
CHAPTER 1

Introduction

My aim in this introduction is to describe a number of fundamental aspects and techniques of surface modification that are built upon in subsequent chapters. Techniques range from the adsorption of small or large molecules onto surfaces, through the incorporation of layer-forming additives into a fluid layer above the surface, to the deliberate roughening or morphological modification of the surface. Gradual or abrupt spatial control of surface modification is also addressed and the impact of surface modification in application areas such as tribology, medicine, and catalysis is emphasized.

Materials properties can be broadly classified into those resulting from the nature of the bulk and those resulting from the characteristics of the surface. Examples of bulk properties include tensile strength, magnetic susceptibility, density, heat capacity, and even price (since materials are generally sold by the kg rather than the m²). Examples of properties where surface effects dominate include wear-resistance, frictional behavior, wettability, paintability or printability, biocompatibility, corrosion resistance, and, to some extent, aesthetic appearance.

It often happens that the ideal properties for a particular application cannot be found in a single material, but that the best solution is to coat a material possessing ideal bulk properties with a substance that imparts the desirable surface performance. The application of coatings represents an important industrial activity that navigates the often-tortuous path between the optimization of bulk and surface properties and the realities of bulk-material cost and coating-process economics. Further constraints that add to the challenges facing the industrial coater include adhesion between coating and bulk, the speed of the process and evenness of coating, the temperature required during coating, and the toxicity of the materials used in the process.

Many industrial coatings can be micrometers thick, this book focuses on surface modification on the molecular scale. This is where the most drastic changes occur: Many of the surface properties described above are fully established after only a single molecular layer of the coating has been applied. Molecular-scale coating studies require a “surface-science approach” to the subject, since well-defined, clean surfaces of the bulk material, or “substrate” are essential, if the properties of the coated object are to be predictable and the coating is to be readily characterized.

Many coating processes, such as painting or galvanizing, have histories going back several centuries. However, the surface-science approach to surface

modification really started to develop in the second half of the twentieth century, as ultrahigh vacuum (UHV) analytical techniques — such as Auger electron spectroscopy, X-ray photoelectron spectroscopy and low-energy electron diffraction — started to become available^{1,2}, enabling the quantitative characterization of monolayer coatings for the first time. In those early days of surface science, monomolecular layers of simple substances, such as oxygen, carbon monoxide, or halogens, were typically applied to well-characterized surfaces in the analytical UHV chamber². The past half-century has witnessed a steady increase in the complexity and applicability of systems that can be studied by a rigorous, surface-science approach, which has grown from a field dealing with solid surfaces in vacuum, to encompass interfaces between solids and other condensed phases (see Chapter 5).

1a. Self-assembled monolayers

The invention of self-assembled monolayers (SAMs) (see Chapter 2a) represented a major step forward in the fabrication of monomolecular layers, since they allow a surface to be readily and reproducibly functionalized with a monolayer, without the use of a UHV chamber³. The essential components of SAMs (Figure 1) are the anchoring group, which attaches the molecules to the surface, the head group, which defines the state of functionalization of the new outer surface following modification, and the linking group, which, via van der Waals' interactions, provides an additional driving force for the adsorption reaction, and can create a certain degree of order in the system. Many head groups have been reported⁴ including $-\text{CH}_3$, $-\text{CF}_3$, $-\text{OH}$, $-\text{COOH}$, $-\text{NH}_2$, and biotin. The linking groups generally consist of hydrocarbon (or fluorocarbon) chains with > 8 carbon atoms, at which point the total van der Waals interaction between the chains becomes large enough to lead to ordering phenomena. Anchoring groups depend on the substrate, since it is generally a covalent or coordination bond that is being formed, and include thiols⁵ (on gold and other noble metals), silanes⁶ (on hydroxyl-terminated oxides),

¹*Surface Analysis: The Principal Techniques*, John C. Vickerman, Ian Gilmore (Editors), 2nd Ed., John Wiley & Sons, 2009.

²*Introduction to Surface Chemistry and Catalysis*, Gabor A. Somorjai, John Wiley & Sons, 1994.

³W.C. Bigelow, D.L. Pickett, W.A. Zisman, Oleophobic Monolayers 1. Films Adsorbed From Solution In Non-Polar Liquids. *J Coll Sci Imp U Tok* (1946) Vol. 1(6) pp. 513–538; R.G. Nuzzo, D.L. Allara, Adsorption of Bifunctional Organic Disulfides on Gold Surfaces. *J Am Chem Soc* (1983) Vol. 105(13) pp. 4481–4483; R. Maoz, J. Sagiv. On The Formation and Structure of Self-Assembling Monolayers A Comparative ATR-Wettability Study of Langmuir-Blodgett and Adsorbed Films on Flat Substrates and Glass Microbeads. *J Colloid Interf Sci* (1984) Vol. 100(2) pp. 465–496

⁴D. Witt, R. Klajn, P. Barski, B.A. Grzybowski, Applications, Properties, and Synthesis of Omega-Functionalized n-Alkanethiols and Disulfides – the Building Blocks of Self-Assembled Monolayers. *Curr Org Chem* (2004) Vol. 8(18) pp. 1763–1797.

⁵J.C. Love, L.A. Estroff, J.K. Kriebel, R.G. Nuzzo, G.M. Whitesides, Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology. *Chem Rev* (2005) Vol. 105(4) pp. 1103–1169.

⁶A. Ulman, Formation and Structure of Self-Assembled Monolayers. *Chem Rev* (1996) Vol. 96(4) pp. 1533–1554.

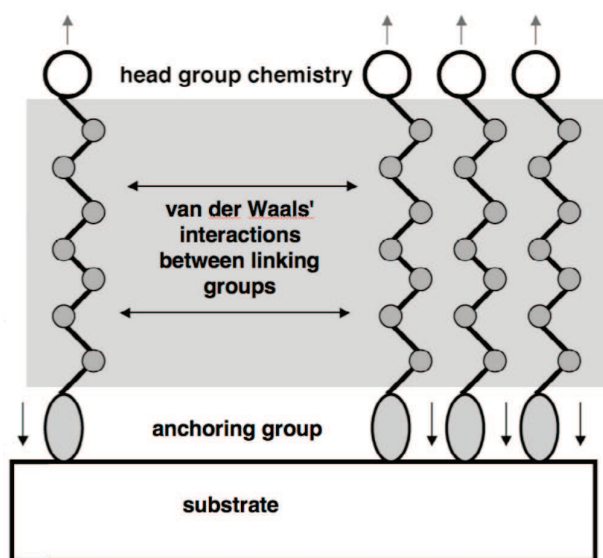


Figure 1: Diagram of the interactions involved in a self-assembled monolayer (courtesy of Dr. S. Tosatti, SuSoS AG).

phosphates⁷ or phosphonates⁸ (on many oxides) and catechols⁹ (on transition metal oxides) (Figure 2). Self assembly of these systems occurs rapidly (typically minutes to hours), although the molecular order in the monolayer often develops with slower kinetics¹⁰.

