

From Surface Science to Nanotechnology

M.A. Van Hove*

Materials Sciences Division, Lawrence Berkeley National Laboratory,
Berkeley, CA 94720, USA

and

Advanced Light Source, Lawrence Berkeley National Laboratory,
Berkeley, CA 94720, USA

and

Department of Physics, University of California,
Davis, CA 95616, USA

Abstract

This overview sketches the historical development of surface science through nanoscience toward nanotechnology. It spans about 50 years of evolution and emphasizes the multidisciplinary nature of this field, as well as its closely-knit interactions with technology, scientific disciplines, phenomena and techniques. A series of examples is given, drawn mainly from work performed in Berkeley, to highlight various stages in the field: surfaces, interfaces, clusters, thin films, superlattices, nanostructures and “bionano”.

Introduction

Nanoscience can be viewed as the evolutionary outgrowth of surface science. Similarly, nanotechnology can be seen as a development of “applied surface science”. In fact, this field has continuously changed its character and substance over 50 years. To start off a review of this evolution, it may be useful to cite a few definitions taken from the web:

- Surface science studies “solid surfaces and interfaces, as well as gas-solid interactions” (International Union for Vacuum Science, Technique, and Applications[1]).
- Nanoscience is “the scientific discipline seeking to increase our knowledge and understanding of nanoscale phenomena, i.e. science on the scale of 0.1 nm to 100 nm”[2].

- Nanotechnology is “the creation of functional materials, devices and systems through control of matter on the nanometer length scale (1-100 nm), and exploitation of novel phenomena and properties (physical, chemical, biological) at that length scale” (National Aeronautics and Space Administration[3]).

One interesting aspect of these definitions is their vagueness. For instance, no length scale is specified for surface science. And neither surface science nor nanoscience are limited to particular disciplines such as physics or chemistry. This vagueness is quite convenient as it allows continuous development and evolution into new directions, without requiring frequent changes in names. On the other hand, the definitions of nanoscience and nanotechnology are so general that they cover molecular chemistry and biology as already practiced for many decades before the introduction of these names.

It is therefore useful to limit the scope of these definitions to describe the present state of these fields. Thus, in practice, surface science, which includes interface science, has focused on the scale of 0.01 to 10 nm (0.1 to 100 Å) in the single dimension perpendicular to the surface or interface. Surface science thus restricts itself to the nanometer scale in one dimension, studying structures that are spatially extended in two dimensions (“2D” structures). Surface science has concentrated on solid/vacuum, solid/gas and solid/solid interfaces, with relatively less emphasis on interfaces that involve liquids or soft matter (soft matter being polymeric and biological materials, for example).

By contrast, nanoscience and nanotechnology involve the nanometer scale in 2 or 3 dimensions, and thus study “one-dimensional” (“1D”) or “zero-dimensional” (“0D”) structures, such as nanowires and nanodots, respectively. In addition to the interfaces of interest to surface science, nanoscience and nanotechnology also investigate solid/liquid, solid/soft and soft/fluid interfaces.

To exemplify more specific subjects covered in nanoscience and nanotechnology, we may list the projects included in a nanoscience center, the Molecular Foundry[4], which is now under construction at the Lawrence Berkeley National Laboratory of the U.S. Department of Energy, in Berkeley, California. Its program, scheduled to start in 2006, is organized around the following six major themes:

- Inorganic Nanostructures: optimal preparation of metal, carbon and semiconductor nanostructures.

- Organic Nanostructures: study of soft materials, including organic molecules, macromolecules, and their assemblies.
- Biological Nanostructures: integration of biological components into functional nanoscale materials.
- Nanofabrication: state-of-the-art lithographic and thin-film processing.
- Imaging and Manipulation of Nanostructures: characterization and manipulation of a broad variety of nanostructures, from hard to very soft matter including liquid structures.
- Theory of Nanostructured Materials: theoretical support to complement experiments, guide the development of new principles, and predict new behavior and applications.

Who drives whom?

The title of this review, “From Surface Science to Nanotechnology”, might be interpreted to imply that science drives technology. This is certainly an oversimplification: in fact, there are many two-way interactions between the science and the technology. For example, surface science itself arose out of the invention of the transistor and the technological need for a higher reliability of this device, since it was rapidly discovered that uncontrolled surface impurities prevented reproducible performance. Space exploration then contributed vacuum technology and techniques, essential for controlling and characterizing surfaces. Many other technologies have spurred surface science into a multitude of new directions, such as: clusters, due to their importance in heterogeneous catalysis; interfaces, which dominate interconnects and junctions; thin films and coatings, relevant to sensors and objects in mechanical contact; and superlattices, used in lasers. This sequence of new driving forces continues into nanostructures, including bionanomaterials.

