

# Overview of Nanoelectronic Devices

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*This paper provides an overview of research developments toward nanometer-scale electronic switching devices for use in building ultra-densely integrated electronic computers. Specifically, two classes of alternatives to the field-effect transistor are considered: 1) quantum-effect and single-electron solid-state devices and 2) molecular electronic devices. A taxonomy of devices in each class is provided, operational principles are described and compared for the various types of devices, and the literature about each is surveyed. This information is presented in nonmathematical terms intended for a general, technically interested readership.*

**Keywords**— *Molecular electronics, nanoelectronics, quantum dots, quantum-effect devices, resonant tunneling, single-electron transistors.*

## I. INTRODUCTION

For the past 40 years, electronic computers have grown more powerful as their basic subunit, the transistor, has shrunk [1]. However, the laws of quantum mechanics and the limitations of fabrication techniques may soon prevent further reduction in the size of today's conventional field-effect transistors (FET's). Many investigators in the field of next-generation electronics project that during the next 10 to 15 years, as the smallest features on mass-produced transistors shrink from their present lengths of 250 nm to 100 nm and below, the devices will become more difficult and costly to fabricate. In addition, they may no longer function effectively in ultra-densely integrated electronic circuits [2]–[11]. (Note: 1 nm is 1 billionth of a meter, approximately 10 atomic diameters.)

In order to continue the miniaturization of circuit elements down to the nanometer scale, perhaps even to the molecular scale, researchers are investigating several alternatives to the transistor for ultra-dense circuitry. These new nanometer-scale electronic (nanoelectronic) devices perform as both switches and amplifiers, just like today's transistors. However, unlike today's FET's, which operate based on the movement of masses of electrons in bulk matter, the new devices take advantage of quantum mechanical phenomena that emerge on the nanometer scale, including the discreteness of electrons.

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What will such alternative next-generation nanodevices look like? Upon what operating principles will they function? How will they resemble present-day transistors, and how will they differ? This paper addresses these questions by surveying the literature about novel nanoelectronic devices that could replace the transistor in tomorrow's smaller, denser, and faster digital computers. The answers are presented in nonmathematical terms intended for a general, technically interested readership. However, this overview builds upon several earlier, more technical and specialized reviews [12]–[25] and treatises [26]–[29], as well as the work of numerous research groups.

Specifically, we will survey two broad classes of alternative nanoelectronic switches and amplifiers:

- *solid-state quantum-effect and single-electron devices;*
- *molecular electronic devices.*

Devices in both classes take advantage of the various quantum effects that begin to dominate electron dynamics on the nanometer scale.

Fabricating quantum-effect and single-electron devices in solids is the approach taken by most research groups exploring new-technology nanoelectronic devices [20]. It makes novel devices out of the same semiconductors used for transistors. Despite the novelty of the designs, researchers already have been able to develop, fabricate, and employ in circuitry several promising new device types by building upon 50 years of industrial experience with bulk semiconductors.

Molecular electronics is a relatively new approach that would change both the operating principles *and* the materials used in electronic devices [17], [25], [30]–[37]. The incentive for such radical change is that molecules are naturally occurring nanometer-scale structures. Unlike nanostructures built from bulk solids, molecules can be made identically, cheaply, and easily, by the billions of trillions that will be needed for industrial-scale production of ultra-dense nanoelectronic computers. Two significant challenges are to devise molecular structures which act as electrical switches, and to assemble these molecules into the precise extended structures needed for reliable computation. Exciting theoretical and experimental progress toward these goals is just beginning.

To simplify the terminology, in focusing upon these two alternative types of nanoelectronic devices, we will not include nanometer-scale FET's in the category of "nanoelectronics." However, this work does not discount the important point of view that envisions the aggressive miniaturization of FET's down to the nanometer scale [21], [38]–[41]. Rather, this work attempts to complement articles on that topic elsewhere in this issue of the *Proceedings* [43], [171]. In so doing, this paper compares and contrasts the alternatives with FET's to arrive at a technology vision that is complementary to a vision of nanometer-scale circuitry based upon the continued miniaturization of FET's.

Thus, before examining the designs for quantum-effect and single-electron nanoelectronic devices, we must examine the structure and function of conventional microelectronic transistors [27], [161], [213], as well as their possible limitations.

## II. MICROELECTRONIC TRANSISTORS: STRUCTURE, OPERATION, OBSTACLES TO MINIATURIZATION

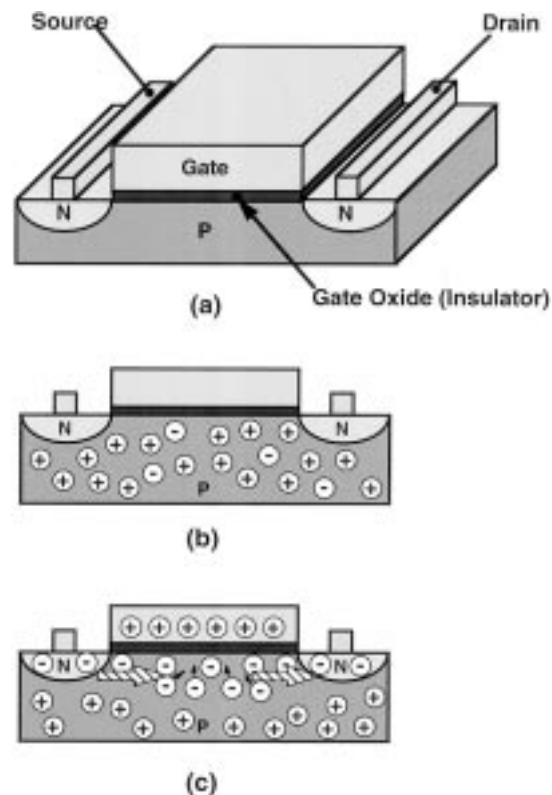
In digital circuits, the transistor usually is used as a two-state device, or switch. The state of a transistor can be used to set the voltage on a wire to be either high or low, representing a binary one or zero, respectively, in the computer. Logical and arithmetic functions are implemented in a circuit built using transistors as switches.

The transistor's second function in a computer is amplification. A small input electrical signal can control an output signal many times larger. Amplification allows signals to be transmitted through switches inside the computer without loss of strength [6]. The primary types of transistors in use today are the FET, in which a voltage is imposed on the device to control a second output voltage or current, and the bipolar junction transistor (BJT), in which a current is used to control another current.

### A. Structure and Operation of a MOSFET

The metal-oxide semiconductor FET (MOSFET) has been by far the most common type of transistor in modern microelectronic digital circuits, since Shockley's explanation of the device in 1952 [134], [135]. Properly designed MOSFET circuits use very little power and are economical to fabricate. As shown in Fig. 1, the field effect transistor has three terminals which are called the source, the drain, and the gate.

Although the novel designs that are discussed below for nanometer-scale electronic switching devices operate according to principles quite different from a MOSFET, all retain the same essential features: a source, drain, and (usually) a gate in the same conceptual roles as in a MOSFET. The channel through which current may flow from source and drain is altered more drastically in making the transition to nanoelectronic devices. Thus, to introduce the device components in a relatively familiar context and to establish a basis for comparison with conventional technology, we briefly explain the operation of a MOSFET.



**Fig. 1.** Schematic cross section of a NMOS transistor. (a) The transistor shown in the schematic cross section is the basic building block of microcomputers. (b) When there is no voltage applied to the gate electrode, no current can flow through the semiconductor. (c) However, when voltage is applied to the gate electrode, the electrons (negative circles) segregate from the holes (positive circles) to form a "channel" which permits current (large white hatched arrows) to flow between the source and the drain.

The name "metal-oxide-semiconductor field effect transistor" stems from its constituent materials. MOSFET's are built upon a crystalline substrate of the doped semiconductor silicon. Pure silicon is a very poor conductor, so dopant impurities, such as boron or arsenic, are introduced into the silicon to create an excess of mobile positive or negative charges. Negatively doped (N-doped) silicon contains free electrons that are able to move through the bulk semiconductor. Positively doped (P-doped) silicon contains electron vacancies, commonly known as "holes," which act as positive charges that move freely through the bulk material.

A metal electrode separated from the semiconductor below by an insulating oxide barrier serves as the gate of the MOSFET, whose voltage and associated electric field controls the flow of current from the source to the drain [27]. This is why the device is called a "field-effect" transistor. When the voltage on the gate is low, the region between source and drain contains few mobile negative charges, and very little current can flow. This is shown in Fig. 1(b). However, as illustrated in Fig. 1(c), increasing this voltage sufficiently attracts electrons to the region under the gate, opening the channel and allowing masses of electrons to flow from the source to the drain. This corresponds to a dramatic rise in current.

