

Nanoscience: The Role of “Making” New Forms of Matter

Christopher E. D. Chidsey

Department of Chemistry, Stanford University

Introduction: What Nanoscience is and is not.

“Nano” of course means “billionth of”. Nanoscience has been defined as the science of matter with characteristic lengths ranging from 1nm to 100nm. In practice, nanoscience is a collection of portions of traditional disciplines. That is, it is a union of subdisciplines. Here are just a few of the component subdisciplines: materials chemistry, polymer science, colloid chemistry, crystal growth, surface science, solid-state physics, microelectronics, structural biology, ...

A key question to ask is why nanoscience has emerged with the global enthusiasm and fear that it has? Clearly the reason is the promise and, as some see it, threat of a nanotechnology, or more aptly nanotechnologies. For this reason, most discussions of nanoscience eventually turn to technology. However, I would like to suggest that technology is not fundamentally what is driving nanoscience. Technology is oblivious to both the 1nm and the 100nm boundaries and avidly embraces whatever the “right size”¹ may be. In his recent article entitled “Nanoscience, Nanotechnology, and Chemistry”,¹ Whitesides concludes with the useful insight that: “Research and development must be focused on the development of science and technology at the right size—and that size may range from nanometers to millimeters (for the technologies of small things): ‘nano’ is not always the best or only answer.” I will go further and claim that a dispassionate examination of current technological innovation, from biotechnology, to information technology to energy technology, will reveal that nanoscale phenomena often play a role, but rarely an exclusive role. Moreover, there is often an accidental quality to whether or not “nano” enters the picture. I am particularly fond of the irony of biotech instrument companies with names like “Nanodrop” and “Nanostream”. To the extent that ‘nano’ is at all relevant to these firms technologies, it is in the context of nanoliters (1nL = (100µm)³). This is three orders of magnitude larger in length and nine orders of magnitude larger in volume than the upper end of the officially defined nanoscale.

The fundamental driver of nanoscience is not technology, but rather a political effort to provide an inspiring agenda for major portions of the physical sciences, which have by some measures languished in recent decades. The question of how and why to provide public funding for research in the physical sciences is of course central to that agenda. While this political agenda should not be ignored in discussions of science and ethics, I do not want to see it confused with either science or ethics. Balzani, in another recent article on nanoscience and chemistry,² provides a definition of science that I find useful in this regard: “Science is a human activity aimed at knowing the laws of Nature and then using such a knowledge to change the world”. To this, I add my own, unschooled, personal definition of ethics: “Ethics is the human activity of considering and regulating how we change the world”. “World” in both these definitions is a very broad concept. It certainly encompasses human society as well as the physical and biological geosphere, but can as well be taken to mean all that human action can affect. “Laws of Nature” is a

quaint term of art meaning a reductive, mechanistic explanation of how the world works – the implication being that we don't get to change the laws of Nature, that we can change the world only within their boundaries.

In my view, nanoscience is not yet a scientific discipline of its own, and may never become one, because it is not yet clear that the Laws of Nature are particularly special between 1nm and 100nm. By contrast, let us remember that 0.1nm is a truly important characteristic length. It is the diameter of delocalization of electrons about protons and other nucleons to which they are electrostatically attracted. Electrons, nucleons and the photons that carry energy among them are the essential components from which our “world” is composed and *0.1nm is the characteristic length of this world*. The most important exceptions are of course the nuclear and cosmological processes (1) that gave us the particular numbers of nucleons on our particular planet and (2) that gave us a nuclear inferno in a sun located at a particular distance to power our planet with its thermal photons.

Of course, 0.1nm is the characteristic length of chemistry. Being the chemist that I am, you will not be surprised that I claim that the subdisciplines that comprise nanoscience are all just working out how the particular “laws of Nature” that comprise chemistry apply to matter on the 1nm to 100nm length scale. While it is true that certain interesting transitions in properties occur in this range in some materials, such as the transition from energy level spacings greater than room temperature to less than room temperature, it is by no means clear that this range of multiples of 0.1nm is at all fundamental. To the extent that *some multiple* of the fundamental delocalization length of electrons is of fundamental importance, the earlier term “mesoscale”, would have been the better choice, implying as it does a length-dependent transition in properties that depends on the particular property in question. This is another version of Whitesides' “right size”. However, “mesoscale” carried with it the baggage of the subdisciplines that had adopted it – primarily solid-state physics. Nanoscience has the political virtue of being an ecumenical, and perhaps deliberately ambiguous, term that many subdisciplines of the physical sciences can rally around.

