Bottom-up Nanoelectronics

Peter Hadley

Kavli Institute of Nanoscience, Delft University of Technology, Delft, The Netherlands

Abstract — **Nanoelectronics is a broad topic that spans molecular devices to silicon field-effect transistors. While the development of nanoscale silicon devices is an important topic, the focus here will be on the challengers to silicon such as molecules, carbon nanotubes, and nanowires. In high performance applications like computation or communications, the challengers might be able to provide devices that are about as fast, and about as small as those that will be made in the near future in silicon. It is not in terms of performance that silicon will be challenged. The real potential of the challengers is that they may eventually provide about the same performance as silicon for a lower price.**

I. INTRODUCTION

The nanometer scale is important for technology because atoms are a fraction of a nanometer in size and as soon as a few atoms are put together to make a device, that device has the dimensions of nanometers. The smallest transistors, lasers, sensors, motors, memory cells, and pumps are all a few nanometers in size. Electronic devices already have critical dimensions in the nanometer range and the control of fabrication at this scale is very important.

Broadly speaking, there are two routes to constructing nanoscale electronic devices: from the top down and from the bottom up. In top-down technologies, devices are carved out of bulk materials. The best example of this is silicon integrated circuit technology. By selectively depositing layers and etching material away, fantastically complex circuits can be made. The other route to making nanostructures is the bottom-up route. In this case, molecular building blocks are placed in the right environment and they assemble themselves into complicated structures. The best examples of bottom-up structures are living cells. The different routes have their advantages and disadvantages. Historically, the top-down route has been more relevant for electronics and presently all complex circuits are made this way. However, there has been much interest lately in the bottom-up route.

Making electronic circuits by bottom-up techniques using molecules as electronic components was first seriously discussed in the 1970s when top-down integrated circuits still had fairly large dimensions. [1] At that time, one of the major advantages of molecular electronics was said to be that it would result in circuits much denser than those possible by top-down technology. Since that time, spectacular advances have been made using top-down technologies. Some critical components, like the gate oxide, are only a few atoms thick. It now seems unlikely that molecular devices could be made significantly smaller than silicon devices. The miniaturization of electronics will end with the miniaturization of CMOS. However, there are other good reasons for pursuing the bottom-up approach. When devices are synthesized chemically, the position of every atom in the device is known and the devices can be optimized on the atomic scale. Chemical synthesis is also a process that can be scaled up easily. Once it is possible to make transistors by chemical synthesis, more transistors will be made in one day than will ever be made by photolithography. The cost per transistor will drop by orders of magnitude and this will lead to new applications.

Once bottom-up devices are synthesized, they can either be added to silicon technology or they could be used to build circuits independently of silicon. When combined with silicon, nanoelectronic elements will provide useful functionality. Single-electron transistors can measure charge, spin transistors can measure magnetic field, nanomechanical sensors can detect motion or mass, quantum dots can absorb or emit light, and molecules can act as chemical sensors. While these enhancements to silicon may be important, they will always be tied to the economics of silicon technology. A real breakthrough will occur when the bottom-up components can be self-assembled into circuit independently of top-down silicon technology.

Obviously it will be a great challenge to arrange chemically synthesized electronic components into circuits. The first circuits that are likely to appear will be very simple and probably will not be deposited on a substrate the way conventional circuits are. Examples would be temperature or humidity sensors that could be incorporated into cloth to enable the cloth to respond to various conditions. Another possible application is a molecular photovoltaic cell. If this cell was sensitive to infrared radiation, several could be stacked in series and then used to power a molecular light emitting diode that emits visible light. By incorporating such structures into paint, the paint would glow where an infrared beam fell on it. Similarly, photovoltaic cells suspended in a solution could be used to generate the voltage needed to initiate polymerization. This way a light signal could be used to thicken a liquid. These are just a few examples of the many things that could be done with a few simple electronic components if they were available in bulk quantities.