This tight interaction between science and technology is sketched in Figs. 1 and 2, which draw a historical overview of the evolution of surface science toward nanoscience and nanotechnology. The time axis covers approximately a half century, from the 1950s to the early 21st century. These two figures illustrate the many interactions between the field itself, the technologies that feed into it and benefit from it, the scientific disciplines that are attracted to it, the phenomena that sustain it, and the techniques that make it all possible. These two figures roughly follow the historical timeline.

The mutual interdependence between science and technology is one reason that the field of surface science has continued to evolve over a half century, and gradually “morphed” toward the fields of nanoscience and nanotechnology. There has been a continuous flux of new challenges, results and techniques between the scientific and technological communities.

Figs. 1 and 2 also exhibit the trend toward growing complexity over time, again spurred by technological needs. Indeed, the traditional “surface” of surface science is the simplest possible geometry, involving just a solid terminated at a solid/vacuum interface: that simple geometry already provides much variety of structures and phenomena, such as surface reconstructions, surface segregation, physical and chemical adsorption, growth, all defined by thermodynamics, geometric structure, electronic structure, magnetic structure, vibrations, dynamics, etc. Progressing to interfaces adds the complexities of having different solids in contact. Studying clusters requires simultaneously considering a variety of crystallographic faces as well as their mutual edges and corners. Thin films and coatings also involve combinations of materials and their sometimes diffuse interfaces. Superlattices add the complexity of multiple interfaces. With nanostructures, the lower dimensionality comes into play much more prominently (as already foreshadowed by clusters).

In Figs. 1 and 2, the central broad arrow suggests the evolution of the field in terms of the following major types of structure that it has focused on at different times: solid/vacuum surfaces, solid/solid interfaces, small clusters, thin films and coatings, superlattices, nanostructures, and more specifically nanobiological structures. Fig. 1 shows above the same arrow a long list of technologies that have incited developments in this field, while also benefiting from its progress in return, as we have just discussed. Below the arrow are listed major scientific disciplines that have been attracted to the field, usually in concert with the technologies themselves. It is hard to think of any science or field of engineering that is not in some way involved in surface science. This also clearly illustrates the multidisciplinary character of the field, which continues to diversify as it progresses toward nanoscience and nanotechnology.

Fig. 2 lists, above the same central arrow, major physical, chemical and other phenomena that have been explored by scientists from the various disciplines: such phenomena of course underlie the technologies mentioned earlier. These phenomena are often studied for their own interest, in addition to the technological relevance: many challenging, purely scientific problems have emerged at surfaces and interfaces.

Below the arrow in Fig. 2, appears a series of techniques that are essential to performing the scientific research in this field: many of these techniques were developed specifically for the particular needs of this field, while others were

adapted from other fields. The major challenge has often been to detect a small quantity of matter (the surface or interface atoms) in the presence of large amounts of matter (the underlying bulk material). This particular challenge is further amplified in the case of nanoscience and nanotechnology, where zero- or one-dimensional structures need to be studied.

Faced with the impossibility of comprehensively covering this immense field of scientific and technological activity here, I shall in the following briefly describe individual examples in the evolution from surface science toward nanotechnology. Some examples are chosen from my own work, while most are selected from other studies performed in Berkeley. Rather than illustrating each example with figures, I provide selected bibliographic references, as well as web links to the corresponding research groups.

Surfaces

One fundamental aspect of understanding matter is its geometric structure: bond lengths, bond angles, interlayer distances, etc. Among the many techniques that have been developed to determine the structure of surfaces are low-energy electron diffraction (LEED) and photoelectron diffraction (PED). These methods have contributed the most surface structures to our knowledge base, namely over two thirds of the total[5].

LEED, by virtue of its low electron energies in the range 10-400 eV, affords shallow penetration into surfaces, on the order of 0.5 to 1 nm (5 to 10 Å). Advanced theoretical methods are required to extract the structural information from the experimental data. While LEED experiment and theory are highly developed, one drawback of the technique is the need for a solid/vacuum surface.