This distinct change in conductivity makes the MOSFET a two-state device. Since small changes of gate voltage result in large changes in conductivity, the MOSFET also can be used as an amplifier. Nanoelectronic devices for use in computers must function in these same two roles of two-state device and amplifier.

In the past, the most common way to make smaller electronic circuits has been simply to shrink the dimensions of all of the circuit components by a constant factor, a process called “scaling.” The MOSFET has remained popular because its operation changes very little and it maintains very favorable cost-to-performance ratios as it is scaled down to much smaller sizes. This scaling has proceeded at an exponential rate, doubling the number of transistors on a chip approximately every 18 months since the invention of the integrated circuit by Kilby in 1958. This has produced today’s commercial, mass-produced integrated circuits, such as Intel’s Pentium chip, which contains over 3.2 million transistors with a minimum feature size of approximately 350 nm [144]. However, as MOSFET’s reach minimum feature sizes of 100 nm and less, this rapid, cost-effective scaling of dense circuitry may not persist [7], [8].

### B. Obstacles to Further Miniaturization of FET’s

Despite formidable challenges, however, many of those in the research community and industry do envision close variants of conventional microelectronic transistors becoming miniaturized into the nanometer-scale regime [38]–[41], [171]. For example, the *The National Technology Roadmap for Semiconductors*, published by the Semiconductor Industry Association, projects that chips will be made from transistors with major features (gate lengths) of 70 nm in the year 2010 [21]. (Revisions of that document now in progress may be even more optimistic [44].)

Individual working transistors with 40 nm gate lengths have already been demonstrated in silicon [45], [46]. Transistors with gate lengths as small as 25 nm have been made using gallium arsenide [47]. It is unclear, though, whether such transistors can be made sufficiently uniform and reliable to build a densely integrated computer containing a billion or more of them. Additionally, a dense network of such transistors could be slowed down by the flow of current through extremely narrow wires from one device to the next. Detailed treatments of the fundamental limitations upon small electronic circuitry [4]–[9], [49] and of the scaling problem for FET’s may be found elsewhere in the literature [39], [109], including this issue of the *Proceedings* [43], [171].

However, to provide points of reference for contrasting nanoelectronic devices with scaled-down FET’s, a few of the obstacles to FET scaling are simply enumerated below, in increasing order of their intractability.

- *High electric fields*, due to a bias voltage being applied over very short distances, can cause “avalanche breakdown” by knocking large numbers of electrons out of the semiconductor at high energies, thus causing

current surges and progressive damage to devices [5], [6]. This may remain a problem in nanoelectronic devices made from bulk semiconductors.

- *Heat dissipation* of transistors (and other switching devices), due to their necessarily limited thermodynamic efficiency, limits their density in circuits, since overheating can cause them to malfunction. This is likely to be a problem for any type of densely packed nanodevices [133], [141], [142].
- *Vanishing bulk properties* and nonuniformity of doped semiconductors on small scales. This can only be overcome either by not doping at all (accumulating electrons purely using gates, as has been demonstrated in a GaAs heterostructure) [214] or by making the dopant atoms form a regular array. Molecular nanoelectronics is one path to the latter option.
- *Shrinkage of depletion regions* until they are too thin to prevent quantum mechanical tunneling of electrons from source to drain when the device supposedly is turned off [3]. The function of nanoelectronic devices is not similarly impaired, because it depends on such tunneling of electrons through barriers.
- *Shrinkage and unevenness of the thin oxide layer* beneath the gate that prevents electrons from leaking out of the gate to the drain. This leakage through thin spots in the oxide also involves electron tunneling.

The thermodynamic obstacle to FET scaling, heat dissipation, suggests that it would be desirable to find replacements for FET’s that might permit the construction of circuits that require fewer switching devices in order to perform the same functions. Below, it is discussed how alternative nanoelectronic devices can accomplish this.

Further, all but one of the other obstacles to scaling result from the simultaneous decrease in the effectiveness of doping and the increase in the significance of quantum mechanical effects. Once electronic devices approach the nanometer and the molecular scale, the bulk properties of solids are replaced by the quantum mechanical properties of a relatively few atoms. Properties associated with uniformly doped semiconductors will become less evident and influential in the operation of an electronic device. Quantum mechanical effects, such as energy quantization and tunneling, become much more significant. In order for a transistor-like device to operate on the nanometer-scale and, ultimately, on the molecular scale, it would be advantageous if it did not depend upon doped materials and if it operated based on quantum mechanical effects, rather than in spite of them [12]. This is the nature and the strength of the nanoelectronic alternatives to FET’s that are discussed below.

### III. SOLID-STATE QUANTUM-EFFECT AND SINGLE-ELECTRON NANO-ELECTRONIC DEVICES

A number of nanometer-scale solid-state replacements for the bulk-effect semiconductor transistor have been suggested to overcome the difficulties discussed above. All of these devices function by taking advantage of effects that

occur on the nanometer-scale due to quantum mechanics [129], [130], [151], [173], [174].

The essential structural feature that all of these devices have in common is a small “island” composed of semiconductor or metal in which electrons may be confined. This island of a nanoelectronic device assumes a role analogous to that of the channel in an FET. As is explained in greater detail below, the extent of confinement of the electrons in the island defines three basic categories of solid-state nanoelectronic devices.

- *Quantum Dots* (QD’s or “artificial atoms”) [28], [57], [58], [140], [156], [216], [217], [218], [219], [220]. Island confines electrons with *zero* classical degrees of freedom remaining.
- *Resonant Tunneling Devices* (RTD’s) [20], [28], [123], [124], [180]. Island confines electrons with *one or two* classical degrees of freedom.
- *Single-Electron Transistors* (SET’s) [15], [23], [76], [125]. Island confines electrons with *three* classical degrees of freedom.

The composition, shape, and size of the island gives the different types of solid-state nanoelectronic devices their distinct properties. Controlling these factors permits the designer of the device to employ quantum effects in different ways to control the passage of electrons on to and off of the island. For example, the mean free path of mobile electrons can be much greater in semiconductors than in metals. Thus a mobile electron might travel coherently all the way across a semiconductor island, without severe collisions. This means that conductivity of a device can be strongly enhanced or suppressed by quantum mechanical interference between separate paths an electron might take through the device.

As is well known, microelectronic devices are made primarily from silicon (Si), an element in group IV of the periodic table. Presently, however, most solid-state nanoelectronic devices incorporate semiconductors made from combinations of elements from groups III and V of the periodic table—e.g., gallium arsenide (GaAs) and aluminum arsenide (AlAs) [29], [124]. The mobilities of electrons are higher in these III–V semiconductors [132], and it is also easier to fabricate defect-free junctions between different III–V semiconductors than it is for junctions between two group IV semiconductors, such as Si and Ge.

#### A. Islands, Potential Wells, and Quantum Effects

The smallest dimension of the island in a solid-state nanoelectronic device ranges from approximately 5–100 nm. The island may consist of a small region or layer different from the surrounding material. Otherwise, edges of the island may be defined by electric fields from small electrodes patterned in the shape of the desired island boundary. Often, the island is embedded between two narrow walls of some other material, or an insulating oxide of the island material, or an insulating defect zone in the substrate. In any case, therefore, the island is surrounded by potential energy barriers, which impede the movement of

electrons in and out of the island region. This is illustrated in Fig. 2, in which the energy barriers arise from walls of a different material.

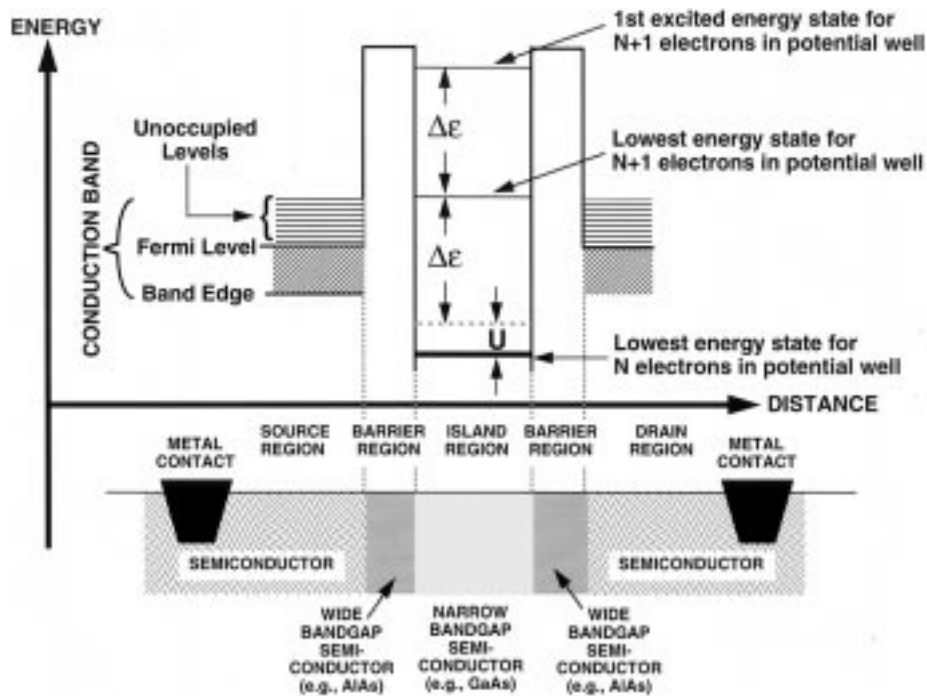
Within the island, mobile electrons will tend to form a puddle that usually is much smaller than the dimensions of the island. The puddle is surrounded by a depletion region that forms (for example) because electrons in the puddle are repelled from surface charges that collect on the boundaries of the island. Thus, the physical features that form the island may have to be fabricated many times the size of the useful region for electron confinement [156]. This is one factor that works against the miniaturization of such quantum-effect and single-electron solid-state devices. (Despite the fact that the depletion region confines mobile electrons to only a portion of the island, we shall not make a distinction in our terminology between the shape and size of the island and those of the potential well for electrons on the island.)

