

# Fabrication of nanoscale structures

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Now that we've surveyed some of the physics ideas we'll need and some methods of seeing what's going on on nanometer scales, it's time to discuss the ways in which nanoscale structures are made. We can divide fabrication techniques into two broad categories: "top-down" and "bottom-up". Since nanoscale top-down techniques are mostly extensions of *microfabrication* methods, we'll start by reviewing approaches to small-scale assembly at the micron scale.

## 1 Microfabrication - photolithography

The standard fabrication method used to make essentially all microelectronic devices today is *photolithography*. Actually, the term photolithography strictly refers to only the pattern-definition step in the process. The silicon or other wafer on which devices are being created is referred to as the *substrate*.

### 1.1 Pattern definition

Photolithography uses light-activated chemistry to define the pattern that will be transferred to the substrate. The keys to this are polymers called *photoresists*. Thousands of chemical engineers have labored thousands of hours to produce many varieties of resist, each with subtly different properties.

The general idea is the following: start with a clean substrate, and place it on a vacuum chuck in a spinner. Squirt a healthy puddle of resist onto the center of the substrate, and spin it at high speeds (typically a few thousand r.p.m.) for something like 30 sec. The resist spreads out across the substrate, forming a nearly uniform layer usually a few hundred nm thick (usually resists are carefully characterized by viscosity so that the curve of layer

thickness vs. spin rate is known). After spinning is complete, the resist is baked at a carefully controlled temperature ( $\sim 120^\circ\text{C}$ ) for a prescribed time ( $\sim 30$  sec) to drive off the carrier solvent, leaving a hard layer of polymer.

The polymer chains have been carefully designed so that exposure to ultraviolet light produces chemical changes in the resist. For “positive tone” resists, exposure breaks down the polymer chains into shorter units that are soluble in some kind of developer. Exposed resist will be dissolved and washed away in the development process, leaving holes in the resist layer wherever exposure has occurred. In “negative tone” resists, UV light causes cross-linking of the polymer chains, and unexposed resist is washed away. In this case exposed areas are all that remain covered with resist after development. Some resists can reverse their tone depending on baking temperatures and times and post-exposure baking.

The desired pattern is originally defined on a *mask*, often (especially in industry) at a size substantially larger than the desired final pattern. The patterned mask is opaque to UV light in the shape of the pattern. UV light is projected through this mask, and reducing optics are used to project the image of the mask onto the resist layer.

This exposure step defines the limits of conventional photolithography because of the diffraction limit of the projection optics. Working at shorter wavelengths than the near-UV is very difficult because conventional glasses absorb rather than transmit at such scales.

After exposure and development, a further step is frequently used called “descumming”. The resist that gets washed away in the development process often leaves behind a monolayer of organic residue that can interfere with subsequent steps. Brief exposure to ozone or an oxygen plasma can remove this contamination.

## 1.2 Pattern transfer

Now we have a substrate coated with a resist stencil. The stencil can be used to protect parts of the substrate during an *additive* step like a metal deposition. Alternately, the stencil can allow some etching procedure to reach the substrate in well-defined locations in a *subtractive* step.

*Additive steps.* These are most commonly deposition of insulating or metal layers. The deposited material coats the entire wafer, resist and all. The resist layer is then *lifted off* by dissolving the polymer in a solvent like acetone, leaving the deposited material only where holes had existed in the resist layer.

Deposition is usually through *evaporation* or *sputtering*. In evaporation

(*physical vapor deposition (PVD)*), the wafer is placed in vacuum facing a heated piece of source material. The source is heated either by a tungsten or molybdenum filament, or via an electron beam, until its temperature is high enough that it has a nonnegligible vapor pressure. Metals are more commonly evaporated than insulators. The material vapor hits the wafer surface and sticks. In sputtering (*plasma-enhanced PVD (PEPVD)*), an argon plasma is used to knock atoms off the source material, rather than simple heating.

In both cases the thickness of deposited material is monitored through a quartz oscillator thickness monitor. The addition of material to the surface of a quartz resonator shifts its frequency by an amount that can be calibrated against thickness.