A recent discovery made with LEED has special practical implications. It is the observation of unusually large vibration amplitudes at certain surfaces: H₂O(0001), Al₂O₃(0001), Ga (010) and Si(111)-(2x1). The earliest of these observations, for H₂O(0001)[6], is also the most interesting, since the surface properties of ice are very important in several ways. For instance, the surface of ice particles is thought to catalyze a crucial step in the formation of the ozone hole over Antarctica: ice particles decompose chlorine-containing manmade molecules to form Cl₂ molecules, which in turn are decomposed by sunlight into Cl atoms that destroy ozone, resulting in less protection on the ground from harmful UV radiation. Enhanced surface vibrations lead to the presence of an “amorphous” form of surface ice in the temperature range in question, 180 – 200 K, and this amorphous layer may be responsible for the catalytic action of ice.

Another property of ice, its slipperiness, can also be traced to enhanced surface vibrations, in this case generating a liquid-like surface layer between about 240 and 273 K; this layer acts like a slippery banana peel. By contrast, the surface solidification expected below 240 K causes a rough doubling of the friction coefficient of ice, as experienced by brave skiers. This may have been the single largest factor contributing to the tragic fate of the Scott expedition trying to first reach the South Pole in 1911-1912 (where they arrived a month after Amundsen): during their return to the Antarctic coast, unusually low temperatures (even for Antarctica) halved the expedition's speed on skis during many weeks; insufficient food had been prepositioned for this unexpected slow pace, resulting in the death of Scott and his team members[7].

An example of surface structure determination with photoelectron diffraction (PED) concerns the intriguing class of materials called quasicrystals: these have non-periodic structures that nonetheless show a large amount of orientational order; a unique characteristic of these materials is the occurrence of 5-fold or other symmetries that are normally forbidden in solids. Quasicrystals are hard, similar to tungsten, and their surfaces have other important properties: they are slippery and chemically rather inert, similar to Teflon. As a result, quasicrystals have been used industrially as hard, inert and slippery coatings, including in frying pans. Are these useful properties related to their unusual quasicrystalline structure?

We studied this question with PED[8] as well as LEED[9]. PED uses incident photons to eject electrons that are surface-sensitive, as in the case of LEED. Again, vacuum is required, and the experiment and theory are well developed. One advantage of PED over LEED is its chemical sensitivity: the signal from a single chemical element can be selected. Using these methods, the surface structure of a quasicrystalline AlPdMn alloy was studied: the crucial results are that the surface is as quasicrystalline as is the bulk material, and that the outermost atomic layer is predominantly composed of aluminum. These findings imply great hardness of the surface (because the quasicrystalline structure allows no easy slip planes), which in turn is known empirically to imply a low friction coefficient. In air, the surface abundance of aluminum produces a chemically inert surface protection, similar to that of pure aluminum and its oxidized surface. So the special surface properties of quasicrystals indeed seem to be related to their peculiar quasicrystalline structure.

Spatial resolution in microscopies

To move toward nanoscience and nanotechnology requires microscopic observations: the lower dimensionality of nanostructures implies that most conventional surface science techniques cannot resolve individual

nanostructures. A series of techniques offering increasingly higher spatial resolution has been developed over the years.

Among techniques using photons only, one may list x-ray microscopy (XRM) and scanning near-field optical microscopy (SNOM). These can offer both structural and chemical distinction. Their resolution is ultimately limited to distances about equal to the skin depth of ~ 10 nm, in practice ~ 20 - 30 nm.

Techniques that use electrons only include transmission electron microscopy (TEM), often in the form of high-resolution electron microscopy (HREM), low-energy electron microscopy (LEEM), LEED in LEEM, mirror electron microscopy (MEM), and convergent-beam LEED. These permit structural rather than chemical distinction. Their resolution is limited by electron optics to ~ 8 - 25 nm, but TEM/HREM achieves a resolution of better than 0.1 nm (1 \AA) when viewing columns of atoms and applying theoretical image reconstruction. An alternative approach is tomography: atomic-scale resolution in three dimensions is an exciting possibility for the future with electron tomography, but requires much development, including on the theoretical side.

If we allow a combination of both photons and electrons, we find techniques such as photoelectron emission microscopy (PEEM), x-ray PEEM, and PED in LEEM. These allow both chemical and structural distinction on the scale of ~ 10 - 50 nm.