Other early applications of bottom-up nanoelectronic devices will probably consist of simple regular arrays of elements. Solar panels can be made by chemically synthesizing diodes and then arranging the diodes in parallel between planar electrodes. It is important that the diodes used in solar cells are inexpensive and following a bottom-up route is a good way to realize this. A related application is lighting panels. These also consist of many diodes in parallel. The challenge is to make light sources that are more efficient and cheaper than normal light bulbs. Once lighting panels are made, displays and sensor arrays made with bottom-up components are likely to follow.

The architecture of a display made from bottom-up elements might be quite different from a conventional display. The display would consist of many identical pixel elements, each capable of exchanging information with its neighbors and displaying color information. These pixel elements would be designed so that, under the right conditions, they arrange themselves into a two-dimensional planar array. Image information would then be passed to some random pixel near the lower left corner. The image information would specify the color that should be displayed and the position (x,y) where that color should be displayed. Each element would be programmed to subtract 1 from the x coordinate and pass the information to the right and to subtract 1 from the y coordinate and pass the pass the information up. If an element receives information with the coordinates (0,0), that element displays the color information. In this architecture, there is no complex wiring, only nearest neighbor connections. No pixel element knows its position yet it displays the correct information. The elements could be powered by sandwiching them between two planar electrodes that act as power and ground. If the elements were produced purely by chemical synthesis, large cheap displays could be made.

A memory could be made using similar elements to those described above but instead of displaying the information, small chunks of information would be stored in each element. The information would be stored until a request for that information was passed to the element to pass the information to the edge of the array where it could be read. If a global signal were given that every element should pass their current information to the right and receive new information from the left, large amounts of information could be written into or read out of the memory quickly. A real breakthrough in memory storage would be achieved if this kind of memory could be made using a three-dimensional array of elements.

A self-assembled processor could be based on the same principles. A processor element would store two kinds of information, data and instructions. The processing element would manipulate the data based on the instructions and pass information to its neighbors. In architectures such as this consisting of many identical elements, it is easier to implement error correction and fault tolerance since every element can take on the duties of any other element. It is also conceivable that nanomachines could be made that implement repairs by replacing faulty elements with new ones.

Since so many devices can be produced simultaneously by chemical synthesis, the more complexity that can be included in a circuit chemically, the lower the costs of the final circuit will be. This could well be the successor to Moore's law. Instead of improving electronics by making the components smaller, we will start with atomically precise components and build ever more complex circuits out of them.

In order to produce the self-assembled circuits described above, there three challenges must be met: fabricating the devices, mastering self-assembly techniques, and developing circuit architectures that use arrays of identical devices. At this point, the bottleneck appears to be constructing suitable nanoscale devices. In particular, the lack of signal gain in nanoscale transistors is preventing us from building electronic circuits from the bottom up. The following section examines some of the problems of very small transistors.

II. SMALL TRANSISTORS

Some dimensions in a transistor are more critical for performance than others. Three important lengths in a field-effect transistor are the gate length, the transistor width, and the gate oxide thickness. The gate length is the distance from source to drain. It is measured in the direction that the current flows. The shorter the gate length, the faster the transistor and the less power it dissipates. CMOS transistors in production have a physical gate length of about 50 nm. Prototype field effect transistors have been made with a gate length of 6 nm. [2] The width of a transistor in the direction perpendicular to the current flow is mostly unrelated to the speed of the device. A typical field-effect transistor has a width about three times the gate length. The current a transistor can provide is proportional to the width transverse to the current flow so sometimes a wider transistor is chosen to provide more current. The gate oxide thickness is smallest critical length in a field-effect transistor. This isolates the gate electrode from the channel. In the transistors now in production, the gate oxide is about 1 nm thick. This is only a few atoms thick and cannot be made much thinner before quantum mechanical tunneling through the gate oxide causes a significant problem of current leaking through the oxide.