Two essential quantum mechanical effects are exhibited by electrons confined to nanometer-scale islands between closely spaced potential energy barriers [16], [124], [129], [176]. First, quantum mechanics restricts each electron’s energy to one of a finite number of one-electron energy levels (quantum states with discrete, “quantized” energies). The smaller the distance between the barriers (i.e., the smaller the island), the more widely spaced in energy are the levels for the electrons in the potential well between the barriers. In Fig. 2, the symbol  $\Delta\epsilon$  is used to represent the energy spacing between two energy levels in such a potential well.

Second, if the potential barriers are thin enough (approximately 5–10 nm or less, depending on the height of the barriers), electrons occupying energy levels lower than the height of the barrier have a finite probability of “tunneling” through the barrier to get on or off the island. However, for an electron of a given energy to tunnel through a barrier, there must be an empty state with that same energy waiting on the other side.

These two effects, energy quantization and tunneling, strongly influence the flow of electrons through a nanoelectronic device. When a bias voltage is applied across the island, it induces mobile electrons in the conduction band of the source region to attempt to move through the potential well in the island region to get to the region of lower potential in the drain region. The only way for electrons to pass through the device is to tunnel on to and off of the island through the two high potential barriers that define the island and separate it from the source and the drain..

But tunneling can occur and charge can flow toward the drain only if there is an unoccupied quantum energy level in the well at an energy that matches one of the occupied energy levels in the source band. (In extended systems, such as the bulk metals or semiconductors in the source and drain, the allowed energy levels for electrons are so closely spaced that they form bands over a range energies, in contrast to the discrete energy levels in a single atom or in a nanometer-scale potential well. As shown schematically in Fig. 2, the electrons occupying the source conduction



**Fig. 2.** Quantum well for a resonant tunneling diode (RTD). The barrier regions around the island in the RTD shown at the bottom of the figure create the potential energy “well” graphed in the top part of the figure. Energies of the electrons trapped in the well on the island are “quantized”—they can only have the energy states or “levels” shown. Mobile electrons in the source region (and the drain region) occupy the energy levels between the band edge and the Fermi level, with unoccupied energy levels above that in energy. If  $N$  mobile electrons are on the island, the energy cost of adding one more from the source has two components: the charging energy  $U$ , plus the excitation energy  $\Delta\epsilon$ . For an RTD,  $U$  usually is even smaller, relative to  $\Delta\epsilon$ , than is shown in the figure.

band range continuously in energy from that of the lowest energy level in the band at the “band edge” to the level of the highest energy conduction electrons at the “Fermi level”).

As is also shown in Fig. 2, a similar energy band contains the conduction electrons on the drain, and usually there are many available unoccupied one-electron quantum states at energies above this band, as well. So, once an electron is able to tunnel from the source to the island under a bias, it is usually free to complete its passage through the device by tunneling once again from the well onto the drain.

### B. Resonant Tunneling Devices

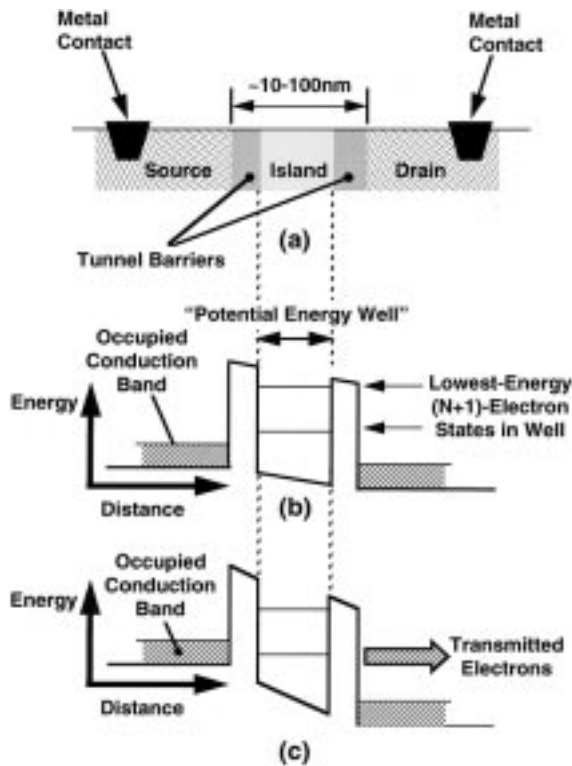
Although resonant tunneling devices [16], [28], [123], [124] were not the first category of solid-state nanoelectronic device listed above, we explain their operation in detail first, because it illustrates energy quantization and tunneling in their simplest form.

It is crucial to the operation of resonant tunneling devices (and the other categories of nanoelectronic devices) that the energy of the quantum states in the potential well on the island can be adjusted relative to the energy of the bands in the source and drain. An example of this is diagrammed in Fig. 3 for the two-terminal nanoelectronic device shown in Fig. 3(a). Increasing the applied voltage bias across the device progressively lowers the energy of all the states in the well relative to the energies the electrons in the source. This is shown in Fig. 3(b) and (c).

When the bias potential is sufficient to lower the energy of an unoccupied one-electron quantum state inside the well to be within the range of energies for the source conduction band, the quantum well is said to be “in resonance” or “on,” and current can flow onto the island and out to the drain. This is shown schematically in Fig. 3(c). Otherwise, current through the device is blocked—the device is “out of resonance” or switched “off,” as in Fig. 3(b). This use of a variable applied bias to switch a tunneling current on and off characterizes the operation of a two terminal resonant-tunneling device called a resonant-tunneling diode or RTD.

Similar adjustment of the energy levels in the potential well relative to those in the source also can be achieved by varying the voltage on a third (gate) terminal, rather than the voltage on the source. This is illustrated in Fig. 4. In this three-terminal configuration, shown in Fig. 4(a) and termed a resonant tunneling transistor (RTT), a small gate voltage can control a large current across the device [Fig. 4(b) and (c)]. Thus, an RTT can perform as both switch and amplifier, just like the conventional MOSFET described above.

Actually, nanometer-scale, quantum-effect devices such as these can have switching properties that are superior in some ways to those of MOSFET’s. RTD’s and RTT’s can have *multiple* on and off states associated with multiple discrete quantum levels inside the potential well on a very small or very narrow island. If these levels are spaced

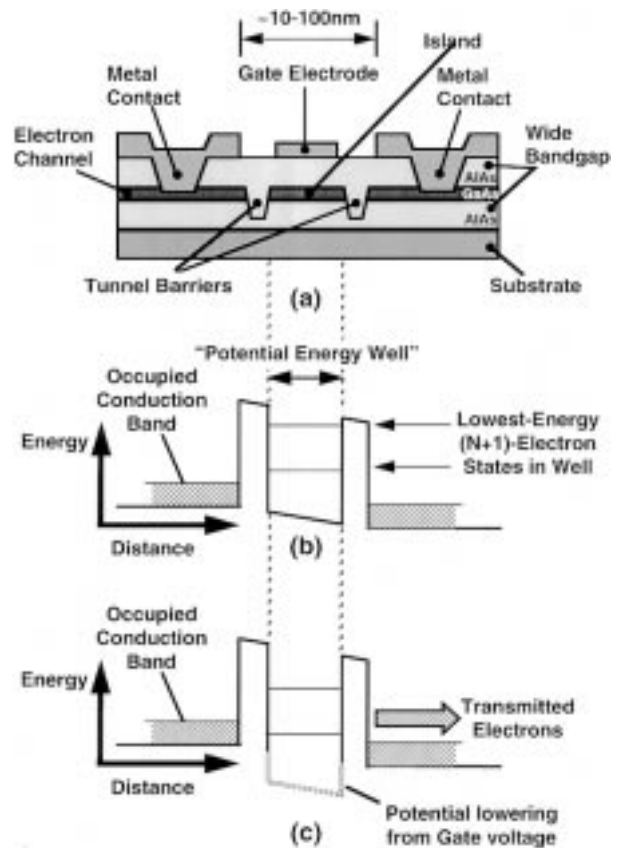


**Fig. 3.** Schematic of cross section and operation for an RTD. (a) RTD, shown in cross section, consists of a small island region between thin barriers. (b) Barriers create a potential well around the island, and usually prevent charge from flowing through the device, even when it is under a small voltage bias (downward slope in energy from source to drain), as shown. (c) Increasing the bias shifts down the energy for all the states in the well and brings them into resonance with the mobile electrons in the occupied conduction band in the source, so that an electron current can be transmitted through the device.

widely enough in energy (that is, if  $\Delta\epsilon$  is greater than the energetic difference between the band edge and the Fermi level for the source), then each of the different levels in the well can be brought successively into and out of resonance with the source conduction band in succession, as the bias voltage (or gate voltage) is increased.

