films. The darker gray areas originate from the holes in the carbon film on the TEM grid. The black spots in image (b) show the iron oxide core of ferritin. The films have cracks, and on image (b) the free-standing film is rolled up from the side, which was caused by the electron beam from the TEM. Image reprinted with permission from *Nano Lett.* **2006**, *6*, 1172–1177. Copyright 2006 American Chemical Society.

Further work showed the possibility to coat nanostructured butterfly wings with Al_2O_3 and thus to obtain structured samples with various colors that depend on the thickness of the coating.²² Although this field is emerging slowly, it is expected that there will be much more activity and progress in the near future.

Novel Processes

Since the development of ALD, much of the work was dedicated to the development of new processes. A large number of materials, mainly metal-oxides, but also nitrides, carbides, sulfides, phosphides and metals have been successfully deposited. The known instances cover a major part of the Periodic Table either as pure elements or as binary or ternary compounds.

While most of the developed processes concentrated on materials, which in one way or another are interesting for electronic or optical applications, there are also other important areas of application. A particularly attractive new process, the deposition of apatite by ALD, may find broad application in the synthesis of biocompatible materials.²³ There will be a large number of possible applications if such processes can be applied routinely and in a controlled manner.

Another highly interesting novel group of materials deposited by ALD are polymers or their derivatives. In 1991, the principle of polymer-ALD, the so-called molecular layer deposition (MLD) was demonstrated.²⁴ However, not much attention was paid to this work until about 15 years later when new attempts were made to produce very thin polymer films. Since then the ALD process has become a really versatile tool for thin film deposition, as not only inorganic materials can be deposited, but also organic molecules. Moreover, studies on the synthesis of hybrid materials of organic and inorganic molecules stacked in a layer-by-layer manner were performed. More insight into this particular field of ALD (MLD) is given in the article on page 34 by S.M. George et al. in this issue of Material Matters.

Further development in this direction will be of high interest, since hybrid organic-inorganic materials may exhibit unique properties and prove useful for a variety of biomedical or environmental applications.

Conclusion

ALD has emerged as the method of choice for the controlled and conformal deposition of very thin layers involving micro- or nanostructures. A large number of materials can be deposited by ALD. The possibility of obtaining a reactor commercially as well as the steadily increasing number of precursors make the ALD process especially convenient and attractive for newcomers to this field. Even though there are still limitations in particular processes or precursors for very special purposes, in general, the only limitation to further applications of ALD appears to be the imagination and creativity of the researchers involved.

Acknowledgment

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Materials for Vapor Deposition of Thin Films*

Metal	Name	Purity	Prod. No.
Aluminum (Al)	Trimethylaluminum	97%	257222-100G
	Trimethylaluminum	99.9999+%	597775-5G 597775-25G
	Tris(dimethylamido)aluminum(III)	99%	469947-10G
Antimony (Sb)	Triphenylantimony(III)	99%	T81809-25G T81809-100G
	Tris(dimethylamido)antimony(III)	99.99%	553972-25ML
Arsenic (As)	Triphenylarsine	99.99%	492736-5G
Boron (B)	Diborane	99.99% (diborane only), 10% in hydrogen	463051-24L 463051-48L
	Boron trifluoride	99.99+%	463086-20G 463086-100G
Barium (Ba)	Barium bis(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate)	99.99%	495174-5G 495174-25G
Calcium (Ca)	Calcium bis(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate)	99.9%	495158-5G 495158-25G
Cadmium (Cd)	Cadmium acetylacetonate hydrate	99.9+%	517585-50G
Gadolinium (Gd)	Tris(cyclopentadienyl)gadolinium(III)	99.9%	492566-1G 492566-5G
	Tris(ethylcyclopentadienyl)gadolinium(III)	99.9%	517437-1G
	Tris(tetramethylcyclopentadienyl)gadolinium(III)	99.9%	511366-1G
Cobalt (Co)	Bis(pentamethylcyclopentadienyl)cobalt(II)	> 97%	401781-1G
	Bis(ethylcyclopentadienyl)cobalt(II)	> 97%	510645-1G 510645-5G
Copper (Cu)	Copper bis(2,2,6,6-tetramethyl-3,5-heptanedionate)	99%	345083-1G 345083-5G
	Copper bis(6,6,7,7,8,8,8-Heptafluoro-2,2-dimethyl-3,5-octanedionate)	≥ 99.99%	541761-1G 541761-5G
Erbium (Er)	Erbium(III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate)	99.9+%	434078-1G
	Tris(cyclopentadienyl)erbium(III)	99.99%	491918-1G 491918-5G
	Tris(isopropylcyclopentadienyl)erbium(III)	99.9+%	495980-1G 495980-5G
	Tris(butylcyclopentadienyl)erbium(III)	99.9+%	495999-1G 495999-5G
Europium (Eu)	Tris(tetramethylcyclopentadienyl)europium(III)	99.9%	511374-1G
Gadolinium (Gd)	Tris(cyclopentadienyl)gadolinium(III)	99.9%	492566-1G
	Tris(tetramethylcyclopentadienyl)gadolinium(III)	99.9%	511366-1G
	Tris[N,N-Bis(trimethylsilyl)amide]gadolinium(III)	98%	547824-1G
Gallium (Ga)	Tris(dimethylamido)gallium(III)	> 98%	546534-1G 546534-5G
Germanium (Ge)	Germanium(IV) fluoride electronic grade	99.9%	463000-5G 463000-15G
	Tetraethylgermanium	99%	401706-1G 401706-5G
	Tributylgermanium hydride	99%	409170-250MG 409170-1G
Hafnium (Hf)	Hafnium(IV) tert-butoxide	99.99% (purity excludes ~2000 ppm zirconium.)	445541-5G
	Tetrakis(dimethylamido)hafnium(IV)	99.99+%	455199-5G 455199-25G
	Tetrakis(diethylamido)hafnium(IV)	99.99%	455202-10G 455202-25G 455202-100G
	Tetrakis(ethylmethylamido)hafnium(IV)	99.99+%	553123-5ML 553123-25ML
	Bis(trimethylsilyl)amidohafnium(IV) chloride	99.99+% as metals	J100005-5G
Holmium (Ho)	Tris(cyclopentadienyl)holmium(III)	99.9%	554014-5G



Metal	Name	Purity	Prod. No.	
Indium (In)	Indium(III) acetylacetonate	99.99+%	I3300-1G	
			I3300-5G	
Iron (Fe)	Iron(II) acetylacetonate	99.95%	413402-10G	
			517003-10G	
	Iron(III) acetylacetonate	99.9+%	517003-50G	
			481718-25ML	
	Iron(0)pentacarbonyl	99.999%	481718-100ML	
Iron(III) tert-butoxide	99.9%	698520-1G		
Lanthanum (La)	Tris(cyclopentadienyl)lanthanum(III)	99.9%	493597-1G	
			493597-5G	
Magnesium (Mg)	Tris(tetramethylcyclopentadienyl)lanthanum(III)	99.9%	513180-1G	
Magnesium (Mg)	Bis(cyclopentadienyl)magnesium(II)	≥ 95%, 99.99+% as metals (excludes ~300ppm Al)	J100042-10G	
Magnesium (Mg)	Bis(pentamethylcyclopentadienyl)magnesium electronic grade	99.999%	512540-1G	
			512540-5G	
Manganese (Mn)	Manganese(0) carbonyl	> 98%	63541-1G	
			63541-5G	
Molybdenum (Mo)	Molybdenumhexacarbonyl	99.9+%	577766-5G	
			577766-25G	
Neodymium (Nd)	Tris(isopropylcyclopentadienyl)neodymium(III)	99.9%	496014-1G	
			496014-5G	
Nickel (Ni)	Bis(ethylcyclopentadienyl)nickel(II)	> 98%	510483-5G	
Phosphorous (P)	Phosphine electronic grade	99.9995+%	295647-10G	
			295647-50G	
			431249-25ML	
	Trimethyl phosphite	99.999+% (metals basis purity)	431249-100ML	
Palladium (Pd)	Palladium(II) acetylacetonate	99%	209015-1G	
			209015-5G	
Praseodymium (Pr)	Tris(cyclopentadienyl)praseodymium(III)	99.9%	475173-1G	
Platinum (Pt)	Trimethyl(methylcyclopentadienyl)platinum(IV)	> 98%	645605-2G	
Rhodium (Rh)	(Acetylacetonato)(1,5-cyclooctadiene)rhodium(I)	99%	335029-100MG	
			335029-500MG	
Ruthenium (Ru)	Bis(ethylcyclopentadienyl)ruthenium(II)	> 98%	648663-2G	
			Triruthenium dodecacarbonyl 99%	245011-1G
			245011-5G	
Samarium (Sm)	Tris(cyclopentadienyl)samarium(III)	99.9%	553999-5G	
Scandium (Sc)	Tris(cyclopentadienyl)scandium(III)	99.9%	410152-1G	
Selenium (Se)	Dimethyl selenide	≥ 99% (GC)	41572-1ML	
			41572-5ML	
	Di-tert-butyl selenide	99.99+%, electronic grade	511501-5G	
	Diethyl selenide	100%	550434-5G	
			550434-25G	
Silicon (Si)	Silane	99.998+%, electronic grade	333891-10G	
			333891-50G	
	2,4,6,8-Tetramethylcyclotetrasiloxane	≥ 99.5%, ≥ 99.999% as metals	512990-25ML	
	2,4,6-Trimethylcyclotrisiloxane	99%	517798-25ML	
	Tetramethylsilane electronic grade	99.99+%	523771-100ML	
	Tris(tert-pentoxy)silanol	99.99+%	553441-5G	
			553441-10G	
			553441-25G	
	Tetraethyl orthosilicate	99.999% (Purity based on metals analysis)	333859-25ML	
			333859-100ML	
	Tris(tert-butoxy)silanol	99.999%	553468-5G	
		553468-25G		
Disilane electronic grade	99.998%	463043-10G		
		463043-20G		