Note that oxygen contamination during deposition must be minimized for materials like copper and aluminum. A good rule of thumb is that a partial pressure of oxygen of  $10^{-6}$  torr corresponds to one monolayer of oxygen hitting the surface per second.

*Subtractive steps.* There are two types of subtractive steps, wet and dry etching. In wet etching, the wafer is exposed to some wet chemistry (such as a buffered HF solution to dissolve  $\text{SiO}_2$ ) which can only reach the substrate through the holes in the resist. In dry etching a plasma or ion beam is used to chemically (in reactive ion etching (RIE)) or kinetically remove exposed material. Again, at the conclusion of the subtractive step, the resist layer is removed with a solvent.

### 1.3 Concluding notes

Other steps are important in commercial device fabrication (ion implantation, annealing, damascene polishing) but won't be discussed here. The amazing thing about this whole business is that there are no less than 37 separate lithography steps (each followed by an additive or subtractive step) involved in the production of a wafer full of Pentium III chips. Since the smallest feature sizes are approaching  $0.1 \mu\text{m}$ , layers must be aligned with a precision approaching that level uniformly across a 12" diameter Si wafer. These requirements get more and more stringent with each succeeding generation of chips, as features shrink and complexity grows. Further, in just a few years the fab industry will run into the end of the road for 193 nm UV light. Something new must happen to work at progressively smaller lengthscales....

## 2 Top-down nanofabrication methods

The procedure described above is “top-down”, and many of its elements are relevant at sub-100 nm scales. We discuss a few examples of top-down nanofabrication methods below.

### 2.1 Extensions of photolithography

Photolithography can be used to produce features at sub-100 nm scales, but the difficulty is high. Work is being done on using dielectric mirrors for reflectively focussing extreme-UV (EUV) light through masks. Further, the wave nature of light can be used in certain clever ways to produce interference effects as small as  $\lambda/4$ . Some “chemically amplified” resists require two-photon events to be exposed, resulting in patterns that vary like the light intensity squared, rather than simply the intensity. Most nanoscale work doesn’t currently use these techniques, however.

### 2.2 Electron-beam lithography

The most common nanopatterning method out there these days is *electron-beam lithography (EBL)*. This is a direct analogy with photolithography, where electron beam exposure alters the chemistry of the resist instead of light exposure. The most common (positive tone) EBL resist is polymethyl(methacrylate), abbreviated PMMA. Most university-based EBL systems are based on modified SEMs, in which computers are used to steer the electron beam over the surface of the sample. Commercial EBL systems do exist and frequently resemble TEMS in their beam energies and electron optics.

*Limitations.* EBL can routinely produce lines as narrow as 20-30 nm in PMMA. Smaller features are possible in certain circumstances. Limiting factors include feature broadening from secondary electron yields (proximity exposure), finite monomer size, and difficulties in developing such small features.

The biggest problem with EBL on the large scale is speed. In photolithography, a whole wafer can be exposed simultaneously, while EBL requires the e-beam to draw each feature one at a time. It remains an ideal technique for producing small patterns on few-mm sized substrates, however, that are most relevant in university-based nanostructure work.



Figure 1: A nice example of EBL from Prof. Rimberg's research group.

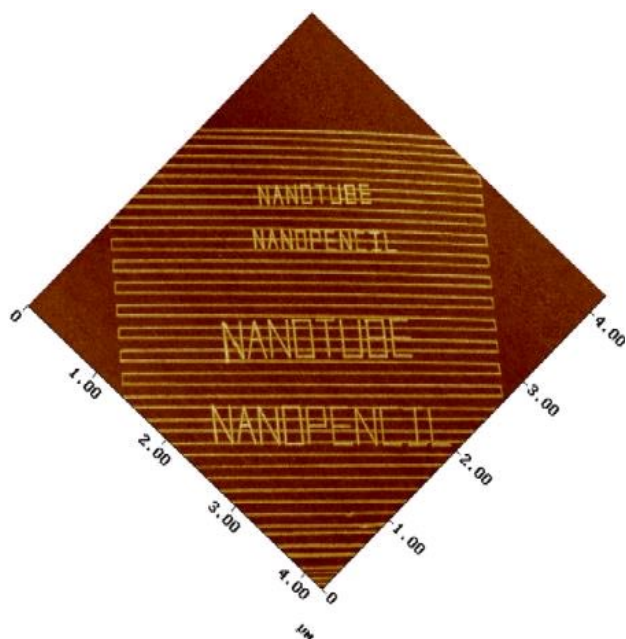


Figure 2: A pattern drawn with SiO<sub>2</sub> in Si using a nanotube as a conducting AFM tip for local oxidation. From Dai's group at Stanford.