These multiple on and off states are illustrated for an RTD in Fig. 5. The peaks in the plot correspond to the alignment of the energy levels in the well with the occupied part of the conduction band for the source. The current falls off between the peaks on the curve as the voltage is varied to make the energy of a quantum level in the well pass below the energy of the conduction band edge.

Two current peaks are shown in Fig. 5(b), corresponding to resonance with each of the two energy states in the potential well shown in Fig. 5(a). Comparable multistate behavior can be obtained by varying the gate voltage in an RTT [20], [124], [176], [179]. Fewer devices are required to implement a given logic function when using such multistate devices rather than two-state MOSFET's. This generates circuitry with a higher density of logic functions per switching device [20], [110], [177]. (Fewer devices per logic function could also imply less heat dissipation per function, which might help these nanoelectronic devices

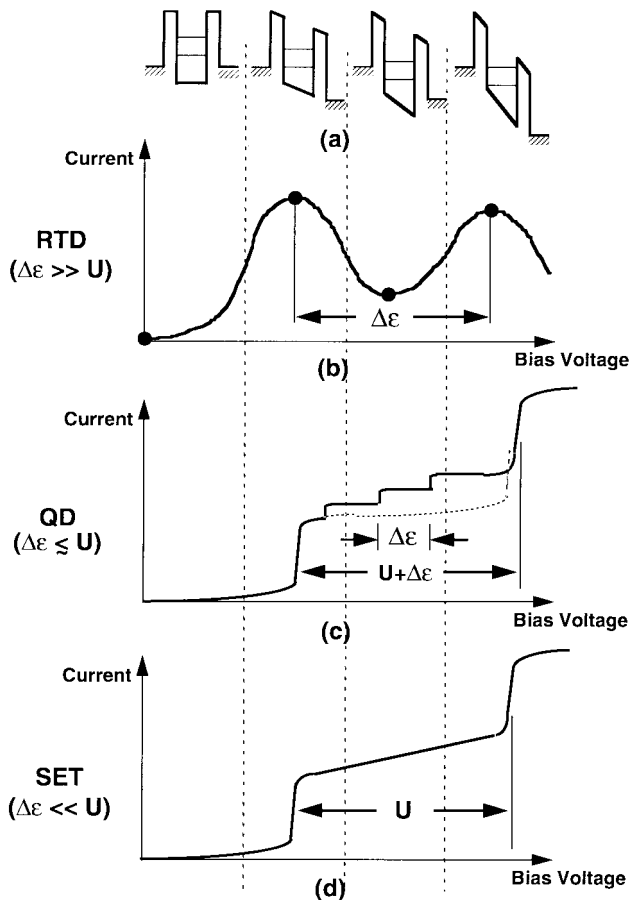


**Fig. 4.** Schematic of cross section and operation for the resonant tunneling transistor (RTT). (a) Cross section is for a lateral RTT of the type constructed by Randall *et al.* [155]. (b) Barriers in device create potential well around the island, and usually prevent charge from flowing through the device, even when it is under a voltage bias (downward slope in energy from source to drain), as shown. (c) Potential well has configuration similar to that for the RTD shown in Fig. 3 until the gate electrode is charged, lowering the energy for all the states in the well and bringing them into resonance with the mobile electrons in the occupied conduction band in the source, so that an electron current can be transmitted through the device.

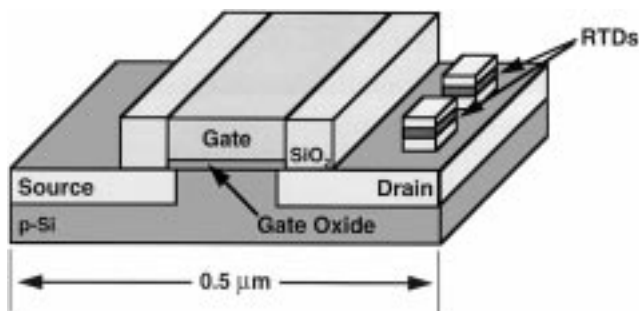
circumvent one of the FET scaling problems enumerated above.)

This advantage for logic that includes quantum-effect devices has led investigators to build *hybrid* microelectronic-nanoelectronic devices, in which tiny quantum-effect RTD's are built into the drain (or source) of a micron-scale MOSFET. A schematic of such a device is shown in Fig. 6. The hybrid RTT also exhibits multistate behavior—the drain current can be switched on and off several times for various values of the bias voltage. Thus, the logic density of circuitry containing such hybrid devices can be made much higher without a significant decrease in the feature sizes on the chip [20], [178], [179].

Fabricating circuits with this relatively large, hybrid type of three-terminal RTT is easier than fabricating circuits with the much tinier, complex structures for purely nanoelectronic RTT's, such as the one shown in Fig. 4. For this reason a number of groups are experimenting with such devices. Seabaugh *et al.* have constructed such devices, used them in circuitry [20], [78], [180]–[183] and even



**Fig. 5.** Current ( $I$ ) versus bias potential ( $V$ ) plotted for three categories of solid-state nanoelectronic devices. (a) Snapshots of the variation in the quantum well due to the change in the applied bias potential; (b)  $I$  versus  $V$  plot for RTD; (c)  $I$  versus  $V$  plot for QD; (d)  $I$  versus  $V$  plot for SET.



**Fig. 6.** Schematic of hybrid RTD-FET. Nanometer-scale RTD's are built into the drain of a micron-scale FET, creating a "hybrid" microelectronic-nanoelectronic device which has more logic states than a regular FET and is easier to build into circuitry than the tiny RTD.

demonstrated their operation at room temperature [178]. Hybrid logic can be viewed as a practical engineering step on an evolutionary path toward nanoelectronics. It could accelerate the availability of quantum-effect devices in integrated circuits with very dense functionality.

This progress on resonant tunneling devices is based upon research dating back to the early 1970's, when Esaki and his collaborators first reported the observation and use of

the resonant tunneling effect in a device. However, for nearly a decade, such devices were thought to be limited by problems such as low current density on-resonance, until work on RTD's by Sollner and his collaborators [96] at the MIT Lincoln Laboratory demonstrated otherwise. That breakthrough and the results of simultaneous investigations by Reed [97] led Capasso and Kiehl [123] to develop an early RTT. Work on resonant tunneling devices is being carried on by a number of groups [16], [176], [211], with particular progress on the hybrid RTT's and circuitry by Seabaugh and his collaborators at Texas Instruments [20], [78]. Also notable is MIT Lincoln Laboratory's construction of a fabrication facility that is producing very large scale integration (VLSI) wafers containing large numbers of RTD's in high-speed circuits intended for digital signal processing applications [77], [93].

### C. Distinctions Among Types of Devices: Other Energetic Effects

To explain the distinctions among the three broad categories of devices (QD's, RTD's, and SET's), we must admit that the factors determining the energy of electrons on a small island are somewhat more complicated than is explained above. To begin with, since an island may have different dimensions along each axis— $x$ ,  $y$ , and  $z$ —the electron's energy levels may be quantized separately in each direction—with spacings  $\Delta\epsilon_x$ ,  $\Delta\epsilon_y$ , and  $\Delta\epsilon_z$ , respectively.

To further complicate things,  $\Delta\epsilon$  is calculated for a hypothetical lone electron on the island, ignoring repulsive interactions that occur when more than one electron resides there. In fact, an extra ( $N+1$ )st electron attempting to enter an island that was not previously empty needs extra energy to overcome its electrostatic repulsion with the  $N$  electrons already on the island. This energy of repulsion or "charging energy" is symbolized on Fig. 2 by the letter  $U$ .