Metal	Name	Purity	Prod. No.
Strontium (Sr)	Strontium bis(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate)	99.99%	495166-5G 495166-25G
	Strontium tetramethylheptanedionate	99%	697524-1G
Tantalum (Ta)	Pentakis(dimethylamino)tantalum(V)	99.9%	496863-5G
	Tris(diethylamido)(ethylimido)tantalum(V)	99.99%	517836-5ML
	Tris(diethylamido)(<i>tert</i> -butylimido)tantalum(V)	99%, 99.99+% as metals	521280-5ML
	Tris(ethylmethylamido)(<i>tert</i> -butylimido)tantalum(V) electronic grade	≥ 95% (CP), 99.99+% as metals	J100043-5G
Tellurium (Te)	Tellurium tetrabromide anhydrous, beads, –10 mesh,	99.995%	451576-5G 451576-25G
	Tellurium tetrabromide anhydrous, powder,	99.999%	464589-5G 464589-25G
	Tellurium tetrachloride	≥ 99.999%	518190-5G 518190-25G
	Tellurium tetrachloride	99%	205338-5G 205338-25G 205338-100G
Terbium (Tb)	Tris(isopropylcyclopentadienyl)terbium(III)	99.9%	496006-1G 496006-5G
	Tris(cyclopentadienyl)terbium(III)	99.9%	554006-5G
	Tris(tetramethylcyclopentadienyl)terbium(III)	99.9%	525065-1G
Thulium (Tm)	Tris(cyclopentadienyl)thulium(III)	99.9%	553980-5G
Tin (Sn)	Trimethyl(phenyl)tin	98%	366331-1G 366331-5G
	Terakis(dimethylamido)tin		698431-1G
	Tin acetylacetonate		697478-5G
Titanium (Ti)	Titanium(IV) isopropoxide	99.999%	377996-5ML 377996-25ML 377996-100ML
	Titanium(IV) methoxide	99.99+%	463582-25G
	Tetrakis(dimethylamido)titanium(IV)	99.999%	469858-5G 469858-25G
	Tetrakis(diethylamido)titanium(IV)	99.999%	469866-5G 469866-25G
	Tetrakis(ethylmethylamido)titanium(IV) electronic grade	99.99+%	473537-5G 473537-25G
	Bis(diethylamido)bis(dimethylamido)titanium(IV)	≥ 95%, 99.99+% as metals	J100026-10G
Tungsten (W)	Tungsten hexacarbonyl	99.9+% , purified by sublimation	472956-5G 472956-25G
	Tris(diethylamido)(<i>tert</i> -butylimido)tantalum(V)	99%, 99.99+% as metals	521280-5ML
	Tungsten(0) pentacarbonyl- <i>N</i> -pentylisonitrile	99%	535567-5ML
Vanadium (V)	Vanadyl acetylacetonate	99.99%	574562-5G 574562-25G
Ytterbium (Yt)	Tris(cyclopentadienyl)ytterbium(III)	99.9%	492434-1G 492434-5G
Yttrium (Y)	Yttrium(III) acetylacetonate hydrate	99.99%	438790-5G
	Tris(cyclopentadienyl)yttrium(III)	99.9%	491969-1G 491969-5G
	Tris(butylcyclopentadienyl)yttrium(III)	99.9%	524522-5ML
Zinc (Zn)	Diethylzinc	> 98%	256781-100G
Zirconium (Zr)	Tetrakis(diethylamino)zirconium(IV)	99.99+%	453153-5ML 453153-25ML
	Zirconium tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionate)	99.99+%	478865-5G 478865-25G
	Zirconium(IV) diisopropoxidebis(2,2,6,6-tetramethyl-3,5-heptanedionate)	99.99+%	494151-5G 494151-25G
	Tetrakis(ethylmethylamido)zirconium(IV)	≥ 99%, 99.99+% as metals	553131-5G 553131-25G
	Tetrakis(dimethylamido)zirconium(IV)	99.99+%	579211-1G 579211-5G

*Also see Volatile Precursors for Vapor Deposition Systems on page 37.

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Molecular Layer Deposition of Organic and Hybrid Organic-Inorganic Polymers



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Introduction

Atomic layer deposition (ALD) techniques have emerged in the last ten years to meet various needs including semiconductor device miniaturization, conformal deposition on porous structures and coating of nanoparticles. ALD is based on two sequential self-limiting surface reactions.^{1,2} Because the surface chemical reactions are self-limiting, ALD can deposit very conformal ultra-thin films on high aspect ratio structures.³ The control of the ALD growth is ~ 1 Å per reaction cycle and the resulting ALD films are continuous and pinhole-free.⁴

ALD processes have been developed for a wide variety of inorganic materials. Because of the binary nature of the ALD reaction sequence, most ALD materials are binary compounds such as Al_2O_3 and TiN. For example, Al_2O_3 ALD is usually performed using $\text{Al}(\text{CH}_3)_3$ (TMA, **Aldrich Prod. No. 663301**) and H_2O as the two reactants.^{5,6} TiN ALD can be performed using TiCl_4 (**Aldrich Prod. No. 254312**) and NH_3 (**Aldrich Prod. No. 294993**) as the two reactants.⁷ The most common ALD materials are metal oxides and metal nitrides. Several reviews have detailed the many inorganic materials that have been deposited using ALD techniques.^{8,9}

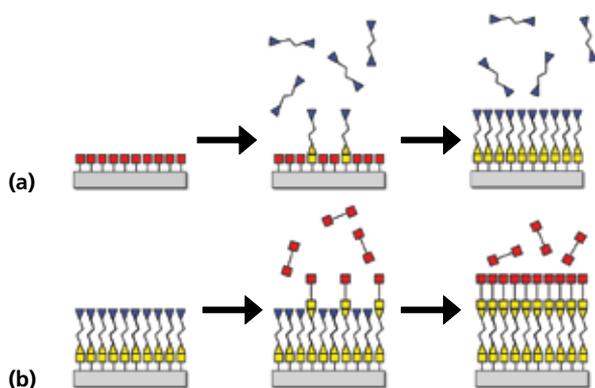


Figure 1. Schematic of the molecular layer deposition (MLD) method based on sequential, self-limiting surface reactions.

Molecular layer deposition (MLD) is closely related to ALD.^{10,11} MLD is also based on sequential, self-limiting surface reactions. However, a "molecular" fragment is deposited during MLD reactions as shown by the schematic in **Figure 1**.¹⁰ This molecular fragment is organic and can contain inorganic constituents. The deposition of purely organic polymer MLD

films can be achieved using step-wise condensation reactions. The growth of these organic polymer MLD films was first demonstrated by several groups in Japan.¹¹⁻¹⁵ Hybrid organic-inorganic films can be deposited by simply mixing organic and inorganic reactants.

Molecular Layer Deposition of Organic Polymers

The initial investigations of the MLD of organic polymers concentrated on polyimides¹¹ and polyamides.¹⁴ These early demonstrations of MLD were also known as alternating vapor deposition polymerization.¹⁴ The basic strategy was to utilize homobifunctional reactants with two chemical functionalities such as X-A-X and Y-B-Y. "X" and "Y" are chemical functional groups and "A" and "B" are organic fragments. A two-step AB cycle with two homobifunctional reactants is as follows:



where the asterisks indicate the surface species. The underlying substrate and deposited film are represented by "S". In the A reaction, the X chemical functionality reacts with SBY^* species to deposit SB-AX^* species. In the B reaction, the Y chemical functionality reacts with SAX^* species to deposit SA-BY^* species.

Recent work has explored the MLD of two polyamides: nylon 66 (**Aldrich Prod. No. 429244**)¹⁰ and poly(*p*-phenylene terephthalamide) (PPTA).¹⁶ The reactants for nylon 66 MLD are adipoyl chloride ($\text{ClOC}-(\text{CH}_2)_4-\text{COCl}$) (AC, **Aldrich Prod. No. 165212**) and 1,6-hexanediamine ($\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$) (**Aldrich Prod. No. H1169-6**).¹⁰ The reactants for PPTA MLD are terephthaloyl chloride (TC, **Aldrich Prod. No. 120871**) and *p*-phenylenediamine (PD, **Aldrich Prod. No. 695106**).¹⁶ In both cases, the acid chloride and amine functional groups react to form an amide linkage. Sequential exposures of AC and HD for nylon 66 MLD or TC and PD for PPTA MLD were used to deposit these polyamide films.^{10,16} A schematic of the surface chemistry during PPTA MLD is shown in **Figure 2**.¹⁶

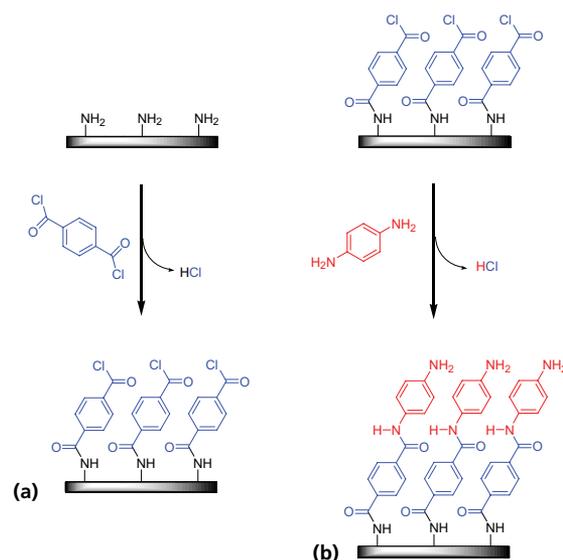


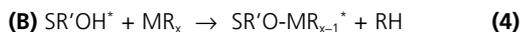
Figure 2. Illustration of the surface chemistry for poly(*p*-phenylene terephthalamide) MLD using (a) terephthaloyl chloride and (b) *p*-phenylenediamine as the homobifunctional reactants.

One of the difficulties with using homobifunctional reactants for polymer MLD is that the homobifunctional reactant can react twice with two chemical groups on the surface.¹⁶ These “double” reactions remove two surface chemical groups from further reaction. The number of reactants that can react with the surface is reduced considerably after a number of double reactions. Consequently, future strategies for organic polymer MLD could employ heterobifunctional reactants or reactants with masked or protected functionalities.¹⁶

Extension to Hybrid and Organic-Inorganic Polymers

The MLD of hybrid organic-inorganic polymers can be achieved by using an inorganic reactant together with an organic reactant.¹⁷ This extension is achieved by combining one of the reactants used in a typical ALD process with one of the reactants used in a MLD process for an organic polymer. For example, $\text{Al}(\text{CH}_3)_3$, trimethylaluminum (TMA), is a very common reactant used for Al_2O_3 ALD.^{5,6} TMA reacts readily with oxygen containing species. A diol, such as ethylene glycol ($\text{HO}-(\text{CH}_2)_2-\text{OH}$), (EG, **Aldrich Prod. No. 324558**) is a homobifunctional reactant that could be used together with a carboxylic acid or acid chloride to deposit a polyester in a step-wise MLD process. Together, TMA and EG can be used in a sequential, step-wise process to deposit a hybrid organic-inorganic polymer known as an alucone.¹⁸

A new family of reactions is possible between metal alkyls such as TMA with diols such as EG. The general two-step MLD reaction between the metal alkyl and the diol can be written as follows.¹⁷



In the A reaction, the reaction stops when all the SMR^* species have completely reacted to produce $\text{SM-OR}'\text{OH}^*$ species. In the B reaction, the reaction stops when all the $\text{SR}'\text{OH}^*$ species have completely reacted to produce $\text{SR}'\text{O-MR}_{x-1}^*$ species. The sequential reactions of TMA and EG during MLD yield a polymeric film described by $(\text{Al-O-CH}_2\text{-CH}_2\text{-O})_n$. This new polymer is an alucone¹⁸ and can be called poly(aluminum ethylene glycol).¹⁷ A schematic illustrating the growth of poly(aluminum ethylene glycol) is shown in **Figure 3**.¹⁷

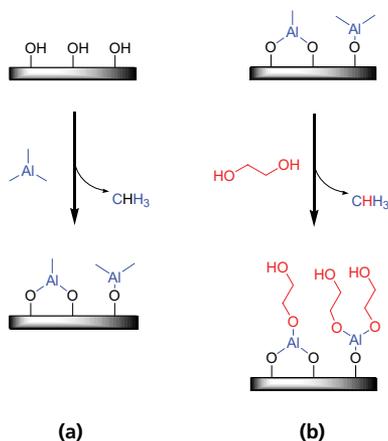


Figure 3. Illustration of the surface chemistry for poly(aluminum ethylene glycol) MLD using (a) trimethylaluminum as a homotrifunctional reactant and (b) ethylene glycol as a homobifunctional reactant.