SAMs represent a powerful approach to covering a surface in a layer of a given functionality. In many cases moderate surface contamination is displaced by the SAM-forming reaction⁵, meaning that surface functionalization with a high degree of perfection can be achieved under ambient conditions.

It is, of course possible to adsorb more than one single SAM-forming molecule (with different head groups) on a surface, in order to have more control over the precise functionality that is exposed. The *density* of the functionality can also be tuned by mixing the adsorbate containing the desired head group with an adsorbate terminated in an “inert” head group that has no function for the particular applica-

⁷D. Brovelli, G. Hähner, L. Ruiz, R. Hofer, G. Kraus, A. Waldner, J. Schlosser, P. Oroszlan, M. Ehrat, N.D. Spencer, Highly Oriented, Self-Assembled Alkanephosphate Monolayers on Tantalum(V) Oxide Surfaces. *Langmuir* (1999) Vol. 15 pp. 4324–4327.

⁸J.T. Woodward, A. Ulman, D.K. Schwartz, Self-Assembled Monolayer Growth of Octadecylphosphonic Acid on Mica. *Langmuir* (1996) Vol. 12(15) pp. 3626–3629; W. Gao, L. Dickinson, C. Grozinger, F.G. Morin, L. Reven, Self-Assembled Monolayers of Alkylphosphonic Acids on Metal Oxides. *Langmuir* (1996) Vol. 12(26) pp. 6429–6435.

⁹J.L. Dalsin, B.H. Hu, B.P. Lee, P.B. Messersmith, Mussel Adhesive Protein Mimetic Polymers for the Preparation of Nonfouling Surfaces. *J Am Chem Soc* (2003) Vol. 125(14) pp. 4253–4258; J.-Y. Wach, B. Malisova, S. Bonazzi, S. Tosatti, M. Textor, S. Zuercher, K. Gademann, Protein-Resistant Surfaces through Mild Dopamine Surface Functionalization. *Chem-Eur J* (2008) Vol. 14(34) pp. 10579–10584.

¹⁰D.K. Schwartz, Mechanisms and Kinetics of Self-Assembled Monolayer Formation. *Annu Rev Phys Chem* (2001) Vol. 52 pp. 107–137.

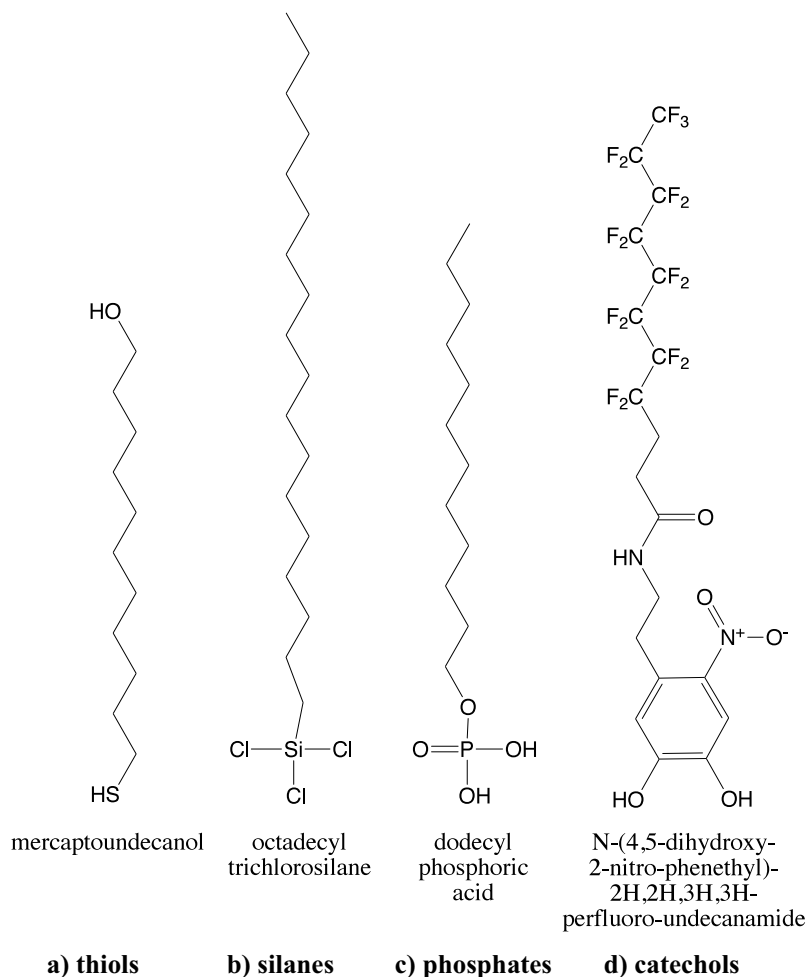


Figure 2: Examples of molecules that have been used to produce self-assembled monolayers on various surfaces. a) Thiols have been used extensively to functionalize gold, silver, and other metals⁵. b) Trichloro- and trialkoxy silanes are used to functionalize many oxide surfaces⁶ and are used industrially as adhesion promoters. c) Phosphates and phosphonates^{7,8} and d) catechols⁹ have been used to functionalize a number of transition metal oxides.

tion.¹¹ This dilution can also be spatially varied, leading to a concentration gradient in the functionality¹². SAMs can also be printed in patterns on surfaces, for example by microcontact printing, which involves using an elastomeric stamp to print SAM-forming molecules onto substrates¹³, or ink-jet printing, where the adsorbing

¹¹C.D. Bain, G.M. Whitesides, Formation of 2-Component Surfaces by the Spontaneous Assembly of Monolayers on Gold from Solutions Containing Mixtures of Organic Thiols. *J Am Chem Soc* (1988) Vol. 110(19) pp. 6560–6561.

¹²S. Morgenthaler, C. Zink, N.D. Spencer, Surface-Chemical and -Morphological Gradients. *Soft Matter* (2008) Vol. 4 pp. 419–434.

¹³Y.N. Xia, G.M. Whitesides, Soft Lithography. *Angew Chem Int Edit* (1998) Vol. 37(5) pp. 551–575.