To end this introduction about the identity of nanoscience, I want to return to a key aspect of my fellow chemist Balzani's definition of science that I believe will help to set both the political origins of nanoscience and its intellectual and ethical implications in a useful perspective. Balzani makes “using such a knowledge (of the laws of Nature) to change the world” a co-equal part of his definition of science. This activist understanding of science has been endemic to chemistry since it emerged in the 18th century from the fantastical ambitions of alchemists and the practical successes of the smith, the glassmaker, the potter, the brewer and all the other makers of modified forms of matter. As an early exemplar of chemistry, it is hard to beat Lavoisier. At the Royal Gunpowder and Saltpeter Administration in Paris, he perfected the defining method of chemistry -- a repeated cycle of the ancient practice of *making*, the Galilean instinct of *measuring* and the Newtonian instinct of *modeling* the results with as general a theory as Nature will sustain. It was not until he had painstakingly explored and purified many candidate materials that Lavoisier could do the experiments that established oxygen as an element.

Indeed, there are very few pure substances in our world and, due to the small characteristic length of matter, it is very hard to tell when a substance is pure. Thus, the synthesis and preparation of pure substances has been and remains a non-trivial and absolutely essential element of chemical science. Indeed, chemistry, unlike some other sciences, sees synthesis as the third leg of its scientific stool. The scientific method generally requires the iterative process of measuring and modeling Nature, but chemistry proudly proclaims itself the science of *making*, measuring and modeling matter. With making new forms of matter such a central component of its identity, it is hardly surprising that Balzani and many others, including me, take the next step and identify *changing the world* as a central aspect of the human activity we call science. In a sense, having made new forms of matter, we have already changed the world, at least within the domain of our own experiments. Embracing “changing the world” as a central aim of science can thus be seen as making explicit, and hopefully ethical, that which we would nonetheless do implicitly.

The role of *making* in nanoscience can hardly be overemphasized. As an essentially chemical science, nanoscience is predicated on making new forms of matter with feature sizes on the 1nm to 100nm length scale. At the moment, the measuring and modeling aspects of nanoscience are often crude, but that is in large measure because the level of control in making the nanoscale materials is even cruder. With time, the purity, or what is known to chemists as the *chemical homogeneity*, of the newly made forms of matter will rise, and nanoscience will be able to more precisely measure and model phenomena on the nanoscale. I expect that the results will sustain my suspicion that mesoscale would have been the more apt scientific designator and that there are few, if any, new *laws of Nature* lurking specifically in the nanoscale. Nonetheless, we will be left with a much broadened appreciation for the role of *synthesis* in science. Anticipating this development, I propose that it is to *making new forms of matter* (what chemists call *synthesis*) on whatever is the “right size” scale, rather than to *nanoscience*, that we should turn our ethical considerations.

Examples of *Making* from the field of 1-dimensional semiconductor nanostructures

I can scarcely do justice to the vast array of new materials being synthesized in nanoscience. All I hope to do here is provide a few examples that are in some measure illustrative of the synthetic chemistry underlying all the fuss about nanoscience. By and large, the methods that directly form nanoscale materials are crude by comparison with better developed fields of chemistry such as the synthesis of bulk commodity chemicals, fine chemicals, pharmaceuticals, oligonucleotides or electronic-grade single crystals and epitaxial heterostructures. Even in those areas where the same synthetic methods are lifted directly from these highly refined fields, their application to form nanoscale entities currently produces only crudely homogeneous materials. As will become apparent by example, the difficulty in making chemically homogeneous materials is in large measure due to the vastly increased number of degrees of freedom available at the nanoscale. The *heterogeneity* of possible atomic assemblies is huge once one passes the 1nm mark but before one settles for the traditional bulk solid-state approximation of infinitely repeating lattices with a small number of unique atoms in each unit cell. Indeed, the broader

recognition by non-chemists of the vast heterogeneity of possible atomic arrangement may be the most important contribution of this era of nanoscience to the future of science.