Previous investigations have shown that alucone MLD using TMA and EG is very efficient.¹⁷ *Ex situ* x-ray reflectivity (XRR) analysis revealed that the MLD growth rate was temperature dependent.¹⁷ The alucone MLD growth rates decreased from 4.0 Å per TMA/EG cycle at 85 °C to 0.4 Å per TMA/EG cycle at 175 °C. **Figure 4** shows that the alucone MLD is very linear versus number of TMA/EG cycles.¹⁷ The XRR analysis also determined that the density of these alucone films was independent of the deposition temperature and constant at $\sim 1.5 \text{ g/cm}^3$. This measured density for the hybrid organic-inorganic alucone MLD film¹⁷ is much less than the density of $\sim 3.0 \text{ g/cm}^3$ for an Al_2O_3 ALD film grown at 177 °C.¹⁹

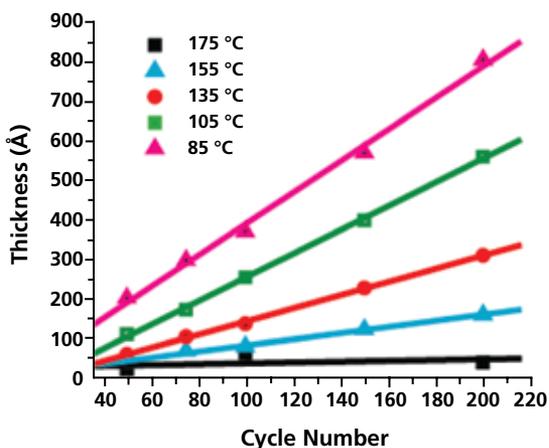


Figure 4. Thickness of the poly(aluminum ethylene glycol) MLD film versus number of cycles of trimethylaluminum and ethylene glycol at different growth temperatures determined using x-ray reflectivity measurements.

Many other organometallic precursors can be used to define hybrid organic-inorganic MLD polymers. For example, zinc alkyls such as $\text{Zn}(\text{CH}_2\text{CH}_3)_2$, diethylzinc (DEZ, **Aldrich Prod. No. 668729**), can react with diols such as EG in a similar MLD process.²⁰ Various other metal alkyls that can easily react with oxygen are also possible candidates for hybrid organic-inorganic polymer MLD. For example, metal alkyls based on magnesium (Mg) and manganese (Mn) react readily with oxygen and are possible candidates to react with diols. Metal alkyls of Mg and Mn are available as $\text{Mg}(\text{Cp})_2$ (**Aldrich Prod. No. J100042**) and $\text{Mn}(\text{Cp})_2$ (**Aldrich Prod. No. 415405**) where Cp is the cyclopentadienyl ligand. Other possible metal alkyls are ferrocene, $\text{Fe}(\text{Cp})_2$ (**Aldrich Prod. No. F408**), nickelocene, $\text{Ni}(\text{Cp})_2$ (**Aldrich Prod. No. N7524**), and cobaltocene, $\text{Co}(\text{Cp})_2$ (**Aldrich Prod. No. 339164**). The possibilities are virtually unlimited given all the metals on the periodic table.

The reactions based on diols will produce hybrid organic-inorganic MLD films that will be composed of a metal oxide and an organic constituent. Other homobifunctional organic reactants are possible that would further expand the generality of these reactions. For example, the homobifunctional organic reactant could be a diamine or a dithiol. For the diamines and the dithiols, the hybrid organic-inorganic MLD film would be composed of a metal nitride or metal sulfide and an organic constituent.

Future Prospects for Additional Organic and Organic-Inorganic Polymers

To prevent “double” reactions, MLD reactions can utilize heterobifunctional reactants.¹⁶ These reactants have two chemical functional groups that are different. One of the chemical functional groups can react with the surface species. The second chemical functional group cannot react with the surface species. The heterobifunctional reactants react only monofunctionally and prevent double reactions and polymer chain termination.

The simplest two-step AB cycle using heterobifunctional reactants is:



In the A reaction, the W chemical functionality (but not the X chemical functionality) reacts with the SBZ^{*} species to deposit SB-AX^{*} species. In the B reaction, the Y chemical functionality (but not the Z chemical functionality) reacts with the SAX^{*} species to deposit SA-BZ^{*} species. There are a variety of examples of heterobifunctional reactants that display two separate chemical reactivities on the same molecule. Possible chemical functional groups are amine, allyl, hydroxyl, isocyanate, epoxy, succinimide ester, maleimide and thiol.

In addition to heterobifunctional reactants, the reactant can also avoid a double reaction by containing a concealed functionality that only expresses itself upon reaction. There are a variety of ring-opening reactions that react to yield a new hydroxyl (-OH), amine (-NH₂) or carboxylic acid (-COOH). For example, an epoxy ring can react with a surface amine to yield a hydroxyl group. A cyclic azasilane, such as 2,2-dimethoxy-1,6-diaza-2-silacyclooctane, can react with a surface hydroxyl to yield amine groups.¹⁶ A cyclic carbonate, such as ethylene carbonate, can react with a surface amine to yield a hydroxyl group.¹⁶ Examples of various reactions involving ring-opening or heterobifunctional reactants are shown in **Figure 5**.

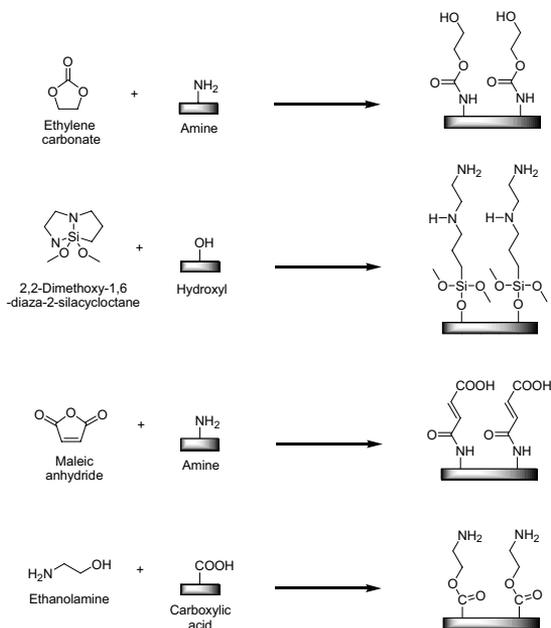


Figure 5. Examples of various reactions involving ring-opening or heterobifunctional reactants.

The MLD of organic and hybrid organic-inorganic polymers can also be accomplished using a three-step reaction sequence. Possible three-step ABC reactions increase the flexibility of MLD reactions to include various organic compositions. In addition, three-step ABC reactions also increase the number of different combinations of possible heterobifunctional reactants that can be utilized to define the MLD process. One example of a three-step ABC reaction is the sequential reaction of TMA, ethanolamine (EA, **Aldrich Prod. No. 398136**) and maleic anhydride (MA, **Aldrich Prod. No. M188**).²¹ This reaction sequence incorporates a metal alkyl reactant, a heterobifunctional reactant and a ring-opening reactant. A schematic of the three-step ABC reaction is shown in **Figure 6**.²¹

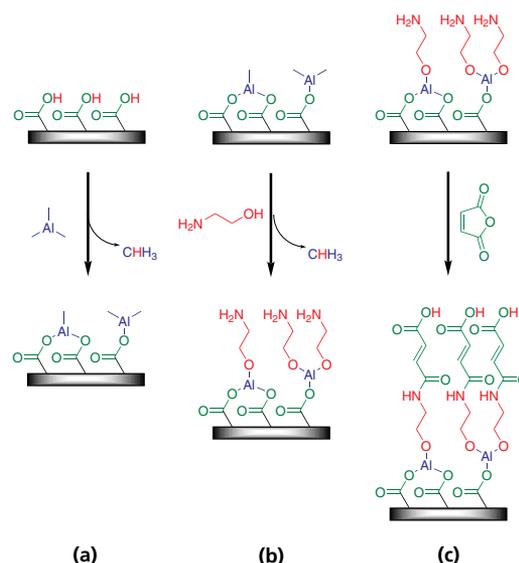


Figure 6. Illustration of the surface chemistry for the three-step ABC reaction involving (a) trimethylaluminum as a homotrifunctional reactant, (b) ethanolamine as a heterobifunctional reactant and (c) maleic anhydride as a ring-opening reactant.

This three-step ABC reaction sequence avoids the possibility of double reactions and leads to very robust and linear MLD growth. Recent studies have shown that this ABC alucone MLD film grows at temperatures of 90–150 °C and yields MLD growth rates of 23–8 Å per ABC reaction cycle, respectively.²¹ Other possible three-step ABC reaction sequences using heterobifunctional reactants, ring-opening reactants and reactants with masked or protected functionalities will offer a wide range of possibilities for the MLD of organic and hybrid organic-inorganic MLD films. These new combinations, together with previous ALD processes, will significantly increase the range of thin film materials that can be deposited conformally with precise thickness control.

Acknowledgments

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Volatile Precursors for Vapor Deposition Tools

Packaged in cylinders for use with deposition systems.