As shown in the figure, the total difference in energy between the lowest quantum state for an island with only  $N$  mobile electrons and the lowest quantum state for an island with  $N+1$  mobile electrons is the *sum* of  $U$  plus  $\Delta\epsilon$ . The requirement for the additional amount of energy  $\Delta\epsilon$ , beyond the charging energy, arises from the Pauli exclusion principle. Even when repulsive interactions are ignored, the exclusion principle prohibits the ( $N+1$ )st electron from occupying the same one-electron energy state as any of the electrons already on the island. Thus, this extra electron must be elevated in energy by  $\Delta\epsilon$  to the next higher noninteracting one-electron quantum state.<sup>1</sup>

The relative sizes of  $U$  and  $\Delta\epsilon$  are sensitive to the shape and size of the island. Shorter dimensions have larger  $\Delta\epsilon$  (they are more strongly quantized), while longer dimensions

<sup>1</sup>Not every new electron added to the island of an RTD will require an additional amount of energy  $\Delta\epsilon$ . Electrons on an RTD's island have extra degrees of freedom, such as motion along the island's long axes, or spin. Hence, if we can neglect the charging energy  $U$ , multiple electrons can occupy the island all at essentially the same energy. But after all these closely packed states have been filled, an extra energy  $\Delta\epsilon$  (determined by the island's shortest dimension) is needed to add the next electron. Thus, the  $I$ - $V$  characteristics are still dominated by the island's shortest dimension, as claimed in the main text.

have smaller  $\Delta\epsilon$  (the allowed quantum-mechanical energies are more nearly continuous). For our purposes,  $\Delta\epsilon$  varies inversely as the square of the shortest dimension of the island. Shorter dimensions and smaller islands also increase  $U$ , which varies inversely as  $R$ , the effective radius of the island, which may be approximated by its longest dimension. Viewed another way,  $U$  grows large as the mean distance  $\langle r \rangle$  between pairs of mobile electrons on the island grows small—i.e., as the electrons are squeezed close together. So long as the island has at least one long dimension, electrons can spread out along that axis to avoid each other and keep  $U$  small. In contrast, even one short dimension is enough to create a large effective  $\Delta\epsilon$ .

Thus, since the relative magnitudes of  $U$  and  $\Delta\epsilon$  govern device behavior, and the island shape strongly influences the relative magnitudes of these two energies, island shape is a convenient basis for distinguishing the three categories of solid-state nanoelectronic devices. On that basis, we can reconsider the resonant tunneling devices discussed above and contrast them with the other categories of nanoelectronic devices.

#### D. Taxonomy of Nanoelectronic Devices

1) *Resonant Tunneling Devices Further Explained:* A resonant-tunneling device [16], [28], [123], [124] usually has a long and narrow island (i.e., a “quantum wire” or “pancake”) with shortest dimension 5–10 nm [184]. The island is made from a semiconductor containing many mobile electrons. The short dimension(s) make  $\Delta\epsilon$  large, while the large dimension(s) keep  $U$  small. (That is,  $\Delta\epsilon \gg U$ .) This means that the spacings between allowed energies of collections of electrons on the island are determined solely by  $\Delta\epsilon$ , because  $U$  is a negligible term in calculating the total energy  $U + \Delta\epsilon$  for adding an electron to the island. Thus, when a resonant-tunneling device is subject to a voltage bias between the source and the drain, it produces a current versus voltage plot like that sketched in Fig. 5(b), in which the distance between current peaks is dominated by  $\Delta\epsilon$  and there is little effect of the charging energy observable. Fig. 5 also contrasts the current versus voltage behavior of a resonant tunneling diode with the behaviors of a QD and an SET, both discussed in greater detail below.

2) *Quantum Dots (QD's):* QD's are constructed with islands that are short in all three dimensions, confining the electrons with *zero* classical degrees of freedom—electronic states are quantized in all three dimensions. The dot-like island may be made of either metal or semiconductor. It can consist of small deposited or lithographically defined regions [218]; small, self-organized droplets [219], [220]; or nanocrystallites grown *in situ* or deposited in a film [216], [217]. Using the physical ideas outlined above, we observe that making an island short in all three dimensions leads to widely spaced quantum energy levels for an electron on the island—i.e.,  $\Delta\epsilon_x$ ,  $\Delta\epsilon_y$ , and  $\Delta\epsilon_z$  are all large. The charging energy  $U$  is also large, because there is no way for a pair of electrons to get far from each other. As a result, both the interaction among the electrons on a QD and the energy

levels for each individual electron influence the flow of current through the dot. A schematic plot of current versus voltage for a typical QD is shown in Fig. 5(b). Because  $U$  and  $\Delta\epsilon$  are comparable in magnitude, a sequence of steps in current associated with each of the two energy scales is observed as the bias voltage is varied. The current jumps to a finite value when electrons can first travel through the island one at a time, and further large jumps herald the ability of electrons to go through two, then three at a time. This series of jumps in current is spaced by a voltage proportional to  $U$ . The smaller and more frequent jumps occur when an electron can travel across the dot not just in the island's lowest-lying vacant quantum state but also in one or more excited states. The more paths available, the greater the current flow.

In the category of QD's we include individual dots, also known as “artificial atoms” [28], [140], [156], as well as coupled dots (“quantum-dot molecules”) [184], and a kind of composite device called a “QD cell,” in which four or five QDs form a single two-state device. (QD cells [185], the clever logic designs based upon them [18], and related composite structures that might be built from QD's [186] are beyond the scope of this overview. However, they are discussed in detail elsewhere in this issue of the *Proceedings* [187].)

3) *Single-Electron Transistors:* A single-electron transistor (SET) [15], [125] is always a three-terminal device, with gate, source, and drain, unlike QD's and RTD's, which may be two terminal devices without gates. An SET switches the source-to-drain current on and off in response to small changes in the charge on the gate amounting to a single electron or less (hence, the name). Unfortunately, the terms SET and QD are sometimes used interchangeably in the literature. But we will draw a clear distinction between the two based on the number of classical degrees of freedom retained by electrons on the island, zero for the QD and three for the SET, and the difference in behavior that results.

SET's are based around an island, usually of metal, and usually containing a million or more mobile electrons. As opposed to a QD or RTD, an SET's island has no very short dimension and no very long one, either. Nonetheless, QD's may be physically just as large as SET's—what counts as “short” or “long” depends strongly on the materials used. An island with “short” dimensions will have well-separated quantized energy levels for electrons, but in a semiconductor this may occur at lengths of 100 nm while for metals the lengths must be at least ten times smaller. Hence, making “small” metal particles requires heroic efforts [92]. Since  $U$  is much less sensitive than  $\Delta\epsilon$  to choice of material for the island, this choice may be used to tune the relative sizes of the two energies. Metal islands emphasize  $U$  over  $\Delta\epsilon$ , another defining characteristic of SET's. This limit is called “Coulomb blockade,” since the Coulomb interactions among electrons (represented in  $U$ ) block electrons from tunneling onto the island at low bias voltage. As depicted schematically in Fig. 5(d), the current versus potential curve for a biased SET exhibits

only thresholds associated with  $U$ , not with  $\Delta\epsilon$ , which is negligibly small for such a device.

Increasing the gate voltage for an SET to a critical value suddenly allows current to flow from source to drain, but a further increase turns off the current just as suddenly. Additional increases in gate voltage repeat this on/off cycle [15], [125], [140], [188]–[192]. Despite these similarities to an RTD, SET's operate according to a completely different physical principle.

Electrons could, in principle, tunnel onto the island one at a time from the source, and then off onto the drain. This would produce a measurable flow of current. However, extra electrons generally cannot tunnel onto the island due to the electrostatic repulsion of the electrons already there, so no current flows. This Coulomb blockade is a classical effect, depending on the island being sufficiently isolated that an electron cannot quantum mechanically spread over both the island and the source or drain. Recall that in RTD's the opposition to current flow depends on quite different quantum mechanical effects, though the result appears quite similar.

In order to control the number of electrons on the island, a metal gate electrode is placed nearby. A sufficient increase in the voltage of the gate electrode induces an additional electron to tunnel onto the island from the source. The extra electron soon tunnels off onto the drain. This double-tunneling process repeats millions of times a second, creating a measurable current through the island. Since the current between the source and drain is sensitive to the charge of single electrons on the gate, the amplification ratio, or "gain," can be extremely high.

As the gate voltage is increased further, the number of electrons on the island stabilizes at a value one higher than before, and again no current flows. Yet further increases in gate voltage cause more electrons to migrate to the island, and each one-electron increase is heralded by a spike in current flow. Thus, in contrast to the RTD, which exhibits peaks in a plot of the current versus the *bias* voltage, an SET would exhibit current peaks similar to those in Fig. 5(b) in a plot of current versus its *gate* voltage.