Carbon Nanotubes

Carbon nanotubes are perhaps the quintessential nanoscale material. The single-walled variants, which consist of a single tube of carbon atoms bonded in the hexagonal manner found in graphite, have attracted particular attention for their exceptional electronic properties, which rival and may indeed exceed all known metals and semiconductors at room temperature. The chemical inertness of the tubes' surfaces are central to these remarkable properties. Without that the impurities and structural defects at the surface of the tubes would destroy the remarkable electronic properties. Figure 1 shows some key results from an important paper by Dai and collaborators showing that very high performance transistors can be made from single tubes coated in a thin layer of zirconium dioxide, an insulator that allows the influence of a controlling gate electrode to determine the conductivity of the tube. The 2nm-diameter semiconducting tube is switchable with a switching sensitivity significantly better than current generation commercial microelectronic devices: the results in Figure 1c correspond to a figure of merit of 3 milliamperes of current per volt applied to the gate per micron of semiconductor width.

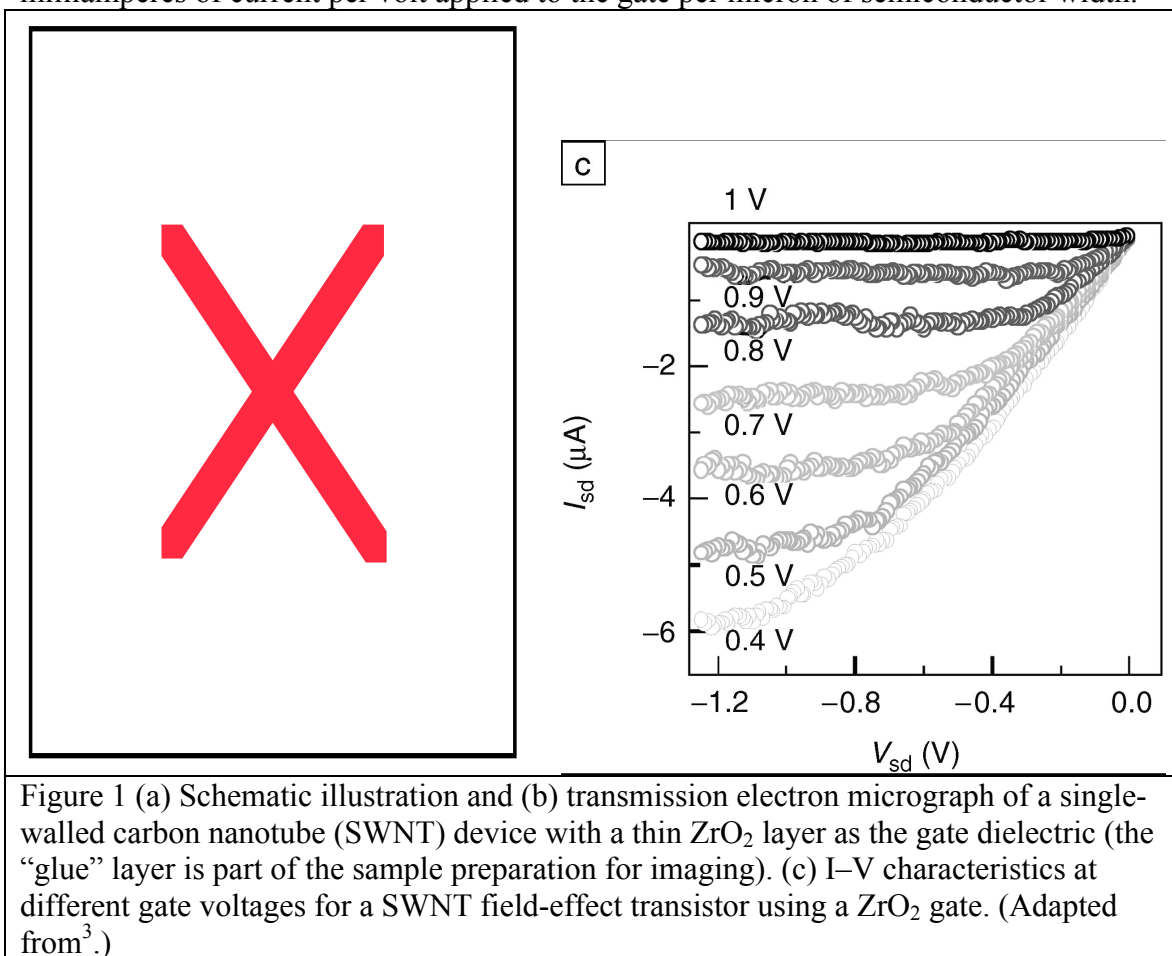


Figure 1 (a) Schematic illustration and (b) transmission electron micrograph of a single-walled carbon nanotube (SWNT) device with a thin ZrO₂ layer as the gate dielectric (the “glue” layer is part of the sample preparation for imaging). (c) I–V characteristics at different gate voltages for a SWNT field-effect transistor using a ZrO₂ gate. (Adapted from³.)