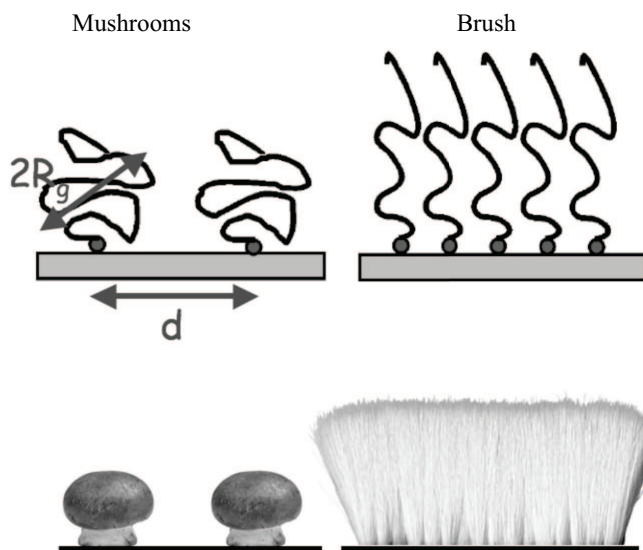


Figure 3: End-grafted polymer chains in a good solvent. If $d > 2R_g$, the chains assume a conformation similar to that of free chains in solution, for which R_g is the radius of gyration. This is known as the “mushroom” conformation. If $d < 2R_g$, the chains stretch out into the solvent to form a polymer “brush”.

molecule is used as ink in a conventional ink-jet printer¹⁴. A very broad range of applications for SAMs has been reported, ranging from biosensors¹⁵ to lubricants for microelectromechanical devices¹⁶ and they have been crucial in the development of a number of new fields, from nanoparticles¹⁷ to nanowires¹⁸.

1b. Functionalizing surfaces with polymer brushes

When polymer chains are tethered to a surface in the presence of a good solvent, and are spaced closely together (separated by a distance, d , that is less than twice their radii of gyration¹⁹, R_g , measured as the free molecule in a good solvent), they have a tendency to stretch out into the solvent in a brush-like configuration, rather than interacting closely with each other.

¹⁴A. Bietsch, J. Zhang, M. Hegner, H.P. Lang, C. Gerber, Rapid Functionalization of Cantilever Array Sensors by Inkjet Printing. *Nanotechnology* (2004) vol 15 pp. 873–880.

¹⁵N.K. Chaki, K. Vijayamohan, Self-Assembled Monolayers as a Tunable Platform for Biosensor Applications. *Biosens Bioelectron* (2002) Vol. 17(1-2) pp. 1-12.

¹⁶W.R. Ashurst, C. Yau, C. Carraro, R. Maboudian, M.T. Dugger, Dichlorodimethylsilane as an Anti-Stiction Monolayer for MEMS: A Comparison to the Octadecyltrichlorosilane Self-Assembled Monolayer. *J Microelectromech S* (2001) Vol. 10(1) pp. 41–49.

¹⁷G.H. Woehrle, L.O. Brown, J.E. Hutchison, Thiol-Functionalized, 1.5-nm Gold Nanoparticles Through Ligand Exchange Reactions: Scope and Mechanism of Ligand Exchange. *J Am Chem Soc* (2005) Vol. 127(7) pp. 2172–2183.

¹⁸C.N.R. Rao, G.U. Kulkarni, A. Govindaraj, B.C. Satishkumar, P.J. Thomas, Metal Nanoparticles, Nanowires, and Carbon Nanotubes. *Pure Appl Chem* (2000) Vol. 72(1-2) pp. 21–33.

¹⁹*Principles of Polymer Chemistry*, P.J. Flory, Cornell University Press (1953).

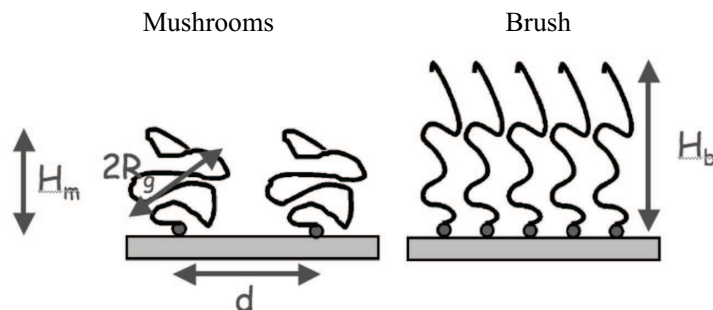


Figure 4: Scaling of polymer height from the substrate surface in both mushroom and brush conformations. The quantity $d/2R_g$ gives an indication of the degree of brush formation. In the mushroom conformation, the height, H_m is independent of the grafting density, while in a brush, the height, H_b scales as the cube root of the grafting density, σ , which is $1/d^2$.

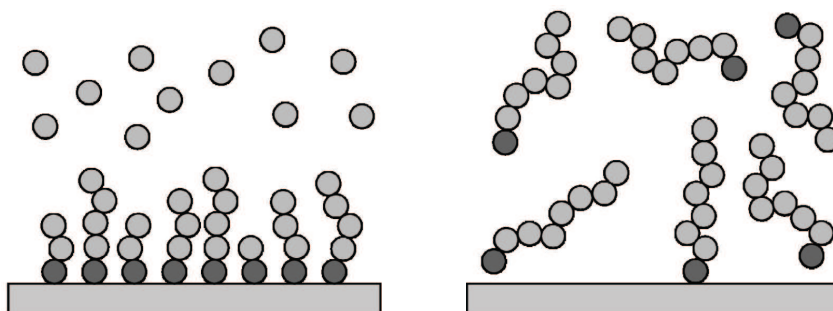


Figure 5: “Grafting-from” (left) and “grafting-to” (right) approaches for the synthesis of polymer brushes.

In other words, the free-energy cost incurred due to interaction between the chains exceeds the contribution due to the entropy elasticity of the chain (Figure 3). In the case of the widely spaced, (or “mushroom”) conformation, the height of the polymer layer above the substrate is independent of the grafting density of the chains (number of attached chains per unit area). In the brush conformation, however, the height scales as the cube root of the grafting density (Figure 4)²⁰, σ , which itself is equivalent to $1/d^2$.²¹

A number of approaches have been described for the preparation of polymer brushes, and these can be broadly described as “grafting from” and “grafting to”²² (Figure 5). In grafting from, an initiator is immobilized on a surface, and

²⁰T. Wu, K. Efimenko, P. Vlcek, V. Subr, J. Genzer, Formation and Properties of Anchored Polymers with a Gradual Variation of Grafting Densities on Flat Substrates. *Macromolecules* (2003) Vol. 36 pp. 2448–2453.

²¹A. Halperin, M. Tirrell, T.P. Lodge, Tethered Chains in Polymer Microstructures. *Adv Polym Sci* (1992) Vol. 100 pp. 31–71; *Polymers at Interfaces*, G.J. Fleer, M.A. Cohen Stuart, J.M.H.M. Scheutjens, T. Cosgrove, B. Vincent, Chapman & Hall, London, 1993.

