

# Engineering atomic and molecular nanostructures at surfaces

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Presented by Guanwen Yang

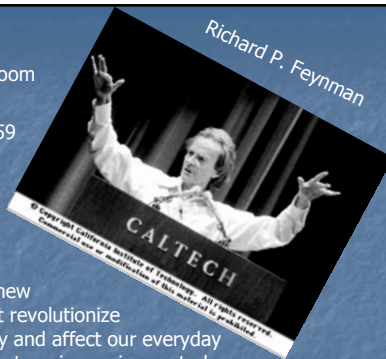
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## Abstract

- The fabrication methods of the microelectronics industry have been refined to produce ever smaller devices, but will soon reach their fundamental limits.
- An alternative way to even smaller functional systems is the autonomous assembly of atoms and molecules on atomically well-defined surfaces.
- Once the mechanisms controlling the self-ordering phenomena are fully understood, the self-assembly and growth processes can be steered to create a wide range of surface nanostructures.
- Today I would like to introduce some useful fabrication methods in surface engineering and some new features by using them in different fields.

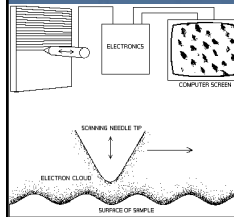
There is "plenty of room at the bottom"

----- 1959



He predicted exciting new phenomena that might revolutionize science and technology and affect our everyday lives — if only we were to gain precise control over matter, down to the atomic level.

The invention of STM allows us to image and manipulate individual molecules and atoms



Tunneling current is the result of the overlapping wavefunctions between the tip atom and surface atom.

The magnitude of tunneling current is extremely sensitive to the gap distance between the tip and sample. As we measure the current with the tip moving across the surface, atomic information of the surface can be mapped out.

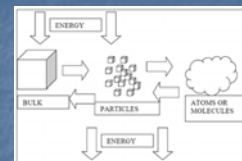
$$I(L) \sim P(L) \sim \psi^2(L) \sim e^{-2\kappa L} \sim e^{-2\sqrt{2m\phi}\hbar^{-1}L}$$

Electrical current  $\phi$  is the work function  $\sim eV$

Bare Graphite

STM is a powerful tool for routinely obtaining atomic structure. Obviously it also can be used to control atoms on different surfaces by moving it here to there. But it still seems unlikely to find industrial use in the near future.

Fabrication Method



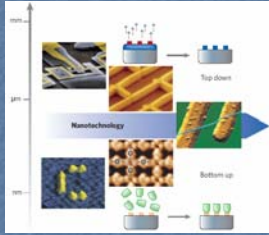
top-down

bottom-up

The first way is to start with a bulk material and then break it into smaller pieces using mechanical, chemical or other form of energy.

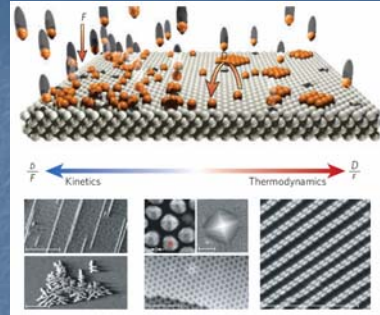
An opposite approach is to synthesise the material from atomic or molecular species via self-assembly of molecules and self-patterning taking place at the surface of the substrate.

Top-down nanotechnology is a natural extension of current methods of microelectronics, such as lithography, writing or stamping. The next-generation production lines used by the semiconductor industry are likely to be based on X-ray lithography, which allows parallel processing. But the upgrade will require huge investments and extensive equipment development.



- An electron microscopy image of a nanomechanical electrometer
- Patterned films of carbon nanotubes
- A single carbon nanotube
- A regular metal-organic nanoporous network
- Seven carbon monoxide molecules forming the letter 'C'

The bottom-up techniques make use of self processes for ordering of supramolecular or solid-state architectures from the atomic to the mesoscopic scale.



The primary mechanism in the growth of surface nanostructures from adsorbed species is the transport of these species on a flat terrace.

This surface diffusion is thermally activated; that is, diffusion barriers need to be surmounted when moving from one stable adsorption configuration to another.

the diffusivity  $D$  - the mean square distance traveled by an adsorbate per unit time. It obeys an Arrhenius law.

$$D = D_0 \exp(-E_m / k_B T)$$

Deposition rate  $F$  - The rate at which atoms or molecules are deposited on a surface

The ratio  $D/F$  determines the average distance that an adsorbed species has to travel to meet another adsorbate, either for nucleation of a new aggregate or attachment to an already formed island. The ratio of deposition to diffusion rate  $D/F$  is thus the key parameter characterizing growth kinetics.