Micron-scale microscopy

An example of micron-scale investigation is the study of quantum well states in ultrathin films of Cu on Co on Cu, in which the outermost film is grown as a wedge with nanoscale thickness ranging from 0 to about 5 nm on a Co film with a similar but fixed thickness. Using incident x-rays focused to about $50 \mu\text{m}$ and scanned across the wedge, photoelectrons are emitted from the thin films as a function of film thickness: the signal shows the addition of individual monolayers along the thickening wedge.

An energy spectrum of those photoelectrons exhibits oscillations corresponding to a sequence of quantum well states: their energy varies with the number of monolayers in the wedge. The quantum well states can be reproduced roughly with the Phase Accumulation Model (which states that the phase accumulated by an electron wave in a round trip across the film should be an integer multiple of 2π), and more accurately with ab initio calculations[10]. Such theoretical modeling will allow “wave function engineering” to tailor nanostructures with desired properties

Atomic-scale microscopy

None of the abovementioned microscopies currently delivers single-atom imaging. This crucial capability for nanoscience and nanotechnology is offered by scanning tunneling microscopy (STM) and other scanning-probe methods related to it.

These methods were first developed for surfaces, and found many applications in surface science. I mention here three such applications that probe the dynamics of molecular interactions with surfaces, as well as tip effects on the surface: these illustrate the value of atomic-scale imaging to understand the basic processes that are central to many phenomena important in nanoscience and nanotechnology.

Acetylene adsorbs intact on Pd(111), but does not rotate freely at low temperatures of ~ 30 K. However, the tunneling current near such an adsorbed molecule supplies sufficient energy for it to rotate around the surface normal[11]. Similarly, oxygen molecules on Pd(111) can be excited by a tunneling current, resulting in their decomposition, as witnessed by the appearance of pairs of O atoms[12]. And hydrogen molecules have been shown by STM imaging to require at least three adjoining H-free sites to spontaneously adsorb and decompose into H atoms[13].

An important point to make here is that STM imaging is a complicated process that can easily lead to serious misinterpretations. This is well illustrated by the fact that different atoms adsorbed in similar positions on the same surface can show up in STM in radically different ways: for instance, carbon and oxygen atoms adsorbed on many metal surfaces, including Pd(111), appear as bumps and dips, respectively. This can be explained theoretically through different interference effects between tunneling paths from tip to surface: the net result is that C appears as bumps, while O appears as dips[14].

Despite such complications of interpretation, STM is of immense value for imaging atomic-scale features of nanostructures. A perfect example is given by the imaging and analysis of Si nanowires[15]: the images in this case could be interpreted to show the positions of individual hydrogen atoms capping (100) and (111) facets of the nanowires.

Nanocatalyst synthesis

The synthesis of nanostructures is currently one of the most active aspects of nanoscience. Controlling individual atoms and molecules is still a challenge, particularly when the process must be repeated for large numbers of atoms and molecules. Self-assembly is therefore an attractive alternative: it relies on learning to harness nature's own forces to steer the atoms and molecules where they are desired. Among the many methodologies being explored are growth of nanostructures in solution and lithographic synthesis.

For example, metallic nanoparticles of reasonably uniform size and shape can be grown in suitable solutions. Thus, Pt nanoparticles have been grown in sizes ranging from 1.7 to 7 nm (with 10% size variation in each batch) using poly(vinylpyrrolidone); and their shapes can be continuously tailored from cubic to octahedral by varying the concentration of AgNO_3 . Using lithographic techniques, more familiar in electronic chip manufacture, millions of nearly identical Pt nanodots have been created on a SiO_2 substrate in sizes around 25 nm, arranged in a regular array with controllable mutual distances. Importantly, it is found that the size of and distance between the nanoparticles have significant effects on their catalytic activity and selectivity[16].

Computational modeling

Due to the difficulty of measuring structure and processes at the nanoscale, it is extremely valuable to be able to perform computational modeling. Such simulation can offer proofs of principles and guide the experiment, as well as explain observations. The level of sophistication of the theoretical methods used in simulations can vary widely, and depends in large measure on the complexity of the problem, as well as the needed accuracy.

As an example, consider metallic alloy nanoparticles, useful in heterogeneous catalysis. Suppose that the goal is to make the chemically active metal, such as Pt, segregate to the surface, while keeping a less active, and cheaper, metal inside the nanoparticle. Such particles can be synthesized and are often imaged by TEM, but no technique has imaged the surface composition of the particles, so that it is difficult to experimentally explore their structure and composition. We have simulated the surface segregation in this system for particles of hundreds to thousands of atoms. Because of the vast number of possible configurations, we used a simple theoretical scheme with empirical interaction forces between atoms, namely the Modified Embedded Atom Method, coupled with Monte Carlo iterations to let the system evolve toward a lower total energy. After millions of iterations, a stable equilibrium segregation is obtained.