Metal	Name	Structure	Physical State	Prod. No.
Aluminum (Al)	Trimethylaluminum	(CH ₃) ₃ Al	Liquid, pyrophoric	663301-25G
Hafnium (Hf)	Tetrakis(dimethylamido)hafnium(IV)	Hf[N(CH ₃) ₂] ₄	Solid, air-sensitive	666610-25G
Iron (Fe)	Iron (III) <i>tert</i> -butoxide	{(CH ₃) ₂ CO} ₃ Fe ₂	Solid, air-sensitive	698512-10G
Platinum (Pt)	Trimethyl(methylcyclopentadienyl) platinum(IV)	C ₅ H ₄ CH ₃ Pt(CH ₃) ₃	Solid, low melting	697540-10G
Ruthenium (Ru)	Bis(ethylcyclopentadienyl)ruthenium(II)	Ru(C ₅ H ₄ -C ₂ H ₅) ₂	Liquid	679798-10G
Silicon (Si)	Tris(<i>tert</i> -butoxy)silanol	((CH ₃) ₂ CO) ₃ SiOH	Solid	697281-25G
Silicon (Si)	Tris(<i>tert</i> -pentoxy)silanol	(CH ₃ CH ₂ C(CH ₃) ₂ O) ₃ SiOH	Liquid	697303-25G
Silicon (Si)	Silicone tetrachloride	SiCl ₄	Liquid, air-sensitive	688509-25ML
Tantalum (Ta)	Tris(diethylamido)(<i>tert</i> -butylimido) tantalum(V)	(CH ₃) ₃ CN=Ta(N(C ₂ H ₅) ₂) ₃	Liquid, air-sensitive	668990-10G
Titanium (Ti)	Tetrakis(dimethylamido)titanium(IV)	Ti[N(CH ₃) ₂] ₄	Liquid, air-sensitive	669008-25G
Titanium (Ti)	Titanium(IV) isopropoxide	Ti[OCH(CH ₃) ₂] ₄	Liquid, air-sensitive	687502-25G
Titanium (Ti)	Titanium tetrachloride	TiCl ₄	Liquid, air-sensitive	697079-25G
Tungsten (W)	Bis(<i>tert</i> -butylimino)bis(dimethylamino) tungsten(VI)	((CH ₃) ₃ CN) ₂ W(N(CH ₃) ₂) ₂	Liquid, air-sensitive	668885-10G
Zinc (Zn)	Diethylzinc	Zn(C ₂ H ₅) ₂	Liquid, pyrophoric	668729-25G
Zirconium (Zr)	Tetrakis(dimethylamido)zirconium(IV)	Zr[N(CH ₃) ₂] ₄	Solid, air-sensitive	669016-25G
Water	Water	H ₂ O	Stable in air	697125-25ML

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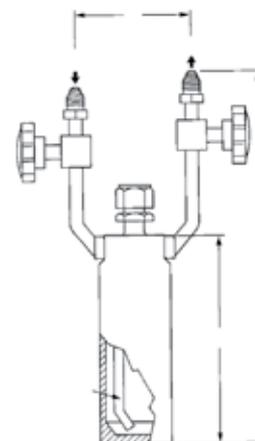
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300 mL	3.25 × 7.36 × 12.81	Z52,706-8
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Molecular Monolayers on Silicon Surfaces



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Introduction

Controlled formation of organic molecular monolayers on silicon surfaces offers the promise of enhancing the functionality of existing and emerging silicon based materials and devices. The synthetic tunability and diversity of properties of organic molecules suggests a range of promising applications for the resulting hybrid organic/silicon structures. At the simplest level, molecular monolayers can serve to passivate the surface, protecting the underlying substrate or structure from unwanted reactions or processes which degrade its properties. However, these monolayers can be much more than passive protective coatings, controllably altering the properties and imparting new functionality to bulk or nanostructured materials. Formation of monolayers with a variety of terminal functional groups can be used, for example, to tailor the wettability of the surface or modulate the electronic properties of the substrate through long-range field effects. Immobilization of biomolecules or other types of selective receptors on the surface offers opportunities for the development of novel sensing platforms based on electrical, optical or mechanical transduction of chemical binding events. Attachment of redox active or other types of "molecular switch" molecules (e.g., photochromic or electrochromic molecules) to silicon could enable fabrication of molecular scale memory or logic elements integrated with conventional silicon based microelectronic devices.

This article briefly reviews the methods and mechanisms for the formation of molecular monolayers on silicon surfaces, the properties of these monolayers and current perspectives regarding their application in molecular electronic and sensing applications.

Monolayer Formation — Methods, Mechanisms and Properties

In 1993, Linford and Chidsey reported the formation of monolayers of long chain alkyl molecules covalently attached directly to silicon surfaces, without an intervening oxide layer.¹ This approach involved the reaction of free radicals, formed by the thermal decomposition of diacyl peroxides, with the atomically flat hydrogen terminated Si(111) surface (H-Si(111)). The H-Si(111) surface can be generated by a straightforward wet chemical etching procedure in ammonium fluoride² and exhibits sufficient stability to permit some degree of manipulation in air and organic solvents. Numerous subsequent studies of the reactivity of H-terminated silicon have led to the development of a range of solution and gas

phase approaches to covalently attach organic molecules to the silicon surface. It is now possible to form monolayers with a wide range of terminal functionality as well as to vary the nature of the linking group (Si-C, Si-O, Si-N)^{3,4}. These chemistries have also been employed to functionalize other H-terminated silicon substrates including Si(100) (the substrate most commonly used in the microelectronics industry) as well as porous silicon, nanowires and nanoparticles.

Following the initial reports of monolayer formation initiated by thermal decomposition of peroxy compounds, subsequent investigations revealed that terminal alkenes react under both thermal⁵ and photochemical conditions⁶ with H-terminated silicon, without the need for a radical initiator. These reactions have been shown to proceed via the radical chain reaction mechanism shown in **Figure 1**. Once an initial Si radical (dangling bond) is formed alkenes react readily at this site, by forming a Si-C covalent bond, breaking the carbon-carbon double bond and creating a carbon-centered radical. This radical can then abstract a hydrogen atom from an adjacent silicon (effectively, a [1,5] hydrogen atom shift) creating a new reactive silicon-dangling bond, continuing the process. Scanning tunnelling microscopy images of partially reacted surfaces (shown in Figure 1) reveal that the reaction

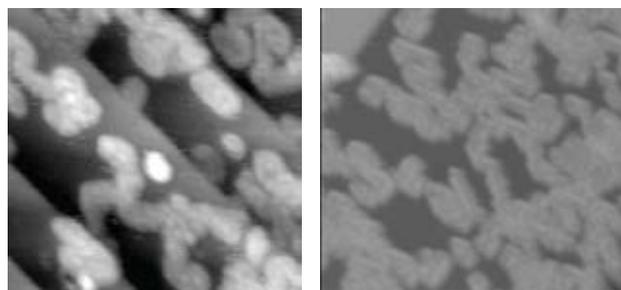
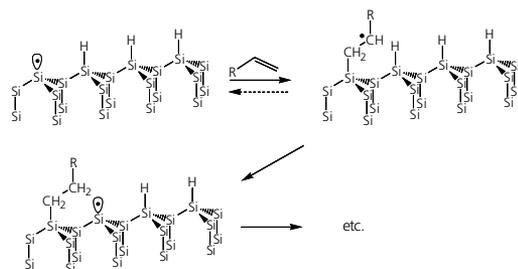


Figure 1. The reaction of alkenes with H-Si(111) proceeds via the radical chain reaction first suggested by Chidsey and co-workers⁵ and depicted schematically above. STM images of partially reacted monolayers show that monolayer growth proceeds via growth of irregularly shaped islands arising from the pseudo random walk progress of this chain reaction. Similar morphologies are observed for reaction in solution⁸ (image at right, 30 min. reaction with decene at 447 nm irradiation) or gas phase⁹ (image at left, 3 min. reaction with hexene at 185 nm irradiation).

does indeed proceed via the formation of irregularly shaped islands, consistent with a pseudo-random walk like progress of the chain reaction.^{7,8} While the reactions propagate via a radical chain reaction, the mechanism of formation of the initial Si radical is a matter of considerable debate. Direct photochemical or thermal induced cleavage of the Si-H bond requires photons at wavelengths < 160 nm or temperatures in

excess of 300 °C, whereas typical conditions for the solution phase hydrosilylation reactions involve ~300nm photons and temperatures in the range of 100–160 °C. Studies of gas phase photochemical reactions of alkenes with Si-H (using 185 nm irradiation) have implicated alkyl radicals produced via photolysis of the alkenes as the initiating species.⁹ In the case of thermal reactions trace oxygen is a possible initiator. The abstraction of H by molecular oxygen to create a silyl radical has indeed been observed in the molecule tris(trimethylsilyl)silane (**Aldrich Prod. No. 360716**),¹⁰ an interesting molecular analog of the H-Si(111) surface. The activation barrier for this process has been calculated to be ~130 kJ/mol,¹¹ implying that this pathway can account for reactions observed at temperatures >100 °C. The mechanism of the solution phase photochemical reactions (particularly those initiated by visible light) remains an open question.

Molecular monolayers made via reactions of alkenes with H-Si(111) are often referred to as “self-assembled” monolayers on silicon surfaces by analogy with thiol monolayers on gold. However, STM imaging shows that the monolayers on silicon do not exhibit the ordered domains observed for thiol-based monolayers on gold surfaces. The lack of order arises from three factors: 1) formation of strong Si-C covalent bonds precludes diffusion of the molecules once bound to the surface, 2) difference in the spacing between Si atoms on Si(111) (0.385 nm) and the diameter of an alkyl chain (0.42 nm) implies that not all Si atoms can bind an alkyl chain (cf., the 0.5 nm spacing on Au(111) for the typical $\sqrt{3}R30$ structures), and 3) the self-limiting pseudo random-walk progress of the radical chain reaction. While the last factor is particular to modification reactions that proceed via the radical chain process, the first two factors will limit the degree of order for alkyl monolayers formed via other routes such as reactions with alkyl Grignards¹² or diazonium compounds.¹³

The density (saturation coverage) of these monolayers has been the subject of some debate. Due to the steric constraint noted above, only methyl groups can occupy all the available silicon sites (i.e., form a complete monolayer). For longer alkyl chains (8–18 methylene groups), experimental estimates of coverage generally fall in the range of 0.30–0.45ML (i.e., replacement of 30–45% of the initial Si-H bonds with alkyl chains).⁷ A coverage of 0.4 ML on Si(111) corresponds to an area per molecule of 32 Å². This is considerably less than the density of ~21 Å² that can be achieved for SAMs on gold substrates or in close packed Langmuir-Blodgett films.

These monolayers are chemically quite robust, withstanding boiling and sonication in various solvents (water, chloroform, aq. HCl, etc.). Monolayers formed via Si-C links are generally stable upon dipping in hydrofluoric acid, although this procedure does remove alkyl chains attached via Si-O-C bonds. While the alkyl monolayers themselves are quite stable, degradation of the underlying silicon substrate has received less attention, particularly in view of the fact that silicon surfaces are known to be highly susceptible to oxidation. X-ray photoelectron (XPS) spectra of even carefully prepared surfaces invariably show a significant O1s core level signal, corresponding to 0.1–0.5 mL of oxygen,⁷ likely arising from oxygen insertion into Si-Si backbonds. The absence of a shifted Si_{2p} core level at ~103eV is often cited as an indication of an absence of silicon oxidation. However, this feature is associated with formation of SiO₂ (Si in a +4 oxidation state) indicative of the later stages of oxidation. In contrast, insertion of an oxygen atom into one out of the three available backbonds

for each Si atom (i.e. 1 mL of oxygen) will only shift the Si_{2p} level by ~1eV which would be difficult to resolve in most reported XPS spectra. As even low levels of oxidation can give rise to electrically active defects (see below), the reduction of oxygen concentrations in these monolayers remains a challenge. In terms of longer-term stability, alkyl termination does significantly slow down the oxidation relative to the unpassivated H-terminated surface although some level of oxidation is still observed, particularly in aqueous environments. This is not surprising in view of the fact that the monolayer is disordered and not close packed, but suggests a possible problem for using these monolayers for biosensor applications requiring extended immersion in aqueous buffer solutions.