Three important problems that small transistors typically have are low gain, low drive current, and large leakage current. A necessary condition for voltage gain in a field-effect transistor is that the source-drain length be significantly longer than the gate oxide thickness. This ensures that the gate voltage is more important in determining the conductivity of the channel than the source-drain voltage. Typically, the gate oxide is about 45 times smaller than the gate length. Since the gate oxide is already 1 nm thick, it can't be made much thinner. It is possible to reduce this factor of 45 by using other materials but source-drain lengths smaller than 1 nm do not seem feasible. This argument holds for any field-effect device. Molecular or nanowire field-effect devices cannot have shorter source-drain lengths than 1 nm or they won't have gain. No other known mechanism, such as single-electron effects, spintronics, or quantum interference has ever been used to make a transistor that exhibits signal gain, has a source-drain length less than 1 nm and operates at room temperature. [3]

There are reports of transistors with source-drain lengths smaller than 1 nm. For instance, transistors based on single molecules [4] or single C_{60} fullerenes [5] have been made. These transistors have no signal gain and cannot be used to amplify signals.

There are also reports of transistors with widths transverse to the current flow of about 1 nm. Carbon nanotube transistors fall in this category. [6] However, all of the carbon nanotube transistors that show gain have a gate length that is longer than the gate length of a typical silicon transistor. There seems to be no real practical advantage to the very small transistor width.

The drive current is another important transistor characteristic to be considered. The drive current is the current the transistor can deliver when it is fully turned on. Sometimes the speed of a transistor is characterized by the gate delay $C_g V/I_{\text{drive}}$. Here C_g is the gate capacitance, V is the signal voltage, and I_{drive} is the current drive of the transistor. This is the amount of time it takes to charge the input of one transistor with the drive current of the same transistor. Typical values for the gate delay in semiconductor transistors are about 1 ps. [7] The greater the drive current, the shorter the switching time.

The gate delay is a lower limit on the speed of the circuit. The real switching speed depends on how long it takes a transistor to charge a voltage node. This time is CV/I_{drive} where C is the capacitance of the node. The capacitance C includes any stray capacitance of the wires plus the input capacitances at the gates of any transistors connected to this node. For signal voltages on the order of 1 V and capacitances of 100 aF, a transistor would have to have a drive current of 10 microamps to achieve a switching speed of 10 ps. Many molecular transistors that have been discussed in the literature provide only a few nanoamps of current. This means that circuits built from these transistors would be significantly slower than conventional silicon circuits. Often a lot of current is needed in an application. Milliamps are needed to drive a transmission line or to drive a signal across a chip. In these cases, very many molecular transistors in parallel would be needed.

Another important characteristic of a transistor is the leakage current. A transistor can be thought of as a sort of switch that can be opened and closed. Even when the switch is nominally open so that no current should flow through it, there is always a small leakage current. Small transistors tend to have more trouble with leakage current than larger transistor because the source and drain electrodes are closer together. This leakage current dissipates energy and causes the circuit to heat up. The heat generated by the leakage current is one of the factors that limit the density of transistors in a circuit. The power dissipated per unit area due to this leakage is, $nI_{\text{leak}}V$, where n is the transistor density, I_{leak} is the leakage current and V is the supply voltage. The leakage current should be responsible for no more than a small fraction of the total power dissipated. An acceptable total power density is about 10 W/cm². This can be expressed as the inequality,

$$n << 10/(I_{\text{leak}}V_{\text{supply}}) \text{ [transistors/cm}^2\text{]}. \qquad (1)$$

Many nanoscale transistors that have been presented in the literature can be rejected as impractical for dense integrated circuits on this basis.

The conclusions that can be drawn from this discussion of gain, drive current, and leakage current is that it is unlikely that devices can be made that are significantly smaller or significantly faster those projected to be realized in the coming decade in silicon. The opportunities for bottom-up transistors are not for smaller devices and denser circuits but for cheaper devices. Large-area/low-cost electronic applications such as solar cells, lighting panels, and displays are the applications where bottom-up have the most potential. Silicon technology has trouble competing in these applications because the costs of a silicon integrated circuit is on the order of \$100/cm². This is too expensive for many large area applications. If the bottom-up electronic components are much cheaper than silicon devices it will not matter that they are not as small or not as fast as silicon.

The next few sections briefly describe the status of various technologies for fabricating electronic components by bottom-up techniques.