This way, for example, we found that large PtNi nanoparticles (with thousands of atoms) produce a "core-shell" structure, in which the inside of the particle is

relatively well ordered, as in the bulk alloy, while the surface layer is enriched in Pt and the second layer is enriched in Ni. For smaller particles (with hundreds of atoms), we predict a “surface-sandwich” structure, in which the surface consists of three layers enriched in Pt, Ni and Pt, respectively, counting from the outside, while the core is disordered: the core is now dominated by the surface, which prevents a bulk-like ordering[17].

Quantum dots, nanorods, tetrapods, nanotubes

Low-dimensional nanoparticles are well known to have unique properties of interest to technologists. For example, quantum dots made of CdSe and similar compounds exhibit color that depends continuously on the particle diameter, because the band gap itself depends on the diameter[18]. Such nanocrystals allow, for example, multicolor biological imaging, thus enabling the mapping out of cell structure with fluorescent labeling. This capability can be achieved by using CdSe nanocrystals of varying sizes, which bind selectively to different parts of a cell, thus “coloring” them[19].

Nanoparticles that are less spherical have a more complex band structure; this in turn can give rise to more complex (mixed) colors, as is the case of nanorods[20]. Even higher structural complexity can be obtained by exploiting differential growth rates: thus, CdSe and CdTe tetrapods (consisting of four nanorods joined in a common point) can be formed by nucleation of a cubic-symmetry zincblende core, from which grow branches of hexagonal wurtzite symmetry in four tetrahedral directions[20]. Optical and other properties of such tetrapods can be studied by calculating their electronic structure, despite the very large number of atoms involved[21].

Nanowires can become nanolasers, as was accomplished with ZnO wires about 50 nm across and several μm in length[22]. Within nanowires, it is also possible to form superlattices, for example by alternating Si and SiGe layers along the wires[23]. Hollow nanotubes have also been grown: ZnO nanowires were coated with GaN, after which the ZnO was thermally removed, leaving hollow GaN tubes[23].

Hybrid nanocrystal-polymer solar cells have been made by blending CdSe nanocrystals with a conducting polymer to form a 200 nm thick film. The nanocrystal shape affects the cell efficiency: monochromatic quantum efficiencies of over 50% are achieved by using rod-like nanocrystals partially aligned with the path of current flow in the device[24].

Carbon nanotubes

Carbon nanotubes have received considerable attention and, together with buckyballs, serve as symbols for nanoscience. One among many potential applications is the use of carbon nanotubes as mass conveyors for nanoscale atomic transport: such transport of indium atoms along the nanotubes was achieved by application of an electric bias; the transport could be reversed by reversing the bias[25].

Multiwalled carbon nanotubes offer additional possibilities. One is the ability of individual nanotubes to telescope with respect to each other, and this with almost no friction[26]. Similarly, almost frictionless rotation is possible, enabling the construction of the first synthetic nanomotor: a submicron gold plate lithographically attached to a multiwalled carbon nanotube could be made to rotate for thousands of cycles without apparent degradation or wear, by applying variable voltages to nearby stators[27].

Carbon nanotubes can be used to construct nanoscale transistors, by coupling a single-walled nanotube to a source and a drain; doping with potassium produced an n-type transistor, while as-grown nanotubes exhibited p-type behavior[28]. Junctions between single-walled carbon nanotubes can have different properties: junctions between two metallic or two semiconducting nanotubes conduct high current densities at low resistance, whereas junctions between metallic and semiconducting nanotubes form diodes that exhibit a Schottky barrier behavior[28].

Another form of nanotube diode has been theoretically shown to exist where a single nanotube changes its structure and thus its conducting properties. This relies on the property that an “even” rolling of a graphite sheet produces a metallic nanotube, while a “spiral” rolling yields semiconducting behavior. A “hybrid” nanotube, which changes from semiconducting to metallic is theoretically predicted to function as a diode: current will only flow from the semiconducting region to the metallic region, not in the opposite direction[29].

The electrical conductance along metallic and semiconducting single-walled carbon nanotubes exhibits interesting contrasting behavior: while scattering centers are observed along semiconducting nanotubes, none are seen along metallic ones. This shows that electrons travel ballistically (unscattered) along metallic carbon nanotubes, but not along semiconducting carbon nanotubes[30].