Functional Monolayers and Biomolecule Immobilization

While methyl terminated monolayers can be useful for passivation and chemical stabilization, the low reactivity of this terminal group makes further manipulation of the surface physical or chemical properties difficult. In order to incorporate more complex organic or bioorganic structures at the interface, new strategies for coupling these molecules to the surface are required. A common approach involves the reaction of bifunctional molecules with the surface, with one end binding to the surface and the other terminal group available for further reaction. However, care must be taken to avoid both terminal groups reacting with the surface or formation of monolayers with mixed termination. In many cases it is necessary to protect one of the terminal groups in order to obtain the desired functionality. For example, amino-terminated monolayers are useful for the binding of biologically relevant molecules such as DNA and proteins. However, since the amine group can react directly with the H-terminated surface, particularly under UV irradiation, it must be protected. A common protecting group is *tert*-butoxycarbonyl (t-Boc), which can be removed by treatment with trifluoroacetic acid (TFA, **Aldrich Prod. No. 299537**). Amine terminated monolayers made by this route have been used to attach thiol-modified DNA oligomers to the silicon surface using a heterobifunctional cross-linker.¹⁴

On the other hand, alkene esters, acids and epoxides do not require protection as they appear to react primarily via the alkene end, leaving the terminal groups available for further reaction.^{15–18} The observation that undecylenic acid (**Aldrich Prod. No. 124672**) reacts preferentially at the alkene end, was somewhat unexpected as the oxophilic nature of silicon should thermodynamically favor reaction with the carboxylic acid group.¹⁸ The preferential reactivity with the alkenyl end is consistent with a free radical, rather than a nucleophilic mechanism. The acid function can be activated with *N*-hydroxysuccinimide (NHS, **Aldrich Prod. No. 130672**) as depicted in **Figure 2** to facilitate coupling with amine tagged molecules. This strategy has been used to attach oligonucleotides as well as methoxytetraethyleneglycol (TEG) (a compound known to inhibit non-specific binding of biomolecules to surfaces).¹⁸ FTIR is a particularly effective probe of this reaction sequence as seen in **Figure 2**. The carbonyl-stretching mode is observed to undergo characteristic changes upon NHS activation from a single adsorption at 1715 cm⁻¹ characteristic of a free acid to peaks at 1815 cm⁻¹, 1787 cm⁻¹ and 1744 cm⁻¹ assigned to the succinimidyl ester. Upon reaction with (TEG) amine the NHS peaks are seen to disappear, replaced by new peaks at 1650 cm⁻¹ and 1550 cm⁻¹ assigned to the carbonyl and CNH vibrations of the amide.



For the attachment of biomolecules or other larger complex molecules it is useful to have the ability to control the density of reactive sites since the molecule to be immobilized typically exhibits a much larger footprint than an alkyl chain. This has been demonstrated in the case of reactions of alkene esters¹⁶ where the density of reactive groups was controlled simply by diluting the “active” molecule in a solution of 1-alkene. While the incorporation of the reactive group has been shown to approximately correspond to the ratio of the two alkenes, whether these reactive groups are randomly distributed or clustered remains an open question.

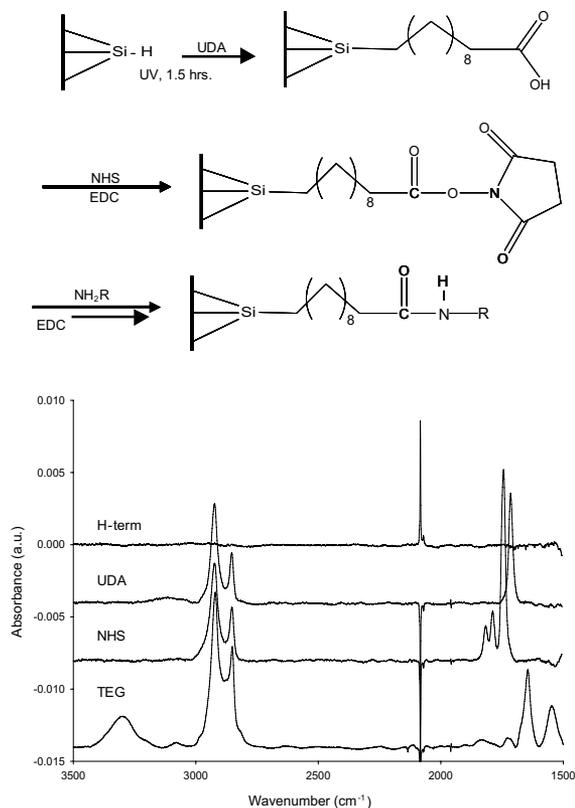


Figure 2. General multi-step reaction scheme for covalent attachment of amine tagged molecules to the silicon surface.¹⁸ The baseline corrected FTIR spectra, obtained in the attenuated total reflection (ATR) geometry, illustrates the changes in the vibrational modes of the monolayer upon passing through the various steps; H-termination followed by photochemical reaction with undecylenic acid (UDA), NHS activation and reaction with tetraethylene glycol (TEG) amine.

Electronic Properties

A primary motivation for using silicon as a substrate for forming molecular monolayers involves exploiting the long-range electric field effects induced by binding events or reactions that involve charge re-distribution at the interface. These field effects arise because, in contrast to metals, electric fields penetrate substantial distances into semiconductors, shifting energy levels in the near surface region. Adsorption of charged or polar molecules on the surface is expected to shift the electronic states (a process referred to as band-bending), altering the conductivity of the substrate, in a manner analogous to the use of an external electric field to control conductivity in a field effect transistor (MOSFET). In principle, this effect can be utilized for label-free detection of chemical or biological species.

Hydrogen terminated silicon surfaces are ideal systems for probing field effects induced by adsorption and reaction events because these interfaces exhibit a low density of electrically active surface states.¹⁹ Surface states are allowed energy levels created in the normally forbidden gap region of a semiconductor which can act as traps for free carriers, reducing the sensitivity of the substrate to external fields. For molecular monolayers to be useful in electrical sensing applications the creation of these electrically active surface states must be minimized during their preparation (i.e., they should maintain the low density of these states observed on H-terminated surfaces). A further requirement for biosensing applications is that this low density of surface states must be maintained upon prolonged exposure to aqueous buffers.

Surface photovoltage (SPV) measurements using a Kelvin probe offer a contactless approach to determining band bending due to surface charges.²⁰ Since photogenerated electron hole pairs act to screen the surface charge responsible for any band-bending, flattening the bands (provided the light intensity is high enough), the difference in surface potential in the dark and under illumination corresponds to the amount of band-bending. As seen in **Figure 3**, H-terminated surfaces typically show a small (<20 mV) photovoltage, which for the low doped wafers ($\sim 1 \times 10^{15} \text{ cm}^{-3}$) used here corresponds to a level of electrically active defects of $\sim 1 \times 10^{10} \text{ cm}^{-2}$ as expected. Upon formation of an alkyl monolayer the SPV is typically seen to increase slightly to 60–100 mV. This small level of band-bending corresponds to a density of trapped charges of $< 5 \times 10^{10} \text{ cm}^{-2}$ which likely arise from unwanted oxidation of the interface during the functionalization reaction. The SPV can be reduced to close to that of the initial H-terminated surface by a brief HF dip (which cleaves Si-O-Si bonds due to oxygen insertion in the backbonds but leaves the monolayer intact as discussed previously). In order to probe the stability of these surfaces, growth of the SPV has been studied upon exposure to phosphate-buffered saline (PBS) solution. As seen in **Figure 3**, the SPV is observed to increase significantly after 1 hour in the PBS solution. The growth of electrically active defects in PBS has also been noted in electrochemical impedance studies of these surfaces.²¹

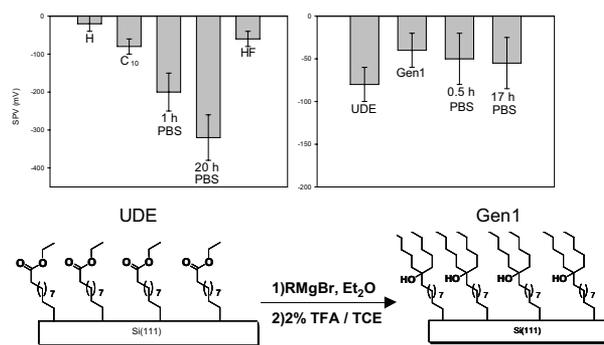


Figure 3. Surface photovoltages for different alkyl monolayers on Si(111). At the top left, the changes in SPV are shown upon formation of a decyl monolayer via photochemical reaction and subsequent exposure to PBS buffer solution followed by an HF dip. The growth of the SPV indicates an increase in the amount of trapped charge at the interface. In contrast, as shown in the bar graph on the right, a branched surface (Gen 1) formed by the reaction of pentyl Grignard with an undecylenic ethyl ester monolayer (UDE) is seen to maintain a stable and low SPV even for extended exposure to PBS buffer.

In order to improve the ability of these monolayers to maintain a low density of electrically active defects in aqueous solutions we have developed a strategy to effectively double the density of alkyl chains on the surface via a branching reaction. As noted above, prepared monolayers on silicon have densities that are typically only 50% of that of a close packed alkyl monolayer. Ester terminated monolayers, however, can react with alkyl Grignards¹⁶ to create the branched structures depicted in Figure 3, leading to an effective coverage of alkyl chains of ~0.8 mL. When the stability of these surfaces is tested the SPV remains low even for prolonged exposures to PBS.

Applications of Molecular Monolayers on Silicon

The progress in developing strategies for the controlled formation of functional monolayers and understanding the properties of the resulting silicon/organic structures has opened up a range of opportunities for designing and fabricating hybrid electronic devices and sensors based on these monolayers. Using the various functionalization strategies outlined above it is now possible to modify a wide range of silicon based structures and devices. Demonstrations of the utility of these monolayers in diverse applications such as molecular electronics and chemical/biomolecular sensing are growing rapidly. For example, monolayers of redox active porphyrin molecules attached to silicon have demonstrated charge storage characteristics that appear promising for molecular scale memory applications.²² In terms of sensing, Si microcantilevers have been modified by robust monolayers with quarternary ammonium termination in order to sense chromate ions in solution.²³ Oligonucleotide hybridization has been detected on functionalized H-terminated surfaces of both Si(111)²⁴ and silicon nanowires,²⁵ demonstrating the potential of these monolayers as platforms for label-free electrical detection of biomolecules.

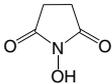
In summary, the future for molecular monolayers on silicon surfaces, nanostructures and devices appears to be full of possibilities, both for fundamental scientific studies

and practical applications. While much progress has been achieved, many open questions remain. We expect that this field will continue to be a vibrant one, continuing to illustrate the potential made possible by the convergence of surface science and organic chemistry.