### 2.3 Scanned probe lithography (SPL)

Another top-down fabrication approach is to use variations on the wonderful scanned probe microscopy techniques we talked about last time. This has some of the same difficulties with speed as EBL, but has produced some impressive patterning.

*“Plowing”*. Some research has been done on using an AFM tip to literally plow a groove through either a very thin resist layer or a special *self-assembled monolayer (SAM)* on the substrate. This can produce lines in these layers as narrow as 20-30 nm, though layers this thin and trenches produced this way make liftoff processing very challenging.

*Local oxidation*. Another approach has been to use either a conductive AFM tip or an STM tip to do local electrochemistry on the substrate, without any resist. This has been used to reduce the conducting cross-section of existing thin metal layers through oxidation. It has also been used to grow SiO<sub>2</sub> patterns on clean Si wafers, as shown in Fig. 2.

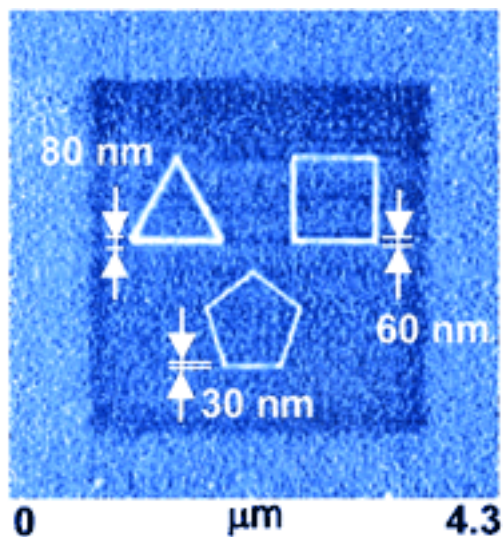


Figure 3: Patterned monolayers from Chad Mirkin’s group at Northwestern.

*Dip-pen lithography.* When AFMs are used in contact mode in ambient conditions, a monolayer film of adsorbed water usually connects the tip and sample. Some researchers have thought of using this property to transfer SAMs from reservoirs down the tip to the substrate, as shown in Fig. 3.

*STM lithography.* There are also two main approaches to using STMs as lithography tools. As noted previously, STMs work best at low temperatures under UHV, and require conducting substrates, all of which are serious constraints on them as fabrication tools.

The first idea is to position individual atoms one at a time to build up structures, as shown in Fig. 4.

The other approach is to chemically modify the surface with the STM (say, by removing passivating H atoms on a Si surface) so that deposited atoms will tend to stick in assigned locations, as in Fig. 5.

### 3 Bottom-up approaches

We’ve now seen a number of top-down fabrication methods for producing sub-100 nm structures. Let’s turn to “bottom-up” fabrication techniques, where chemical and statistical forces can lead to the creation of systems whose “natural” scale is sub-100 nm.

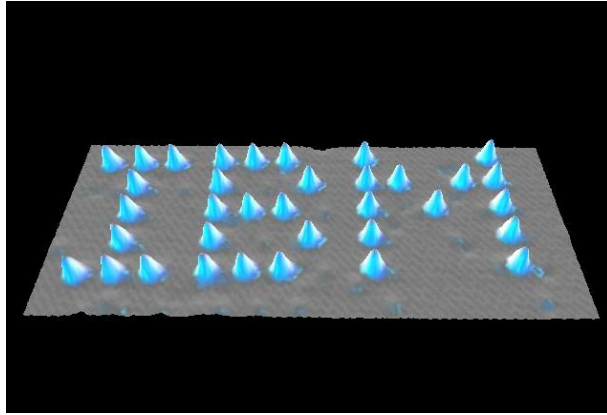


Figure 4: IBM's original demonstration of STM positioning (Eigler). Xe on Ni.