At high temperatures, however, the thermal energy of electrons in the source and drain may overcome the Coulomb blockade, allowing electrons to tunnel onto the island and current to flow under all gate voltage conditions. Thus far, the low temperatures needed to preserve the SET's ability to switch current on or off have been a major obstacle to their practical application. Sufficiently small SET's would work even at room temperature, though. A group at NTT in Japan has succeeded in making such an SET only 30 nm across. It exhibits clear periodic modulations in source-drain current due to Coulomb blockade at 150°K [193], [194]. This is well above the temperature of liquid nitrogen, a relatively cheap coolant which boils at 77°K. The NTT work eventually could lead to more routine use of SET's, and even allow their operation at room temperature (300°K).

### E. Drawbacks and Obstacles to Solid-State Nanoelectronic Devices

As is often the case with successful research investigations, the considerable progress that has been made to date in fabricating and testing solid-state nanoelectronics has illuminated a number of challenging issues and areas for still further study. We enumerate and discuss these issues below in order of the degree of challenge these issues seem to pose to future progress, with the most difficult to resolve issues listed last.

- *Valley Current:* Multistate quantum-confinement devices, like RTD's, do not turn off their current completely when they are off-resonance. There is a residual current in the valley between the current peaks, as seen clearly in Fig. 5(b). This can lead to the possibility of the on and off states not being clearly distinguishable. Circuit architectures must be designed to be tolerant of this potential sensitivity, and, more importantly, devices must be carefully and precisely built to make the peak-to-valley current ratio as large as possible [16], [20].
- *Sensitivity to Input Voltage and Current Fluctuations:* Landauer [101] has pointed out that, unlike in FET's, switching in RTD's or RTT's can be very sensitive to fluctuations in the input voltages, which could accidentally drive devices off-resonance.
- *Cryogenic Operation:* It has been possible to build circuits with hybrid RTD-FET's operating at room temperature [20]. Individual 30 nm silicon SET's show strong oscillations of current versus gate voltage at 150°K (half of room temperature on an absolute scale) [193], [194]. However, most nanoelectronic devices built to date are functional only at cryogenic temperatures—the boiling point of liquid nitrogen and well below. At high temperatures, random thermal motion often provides electrons with the small additional energy they need to get onto the island. Making islands smaller, however, would increase the relevant energy separation  $U$  or  $\Delta\epsilon$  for states on the island, thus reducing the possibility of the device switching on when it should be off. Extrapolating, a device based on an island the size of a single atom (approximately 0.1 nm in radius) could operate at 100 times room temperature (if it would not melt!), but this limit only can be approached with molecular electronics.
- *Materials: III–V Semiconductors Are Less Than Satisfactory and Si Nanoelectronics Are Needed:* Further progress must be made toward fabricating solid-state nanoelectronic devices in silicon rather than in III–V semiconductors. Different III–V semiconductors can be grown in atomically perfect crystalline sandwiches. By contrast, producing clean junctions and barriers in Si-based semiconductors is difficult, because the natural insulator in Si, SiO<sub>2</sub>, is amorphous rather than crystalline, and also tends to have many more impurities than III–V layers do. But SiO<sub>2</sub> is still the best insulator and barrier we have: as little as 5 nm

can be grown uniformly and will prevent electrons from crossing despite several volts applied across it (less than this can be grown as a tunnel barrier). III–V equivalents are far inferior in the electric fields they can withstand. Moreover, despite III–V materials' ultraclean buried interfaces, their exposed top surface will always become contaminated with stray, perhaps mobile, charges, which degrade the stability of devices. In Si applications, thick oxides are always grown to protect devices from such problems. Heterostructures made from Si-based materials, particularly sandwiches of Si/SiGe, are emerging as a promising alternative offering the best of both worlds [215].

- *Background Charge Problem*: Likharev [23], [70] and other investigators have noted that random background charges tend to accumulate in semiconductors in the vicinity of a small operating quantum-effect or single-electron device. These can render the device inoperable. Improved materials are needed to reduce the impact of this effect. Silicon-on-insulator (SOI) technology [194] might be of assistance, as might the relatively nonconductive, nonpolarizable organic compounds that could be used with molecular electronics.
- *Extreme (Exponential) Sensitivity of the Tunneling Current to Width of Potential Barriers* [16], [20]: This is a difficulty intrinsic to the quantum mechanical tunneling effects employed in all the solid-state nanodevices we describe. Its impact can only be mitigated by ensuring that all nanometer-scale barriers are made with extreme precision and uniformity in width [20].
- *Extreme Difficulty of Making Islands and Tunnel Barriers Precisely and Uniformly in Solid-State Devices* [156]: Sufficient precision and uniformity to ensure reliable, predictable behavior of large numbers of devices are very difficult to achieve on a several-nanometer scale in solids. Even the aforementioned heterostructure sandwiches can only achieve such precision in one of the three dimensions [215].

On the other hand, devices made from individual electrically active molecules supported on organic substrates may offer solutions to some of the more serious issues just enumerated, including accumulation of background charge, imprecision or irreproducibility of lengths, and the inability to make small enough quantum confinement structures to achieve room-temperature operation [36].

#### IV. MOLECULAR ELECTRONICS

Molecular electronics uses primarily covalently bonded molecular structures, electrically isolated from a bulk substrate [17], [25], [32], [33], [35]–[37], [59], [69], [146]. Devices of this description, wires and switches composed of individual molecules and nanometer-scale supramolecular structures, sometimes are said to form the basis for an “intramolecular electronics” [17]. (This is to distinguish them from organic microscale transistors and other organic devices that use bulk materials and bulk-effect electron transport just like semiconductor devices. See, for example, [60]–[63].)

As indicated above, solids have the significant disadvantage that it is relatively difficult and expensive to fabricate or “sculpt” in them the many millions or billions of nearly identical nanometer-scale structures that will be needed in each ultra-dense computer chip. Individual molecules, natural nanometer-scale structures, easily can be made *exactly the same* by the trillions of billions. The great power and variety of organic chemistry also should offer more options for designing and fabricating nanometer-scale devices than are available in silicon [14], [30], [31], [33], [35], [36]. Increasingly, this is driving investigators to design, model, fabricate, and test individual molecules [32], [75], [98], [105], [138], [154], [164], [166], [168], [195], [196] and nanometer-scale supramolecular structures [112], [126] that act as electrical switches and even exhibit some of the same properties as small solid-state transistors [98]. Molecular electronics does remain a more speculative research area than solid-state nanoelectronics, but it has achieved steady advances consistent with Aviram's strategy [34] for making molecular electronic circuits viable, inexpensive, and truly integrated on the nanometer scale.

##### A. Molecular Electronic Switching Devices

After more than two decades of work, at least four broad classes of molecular electronic switching devices can be distinguished in the research literature:

- *electric-field controlled molecular electronic switching devices*, including molecular quantum-effect devices [36];
- *electromechanical molecular electronic devices*, employing electrically or mechanically applied forces to change the conformation [98] or to move a switching molecule or group of atoms [121], [170] to turn a current on and off;
- *photoactive/photochromic molecular switching devices* [14], [36], [56], [64]–[66], which use light to change the shape, orientation, or electron configuration of a molecule in order to switch a current;
- *electrochemical molecular devices* [67], [68], [121], which use electrochemical reactions to change the shape, orientation, or electron configuration of a molecule and hence to switch a current.

Many examples and details about the various types of molecular electronic devices are provided in the references cited above and elsewhere [107], [108].

Here, however, we shall focus primarily on the first two categories of molecular electronic devices. The electric-field controlled molecular electronic switches are most closely descended from the solid-state microelectronics and nanoelectronic devices described above and promise to be the fastest and most densely integrated of the four categories. The electromechanical molecular switching devices are also promising, since they too could be laid down in a dense network on a solid substrate.

Each of the other two categories, while quite promising in general, has a major drawback for use in nanocomputers. Photoactive devices in a dense network would be difficult

to switch individually, since light cannot be easily confined on length scales very much below its wavelength (approximately 500 to 1000 nm). Electrochemical molecular devices would likely require immersion in a solvent to operate.

Before we discuss specific device designs, however, we provide some additional background information, plus a discussion on the key topic of the molecular wires that will be needed to link together such molecular switches.

### B. Brief Background on Molecular Electronics

1) *History*: The search for individual molecules that would behave as electrical switches began in 1974, with the pioneering work of Aviram and Ratner, who proposed a theory on molecular rectification [197]. Research on molecular electronics was stimulated in the early 1980's by such visionaries as the late Forrest Carter [30], [31], [95] and by some notable research efforts later in the decade [136]. Aviram's further work in the late 1980's and early 1990's [32], [34] helped enlist a new cadre of investigators and establish a plan for the development of the field.