Despite their remarkable performance, these materials are still very far from commercialization in electronic integrated circuits. The reason is the lack of methods to make chemically homogeneous carbon nanotubes. Figure 2 shows micrographs of typical samples prepared by different methods. All are contaminated to some degree by the catalysts used to make them and by byproducts such as amorphous carbon and multiwalled nanotubes. More fundamentally, the diameters of the tubes are not yet strictly controlled. Even more basic, the orientation of the hexagonal lattice of carbon atoms that forms the tube relative to the tube axis is heterogeneous. This latter heterogeneity is crucial as the orientation of the carbon lattice determines whether a given tube is metallic or semiconducting. One simply cannot mass produce integrated circuits unless the conductivity of the semiconduction and metallic elements used in the switches and wires of the circuit have precisely controlled, and absolutely distinct, conductivities.

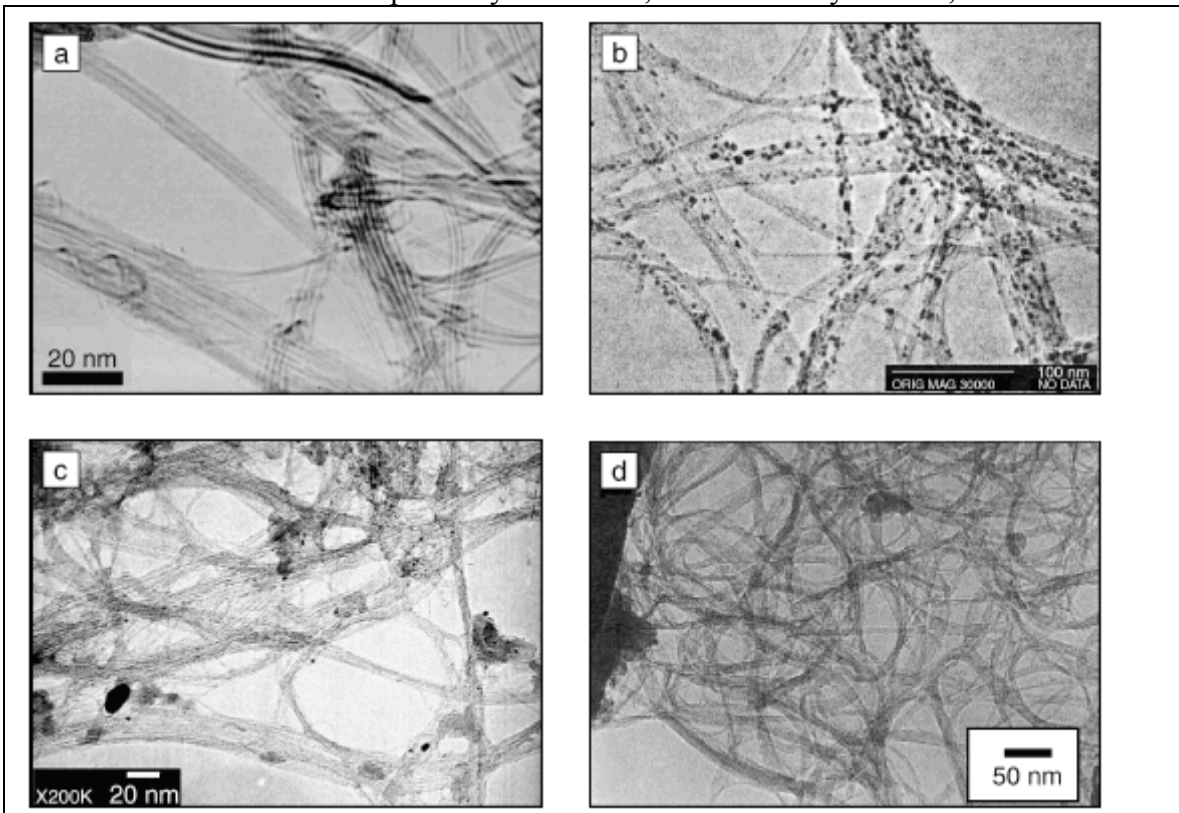


Figure 2. Transmission electron microscopy images of single-walled carbon nanotubes (SWNTs) synthesized by (a) methane chemical vapor deposition (CVD), (b) the HiPCO process (high-pressure catalytic decomposition of carbon monoxide), (c) the CoMoCat CO CVD process, and (d) alcohol CVD. (from ⁴)

A further limitation of carbon nanotubes in electronics is the need to position and orient the tubes with respect to the circuit nodes. At the present time, there are no fully manufacturable way to do this. Work is progressing on two approaches. The first is to purify the tubes in some sort of suspension in a fluid and then deposit them between the nodes of a circuit. The second effort is to grow the tubes from one node and orient the tube to attach to the desired node using electrical or flow fields. Some examples of this approach are illustrated in Figures 3 and 4.