²²*Polymer Brushes: Synthesis, Characterization, Applications*, R.C. Advincula, W.J. Brittain, K.C. Caster, J. Rühle, Wiley-VCH, 2004.

a polymerization reaction then takes place, with the polymer chain growing out from the surface. A number of different synthetic approaches have been taken, including atom-transfer radical polymerization (ATRP)²³ and reversible addition-fragmentation chain transfer (RAFT)²⁴. The grafting-from approach has the advantage of producing a high density of polymer chains on the surface (high σ), but the disadvantage for applications that synthetic chemistry needs to be performed on the surface, whenever a brush is needed.

The grafting-to approach involves the adsorption of ready-synthesized, end-functionalized polymers onto a surface, for example using thiol-modified PEG on a gold surface²⁵. While this approach is much more straightforward, once the end-functionalized polymer has been synthesized, it generally does not yield the high values of σ that are seen with grafting-from approaches, due to the steadily increasing steric inhibition of adsorption — as the coverage increases — by already-adsorbed polymer chains. An improvement in the σ obtainable by grafting-to methods can be achieved via the use of graft copolymers, where multiple brush-forming chains are grafted onto a backbone, to form a bottle-brush-like molecule. The backbone can then provide the adhesion to the surface²⁶ via coulombic, hydrophobic, or covalent interactions, for example. Many examples of this approach will be found throughout this book.

Polymer brushes have a number of fascinating properties that lead to many important applications including biocompatibility, colloidal stabilization, chromatography and control of wetting phenomena (see Chapter 2b). As with self-assembled monolayers, they represent a convenient way of covering a surface with a particular functionality, be it the polymer chains themselves, which may have useful properties related to adhesion or friction, or an end-functionalization on the brush that may be used for subsequent reactions. An example of the former is the widespread use of poly(ethylene glycol) (PEG) brushes to inhibit protein adsorption²⁷; an example of the latter is the use of biotin-end-functionalized PEG brushes to serve as a platform for the immobilization of biomolecules for cells via integrin receptors²⁸, paving the

²³M. Ejaz, S. Yamamoto, K. Ohno, Y. Tsujii, T. Fukuda, Controlled Graft Polymerization of Methyl Methacrylate on Silicon Substrate by the Combined Use of the Langmuir-Blodgett and Atom Transfer Radical Polymerization Techniques. *Macromolecules* (1998) Vol. 31(17) pp. 5934–5936.

²⁴J. Chiefari, Y.K. Chong, F. Ercole, J. Krstina, J. Jeffery, T.P. Le, R.T.A. Mayadunne, G.F. Meijs, C.L. Moad, G. Moad, E. Rizzardo, S.H. Thang, Living Free-Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer: The RAFT Process. *Macromolecules* 31(16) 5559–5562, 1998.

²⁵M. Himmelhaus, T. Bastuck, S. Tokumitsu, M. Grunze, L. Livadaru, H.J. Kreuzer, Growth of a Dense Polymer Brush Layer from Solution. *Europhys Lett* (2003) Vol. 64(3) pp. 378–384.

²⁶G.L. Kenausis, J. Vörös, D.L. Elbert, N.P. Huang, R. Hofer, L. Ruiz, M. Textor, J.A. Hubbell, N.D. Spencer, Poly(L-Lysine)-g-Poly(Ethylene Glycol) Layers on Metal Oxide Surfaces: Attachment Mechanism and Effects of Polymer Architecture on Resistance to Protein Adsorption. *J. Phys. Chem. B* (2000) Vol. 104(14) pp. 3298–3309.

²⁷S.I. Jeon, J.H. Lee, J.D. Andrade, P.G. De Gennes, Protein Surface Interactions in the Presence of Polyethylene Oxide. 1. Simplified Theory. *J Colloid Interf Sci* (1991) Vol. 142(1) pp. 149–158

²⁸N.P. Huang, J. Vörös, S.M. De Paul, M. Textor, N.D. Spencer, Biotin-Derivatized Poly(L-Lysine)-g-Poly(Ethylene Glycol): A Novel Polymeric Interface for Bioaffinity Sensing. *Langmuir* (2002) Vol. 18(1) pp. 220–230.

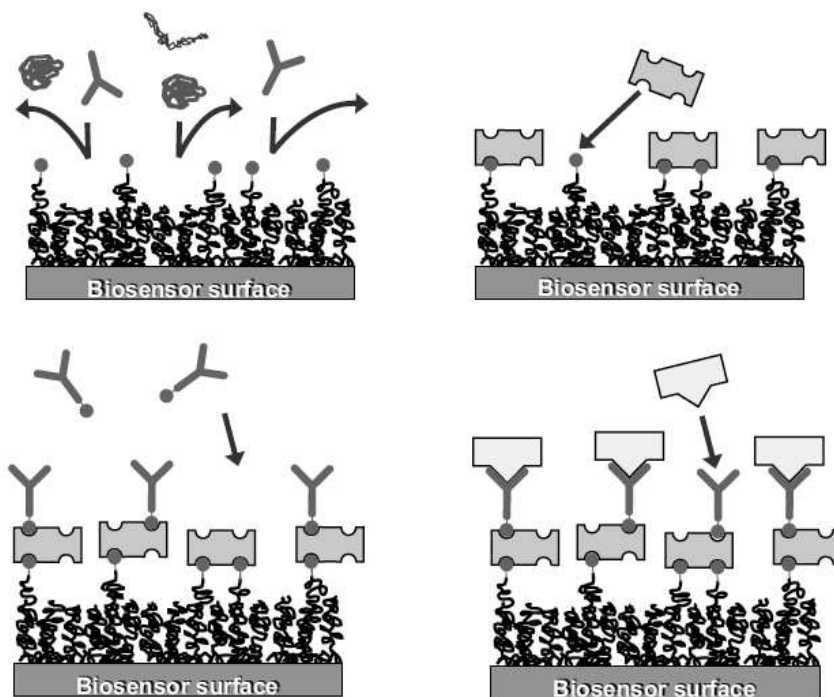


Figure 6: Schematic of the different steps in a model immunoassay. Upper left: a surface coated with a PEG brush, partially terminated with biotin, resists non-specific protein adsorption; upper right: the biotinylated PEG chains specifically adsorb streptavidin; lower left: an antibody attaches to the streptavidin and serves as a capture molecule; lower right: the target molecule binds to the biotinylated antibody through antibody-antigen interactions. Reproduced from Reference 28 with kind permission.

way for proteomics and immunoassay applications (Figure 6). A significant advantage of this approach is that the immobilized biomolecules, which can be used for specific protein or cell interactions, for example, are incorporated in a background of PEG, which suppresses non-specific adsorption to the surface. It is thus a very convenient way to steer the surface towards highly selective interactions with proteins and cells (see Chapter 2c).