Finally, in the 1990's, interest in the field has grown rapidly. Tour *et al.*, have synthesized the spiro-switch proposed by Aviram [166], [196], and different variants of the molecular rectifier have been made [74], [148]. Much work has been done to measure [48], [138], [158], [159], [195], [209] the conductance and other electrical properties of individual molecules or to model [105], [137]–[139], [152]–[154] them. This growth has been driven by recognition of the need for ultra-miniaturization of electronics, and it has been catalyzed by the wide availability of sensitive new methods for imaging, manipulating, and fabricating molecular and supramolecular structures.

2) *Role of New Methods for Nanomanipulation and Nanofabrication*: Although the structure and workings of molecular electronic devices are emphasized in this overview, no discussion of molecular electronics can ignore the exciting new methods for nanofabrication that have made research on molecular electronics feasible and important. Especially significant are the methods for *mechanosynthesis* [198], [199] and *chemosynthesis* [55] of nanometer-scale structures. Mechanosynthesis is the fabrication of nanostructures molecule by molecule using nanoprobes [54], such as the scanning-tunneling electron microscope (STM), the atomic force microscope (AFM), and the new microelectromechanical systems (MEMS) chips that contain arrays of these STM's and AFM's [73], [106].

These sensitive new tools, invented in the 1980's [119], [120], have opened a plethora of new experimental possibilities with molecules. Nanoprobes also have provided realtime visual and tactile feedback and an increased sense of contact with the behavior of the molecular-scale experimental systems that are essential for progress in molecular electronics. By providing a means to image and manipulate individual atoms and molecules, STM's and AFM's have given much impetus to research on molecular electronics. The topic of nanoprobes is discussed more thoroughly in other papers in this issue [85], [87].

Chemosynthesis includes the growing study of the chemical "self-assembly" of nanostructures [71], [72], which also is having considerable impact on the fabrication of solid-state circuit elements. It also includes the application of methods borrowed from biochemistry and molecular genetics [50]–[52], as well as creative and elegant organic syntheses of molecular electronic devices in individual organic molecules [111], [113], [164], [166], [196]. As one example of the application of chemosynthetic self-assembly to molecular electronics, we note that Martin *et al.*, used a self-assembled Langmuir–Blodgett film [148], [162] to demonstrate molecular rectification of the type first suggested in Aviram's and Ratner's theory. Also, in very promising recent work, an interdisciplinary group at Purdue University, West Lafayette, IN, has used self assembly to fabricate and demonstrate functioning arrays of molecular electronic quantum confinement structures connected by molecular wires [112], [200].

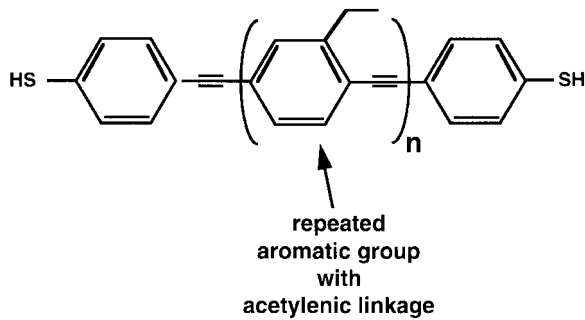
### C. Molecular Wires

The subject of molecular wires is of primary significance, even in an overview of nanoelectronic switching devices. Before one can seriously discuss such electronic devices embedded in single molecules, one must deal with the question of whether a small single molecule can conduct appreciable current. The answer to this question was in doubt, because very narrow wire-like structures often exhibit high resistance, even if they are made from substances that conduct electricity when they are present in bulk. However, a series of very difficult and sensitive experiments [48], [138], [195] and theoretical investigations [105], [137], [139], [152]–[154] over the past few years have answered this question affirmatively.

Extensive experimental work on buckyballs by Joachim and his collaborators established conclusively that one such molecule conducts a current [138]. In very recently reported results, Joachim and Gimzewski have even shown resonant tunneling through a quantum well in a single buckyball, although the switching required deforming the well electromechanically with an STM [98].

Fig. 7 depicts the structure of a molecular wire invented by Tour [164] that was used recently to demonstrate conductance in a single molecule [195]. In that experiment [195], one end of the conducting molecule was adsorbed to a gold surface, but an STM tip was used as the other electrode in the circuit. However, in more recent work by Reed and Tour, each end of a conducting molecule was adsorbed to a different gold electrode mounted on a surface in order to complete a circuit [158], and even to demonstrate quantum-device effects [159]. Wires of this general type also were used in the Purdue self-assembled molecular electronic circuit array mentioned above, in which the characteristic "staircase" pattern of Coulomb blockade [cf. Fig. 5(d)] was observed at room temperature in the plot of current versus bias voltage [112], [126].

The thiol (-SH) functional groups at either end of the molecular wire structure in Fig. 7 adsorb well to gold surfaces and act as "alligator clips" for attaching molecular



**Fig. 7.** Molecular wire. Chain molecule composed of repeating units bound together by conjugated  $\pi$ -bonds was demonstrated to conduct electrical current [195].

electronic units to metal substrates [168], [201]. Such molecular wires also have the desirable property that they can be made quite long, if necessary, because they can be lengthened systematically using chemosynthetic methods [164].

Wires like the one illustrated in Fig. 7 are characterized by extended repeating structures—here a sequence of benzene-like rings connected by acetylene linkages—each part of which is linked to the next by bonds including many  $\pi$ -electrons above and below the plane of the structure. These orbitals or clouds of  $\pi$ -electrons [173] conjugate with each other, or interact, to form a single large orbital throughout the length of the wire to permit mobile electrons to flow [36].

There has been much study of other molecular nanowires, as well. Bein and coworkers [202] used substrates with nanometer-scale pores [203] as templates to create carbon-based conducting polymer wires 3 nm in diameter. A similar method developed by Martin and coworkers [204] also polymerizes wires inside small channels. These nanowires show high conductivity compared to bulk polymers, suggesting that the wires are not amorphous but have regular structure. Tour and his collaborators [168], [195] have more recently shown other potential molecular wires that could be self-assembled onto a gold surface.

Another new type of nanostructure, termed a “buckytube” because of its structural similarity to carbon “buckyballs” [207], also presents possibilities for chemically synthesizing nanowires [205], [206]. Buckytubes are cylindrical carbon nanotubes [91]. These hollow tubes might be used as support for molecular circuit elements—e.g., filled with conducting metal atoms to create among the structurally strongest nanowires chemically possible. The structure of the nanotube derives its strength from the carbon-carbon bonds. The carbon atoms are bonded in virtually flawless hexagonal arrays. Simulations of carbon nanotubes have shown that isolated flaws migrate to the ends of the tube and are eliminated, a phenomenon termed “self-healing” [208].

Alternatively, the tubes might be used to conduct current themselves, as they have been shown to do. A measurement of the conductivity of carbon nanotubes has shown that a tube 10 nm in diameter can carry currents of approximately 10 microamps per molecular strand or “fiber” [209]. More recent work by two research teams shows that, in theory,

carbon nanotubes could even be made to behave like electronic switches [210].

Unfortunately, the commonly studied nested nanotubes show large and uncontrollable variations in electrical properties from one tube to the next [90]. Single-layer nanotubes now starting to be fabricated in quantity offer hope for more reproducible properties and may be useful in molecular electronic devices.

Historically, the field of molecular electronics has focused much attention on understanding and demonstrating the conductance of molecular wires [17], [36], [105], [154], [195]. Also, to manipulate and fabricate tiny molecular switching devices it is convenient to embed them in longer wire-like structures. Thus, much of today’s work on molecular electronic devices is intimately tied to the study of the electrical properties of molecular wires [25].

#### D. Quantum-Effect Molecular Electronic Devices

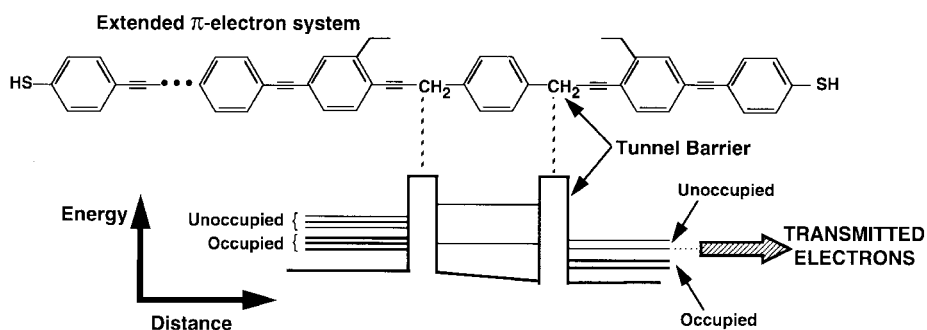
Using molecular structures for quantum confinement might make it possible to manufacture fast, quantum-effect switching devices on a large scale more uniformly and cheaply than has thus far been feasible with solid semiconductors. Early on, investigators in molecular electronics proposed incorporating into molecules and supramolecular structures potential wells for the quantum confinement of mobile electrons [30], and several groups now are working on this approach for molecular switching [159], [200]. The goal has been to implement the electric-field controlled resonant tunneling and single-electron switching effects that have been discussed above for solids.