III. SMALL (<3 NM) MOLECULAR DEVICES

The electrical transport through many different small molecules has been measured under many different conditions. It is difficult to generalize about all these measurements but some trends can be identified. There are often problems with the contacts and the sample-to-sample reproducibility is usually low. This does not mean that it will be impossible to find molecules that are reproducible, but the general experience with molecules that have been studied so far is that molecular devices are rarely reproducible. Clearly, a better understanding of how to make good electrical contact to molecules is needed. At this point, there are no molecules that are widely considered to be suitable for transistor or memory element applications. It seems that molecules smaller than 3 nm are too small to make good transistors.

IV. SUPERMOLECULAR ELECTRONICS

If small molecules are too small to be good transistors, an obvious course of action to take is to try to produce large transistors by bottom-up techniques. Large in this case means transistors with a gate length of 20 - 50 nm. This is a size range where it is known transistors can exhibit good electrical properties.

Creating large structures with atomic precision is the domain of supermolecular chemistry. In supermolecular chemistry, molecules are used as building blocks that are arranged into larger structures. The molecules that serve as the building blocks are chosen to have complementary shapes that fit together like a lock and key. Where one molecule has a bump, the complementary molecule has a hollow that the bump fits into. The molecules form several weak bonds when they fit together in the proper way. It is essential for molecular recognition that weak bonds such as hydrogen bonds or van der Waals bonds be used. When the building blocks are first thrown together in solution they will come together in many conformations and perhaps form a few weak bonds when they do so. A few weak bonds will not be enough to hold the molecules in this conformation and the molecules will assume other conformations until the molecules fit together like a lock and key and many weak bonds are simultaneously formed. If properly design, this structure is stable.

While supermolecular chemistry can produce large molecular structures, they tend to be poor conductors. For instance, DNA can be used to form rather complicated structures but none have been shown to be good electrical conductors. The problem seems to lie with the weak bonding that is needed for the molecular recognition process. Materials held together by weak bonds are typically poor conductors. A solution to this problem may be to create large structures using molecular recognition and then use this structure as a template to create another structure with strong bonds. In any case, the problem of low conductivity in these structures must be overcome before high-quality electronic devices will be made by this route.

V. SINGLE-ELECTRON DEVICES

Single-electron transistors (SETs) are often discussed as elements of nanometer scale electronic circuits because they can be made very small and they can detect the motion of individual electrons. However, SETs have no voltage gain at room temperature. [8] This prevents them from replacing field-effect transistors in most applications. SETs also have a low drive current, usually in the nanoamp range. This makes SET circuits rather slow. The most promising applications for SET's are charge-sensing applications such as the readout of few electron memories, the readout of charge-coupled devices. SETs are particularly well suited for precision charge measurements in metrology that take place at low temperature. However, applications outside the realm of sensitive measurements do not seem very promising.

VI. SEMICONDUCTING NANOWIRES

Semiconducting nanowires are small crystals of semiconductors that typically have diameters of 10 nm - 100 nm and can be up to several microns long. Different semiconductors can be combined in a nanowire to form p-n junctions, quantum dots, transistors, [9] light-emitting diodes, [10] and lasers [11]. What is special about nanowires is how they are grown. By adjusting the growth temperature and pressure it is possible either to grow a long wire of constant diameter or to grow radially so the diameter of the wire increases. By changing the sources during growth, different materials can be layered on top of each other either as layers perpendicular to the axis of the wire or as coaxial shells. [12] The transitions between the materials are nearly atomically sharp. This makes it possible to form three-dimensional structures during growth with sub-nanometer precision. It is possible to grow materials epitaxially on top of each other that do not grow epitaxially in large areas. This is because the cross section of the nanowires is so small that less strain is built up and larger lattice mismatches are possible. Properties such as the band gap of a semiconductor can be tuned by changing the diameter of the nanowires. This gives further flexibility in tailoring the materials for an application.