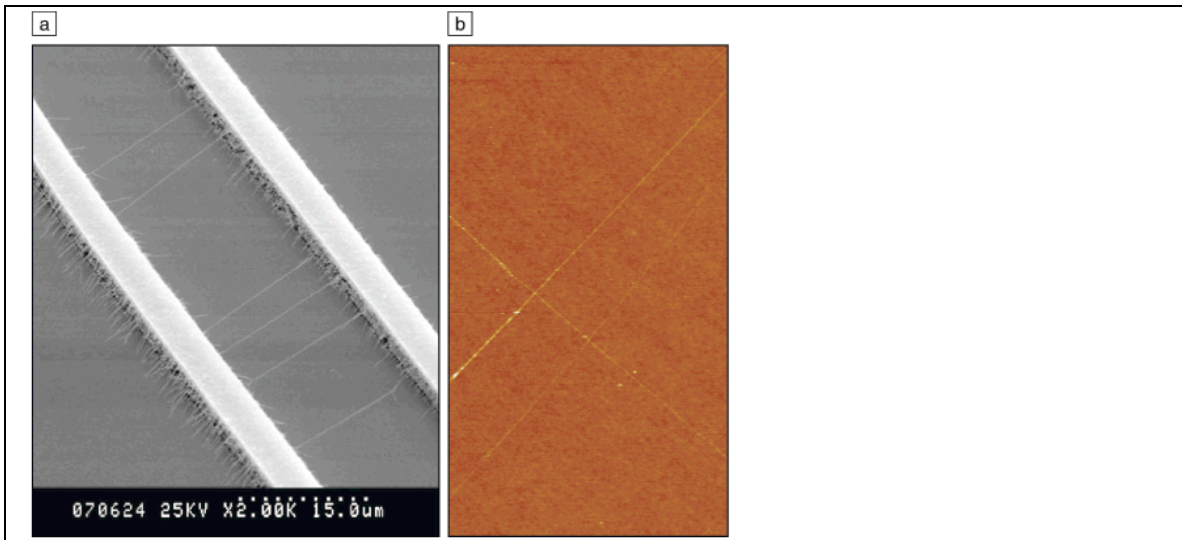


Figure 3. (a) Scanning electron microscopy image of single-walled carbon nanotubes grown under an electric field. (b) Atomic force microscopy image of nanotube crosses produced by two steps of aligned growth in perpendicular electric fields. From⁵