Bionanomaterials

I shall give only one example in the vast and largely unexplored field of nanobiological structures. Using segments of DNA, it has been possible to

construct networks of DNA. For example, a cuboctahedral cage, the edges of which are made up of DNA segments, has been assembled in nanometer scale[31]. The edges are connected at the corners of the cuboctahedron by allowing the twin strands (that form the double helix) to split apart and join different DNA segments. Many such cages could be joined together to form a lattice of cages that serves as a filter or support for other nanoparticles or molecules, among countless other possibilities.

Outlook

It is hard to predict where nanoscience and nanotechnology will lead: the possibilities are endless, given the variety of materials available, as well as the richness of structures that one can imagine. The example of (natural) biology already shows us an amazing range of possibilities. The very notion of interface is the source of a very large set of options: of considerable importance is the opportunity to combine different structures and materials in novel ways. In particular, this allows creating structures with multifunctionality, namely with the ability to perform more than one desired function. As a simple example, one can imagine a nanostructure that both detects and destroys unhealthy molecules.

So the central arrow in Figs. 1 and 2 should really be viewed as a spreading fan. Rather than this field having a constant “width”, we should regard it as continuously broadening and branching out into new territories, in concert with technological demands and opportunities, and in collaboration with new scientific disciplines that investigate an ever expanding set of phenomena. In particular, “bionano” is only one of many directions for the future: biological matter will be far from the only field of research in the nano-era. Biomimetic approaches, which use biological examples to create non-biological nanostructures with similar or novel functions, is just one such important new direction. A different direction will assemble simpler nanostructures into hierarchically more complex structures with much more subtle and precise functions than possible heretofore.

Furthermore, it would be incorrect to view the older root of the field (such as surface science and interface science) to be superseded and made obsolete by the newer directions. As we have seen, the newer directions tend to involve more complex structures and phenomena: to understand them properly will frequently require breaking them up into simpler components, in particular surfaces and interfaces. Thus, surface science and interface science will remain fundamental to the healthy evolution of the field, often providing its basis for understanding.

At present, there is a great need for new experimental techniques to study nanostructures. Most currently used techniques were developed for bulk or surface science. Surface science (and interface science) grew in large part due

to the arrival of new techniques able to sample just a few monolayers of matter, extended infinitely in two dimensions. Nanoscience badly needs techniques that can sample nanoscale assemblies of atoms. As discussed earlier, most microscopies at present only offer resolutions down to the 10 nm range. Scanning tunneling microscopy and a few related scanning probe microscopies now already offer nanoscale or even atomic-scale resolution in limited circumstances. We will need other techniques to perform, for example, spectroscopy on the nanoscale, which at present is possible only in very special circumstances.

Acknowledgement

This work was supported by the Office of Science, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

- * E-mail (since Aug. 2005): vanhove@cityu.edu.hk;
web site: <http://www.sitp.lbl.gov/>
1. <http://www.iuvsta.org/>
 2. <http://www.nanoword.net>
 3. <http://www.ipt.arc.nasa.gov/nanotechnology.html>
 4. <http://foundry.lbl.gov/>
 5. Surface Structure Database: P.R. Watson, M.A. Van Hove, and K. Hermann, NIST Surface Structure Database Ver. 5.0, NIST Standard Reference Data Program, Gaithersburg, MD, USA (2004). <http://www.nist.gov/srd/nist42.htm>
 6. N. Materer, U. Starke, A. Barbieri, M.A. Van Hove, G.A. Somorjai, G.-J. Kroes, and C. Minot, Surf. Sci. 381, 190 (1997).
<http://electron.lbl.gov/leed/leedhigh.html#Ice>
 7. Susan Solomon, "The Coldest March", Yale University Press, New Haven (2001). <http://www.coldestmarch.com/>
 8. J.C. Zheng, C.H.A. Huan, A.T.S. Wee, M.A. Van Hove, C.S. Fadley, F.J. Shi, E. Rotenberg, S.R. Barman, J.J. Paggel, K. Horn, Ph. Ebert, and K. Urban, Phys. Rev. B69, 134107 (2004).
 9. M. Gierer, M.A. Van Hove, A.I. Goldman, Z. Shen, S.-L. Chang, C.J. Jenks, C.-M. Zhang, and P.A. Thiel, Phys. Rev. Lett. 78, 467-70 (1997).
<http://electron.lbl.gov/>
 10. J.M. An, D. Raczkowski, M. Leung, L.-W. Wang, A. Canning, M.A. Van Hove, Z.Q. Qiu, Y.Z. Wu, and E. Rotenberg, Phys. Rev. B68, 045419 (2003).
 11. J.C. Dunphy, M. Rose, S. Behler, D.F. Ogletree, M. Salmeron, and P. Sautet. Phys. Rev. B 57, R12705 (1998). <http://stm.lbl.gov/>
 12. M.K. Rose, A. Borg, J.C. Dunphy, T. Mitsui, D.F. Ogletree, and M. Salmeron, Surf. Sci. 547, 162 (2003). <http://stm.lbl.gov/>
 13. T. Mitsui, M.K. Rose, E. Fomin, D.F. Ogletree, and M. Salmeron, Nature 422, 705 (2003). <http://stm.lbl.gov/>
 14. I.S. Tilinin, M.K. Rose, J.C. Dunphy, M. Salmeron, and M.A. Van Hove, Surf. Sci. 418, 511 (1998). <http://stm.lbl.gov/>