Growing nanowires on conventional semiconducting substrates is a good way to introduce new materials in a technology. Nanowires can also be grown on a separate substrate and then suspended into liquid and deposited much the way molecules might be introduced to a circuit. For instance, light-emitting diodes made from nanowires could be assembled on an electrode in an otherwise completed silicon circuit. This could be used to add light sources to silicon circuits. It is also possible to build transistors using nanowires. Since they are made from single crystals, they have superior electrical properties to organic semiconducting materials presently used in low cost electronics. [13] These transistors could be spun on substrates for applications such as electronic paper, smart packaging, and sensors. Since the nanowires can be formed in one environment and then later deposited on a substrate, they can be used on cheap and flexible substrates. The combination of nanowire LEDs and nanowire transistors could potentially be used to produce cheap and high quality displays.

VII. CARBON NANOTUBES

Carbon nanotubes consist of sheets of carbon atoms in a two-dimensional hexagonal lattice that are rolled up to form tubes. The tubes are typically a few nanometers in diameter and are microns long. They can have different diameters and chiralities. The chirality is the twist of the rows of atoms along the length of the tube. Sometimes the atom rows are parallel to the axis of the tube and sometimes the rows form a helix that winds along the tube. Carbon nanotubes are very strong; they are 10 times as strong as steel for the same weight. The electrical properties of carbon nanotubes depend on their diameter and their chirality. Some tubes are metallic and some are semiconductors.

Both the metallic tubes and the semiconducting tubes are very good conductors. The mean free path in metallic tubes at low bias voltages is 1.6 μm and the resistance of a tube is about 4 kΩ/μm. As the bias voltage is increased, the resistance increases and the current saturates at about 20 μA. The current density under these conditions is about 10^9 A/cm^2. The high bias mean free path is about 10 nm and the resistance is 800 kΩ/μm at high bias. The increase in resistance at high bias is due to the emission of optical phonons. This phonon emission process is only possible when the electrons are accelerated to high energies by the bias. [14]

Semiconducting tubes are also good conductors. Mobilities of 80000 cm²/Vs and a mean free path of 3 µm have been reported in semiconducting tubes. [15] The good conductivity of carbon nanotubes arises from the one-dimensional nature of the tubes combined with their extreme rigidity. The one-dimensionality reduces the number of electron states and phonon states severely. For phonon scattering, a phonon must scatter an electron from an occupied state to an empty state. Because of the reduction in the density of states of electrons and phonons, there are no phonons available with the correct energy and momentum to scatter electrons from the filled states to the empty states. [16] The rigidity of the tubes is important because soft one-dimensional conductors undergo lattice distortions that lead to hopping conduction and/or Peierls transitions. The softness of the materials, and the relative ease with which lattice distortions are formed, are responsible for the relatively poor conductivity observed in organic crystals and conjugated polymers.

A number of groups have made transistors from carbon nanotubes. [6] These transistors have good electrical properties that are on the order of the properties that would be expected of a silicon transistor if it were scaled to the geometry of a carbon nanotube. To perform most functions that silicon transistors do, several semiconducting carbon nanotubes would be needed in parallel to provide sufficient current drive. Carbon nanotubes are presently the best example of a bottom-up structure that shows good electrical conductivity. More work on learning how to have the tubes self-assemble into circuits is needed before carbon nanotube devices can be used in practice. An important lesson that has been learned from the work on carbon nanotubes is that stiff, one-dimensional conductors can be made by bottom-up means with very good electrical characteristics.

VIII. CONCLUSIONS

The trends in the miniaturization of electronics have lead many people to believe that smaller is better. However, there is a lower limit that lies somewhere in the range of a few nanometers. Silicon devices are going to come very close to this lower limit and they are going to leave little possibility for smaller devices to be made in other technologies. The real potential for the challengers to silicon seem to be in large-area/low-cost applications. Solar cells and lighting panels are promising applications for self-assembled arrays of nanoelectronic elements. As bottom-up technologies mature and more low cost nanoelectronic elements become available, silicon will be challenged by circuits that provide about the same performance at lower cost. The bottom-up elements that show the best electrical characteristics at this point are semiconducting nanowires and carbon nanotubes. These are among the largest bottom-up devices demonstrating that smaller is not necessarily better.