The mechanical properties of polymer brushes are also of interest. Klein was among the first to recognize that polymer-brush-coated surfaces displayed exceedingly low friction coefficients under the appropriate good solvent²⁹, and explained this in terms of entropic effects that inhibit both compression and interdigitation of the brush-coated surfaces. Klein began his work with polystyrene brushes, toluene serving as a solvent, but later moved on to PEG/water systems³⁰. The use of water-based brushes was significant, since it mirrors the way in which nature lubricates (see Chapter 2e). This involves the adsorption of glycoproteins to yield oligosaccharide-

²⁹J. Klein, E. Kumacheva, D. Mahalu, D. Perahia, L.J. Fetters, Reduction of Frictional Forces Between Solid-Surfaces Bearing Polymer Brushes. *Nature* (1994) Vol. 370 pp. 634–636.

³⁰U. Raviv, R. Tadmor, J. Klein, Shear and Frictional Interactions Between Adsorbed Polymer Layers in a Good Solvent. *J Phys Chem B* (2001) Vol. 105 pp. 8125–8134.

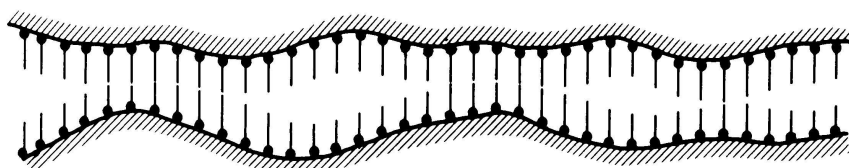


Figure 7: The adsorption of carboxylic acids onto sliding surfaces in a lubricated contact under oil, to produce a low-shear-strength, self-repairing interface. Reproduced from Reference 34 with kind permission.

covered surfaces, which bear a certain resemblance to the man-made, brush-covered systems described above³¹.

1c. Using additives to modify surfaces in a self-repairing way

The traditional life cycle for coatings in most applications begins with the surface-modification process in a manufacturing environment. During use in the field, the coating suffers degradation due to processes such as wear and corrosion, until it reaches the end of its service life.

In contrast, in the case of lubricants, surface modification is frequently a continuous process that takes place as and when it is needed. A simple example is that of friction modifiers such as long-chain carboxylic acids, which are often used in motor oils, in order to reduce friction under conditions that are incapable of producing a hydrodynamic lubricating film. According to the well-established model that originates with Hardy³², the additive molecules adsorb onto the opposed metallic or oxidic surfaces in monolayers (Figure 7), providing a low-shear-strength interface between the hydrocarbon chains, at which sliding can readily occur. This leads to a reduction in friction. Wear of the adsorbed layer does occur to a small extent, but this is rapidly compensated by re-adsorption from the additive-containing oil. Thus the protective system is self repairing. An alternative mechanism involving metal-soap formation appears to occur under certain circumstances, depending on the local water concentration³³.

In the case of antiwear additives and the so-called “extreme-pressure” additives, the situation is more complicated; the crucial reaction that leads to the production of a wear-protective layer may occur only in the case of high pressure and/or locally high temperatures. The precise modes of action of such additives, which are present in virtually every lubricating oil, have been the topic of intensive research for several decades (see Chapter 2d). A significant incentive for such research has been the search for alternative additives that are less damaging to the pollution-control devices on modern automobiles. The commonly used zinc dialkyldithiophosphates

³¹S. Lee, N.D. Spencer, Sweet, Hairy, Soft, and Slippery. *Science* (2008) Vol. 319 pp. 575–576.

³²W.B. Hardy, I. Bircumshaw, Boundary Lubrication, Plane Surfaces and the Limitations of Amontons’ Law. *Proc. R. Soc. Lond.* (1925) Vol. A108 pp. 1–27.

³³M. Ratoi, V. Anghel, C.H. Bovington, H.A. Spikes, Mechanisms of Oiliness Additives. *Tribology Int.* (2000) Vol. 33 pp. 241–247.

(ZnDTPs) have been shown to react, under high tribological stress, to produce a glassy layer on the sliding surfaces, effectively protecting the underlying steel^{34,35}. Worn areas of this layer are replaced by further surface-reactions of the additive, which is always present in the oil solution. Not only are the layers formed in this way self-repairing, but they also seem to display some behavior that can be described as “responsive”: Nanoindentation measurements suggest that the higher the load to which the layers are subjected in tribological tests, the harder — and thus the more protective — the layer becomes³⁶.

An alternative method for lowering friction is the surface attachment of brush-forming polymer chains, as described in Chapter 1b, and a number of different approaches have been taken to realizing this goal. One method is to synthesize brush-forming molecules that spontaneously and reversibly adsorb to the surface from solution, i.e. when dissolved in the lubricant, they can function as friction-reducing additives in a similar way to that described above for the carboxylic acid additives³⁷. These surface-grafted polymers are removed from the surface under extreme mechanical stress, but are then replaced by identical molecules that are present in solution. Thus, such brush systems can also be self-healing, provided that the time constants for removal are slower than those for diffusion to the surface and readsorption. A relatively weak interaction with the surface is actually an advantage in this case, since it ensures that the polymers are removed intact from the surface, leaving behind empty sites for replacement³⁸.

1d. Structure: a new dimension to surface tailoring

Chemical effects of structure

While the chemical composition of a surface is clearly important in determining its properties, the topographical structure of surfaces, from the atomic up to the micrometer scale, can have an additional, but in many cases very significant, effect on surface behavior.

On the atomic level, this is clearly observed in many catalytic reactions on metal surfaces, where the crystal face of the metal concerned can greatly influence the catalyzed rate of reaction (see Chapter 3a). One of the most significant effects of

³⁴A.J. Gellman, N.D. Spencer, Surface Chemistry in Tribology. *P I Mech Eng J-J Eng* (2002) Vol. 216 pp. 443–461.

³⁵H. Spikes. The History and Mechanisms of ZDDP. *Tribology Letters* (2004) Vol. 17(3) pp. 469–489.

³⁶S. Bec, A. Tonck, J.M. Georges, R.C. Coy, J.C. Bell, G.W. Roper. Relationship Between Mechanical Properties and Structures of Zinc Dithiophosphate Anti-Wear Films. *P Roy Soc Lond A Mat* (1999) Vol. 455 (1992) pp. 4181–4203.

³⁷S. Lee, M. Müller, M. Ratoi-Salagean, J. Vörös, S. Pasche, S.M. De Paul, H.A. Spikes, M. Textor, N.D. Spencer. Boundary Lubrication of Oxide Surfaces by Poly(L-Lysine)-g-Poly(Ethylene Glycol) (PLL-g-PEG) in Aqueous Media. *Tribology Letters* (2003) Vol. 15(3), pp. 231–239.