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Select Materials for Deposition of Organic Films on Silicon Surface

Name	Structure	Prod. No.
10-Undecenoic acid	$\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{COOH}$	124672-100ML
		124672-500ML
		94192-50G
		94192-250G
		94192-1KG
Methyl 10-undecenoate	$\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{CO}_2\text{CH}_3$	U8502-5ML
Undecylenic aldehyde	$\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{CHO}$	132276-25G
		132276-100G
10-Undecen-1-ol	$\text{CH}_2=\text{CH}(\text{CH}_2)_9\text{OH}$	U2008-25G
		U2008-100G
Tetraethylene glycol methyl vinyl ether	$\text{CH}_2=\text{CH}(\text{OCH}_2\text{CH}_2)_3\text{OCH}_3$	S603058-1EA
N-Hydroxysuccinimide		130672-5G
		130672-25G
		130672-100G
		130672-250G

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Single Crystal Substrates for Film Deposition

Name	Material/ Composition	Description	Prod. No.
Silicon wafer (single side polished)	Si	(111), diam. × thickness 2 in. × 0.5 mm	647101-1EA 647101-5EA
	Si	(100), diam. × thickness 2 in. × 0.5 mm	646687-1EA 646687-5EA
	Si	(100), diam. × thickness 3 in. × 0.5 mm	647535-5EA
	Si	(111), diam. × thickness 3 in. × 0.5 mm	647543-1EA 647543-5EA
	Si	(100), doped (n-type), diam. × thickness 3 in. × 0.5 mm	647802-1EA 647802-5EA
	Si	(111), doped (n-type), diam. × thickness 3 in. × 0.5 mm	647810-1EA 647810-5EA
	Si	(100), doped (p-type), diam. × thickness 3 in. × 0.5 mm	647764-1EA 647764-5EA
	Si	(111), doped (p-type), diam. × thickness 3 in. × 0.5 mm	647772-1EA 647772-5EA
	Aluminum oxide, single crystal substrate	Al ₂ O ₃	(0001), 99.99% (crystal purity)
Gallium antimonide, single crystal substrate	GaSb	(100), diam. × thickness 2 in. × 0.5 mm	651478-1EA
Gallium arsenide, single crystal substrate	GaAs	(100), diam. × thickness 2 in. × 0.5 mm	651486-1EA
Gallium phosphide, single crystal substrate	GaP	(111), diam. × thickness 2 in. × 0.5 mm	651494-1EA
Magnesium aluminate, single crystal substrate	MgO • Al ₂ O ₃	(111), diam. × thickness 2 in. × 0.5 mm, 99.99%	634832-1EA
	MgO • Al ₂ O ₃	(100), 10 mm × 10 mm × 0.5 mm, 99.99%	635073-1EA
	MgO • Al ₂ O ₃	(110), 10 mm × 10 mm × 0.5 mm, 99.99%	634840-1EA
Magnesium oxide, single crystal substrate	MgO	(100), 10 mm × 10 mm × 0.5 mm, 99.9%	634646-1EA
	MgO	(110), 10 mm × 10 mm × 0.5 mm, 99.9%	634700-1EA
	MgO	(111), 10 mm × 10 mm × 0.5 mm, 99.9%	634697-1EA
Strontium lanthanum aluminate, single crystal substrate	SrLaAlO ₄	(110), 10 mm × 10 mm × 0.5 mm, 99.9%	635111-1EA
	SrLaAlO ₄	(001), 10 mm × 10 mm × 0.5 mm, 99.99%	634891-1EA
Strontium titanate, single crystal substrate	SrTiO ₃	(111), 10 mm × 10 mm × 0.5 mm, 99.99%	638161-1EA
Titanium(IV) oxide, rutile, single crystal substrate	TiO ₂	(001), 10 mm × 10 mm × 0.5 mm, 99.99%	635057-1EA
	TiO ₂	(100), 10 mm × 10 mm × 0.5 mm, 99.99%	635049-1EA
	TiO ₂	(110), 10 mm × 10 mm × 0.5 mm, 99.99%	635065-1EA
Yttrium vanadate single crystal substrate	YVO ₄	(110), 10 mm × 10 mm × 0.5 mm, 99.99%	635103-1EA

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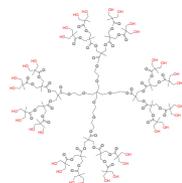
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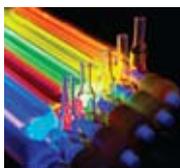
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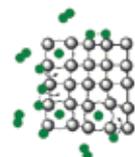
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Universal Platform for Surface Modification Employing Grafted Polymer Layers



Bogdan Zdyrko,¹ Viktor Klep¹ and Igor Luzinov*^{1,2}

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²Center for Optical Materials Science and Engineering Technologies, Clemson University, Clemson, SC 29634
 E-mail: luzinov@clemson.edu

Introduction

Ultrathin (end-) grafted polymer layers are well known to affect dramatically the surface properties of substrates such as adhesion, lubrication, wettability, friction, and biocompatibility. The layers are frequently used to modulate surface properties of various materials without altering their bulk performance.

The present publication focuses on synthesis and characterization of nanothick, chemically grafted polymer films (polymer brushes) on various inorganic and polymeric substrates. The synthesis was conducted employing a recently developed macromolecular anchoring layer approach.¹ Examples of application of the polymer grafting technique to generation of hydrophobic, hydrophilic, and functional surfaces are presented. Functional materials (e.g. optical and ultrahydrophobic) were developed employing the macromolecular anchoring layer approach.

Macromolecular Platform for Nanofabrication of Polymer Grafted Films

The chemical grafting of polymers can be accomplished by "grafting to" or "grafting from" methods.² According to the "grafting to" technique, end-functionalized polymer molecules react with complementary functional groups located on the surface to form tethered chains. The "grafting from" technique utilizes the polymerization initiated from the substrate surface by attached (usually by covalent bonds) initiating groups. Most of the grafting methods developed — "to" and "from" — require attachment of (end-)functionalized polymers or low molecular weight substances (e.g., initiators) to the substrate for synthesis of the polymer brush. Usually the coupling methods are relatively complex and specific for certain substrate/(macro)molecule combinations.

An alternative method for performing the attachment involves a macromolecular anchoring (mono)layer with activity towards both surface and functionalized (macro) molecules.³⁻⁶ The polymer is used for initial surface modification as well as generation of the highly reactive primary anchoring layer. When deposited on a substrate, the primary layer first reacts with the surface through formation of covalent bonds (**Figure 1**). The reactive units located in the "loops" and "tails" sections of the attached macromolecules are not connected to the surface.⁷ These free groups offer a synthetic potential for further chemical modification reactions and serve as reactive sites for the subsequent attachment of functionalized (macro)molecules.

In our research (**Figure 1b**), macromolecules of poly(glycidyl methacrylate) (PGMA) were used to form the primary anchoring polymer layer. The versatile chemistry of the epoxy groups offered flexibility in the selection of necessary initiators/macromolecules to be attached to the surface. The attachment of PGMA to various surfaces was studied and it was determined that a uniform (**Figure 1c**) and homogeneous epoxy-containing polymer layer could be deposited on surfaces by dip-coating.^{1,8-13} The epoxy-containing polymer layer could be deposited as a monolayer on polymeric (PET, polyethylene, PP, PVDF, silicon resin, nylon) and inorganic (silica, glass, titanium, alumina, gold, silver) surfaces. The PGMA layers obtained were smooth and robust, suggesting that PGMA was chemically bonded to the surface. Subsequently, grafted layers were effectively generated from the PGMA platform using "grafting to" and "grafting from" methods.

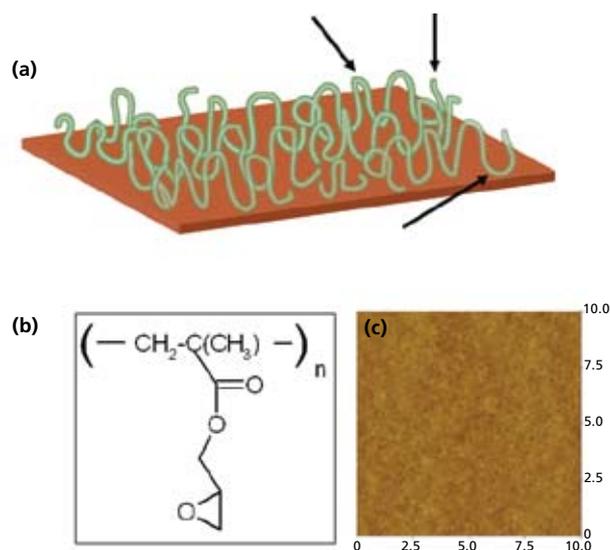


Figure 1. (a) Schematic representation of a reactive polymer attached to a substrate, (b) Chemical structure of the PGMA, (c) AFM image showing topography of PGMA layer deposited by dip-coating on silicon wafer. Size: 10x10 μm .

A "grafting from" approach employing the PGMA primary layer was used to synthesize an effective macroinitiator for controlled/"living" Atom Transfer Radical Polymerization (ATRP).^{8,11,14,15} Initial surface modification was performed

with a thin layer of PGMA. The ATRP macroinitiator was synthesized on the substrate surface by reaction between the epoxy groups of PGMA and the carboxy functionality of bromoacetic acid (BAA) (**Figure 2**, lower row). Polystyrene (**Aldrich Prod. No. 327816**),⁴ poly(oligoethyleneglycol methacrylate)^{8,16}, poly(*N*-isopropylacrylamide) (**Aldrich Prod. No. 535311**),¹⁷ and poly(vinylpyridine) (PVP, **Aldrich Prod. No. 523356**)¹⁸ brushes were synthesized on the PGMA/BAA-modified substrates by ATRP. Following polymerization on the model silicon surface, the approach was developed for synthesis of the grafted layers on polymeric substrates. The surface of PET¹³ and PVDF¹⁸ were modified with polymer brushes synthesized via ATRP.

Effective attachment of end-functionalized polystyrene (PS) and poly(ethylene glycol) (PEG, **Aldrich Prod. No. 202371**) from a melt via the PGMA primary layer (to silicon wafer) by the “grafting to” approach was demonstrated as well (**Figure 2**, upper row).^{10,12,19} Additionally, the grafting approach was employed for attachment of polymers to polymeric films and fibers. Hydrophilic/polar (PEG, polyacrylamide, polyacrylic acid, PEI)¹³ and hydrophobic (polyentafluorostyrene)²⁰ polymers were attached to PET, polyethylene, cotton, and nylon.

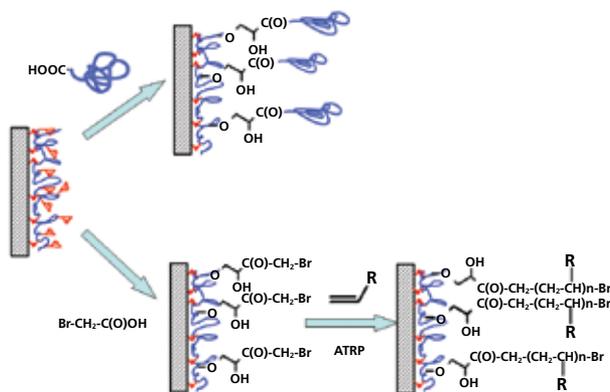


Figure 2. Schematic representation of the “grafting to” (upper row) and “grafting from” (lower row) from the surface activated with PGMA.