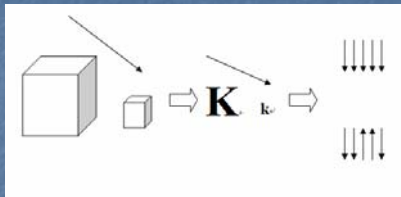
- $D/F$  {
- $\gg 1$  growth occurs close to equilibrium conditions; that is, the adsorbed species have enough time to explore the potential energy surface so that the system reaches a minimum energy configuration.
  - $\ll 1$  the pattern of growth is essentially determined by kinetics; individual processes, notably those leading to metastable structures, are increasingly important.

## Moore's Law



- Improved fabrication technologies resulted in the doubling of the number of silicon field-effect transistors per unit area roughly every 18 months.
- The exponential growth of the information industry relies just as much on improvements in data storage, which uses small regions of ferromagnetic material with opposite magnetization to store 'zeros' and 'ones' in a hard disk.

But in the case of CMOS technologies, the drive for further miniaturization faces fundamental physical limits.

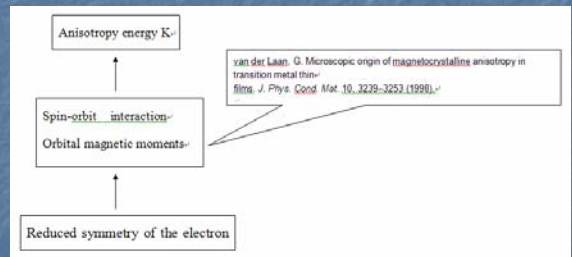


$$K = 40 \mu\text{eV}$$

$$\tau = \tau_0 \exp(nK / k_B T) \quad \tau > 10$$

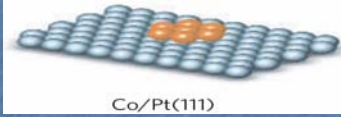
$$n = 10^5$$

An obvious strategy is to develop new materials and structures with a substantially higher anisotropy energy  $K$ .



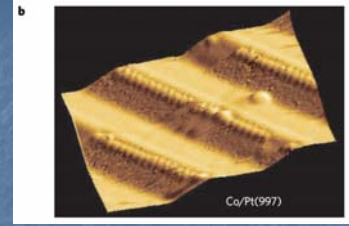
Self-organized metal growth --- **the step decoration method**

the step decoration method allows ready formation of uniform arrays of cobalt chains on a Pt surface. Growth in a well-defined temperature range then results in uniform cobalt chains of monatomic width over the entire sample, forming dense arrays of parallel one-dimensional nanowires. By adjusting the cobalt coverage on the surface and the average step spacing of the platinum surface, width and separation of the nanowires can be independently controlled.



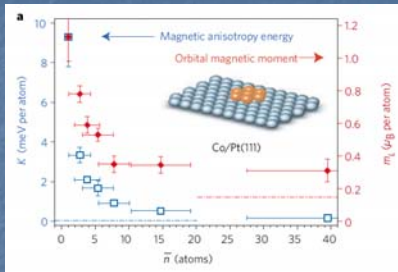
Gambardella, P., Blanc, M., Brune, H., Kuhnke, K. & Kern, K. One-dimensional metal chains on Pt vicinal surfaces. *Phys. Rev. B* 61, 2254–2262 (2000).

Kuhnke, K. & Kern, K. Vicinal metal surfaces as nanotemplates for the growth of lowdimensional structures. *J. Phys. Cond. Mat.* 15, S3311–S3335 (2003).



Scanning tunnelling microscopy image of monatomic cobalt chains decorating the steps of a regularly stepped platinum surface.

Such surface-supported cobalt nanostructures reveal how magnetic properties change as the size of the structures is reduced to a few atoms.



The dashed lines represent the K and mL values for bulk h.c.p.

Co orbital moment and magnetic anisotropy energy increase markedly as the cluster size decreases

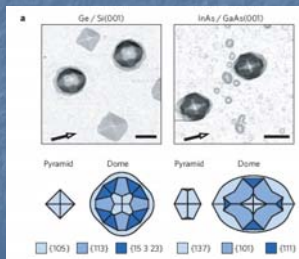
**Quantum Dots**

Solid-state nanostructures, and their energy spectrum, which controls many of the physical properties of interest, can be adjusted over a wide range by tuning composition, size, lattice strain and morphology. These features make semiconductor quantum dots attractive for the design and fabrication of new electronic, magnetic and photonic devices and other functional materials.

Quantum dots can be prepared by using a wide range of methods, including lithography, etching. But fabrication methods based on self-organized growth at surfaces are particularly attractive because they yield quantum dots with virtually no interface defects that might adversely affect performance.