15. D.D.D. Ma, C.S. Lee, F.C.K. Au, S.Y. Tong, and S.T. Lee, *Science* 299, 1874 (2003). <http://www.cityu.edu.hk/cosdaf/>
16. A.S. Eppler, J. Zhu, E.A. Anderson, and G.A. Somorjai, *Top. in Cat.* 13, 33 (2000); J. Grunes, J. Zhu, M. Yang, and G.A. Somorjai, *Cat. Lett.* 86, 157 (2003). <http://www.cchem.berkeley.edu/~gasgrp/>
17. G. Wang, M.A. Van Hove, P.N. Ross, and M.I. Baskes, *J. Chem. Phys.*, in press.
18. S. Empedocles, and M. Bawendi, *Acc. of Chem. Res.* 32, 389 (1999). <http://web.mit.edu/chemistry/nanocluster/>
19. X. Michalet, F. Pinaud, T.D. Lacoste, M. Dahan, M.P. Bruchez, A.P. Alivisatos, and S. Weiss, *Single Molecules* 2, 261 (2001). <http://www.cchem.berkeley.edu/~pagrp/>
20. L. Manna, Erik C. Scher, and A.P. Alivisatos, *J. Am. Chem. Soc.* 122, 12700 (2000). <http://www.cchem.berkeley.edu/~pagrp/>
21. J. Li and L.-W. Wang, *Nanoletters* 3, 1357 (2003). <http://crd.lbl.gov/~linwang/>
22. M. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, *Science* 292, 1897 (2001). <http://www.cchem.berkeley.edu/pdygrp/main.html>
23. Y. Wu, R. Fan, and P. Yang, *Nanoletters* 2, 83, 2002; E. Stach, P. Pauzauskie, T. Kuykendall, J. Goldberger, and P. Yang, *Nanoletters* 3, 867 (2003). <http://www.cchem.berkeley.edu/pdygrp/main.html>
24. W.U. Huynh, J.J. Dittmer, and A.P. Alivisatos, *Science* 295, 2425 (2002). <http://www.cchem.berkeley.edu/pagrp/>
25. B.C. Regan, S. Aloni, R.O. Ritchie, U. Dahmen, and A. Zettl, *Nature* 428, 924 (2004). <http://www.physics.berkeley.edu/research/zettl/>
26. J. Cumings and A. Zettl, *Phys. Rev. Lett.* 93 086801 (2004). <http://www.physics.berkeley.edu/research/zettl/>
27. A.M. Fennimore, T.D. Yuzvinsky, Wei-Qiang Han, M.S. Fuhrer, J. Cumings, and A. Zettl, *Nature* 424, 408 (2003). <http://www.physics.berkeley.edu/research/zettl/>
28. M.S. Fuhrer, J. Nygard, L. Shih, M. Forero, Young-Gui Yoon, M.S.C. Mazzoni, Hyoung Joon Choi, Jisoon Ihm, Steven G. Louie, A. Zettl, and P.L.