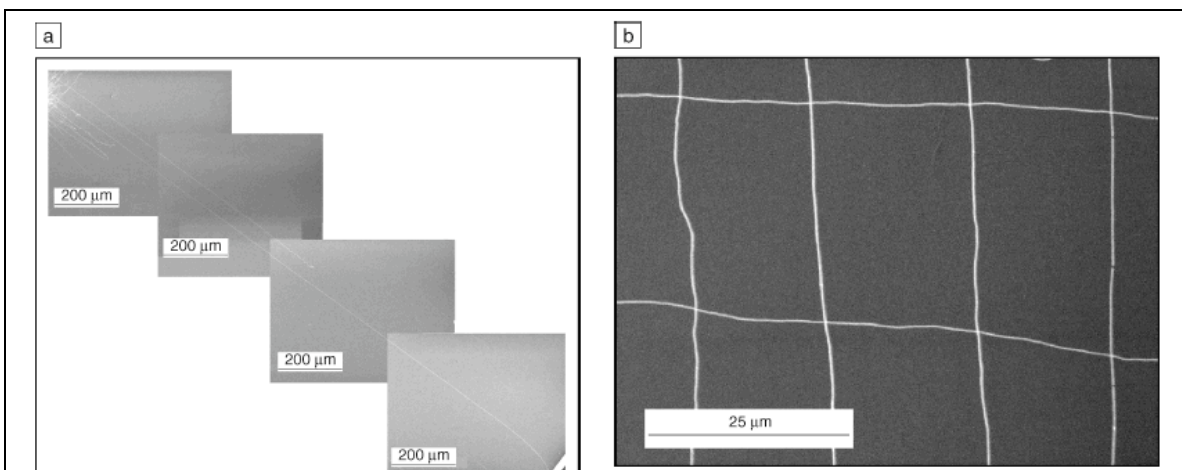


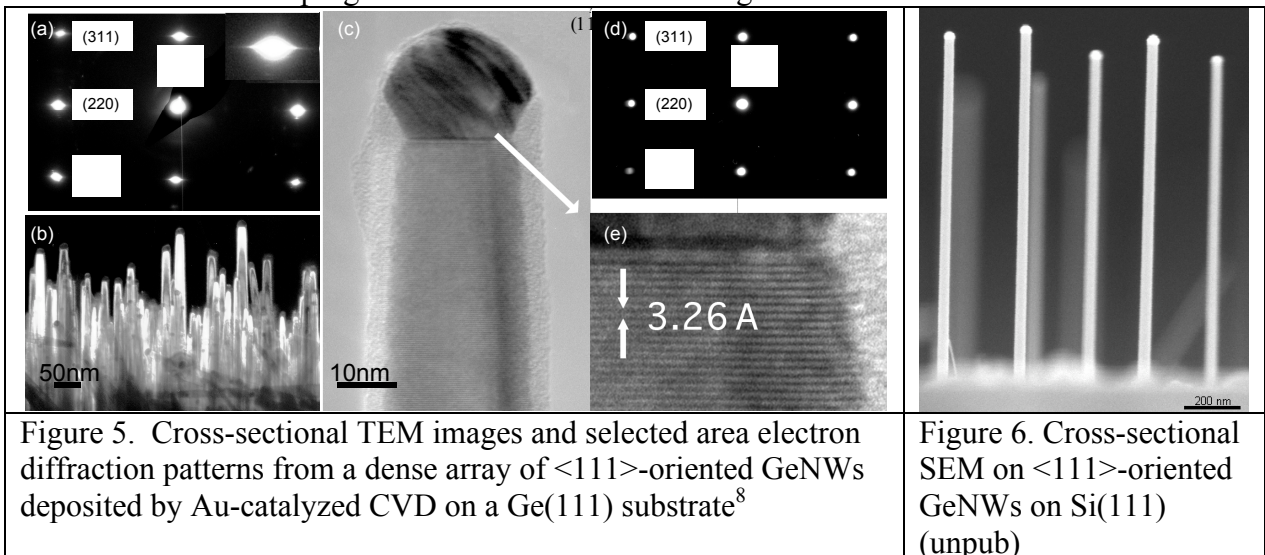
Figure 4. (a) Four connected scanning electron microscopy images showing millimeter-long well-aligned single-walled carbon nanotubes grown by means of chemical vapor deposition (CVD). (b) Scanning electron microscopy image of a two-dimensional nanotube network grown using a “fast-heating” CVD process. From⁶

Germanium Nanowires

Many different types of materials have now been synthesized as one-dimensional wires with nanoscale diameters. As with carbon nanotubes, these nanowires hold promise as electronic elements and may also have other applications, such as photonic, magnetic or thermal uses, determined by their chemical composition. As a second example, I pick a type of nanowire that I know well because my lab has made some of the recent contributions to the study of this material: germanium nanowires (GeNW).

Germanium was the original material used in transistors beginning at Bell Labs in the 1950's. It was eventually replaced when the unique properties on silicon dioxide as an insulator on silicon made silicon a better choice for mass production of integrated circuits. However, the fundamental figures of merit of electron and hole mobility are significantly higher in germanium than silicon, and, if there were manufacturable ways to return to germanium, there is the distinct possibility that it would happen. Recent work to replace silicon dioxide as the insulator on silicon could have the side benefit of enabling germanium and other semiconductor materials to be reconsidered for use in integrated circuits. Germanium offers one very compelling advantage over all other known semiconductors: GeNWs with diameters appropriate for use in nanoelectronic circuits can be grown by gas-phase chemical vapor deposition at temperatures below 300°C⁷. This makes it possible to imagine growing GeNWs at any level among the many levels of nanolithographically defined metal wires currently used to interconnect the devices in an integrated circuit. This would mean that the all-important transistor switches in integrated circuits would no longer be confined to the plane at the top surface of a single crystalline semiconductor substrate. Instead of the current circuit paradigm of sprawling suburban communities of one-story transistors connected by a maze of metallic freeways, 3-dimensional integrated circuits would be comprised of high rise towers of stacked transistors connected by local metal corridors and stairwells. The size and energy consumption per unit operation would drop dramatically. In fact, a single crystalline semiconductor substrate might not even be needed if semiconducting nanowires could be grown wherever they were needed in a 3-D circuit.