³⁸S. Lee, M. Müller, R. Heeb, S. Zürcher, S. Tosatti, M. Heinrich, F. Amstad, S. Pechmann, N.D. Spencer. Self-Healing Behavior of a Polyelectrolyte-Based Lubricant Additive for Aqueous Lubrication of Oxide Materials. *Tribology Letters* (2006) Vol. 24(3), pp. 217–223.

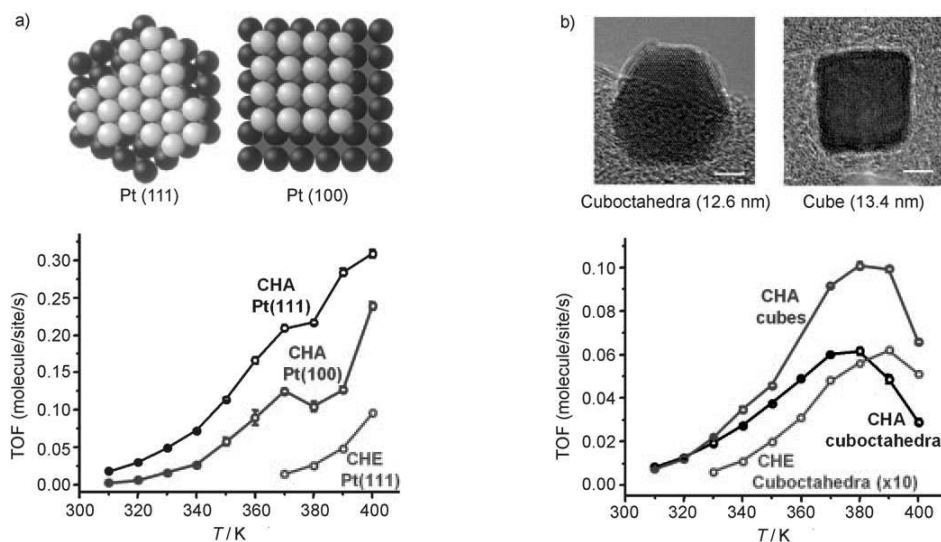


Figure 8: Turnover rates of cyclohexene and cyclohexane formation during the hydrogenation of benzene on Pt(111) and Pt(100) surfaces a), as well as the cubic and cuboctahedra platinum nanoparticles b), which demonstrate the similarities between the single-crystal and nanoparticle surfaces. CHA=cyclohexane, CHE=cyclohexene. Reproduced from Reference 42 with kind permission.

this kind is seen in the iron-catalyzed synthesis of ammonia, where more than a 400-fold difference in catalytic activity can be seen between the different crystal faces of iron³⁹. This behavior can be ascribed to the presence of atoms with different coordination numbers in different crystal faces, those with seven coordinated atoms being only revealed in particularly open crystal faces, such as Fe(111) and constituting the most active sites for both nitrogen adsorption and ammonia synthesis⁴⁰.

In the case of benzene hydrogenation to cyclohexane or cyclohexene on platinum single crystals, a change in selectivity is observed from Pt(111), which catalyzes the formation of both products, to Pt(100), where only cyclohexane is produced. This effect is due to the structure sensitivity of the cyclohexene-forming reaction, while the cyclohexane-forming reaction is structure insensitive. Interestingly, the same effect can be observed on nanoparticles of different shapes; cuboctahedral particles, which contain (111) faces, catalyze the production of both products, whereas cubic nanoparticles (with (100) faces) produce only cyclohexane (Figure 8)^{41,42}.

³⁹N.D. Spencer, R.C. Schoonmaker, G.A. Somorjai. Structure Sensitivity in the Iron Single-Crystal Catalyzed Synthesis of Ammonia. *Nature* (1981) Vol. 294 (5842) pp. 643–644.

⁴⁰N.D. Spencer, R.C. Schoonmaker, G.A. Somorjai. Iron Single-Crystals as Ammonia-Synthesis Catalysts — Effect of Surface-Structure on Catalyst Activity. *J Catal* (1982) Vol. 74(1) pp. 129–135.

⁴¹K.M. Bratlie, H. Lee, K. Komvopoulos, P. Yang, G.A. Somorjai. Platinum Nanoparticle Shape Effects on Benzene Hydrogenation Selectivity, *Nano Lett.* (2007) Vol. 7 pp. 3097–3101.

⁴²G.A. Somorjai, J.Y. Park. Molecular Factors of Catalytic Selectivity. *Angew. Chem. Int. Ed.* (2008) Vol. 47 pp. 9212–9228.

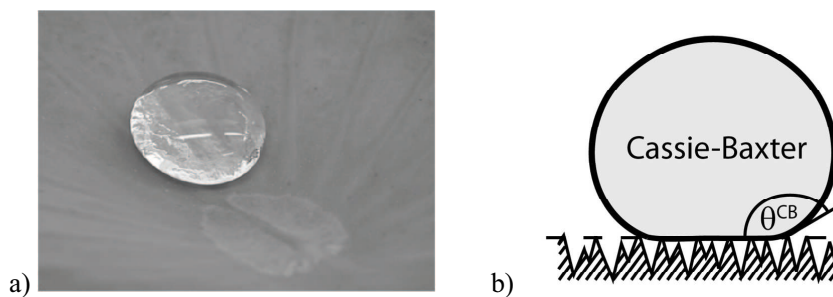


Figure 9: a) A drop of water on a lotus-leaf surface, b) “Cassie & Baxter” state of a droplet on a hydrophobic, rough surface. Note the air enclosed under the drop. Pictures courtesy of Doris Spori, ETH Zurich.

Physical effects of structure

In addition to its influence on surface reactivity, surface structure is also seen to affect wettability on the micrometer scale, as is best illustrated by the “lotus effect”⁴³ (see Chapter 3b). The lotus leaf is superhydrophobic, i.e. has a water contact angle of about 160° , thanks to the combination of the waxes on the surface with a characteristic dual micrometer- and nanometer-scale surface topography. Without the structure, the wax chemistry would only impart mild hydrophobicity to the surface. Superhydrophobicity comes about only when a water droplet is in contact with a rough surface with a substantial enclosure of air beneath the drop (Figure 9). This is the so-called “Cassie-Baxter” state, named after the authors of the work⁴⁴ that described the contact angle of water droplets in this state by means of the equation:

$$\cos(\theta^{CB}) = f_1^* \cos(\theta^Y) - f_2$$

where f_1 and f_2 are fractions of the drop area in contact with the surface and with air, respectively, and θ^Y is the contact angle on a flat surface of the same chemistry. Figure 10 illustrates the effect on the contact angle, of varying the f_1 parameter while maintaining constant surface chemistry⁴⁵.