As so many physical properties depend on quantum dot size and shape, it is essential to know the actual morphology of the 3D semiconductor islands that form on deposition of atoms from the gas phase, and to know how they evolve during post-growth treatments. But the structure of nucleated semiconductor islands and their subsequent morphological evolution remain incompletely understood. Here I would like to introduce two quantum dots that develop in the most studied mode systems: during the growth of Ge on Si(001) and during the growth of InAs on GaAs(001).

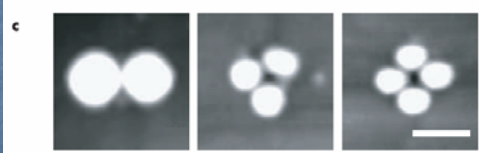
In both systems, only two discrete, well-defined families of islands develop: small islands that are bounded by one type of shallow facets and referred to as pyramids, and larger, multi-faceted islands that are characterized by steeper facets and referred to as domes.



Quantum dots may be laterally organized. highly regular structures are readily obtained by using electron-beam or optical lithography (top-down methods) first to create patterned substrates, which then serve as templates to direct the self-organized Stranski–Krastanov growth of three-dimensional semiconductor islands (a bottom-up method).

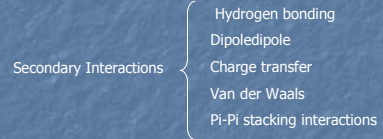


This figure shows quantum dot molecules containing two, three and four dots



## Supramolecular Engineering

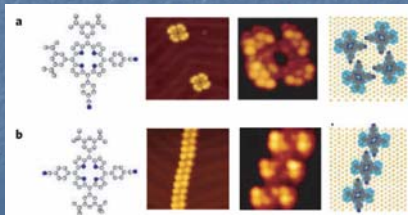
Supramolecular chemistry is talking about how chemists prepare structures of different sizes and shapes with dimension in the range of 1 to 100 nm using spontaneous secondary interactions.



But although much is known about how supramolecular chemistry can be tuned to create desired supramolecular crystals or supramolecular compounds in solution, this knowledge cannot be directly translated to guide the assembly of adsorbed molecules into larger surface structures. **To do so, the influence of the substrate atomic lattice and substrate electronic structure on non-covalent bonds needs to be fully understood.**

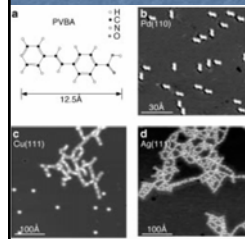
Planar molecules with extended Pi-systems have found particularly wide use. Porphyrins substituted with two functional cyanophenyl moieties in a cis or trans configuration.

a, The cis species assembles in compact clusters of four molecules. Whereas the cis configuration gives rise to discrete clusters made up of four molecules, b, With the trans species linear molecular chains are obtained. the trans configuration produces extended one-dimensional supramolecular chains.



## PVBA on different single-crystal metal substrates

A systematic study of the self-assembly behavior of PVBA illustrates how the materials characteristics and symmetry of the substrate can affect the subtle balance between intermolecular interactions and molecule-surface interactions.



•The rod-like PVBA molecule, which contains a benzoic acid head group and a pyridyl tail group, self-assembles through head-to-tail hydrogen bonding.

•If metallic palladium is used as substrate, molecule-surface coupling is strong and dominates over intermolecular interactions; this prevents the formation of regular surface patterns.

•On close-packed noble-metal surfaces, the PVBA molecules are more mobile and able to assemble into highly regular 1-D supramolecular arrangements.

## Outlook

Even though processes that make use of self-ordering growth have already yielded systems with intriguing functional properties, many challenges still need to be addressed before such strategies find wide practical use.

We would expect that this can be achieved by combining bottom-up and top-down techniques, with the former providing ready access to features with sizes below 10 nm, and the latter allowing for integration of these structures into larger functional systems. This general approach should also result in new materials and devices.

## What is Quantum Dots

Quantum dots are small devices that contain a tiny droplet of free electrons. They are fabricated in semiconductor materials and have typical dimensions between nanometers to a few microns. The size and shape of these structures and therefore the number of electrons they contain, can be precisely controlled;

The physics of quantum dots shows many parallels with the behavior of naturally occurring quantum systems in atomic and nuclear physics. As in an atom, the energy levels in a quantum dot become quantized due to the confinement of electrons. Unlike atoms however, quantum dots can be easily connected to electrodes and are therefore excellent tools to study atomic-like properties. There is a wealth of interesting phenomena that have been measured in quantum dot structures over the past decade. This page shows a few examples from our group. The next paragraph first discusses briefly the parallels between atoms and quantum dots.

These features make semiconductor quantum dots attractive for the design and fabrication of new electronic, magnetic and photonic devices and other functional materials.