Toward this goal, my students, in collaboration with students of Professors Paul McIntyre, Yoshio Nishi and Philip Wong at Stanford, have been working to synthesize GeNWs of controlled diameter and orientation and with precise placement where they are needed. Some of our progress to date is illustrated in Figure 5 and 6.



The diameter of the GeNWs is defined by liquid gold-germanium alloy particles from which the GeNWs crystallize without separate growth of germanium on the sides of the GeNWs. The synthesis of gold nanocrystals (colloids) of well defined diameter from

which the alloy particles can be obtained is a well developed field of nanoscience in its own right. The orientation of the Ge lattice is determined by an epitaxial orientation with the lattice of the (macroscopic) single-crystalline substrate on which the GeNWs are grown. We are currently working to gain control of the location of the GeNWs by lithographically patterning one gold nanoparticle to be located where each GeNW is desired to originate. We believe that the process of patterning the substrate has left impurities on the substrate and we are working to learn how to purify our substrate surfaces prior to growth of the GeNWs so that we can obtain the desired chemical homogeneity of position, diameter, nanowire orientation and Ge lattice orientation.

However, even once we succeed in controlling all the structural parameters of the GeNWs, that will not be enough. We then want to learn to control the impurities in the nanowires including the level of incorporation of the elements in the catalyst particles (currently only gold) and desired dopants that provide chemical control over the properties of semiconductor switches. The good news is that this low temperature synthesis method produces very pure materials; the bad news is that this may make it very difficult to deliberately add impurities where they would be most useful in electronic circuits.

Heterostructured III/V Semiconductor Nanowires

A set of semiconductor nanostructures related to the carbon nanotubes and GeNWs discussed above can be formed from compounds of the group III and V elements. Photonic technologies like solid-state lasers, modulators and detectors have historically been based on these materials. Figure 7 shows some recent work synthesizing axially heterostructured nanowires of GaAs and GaP by Bakkers and colleagues at Philips in the Netherlands⁹. These remarkable structures nonetheless again illustrate the synthetic challenges that remain. The high prevalence of twin dislocations in the GaP segments is not understood and is of concern as they may scatter electrons and holes. Moreover, these beautifully parallel wires were only obtained as an unoriented and unpositioned mass of wires on an amorphous substrates. Some of the most elegant work to date to orient and position nanowires is illustrated by the work from the Samuelson group at Lund shown in Figure 8¹⁰. Here nanoimprint lithography has been used to position Au catalyst particles. Note that despite the positional and orientational control, the wires are tapered due to growth of the semiconductor materials on the nanowire sidewalls. As with the GeNWs, these III/V nanowires will surely continue to yield to on-going synthetic efforts of many groups around the world.

While the 1-dimensional semiconductor nanostructures shown here are only a sampling of only one small set of the many nanostructures under investigation, I hope they at least illustrate the rich opportunity and demanding synthetic challenges facing nanoscience, which is first and foremost the science of making chemically homogeneous structures.