Practical Application of the Polymer Grafting Method

Synthesis of Ultrahydrophobic Coatings

The universality of the anchoring layer approach was used for surface modification of a textile with a rough and hydrophobic layer chemically anchored to the PET fiber boundary.²¹ Basically, the modification process consisted of two primary steps. In the first step of surface modification, silica particles covered with an ultrathin PGMA reactive layer, were deposited on the fiber surface. During the second step, a hydrophobic polymer [poly(styrene-*b*-(ethylene-co-butylene)-*b*-styrene), SEBS] was grafted to the surface of the fibers and nanoparticles, and an ultrathin rough hydrophobic layer chemically anchored to the fiber boundary was generated.

The water repellency of the PET fabric was evaluated via water contact angle (WCA) studies. **Figure 3** illustrates the wettability of the original PET fabric (**Figure 3b**), the fabric

grafted with SEBS (**Figure 3c**), and the fabric modified with nanoparticles with subsequent anchoring of the SEBS monolayer (**Figure 3d**). Clearly, the increase in the WCA is attributed to the introduction of the grafted layer and double roughness, with the initial roughness coming from the fabric structure itself, and the secondary roughness derived from the layer of nanoparticles.

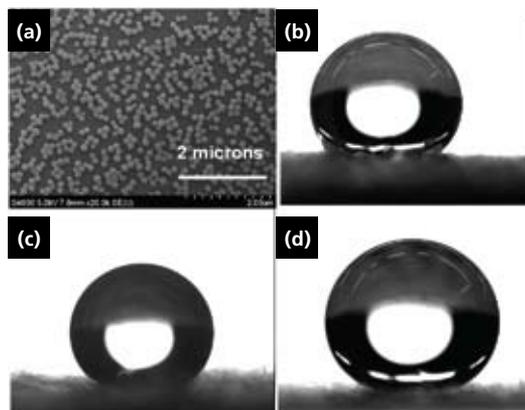


Figure 3. (a) TEH image of PGMA modified silica particles attached to PET fiber, Water Contact Angle Studies (WCA): (b) fabric “as is”, (c) fabric grafted with SEBS only, (d) nanoparticle modification and SEBS grafting.

Optically Active Arrays of Silver Nanoparticles

Optically active, flexible polymer films with embedded chain-like arrays of silver nanoparticles (Ag NP) were fabricated utilizing a PGMA primary anchoring layer.²² Specifically, a patterned PVP-grafted polymer layer (polymer brush), deposited on a flat substrate, was used as a “master” to guide Ag NP assembly. After the ordered layer of nanoparticles was transferred into the PDMS film, the “master” was reused to fabricate the next film.

To create the patterned PVP layer on a flat substrate, the surface of a silicon wafer was modified with a monolayer of PGMA. Subsequently, part of the reactive surface thus created was protected by a polystyrene resist layer employing capillary force lithography (CFL). Thereafter, PVP grafting to the unprotected portion of the surface at low temperatures was performed in the presence of solvent vapor. Namely, carboxy-terminated PVP was anchored to the non-screened areas on the substrate at a temperature of 40 °C, which is approximately 60 degrees below the glass transition temperature (T_g) of both PS and PVP. A lower process temperature was necessary to preserve the PS pattern during grafting. High reactivity of the epoxy groups of the PGMA layer allows attachment of PVP chains and preserves the PS pattern. Ag NP were assembled into an array and transferred into a transparent polymer matrix. Atomic force microscopy (AFM) images of the PVP master, the Ag NPs assembled to PVP stripes and the UV-Vis extinction spectra of the Ag NP one-dimensional structures, embedded into the PDMS transparent matrix, are shown in **Figure 4**. The two maxima in the UV-Vis spectra represent two different plasmon modes: one is a longitudinal mode for which the collective electron oscillations were parallel to the orientation of the structure, and the other is a transverse mode with electron oscillations perpendicular to the structure.

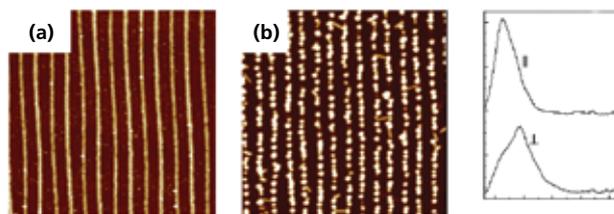


Figure 4. AFM images (all $5 \times 5 \mu\text{m}$, vertical scale – 50nm) of Ag NP preparation process. (a) PVP stripes obtained via solvent-assisted grafting to PGMA; (b) Ag NP adsorbed to PVP pattern; (c) UV-vis extinction spectra of one-dimensional structure of Ag NP in the PDMS matrix measured with two different light polarizations.

Silicone Resin Modification for BaTiO_3 Printing

Based on a primary PGMA anchoring layer, a hydrophilization procedure was designed for PDMS stamps for printing of the BaTiO_3 precursor. Briefly, during the first stage of the modification procedure, PDMS films made of Sylgard 184 (Dow Corning) were treated with a low intensity, radio frequency plasma to create active surface functionalities. Subsequently, a thin layer of the PGMA was deposited on the surface via dip coating and annealed. The epoxy-functionalized PDMS film was modified via the “grafting to” method with a hydrophilic polymer. Poly(acrylamide-co-acrylic acid) was used as the surface modifier.

The low surface energy of the printing stamp is crucial for reliable wettability and transfer of the solution. The AFM surface morphology of the neat and modified PDMS stamp, as well as its wettability with a BaTiO_3 precursor solution is shown in **Figure 5**. Wettability of the stamp was greatly improved after modification. Test-printing with modified PDMS stamps showed excellent pattern transfer, and durability. Moreover, the stamp was demonstrated to be reusable (at least 6 times) without significant deterioration of the transferred pattern. AFM images of the printed BaTiO_3 precursor (**Figure 6**) showed excellent edge sharpness and pattern reproducibility.

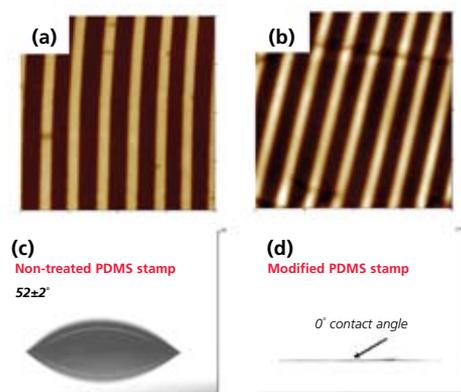


Figure 5. (a) AFM topography images of the model PDMS stamp. (b) Stamp hydrophilization with poly(acrylamide-co-acrylic acid). Vertical scale (a) 500 nm; (b) 200 nm, image size $20 \times 20 \text{ mm}$. (c,d) Wetting of the PDMS stamp with BaTiO_3 precursor solution.

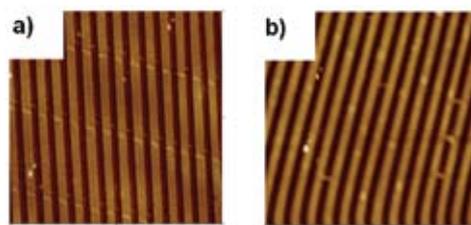


Figure 6. BaTiO_3 precursor printed with modified PDMS stamp onto the Si wafer surface. (a) Morphology of the 1st imprint generation. (b) Morphology of the 6th imprint generation. Vertical scale of the images – 200 nm, image size $20 \times 20 \text{ mm}$.

Conclusions

An overview of recent results in surface modification of various surfaces employing the macromolecular anchoring layer approach was presented. The approach was demonstrated to be useful as a virtually universal method for grafting functionalized polymer layers. The polymer grafting technique developed can be readily applied to surface modification of a wide range of inorganic and polymeric materials including flat surfaces, fibers and textiles. Functional materials were developed based on the macromolecular anchoring layer. Specifically, an ultrahydrophobic textile was made from PET fabric. An optically active array of Ag NPs was synthesized employing a patterned chemical brush synthesized on a PGMA layer. Finally, a BaTiO_3 precursor (high dielectric constant insulator) was printed onto the surface with spatial resolution better than 1.5 micrometers.

Acknowledgments

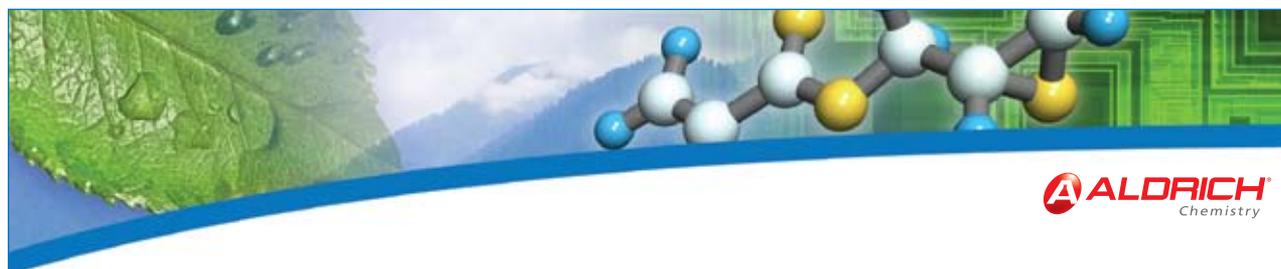
The research presented has been supported by the National Science Foundation CTS-0456550 and DMR-0602528 Grants, ERC Program of National Science Foundation under Award Number EEC-9731680, and Grants M01-CL03, C05-CL01 and C04-CL06 from the Department of Commerce through the National Textile Center. A fraction of this work was supported by Aldrich® Material Science. Authors thank Dr. Viktor Balema and Dr. Shashi Jasty (Sigma-Aldrich Corp.) for collaboration. Igor Luzinov would like to acknowledge present and former members of his research group: K. Swaminatha Iyer, Yong Liu, John Draper, Karthik Ramaratnam, and Oleksandr Burtovy, who conducted a significant fraction of the research presented.

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Kit for Creating Hydrophilic PDMS Surfaces—701912-1KT

Kit Components

- | | |
|---|--------|
| • Solution A (Glycidyl methacrylate based polymer) | 10 mL |
| • Solution B (Acrylamide/acrylic acid based polymer) | 4 mL |
| • Ethanol , Aldrich Prod. No: 245119 | 1 L |
| • Methylethylketone , Aldrich Prod. No: 230294 | 1 L |
| • Water , Aldrich Prod. No: 320072 | 500 mL |

Standard Surface Modification Procedure:

1. Pre-Treatment.

PDMS surface should be activated using a low frequency air plasma treatment for 1 min.

(Recommended plasma cleaners **Aldrich Prod. No.:** Z561673, Z561681, Z561657, Z561665). See page 43.

2. Pre-Rinsing

The plasma activated PDMS sample should be rinsed by washing with ethanol for at least 10 min. The rinsing procedure should be repeated 3 times. Then, the sample should be air-dried for at least 15 min. The water contact angle of such obtained activated PDMS surface is expected to be within a 25–40° range.