REFERENCES

[1] A. Aviram and M. A. Ratner, "Molecular rectifiers," Chem. Phys. Lett. vol. 29 pp. 277-283, 1974.

[2] B. Doris, Meikei Ieong, T. Kanarsky, Ying Zhang, R. A. Roy, O. Dokumaci, Zhibin Ren, Fen-Fen Jamin, Leathen Shi, W. Natzle, Hsiang-Jen Huang, J. Mezzapelle, A. Mocuta, S. Womack, M. Gribelyuk, E. C. Jones, R. J. Miller, H.-S. P. Wong, W. Haensch., "Extreme scaling with ultra-thin Si channel MOSFETs," IEDM '02. Digest. International pp. 267- 270, 2002.

[3] K. K. Likharev, "Electronics below 10 nm," in *Nano and Giga Challenges in Microelectronics*, pp. 27-68, Elsevier, 2003.

[4] Jiwoong Park, Abhay N. Pasupathy, Jonas I. Goldsmith, Connie Chang, Yuval Yaish, Jason R. Petta, Marie Rinkoski, James P. Sethna, Héctor D. Abruña, Paul L. McEuen, and Daniel C. Ralph, "Coulomb blockade and the Kondo effect in single-atom transistors," Nature vol. 417 p. 722, 2002.

[5] Hongkun Park, Jiwoong Park, Andrew K. L. Lim, Erik H. Anderson, A. Paul Alivisatos, and Paul L. McEuen, "Nanomechanical oscillations in a single-C_{60} transistor," Nature vol. 407 p. 57 (2000).

[6] Ph. Avouris, J. Appenzeller, R. Martel, and S. J. Wind, "Carbon nanotube electronics," *Proceedings of the IEEE*, vol. 91 p. 1772, 2003.

[7] International Technology Roadmap for Semiconductors, http://public.itrs.net/.

[8] P. Hadley, Günther Lientschnig, and Ming-Jiunn Lai, "Single-Electron Transistors," *Institute of Physics Conference Series Number 174*, Edited by M. Ilegems, G. Weimann, and J. Wagner, pp. 125 - 132, 2002.

[9] Y. Huang, X. Duan, Y. Cui, L. J. Lauhon, K. Kim, C.M. Lieber, "Logic gates and computation form assembled nanowire building blocks," Science vol. 294 p. 1313, 2001.

[10] X. Duan, Y. Huang, J. Wang, Y. Cui, and C. M. Lieber, "Indium phosphide nanowires as building blocks for nanoscale electronic and optoelectronic devices," Nature vol. 409, pp. 66-69, 2001.

[11] Xiangfeng Duan, Yu Huang, Ritesh Agarwal, and Charles M. Lieber, "Single-nanowire electrically driven lasers," Nature vol. 421 p. 241, 2003.

[12] L. J. Lauhon, M. S. Gudiksen, D. Wang, and C. M. Lieber, "Epitaxial core–shell and core–multishell nanowire heterostructures," Nature vol. 420, 57 - 61, 2002.

[13] Yi Cui, Zhaohui Zhong, Deli Wang, Wayne U. Wang, and Charles M. Lieber, "High Performance Silicon Nanowire Field Effect Transistors," Nano Letters, vol. 3, pp. 149 - 152, 2003.

[14] Ji-Yong Park, Sami Rosenblatt, Yuval Yaish, Vera Sazonova, Hande Ustunel, Stephan Braig, T. A. Arias, Piet Brouwer and Paul L. McEuen, "Electron-phonon scattering in metallic single-walled carbon nanotubes," Nano Letters vol. 4, p. 517, 2004.

[15] T. Dürkop, S. A. Getty, Enrique Cobas, and M. S. Fuhrer, "Extraordinary Mobility in Semiconducting Carbon Nanotubes," Nano Lett. vol. 4, pp.35-39, 2004.

[16] A. B. Kaiser, "Electronic transport properties of conducting polymers and carbon nanotubes," *Rep. Prog. Phys.* vol. 64 p. 1, 2001.