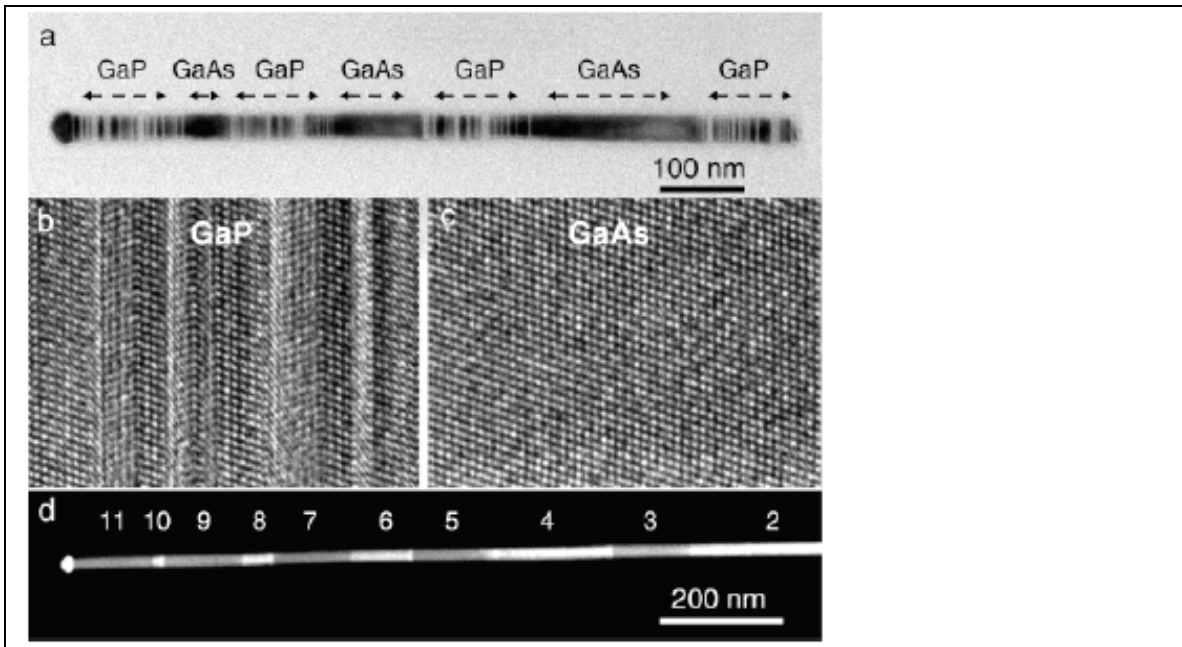


Figure 7. (a) TEM image of a heterostructured GaP-GaAs nanowire. The wire was grown at 420°C. The arrows indicate the segments. Rotational twin dislocations are present in the GaP sections (vertical contrast lines) but not in the GaAs parts. In the insets, typical high-resolution TEM images of a (b) GaP and (c) GaAs segment are shown. (d) HAADF TEM image. GaAs sections are brighter than GaP. From⁹

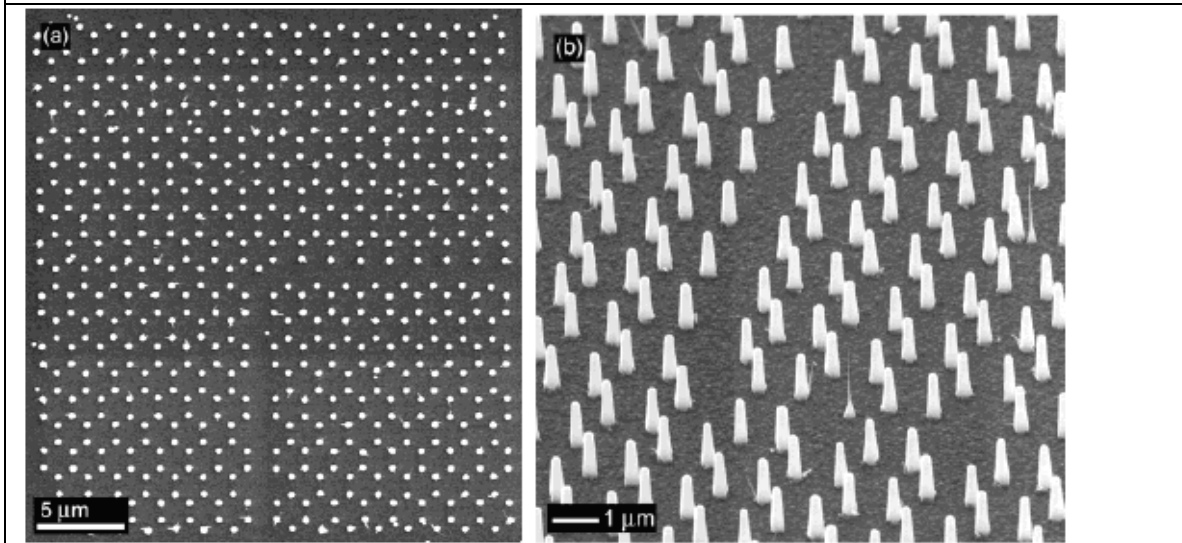


Figure 2. SEM micrographs of nanoimprint-defined InP nanowire arrays as obtained after growth. The nanowires are approximately 1.5 μm long, with a diameter of approximately 290 nm. The dimensions are chosen for a photonic crystal structure operating at wavelengths of 1 μm . Panel (a) shows a top view, displaying the high perfection and uniformity of the arrays; (b) is a zoomed in, tilted image of the bend (45° viewing angle). The few ultrasharp nanowires present are not intentionally formed, and are most probably non-gold catalyzed. From¹⁰

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