3. First Modification Step

The surface of the horizontally positioned sample prepared in the previous step should be covered with Solution A, typically ~1 mL of the solution per square inch of the surface. The sample should be dried under ambient conditions for 20–30 minutes and annealed at 110 °C under nitrogen or argon for 30 minutes.

4. Rinsing

The annealed sample should be rinsed three times with Methylethylketone for 10 min each time. Then, it should be air-dried for at least 30 min.

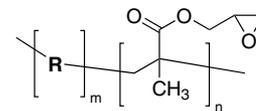


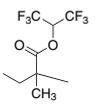
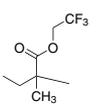
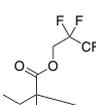
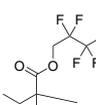
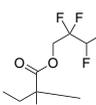
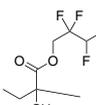
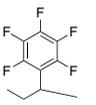
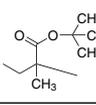
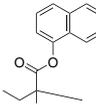
5. Polymer Grafting

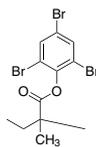
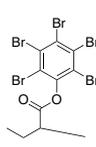
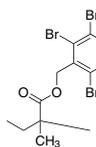
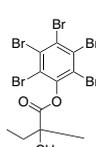
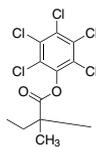
6 mL of ethanol must be added to the container containing Solution B. The mixture should be homogenized by careful stirring. The surface of the horizontally positioned sample prepared in the previous steps should be treated by completely covering the area to be modified with the homogeneous solution, which typically takes ~1 mL per square inch of the surface. The sample should be dried at ambient conditions for 20–30 minutes, then annealed at 80 °C for 14 hrs. Finally, the unattached polymer should be removed from the sample by a thorough rinse with water and the sample air-dried at room temperature.

Functional Glycidyl Co-Polymers

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Co-monomer (R)	Glycidyl Methacrylate (mol %)	Prod. No.
Poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate-co-glycidyl methacrylate)	10	591432
	50	591548
Poly(2,2,2-trifluoroethyl methacrylate-co-glycidyl methacrylate)	10	591866
	50	591750
Poly(2,2,3,3,3-pentafluoropropyl methacrylate-co-glycidyl methacrylate)	10	591106
	50	590894
Poly(2,2,3,3,4,4,4-heptafluorobutyl methacrylate-co-glycidyl methacrylate)	10	592099
	50	592102
Poly(2,2,3,3,3-tetrafluoropropyl methacrylate-co-glycidyl methacrylate)	10	590991
	50	591211
Poly(2,2,3,3,4,4,4-hexafluorobutyl methacrylate-co-glycidyl methacrylate)	10	591769
	50	591874
Poly(pentafluorostyrene-co-glycidyl methacrylate)	10	590878
	30	590975
	50	591084
Poly(tert-butyl methacrylate-co-glycidyl methacrylate)	10	591416
	50	591181
Poly(1-naphthyl methacrylate-co-glycidyl methacrylate)	10	640204
		

Co-monomer (R)	Glycidyl Methacrylate (mol %)	Prod. No.
Poly(2,4,6-tribromophenyl methacrylate-co-glycidyl methacrylate)	10	640255
		
Poly(pentabromophenyl acrylate-co-glycidyl methacrylate)	10	591408
	50	591505
Poly(pentabromobenzyl methacrylate-co-glycidyl methacrylate)	10	640298
		
Poly(pentabromophenyl methacrylate-co-glycidyl methacrylate)	10	591610
	50	591831
Poly(2,6-dichlorostyrene-co-glycidyl methacrylate)	10	640174
		
Poly(pentachlorophenyl methacrylate-co-glycidyl methacrylate)	10	640026
		
Poly(vinyl phenyl sulfide-co-glycidyl methacrylate)	10	640220
		
Poly(ethylene-co-glycidyl methacrylate)	8	430862
		
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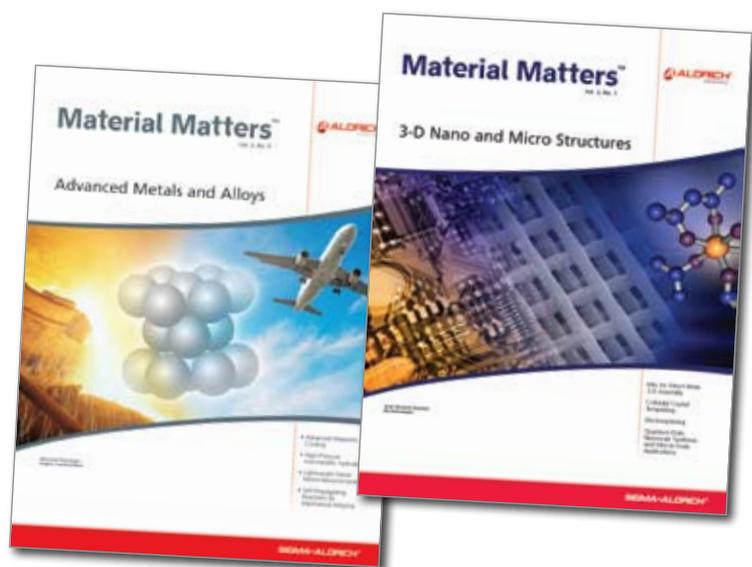
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Molecular Self-Assembly on Gold and Metal-Oxide Surfaces

Molecular Self-Assembly¹ is the assembly of molecules without guidance or management from an outside source. Self-assembly can occur spontaneously in nature, for example the self-assembly of the lipid bi-layer membrane, surrounding cells.

An approach to **Molecular Self-Assembly** that is efficient and that has received ample attention during the last decade is the creation of Self-Assembled Monolayers (or SAMs) using relatively weak intermolecular interactions between certain types of organic molecules, such as thiols or phosphonic acids, and a gold or oxidic surface.

Molecular Self-Assembly on Gold

Several forces are driving assembly of alkyl thiols on a gold surface. First, the sulfur-gold interactions are quite strong, ~45 kcal/mol, which allow for a relatively strong bonding of the film-forming molecules to the surface.

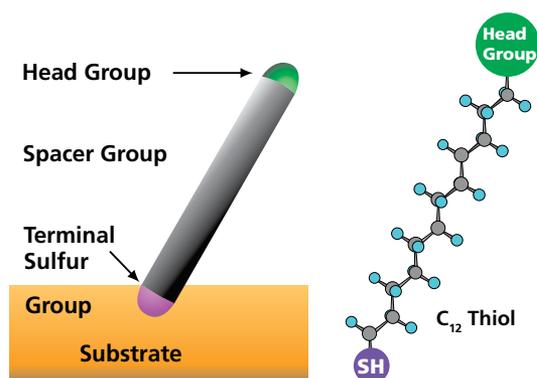


Figure 1. Schematic overview of a thiol molecule on a gold surface.

Furthermore, hydrophobic interactions between carbon and hydrogen atoms in the alkyl thiol molecules can significantly lower the overall surface energy thus promoting the formation of a self-assembled monolayer, especially if the alkyl chains contain at least 10 carbon atoms.^{2,3}

Molecular Self-Assembly on Metal-Oxide Surfaces

Recent advances in the area of micro and nano electronic materials have extended SAMs beyond conventional gold/thiol systems. To expand the choice of the substrates used for the preparation of SAMs, the chemical functionalities in film-forming molecules can be altered by introducing **phosphate or phosphonate-groups**. Such polar acidic molecules are capable of interacting with diverse **metal-oxide surfaces** (e.g. Al_2O_3 , Ta_2O_5 , Nb_2O_5 , ZrO_2 and Ti_2) and form films with a similar degree of ordering as for alkyl thiol SAMs on gold.⁴

Applications of SAMs comprise materials for semiconductor electronics industry such as nano-wires, nano-transistors, and nanosensors in large numbers. A few more examples of SAMs applications include surface wetting, non-fouling property, electrochemistry, surface passivation, protein binding, DNA assembly, corrosion resistance, biological arrays and cell interactions.⁵⁻⁷

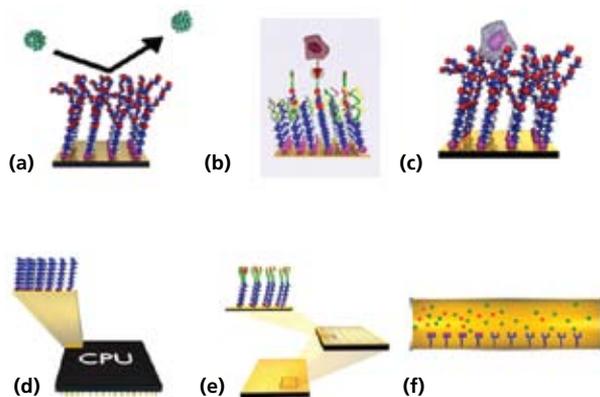


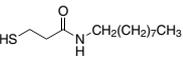
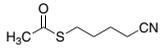
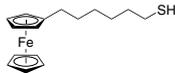
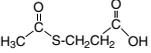
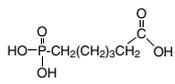
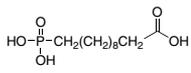
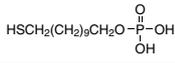
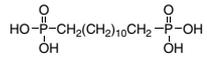
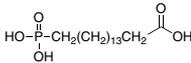
Figure 2. Some applications of self-assembled monolayers.

(a) Non-fouling surfaces (b) SAMs with specific binding receptors (c) Cell supports for native cell growth and studies (d) Molecular electronics (e) Microarrays (f) Separations

References

- (1) *Material Matters*TM, **2006**, Vol.1, No. 2. (2) M.D. Porter et al. *J. Am. Chem. Soc.* **1987**, *109*, 3559. (3) C.D. Bain et al. *J. Am. Chem. Soc.* **1989**, 7155. (4) G. Hahner et al. *17(22):7047-7052*, 2001. (5) J.C. Love et al. *Chem. Rev.* **2005**, *105*, 1103. (6) N.K. Chaki et al. *Biosensors & Bioelectronics* **2002**, *17*, 1 (7) A. Ulman, *Chem. Rev.* **1996**, *96*, 1533.

Materials for Molecular Self-Assembly — Latest Additions

Name	Structure	Prod. No.
Gold surface		
3-Mercapto- <i>N</i> -nonylpropionamide		686492-500MG
4-Cyano-1-butyl thiol		692581-500MG
5-Thiolacetyl-pentanenitrile		694754-1G
6-Ferrocenyl-hexanethiol		682527-250MG
<i>m</i> -Carborane-1-yl thiol		695572-250MG
<i>m</i> -Carborane-9-yl thiol		686506-250MG
Oxidic surface		
3-(Acetylthio)propionic acid		687081-5G
6-Phosphonohexanoic acid		693839-1G
11-Phosphono-undecanoic acid		678031-1G
11-Mercaptoundecylphosphoric acid		674311-50MG
(12-Phosphonodoceyl)phosphonic acid		685437-1G
16-Phosphono-hexadecanoic acid		685801-1G

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