Superhydrophobic surfaces such as the lotus leaf have a particularly interesting property of being “self-cleaning”, since water rolling over the surface tends to remove traces of dirt. This phenomenon lends itself to a number of applications, ranging from self-cleaning textiles to self-cleaning buildings.

Adhesion and friction are also dependent on surface structure in the sense of roughness, although the effect can be difficult to predict. Frictional forces often contain an adhesive component, which tends to decrease as roughness increases, but

⁴³W. Barthlott, C. Neinhuis. The Purity of Sacred Lotus or Escape From Contamination in Biological Surfaces, *Planta* (1997) Vol. 202 pp. 1–8.

⁴⁴A.B.D. Cassie, S. Baxter. Wettability of Porous Surfaces, *Trans. Faraday Soc.* (1944) Vol. 40 pp. 546–550.

⁴⁵D.M. Spori, T. Drobek, S. Zürcher, N.D. Spencer. Cassie-State Wetting Investigated by Means of a Hole-to-Pillar-Density Gradient. *Langmuir* (2010) Vol. 26(12) pp. 9465–9473.

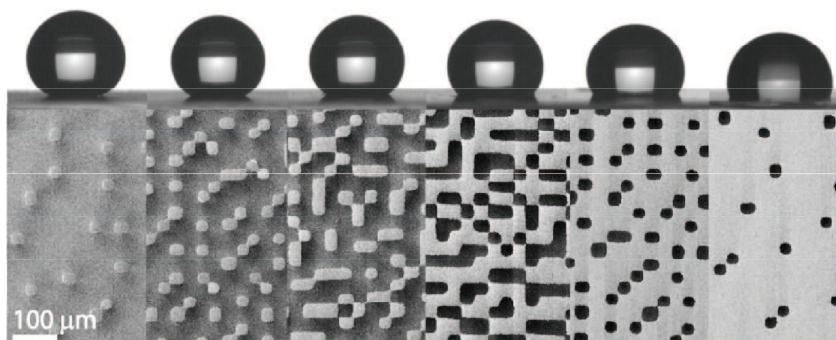


Figure 10: Drops of water in contact with poly(dimethyl siloxane) surfaces of varying hole/pillar densities (shown beneath the drops), corresponding to different fractions of air enclosed beneath the drops (f_2), from Reference 45 with kind permission.

friction itself is also somewhat roughness dependent, especially when interlocking effects⁴⁶ and conformal contacts of elastomers⁴⁷ are involved. The effects are familiar to us in everyday life, but the science remains poorly understood.

In biological adhesion, roughness also plays an important role. For example, roughness is routinely used to enhance cell adhesion to titanium implants that are designed to integrate with bone, such as those in hip-joint or tooth replacements. However, it is also clear that roughness does not affect the adhesion of all cells in a similar manner⁴⁸, and the biochemical aspects of cell responses to roughness remain a much-explored research topic (see Chapter 3c).

Thus, surface structure is an important factor in determining surface properties, and represents an additional parameter that can be varied in order to tailor material surfaces for a particular application. Much research remains to be done in this area.

1e. Spatial distributions on surfaces: from patterns to gradients

There are many reasons why one might want to pattern a surface, chemically or morphologically. Patterns can be used to highlight the contrasting behavior of different surface-chemical modifications, in terms of their chemical reactions or interaction with living organisms, for example. This approach forms the basis of many diagnostic methods, such as gene or protein chips, where different biomolecules are distributed across a surface and their interactions with analytes are followed by fluorescence, for example. Patterned surfaces can also be used to explore biological

⁴⁶P.V.K. Porgess, H. Wilman. The Dependence of Friction on Surface Roughness. *Proc. Roy. Soc. A* Vol. 252 (1959), pp. 35–44.

⁴⁷G.A.D. Briggs, B.J. Briscoe. Surface Roughness and the Friction and Adhesion of Elastomers. *Wear* Vol. 57(2) pp. 269–280.

⁴⁸T.P. Kunzler, T. Drobek, M. Schuler, N.D. Spencer. Systematic Study of Osteoblast and Fibroblast Response to Roughness by Means of Surface Morphology Gradients. *Biomaterials* (2007) Vol. 28 pp. 2175–2182.

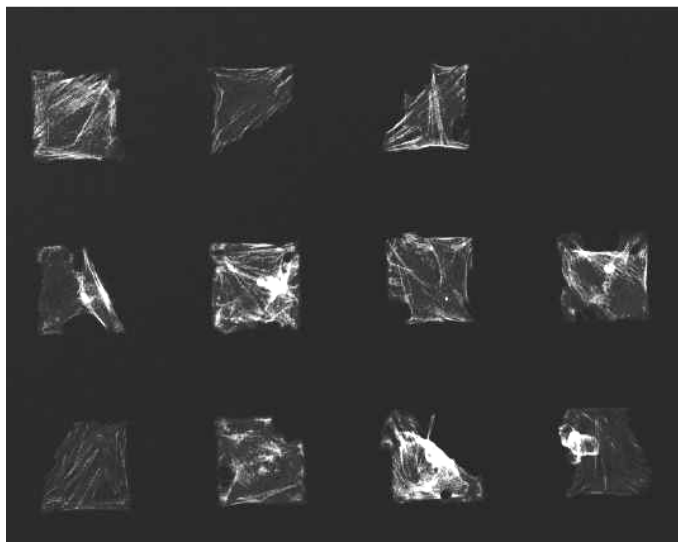


Figure 11: $60 \times 60 \mu\text{m}^2$ features of TiO_2 in a SiO_2 substrate, subsequently functionalized with alkane chains and poly(ethylene glycol) brushes, respectively, and then exposed to human foreskin fibroblasts. Fibroblasts are shown to spread out on the alkane chains to the border of the PEG brushes, and are visualized by immunostaining for f-actin. From Reference 50 with kind permission.

phenomena, such as neurite outgrowth on surfaces⁴⁹, and how adhesion molecules influence such processes. Morphological and chemical patterns have also been explored in terms of their influence on cell adhesion (Figure 11)⁵⁰ and alignment⁵¹, drop dynamics⁵² and wetting phenomena⁵³ (see Chapter 4b).

Approaches to patterning can be roughly divided into two categories: parallel and serial. Approaches such as dip-pen nanolithography (Figure 12)⁵⁴, which uses a modified atomic force microscope tip to write chemical patterns directly onto a surface, can produce features on the nanometer scale, but are inherently serial, one feature being written after another. Fabrication of a macro- or even microscale array is therefore an extremely slow process, unless multiple-tip systems are employed. Parallel approaches, such as photolithography and related techniques, or printing

⁴⁹J.A. Hammarback, S.L. Palm, L.T. Furcht, P.C. Letourneau. Guidance of Neurite Outgrowth by Pathways of Substratum-Adsorbed Laminin. *J. Neurosci. Res.* (1985) Vol. 13(1-2) pp. 213–220.