McEuen, Science 288, 494 (2000).
<http://www.physics.berkeley.edu/research/zettl/>

29. L. Chico, V.H. Crespi, L.X. Benedict, S.G. Louie, and M. L. Cohen, Phys. Rev. Lett. 76, 971 (1996). <http://tiger.berkeley.edu/>

30. H.J. Choi, J. Ihm, S.G. Louie, and M.L. Cohen, Phys. Rev. Lett. 84, 2917 (2000). <http://tiger.berkeley.edu/>

31. N.C. Seeman, Scientific American (June 2004), p. 65.
<http://www.nyu.edu/pages/chemistry/faculty/seeman.html>

Figures

Fig 1. Historical evolution of surface science toward nanotechnology. This sketch spans about 50 years in time, starting in the 1950s and showing the rough time sequence of emphases of the field (these are listed within the central arrow). The rise of the central arrow corresponds to a gradual increase in complexity of the structures and materials being studied. Above the arrow are shown some of the many technological drivers that have fed the field's continuous development and broad diversification. In parallel, as shown below the central arrow, the various technologies have attracted scientists from a wide variety of disciplines to work in and contribute to the field.

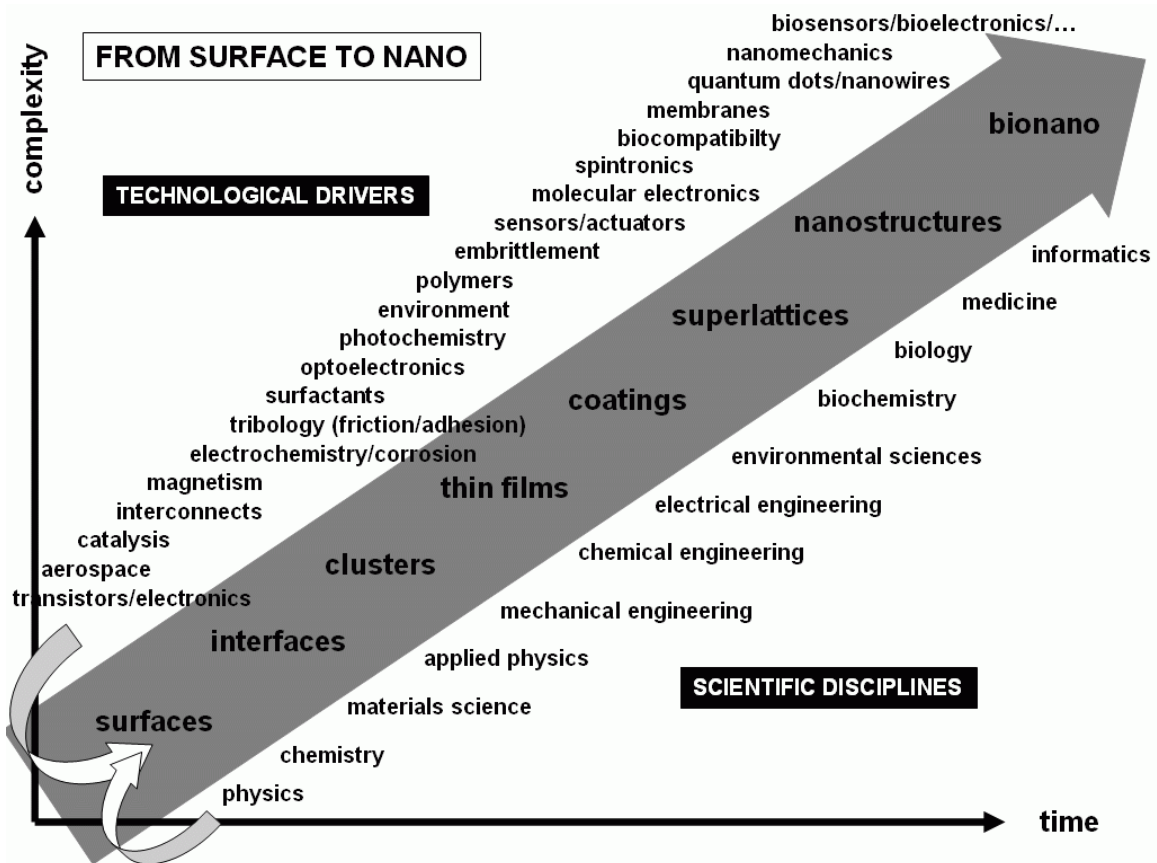


Fig 2. The same evolution of surface science toward nanotechnology as drawn in Fig. 1 is shown here, focusing now on physical phenomena of interest (listed above the central arrow) and on the techniques needed to prepare, characterize, analyze and understand the surface and nano-materials (listed below the central arrow).