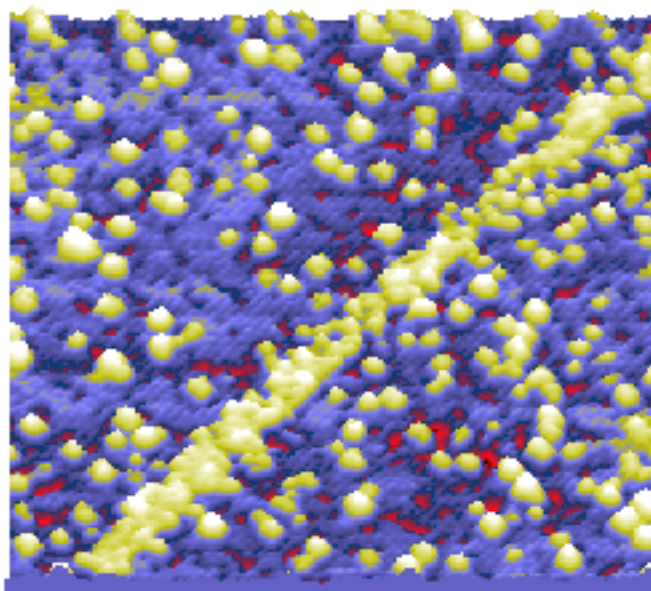


Figure 5: The Delft group's work on deposition onto STM-modified surfaces. Co on Si.

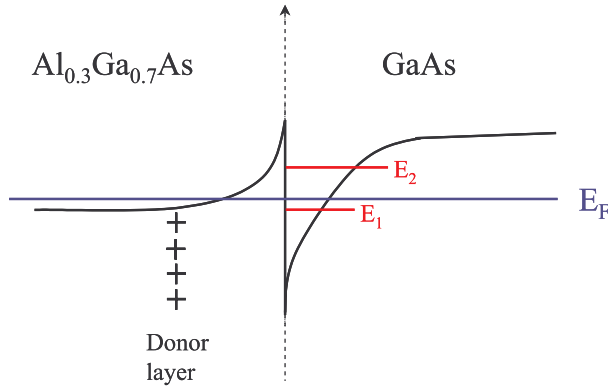


Figure 6: Diagram of energy bands at a semiconductor heterojunction, showing the triangular potential well that results in a 2DEG at the interface.

### 3.1 Crystal growth

As we discussed previously, interfaces between materials of different band gaps can result in charge transfer and band bending. This can be controlled by crystal growers in certain systems, so-called III-V compound semiconductors in particular. The crystal growth technique of choice in these systems is *molecular beam epitaxy*, in which a UHV chamber is combined with substrate heating and exceedingly clean source materials in a very fancy evaporator. With correct growth conditions in the right material system, it is possible to grow crystals literally one atomic layer at a time.

One particular common structure is shown in Fig. 6. Because of band bending at the GaAs/Al<sub>0.3</sub>Ga<sub>0.7</sub>As interface, any electrons injected into the conduction band of the GaAs there sit in a triangular potential well. In this system Si acts as a very shallow donor. As the crystal is grown, a dilute layer of Si atoms is placed a few hundred Å on the AlGaAs side of the interface. Some large fraction of the donated electrons (the rest go to occupy surface states) go to the interface, where they become trapped in the triangular potential well and form a 2DEG. The electron system is truly two dimensional, less than a few nm in  $z$  extent, and at such a low density that only one  $k_z$  mode is occupied. This structure is a *modulation-doped* heterostructure, and forms the backbone of an entire subfield of condensed matter physics research and GaAs semiconductor electronics. They also form the basis for much of ECE565, Quantum Semiconductor Devices.

Extensions of this technique can create truly 1d structures as well. One

can take one of these 2DEG structures, cleave it inside the growth chamber, rotate it by 90 degrees, and *overgrow* onto the cleaved surface. This cleaved-edge overgrowth method has been used to produce a number of 1d quantum wires, and has the advantage of employing atomically flat and uniform boundaries, unlike variations of lithographic approaches.