⁵⁰R. Michel, J.W. Lussi, G. Csúcs, I. Reviakine, G. Danuser, B. Ketterer, J.A. Hubbell, M. Textor, N.D. Spencer. Selective Molecular Assembly Patterning: A New Approach to Micro- and Nanochemical Patterning of Surfaces for Biological Applications. *Langmuir* (2002) Vol. 18(8) pp. 3281–3287.

⁵¹J.L. Charest, M.T. Eliason, A.J. García, W.P. King. Combined Microscale Mechanical Topography and Chemical Patterns on Polymer Cell Culture Substrates. *Biomaterials* (2006) Vol. 27(11) pp. 2487–2494.

⁵²H. Kusumaatmaja, J. Léopoldès, A. Dupuis, J.M. Yeomans. Drop Dynamics on Chemically Patterned Surfaces. *Europhys. Lett.* (2006) Vol. 73(5) pp. 740–746.

⁵³M. Morita, T. Koga, H. Otsuka, A. Takahara. Macroscopic-Wetting Anisotropy on the Line-Patterned Surface of Fluoroalkylsilane Monolayers. *Langmuir* (2005) Vol. 21 pp. 911–918.

⁵⁴R.D. Piner, J. Zhu, F. Xu, S. Hong, C.A. Mirkin. “Dip-Pen” Nanolithography. *Science* (1999) vol 283 pp. 661–663.

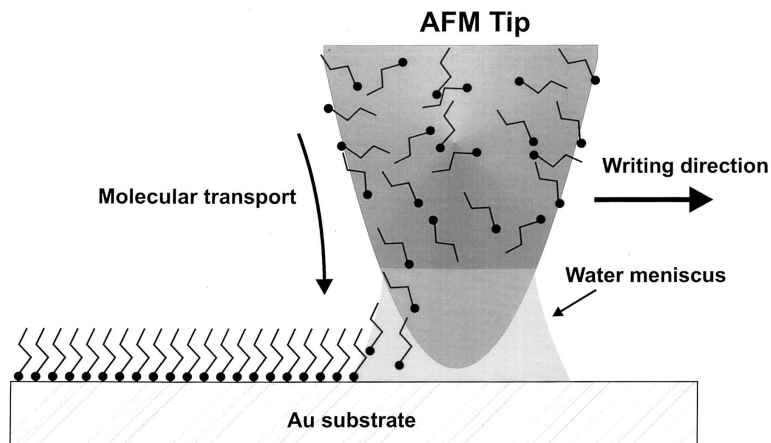


Figure 12: Principle of “dip-pen nanolithography”, whereby SAM-forming molecules are transported to a specific position with nanometer resolution, by means of an AFM tip. The molecules are transported within the water meniscus at the tip-substrate interface. From Reference 54 with kind permission.

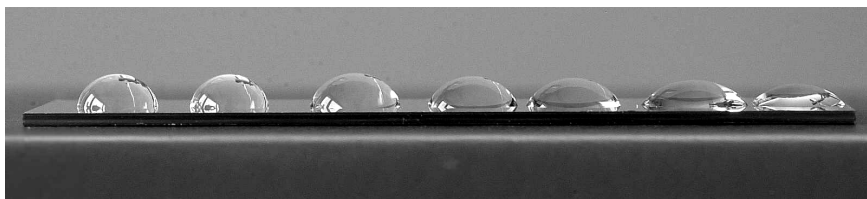


Figure 13: A gradient in hydrophobicity, formed by slow dipping of a gold-covered substrate into a dilute alkanethiol solution, and backfilling with a complementary, OH-terminated thiol. From Reference 60 with kind permission.

processes, such as microcontact printing (Figure 13)^{55,56} or inkjet printing⁵⁷, have much greater potential for patterning large areas, but generally are not suited to nanometer-scale resolution.

Recently, not only molecules, but also particles, have been patterned onto surfaces, by means of a silicone-rubber-based printing step, opening the way to a patterning approach for the fabrication of submicron-scale devices⁵⁸.

Patterning leads to a set of discrete, chemically or morphologically distinct regions on a surface. Sometimes it is more useful to fabricate surfaces where a particular property changes gradually as a function of its spatial location. Such systems

⁵⁵G.M. Whitesides, E. Ostuni, S. Takayama, X. Jiang, D.E. Ingber. Soft Lithography in Biology and Biochemistry. *Ann. Rev. Biomed. Eng.* (2001) Vol. 3 pp. 335–373.

⁵⁶A.P. Quist, E. Pavlovic, S. Oscarsson. Recent Advances in Microcontact Printing. *Anal. Bioanal. Chem.* (2005) Vol. 381 pp. 591–600.

⁵⁷N.E. Sanjana, S.B. Fuller. A Fast Flexible Ink-Jet Printing Method for Patterning Dissociated Neurons in Culture. *J. Neurosci. Meth.* (2004) Vol. 136(2) pp. 151–163.

⁵⁸T. Kraus, L. Malaquin, H. Schmid, W. Riess, N.D. Spencer, H. Wolf. Nanoparticle Printing with Single-Particle Resolution. *Nature Nanotechnology* (2007) Vol. 2 pp. 570–576.

are known as surface gradients, and are finding increasing application in a number of different areas⁵⁹ (see Chapter 4a). On the one hand, gradients allow experiments to be carried out very rapidly as a function of a particular surface property, which is changed along a spatial dimension of the sample. This has the distinct advantage that all other conditions remain the same while this property is being explored. On the other hand, certain dynamic phenomena, such as cell mobility, can be explored as a function of gradient slope. Not only has chemical functionality (leading e.g. to hydrophobicity⁶⁰ (Figure 13) or charge gradients) been explored in this context, but so also have polymer properties (block structure, molecular weight)⁶¹ and surface roughness have also been incorporated into gradients. A large number of different methods have been developed in recent years for the fabrication of chemical and morphological gradients, and their application as combinatorial research tools is now widespread.

⁵⁹S. Morgenthaler, C. Zink, N.D. Spencer. Surface-Chemical and -Morphological Gradients. *Soft Matter* (2008) Vol. 4 pp. 419–434.

⁶⁰S. Morgenthaler, S. Lee, S. Zürcher, N.D. Spencer. A Simple, Reproducible Approach to the Preparation of Surface-Chemical Gradients. *Langmuir* (2003) Vol. 19(25) pp. 10459–10462.

⁶¹J. Genzer, R.R. Bhat. Surface-Bound Soft Matter Gradients. *Langmuir* (2008) Vol. 24(6) pp. 2294–2317.