## 3.2 Chemistry

Synthetic chemistry is, almost by definition, the science of producing structures on the sub-10 nm scale - molecules. The complication is that for most applications chemists are interested in producing very large numbers ( $\sim 10^{22}$ ) of such molecules. Physicists, conversely, would often like to examine much smaller quantities of such systems, usually with some degree of isolation from one another. Here we will just highlight a few particular systems that are made through chemical techniques and actively researched.

*Nanocrystals.* Under certain circumstances chemical reactions can be used to produce large numbers of nanocrystals, typically a few nm in size. Such crystals, particularly semiconducting ones, can exhibit optical and electronic properties significantly different from the bulk due to quantum confinement.

*Conducting polymers.* These long-chain molecules such as polyacetylene can exhibit metallic conduction at room temperature. In crystalline form the molecules align and are bonded to one another relatively weakly through the Van der Waals interaction, forming a highly anisotropic system.

*Fullerenes.* This family of carbon compounds has proven to be a remarkably fruitful source of research, as you all are aware. Buckyballs can be as small as a few Å in diameter, and can be produced in large quantities in a relatively pure form. Carbon nanotubes can be single- or multi-walled, can be metallic, semiconducting, or insulating depending on their structure, and can have diameters as small as a few Å with lengths approaching the micron scale.

*DNA.* DNA is not a very simple family of molecules, but through the labors of biochemists and molecular biologists, it is one of the most controllable. An enormous number of tools exist that allow one to buy DNA strands with base pair sequences literally made to order. It has become a well-studied molecule in physical nanosciences in part because of the ability of scientists to manipulate it.

A large number of researchers are looking to chemical synthesis methods and chemically synthesized materials as eventual replacements for the processes and active elements in the microelectronics industry. In principle the

ability to make trillions of complicated, virtually flawless sub-10 nm structures in parallel makes the idea of molecular electronics quite compelling. As we shall see later, however, going from concept to practicality is extremely nontrivial.

### 3.3 Self-assembly

Closely related to the chemical synthesis techniques mentioned above is the idea of *self-assembly*. Under certain circumstances it is possible to take advantage of the same kinds of energetic and statistical forces that cause crystalline order in solids, and to have the spontaneous formation of arrays of highly ordered nanostructures. Here we list three examples.

*Self-assembled quantum dots.* Above we said that in MBE under the right growth conditions it is possible to assemble large single crystals one atomic layer at a time. Other growth regimes are possible, however, particularly when two materials do not share exactly the same crystalline structure. An example of this is the GaAs/InAs system. InAs has a lattice constant somewhat smaller than GaAs, resulting in a large surface energy cost if InAs is forced to grow epitaxially on GaAs. As a result, if a small amount of InAs is deposited on a GaAs surface, it will spontaneously arrange itself into InAs islands 1-3 nm in diameter and  $< 1$  nm high. Further, these islands can interact with each other elastically through strains in the GaAs, and tend to arrange themselves into regular arrays. These self-assembled quantum dots can have remarkable optical and electrical properties, and such systems are topics of current research.

*Langmuir-Blodgett films.* Certain molecules have hydrophilic and hydrophobic portions. For free energy reasons similar to those above, when placed into water, the molecules spontaneously arrange themselves into an ordered monolayer on the water's surface. By carefully withdrawing a substrate from such a volume of water, the monolayer can be transferred intact onto the substrate.

*Self-assembled monolayers.* Other molecules can do the same sort of trick on different surfaces. For example, a family of relatively big molecules (1-2 nm) called porphyrins will spontaneously form an ordered monolayer on Si if the substrate temperature is increased enough to enhance their surface mobility. On Au surfaces, alkylthiol molecules also tend to form ordered self-assembled monolayers.

## 4 Concluding remarks

We've now seen a number of methods for creating structures on the sub-100 nm scale. Now that we've given an overview of the basics of characterizing and fabricating nanoscale objects, we will turn to the physics of such systems. We'll use papers from the literature to examine a number of physical effects that arise in these systems.