These efforts include embedding in supramolecular structures metal nanoclusters that exhibit properties like QD’s, such as Coulomb blockade. This is the approach adopted in the aforementioned work at Purdue, which showed that large numbers of such QD’s could be manufactured with great uniformity, then self-assembled into an extremely regular structure [112], [126].

Alternatively, a quantum well might be embedded in a molecular wire like that in Fig. 7 by inserting pairs of barrier groups that break the sequence of conjugated  $\pi$ -orbitals discussed above. This has been proposed by Tour [94], who suggests the structure shown in Fig. 8 for a wire with such barriers inserted. That structure would form a two-terminal molecular RTD, but structures for three-terminal RTT-like molecules also have been suggested [53], [169].

A difficulty in realizing such molecular RTD’s and RTT’s is the fact that the charging energy in such a small potential well is sure to be large, perhaps larger than the energy spacing  $\Delta\epsilon$  between the levels in the well. This could make the device much more like a QD than a solid-state RTD. Also, unlike a solid-state RTD, such as is diagrammed in Fig. 3, there is not a near continuum of unoccupied energy levels on the drain side of the molecule to allow an electron in the quantum well to tunnel out, so achieving resonance with the source and drain simultaneously may be difficult.

Still, the flexibility and variety of such organic structures gives the designer many variables with which to optimize



**Fig. 8.** Structure and mechanism for possible molecular RTD proposed by Tour [94]. (a) Conducting chain molecule, like that shown in Fig. 7, but with insulating barrier groups that may generate (b) potential well for quantum confinement that could (c) create a resonant tunneling effect when the molecule is subjected to a voltage bias, permitting a current of electrons to be transmitted through the device. Compare this schematic with that in Fig. 3 for an analogous, but much larger, solid-state device.

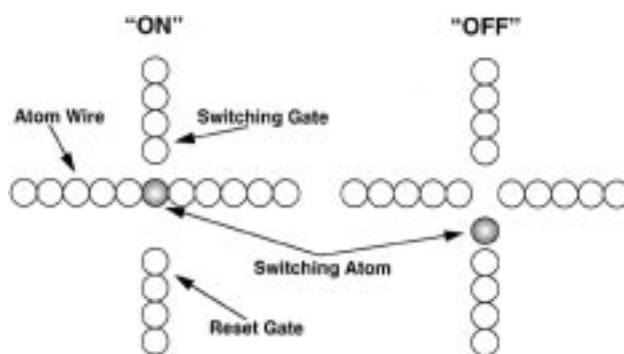
device performance. The recent demonstration of electromechanically controlled resonant tunneling in a molecule also is very encouraging. These facts and the measurements of Reed and Tour [159] on structures like that in Fig. 7 give the authors a sense of optimism that an efficient field-controlled molecular quantum-effect switching device can be engineered successfully in the foreseeable future.

#### E. Electromechanical Molecular Electronic Devices

Electromechanical molecular switching devices are not so closely analogous to microelectronic transistors as are the molecular devices we have considered so far. They are controlled by deforming or reorienting a molecule rather than shifting around electrons. The input may even be mechanical rather than electrical. However, just like all those other switches, they can turn on or off a current between two wires, which makes them interesting for nanocomputing.

1) *Single-Molecule Electromechanical Amplifier:* It is already possible to make such switches composed of only one or a few molecules. In very recently reported results, Joachim and Gimzewski have been able to measure conductance through a single buckyball held between an STM tip and a conducting substrate. By pressing down harder on the STM tip they deformed the buckyball and tuned conduction onto and off of resonance, producing a 50% reduction of current off resonance. The deformation was reversible, a measure of the strength and resilience of the carbon fullerenes. Clearly it would be impractical for computers to use an STM to operate each switch, but Joachim and Gimzewski recommend replacing the STM tip with a small *in-situ* piezoelectric gate or other electromechanical actuator. The only fundamental limit to the speed of such a device would be the vibrational frequency of a buckyball—over 10 THz ( $10^{13}$  Hz), though the prototype misses this goal by 12 orders of magnitude [98].

2) *Atom Relay:* A team of researchers at the Hitachi Corporation in Japan has simulated a two-state electronic switch of atomic dimensions [170]. The concept for this proposed device, termed an “atom relay,” has some simi-



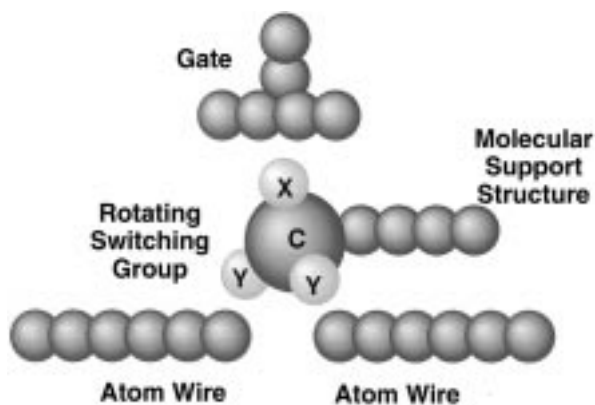
**Fig. 9.** Atom relay proposed and modeled by Wada *et al.* [170]. (a) Upon charging a line of atoms termed a switching gate, a mobile switching atom (shaded circle) is moved into a line of conductive atoms or “atom wire” in order to turn on a current through the wire. (b) The current is turned off by charging the reset gate to move the mobile atom back out of the atom wire.

larities to the molecular shuttle switch. In the atom relay, a mobile atom that is not firmly attached to a substrate would move back and forth between two terminals.

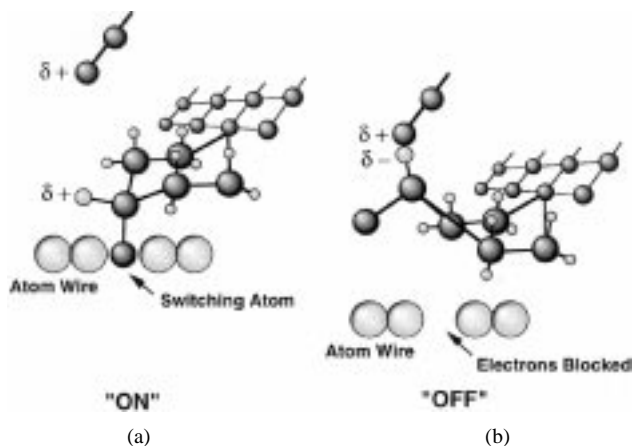
The atom relay would be made from carefully patterned lines of atoms on a substrate. The Hitachi simulations showed that such a line, or “atom wire,” can conduct a small electric current. As shown in Fig. 9, two atom wires connected by a mobile switching atom form the relay. If the switching atom is in place, the whole device can conduct electricity. However, if the switching atom is displaced from the two wires, the resulting gap dramatically reduces the amount of current that can flow through the atom wire.

A third atom wire that passes near the switching atom is termed the “gate” of the atom relay in analogy to the gate of a field effect transistor. Placing a small negative charge on the gate wire moves the switching atom out of its place in the wire. The switching atom is pulled back into place by a second “reset” gate after each use of the switch.

In an actual experiment that approximates this design, Eigler *et al.* created a bistable atom switch with the aid of an STM. In their switch, a xenon atom transfers back and forth between the tip of an STM and a substrate [128], [160]. The location of this switching atom greatly affects the tunneling current that flows from the STM tip to the



**Fig. 10.** Refined molecular switch, Type 1. The atom switch depicted in Fig. 9 might be refined by attaching the switching atom to a rotating molecular group. The orientation of the rotating group is to be controlled by a nearby gate molecule, to which a voltage can be applied for that purpose.



**Fig. 11.** Refined molecular switch, Type 2. Switching atom might be attached to a “rotamer” that permits the atom to (a) be swung into position to turn the switch “on” by filling the gap in the atom wire, or (b) the switching atom is swung up out of the wire to turn “off” the current in the wire. Orientation of the rotamer is to be controlled by adjusting the polarity of the charge on the gate molecule, shown at the very top of both (a) and (b).

surface. While the operation of the switch fabricated by Eigler’s group is different from that of the theoretical atom relay, these experiments have shown that the movement of a single atom can be the basis of a nanometer-scale switch.

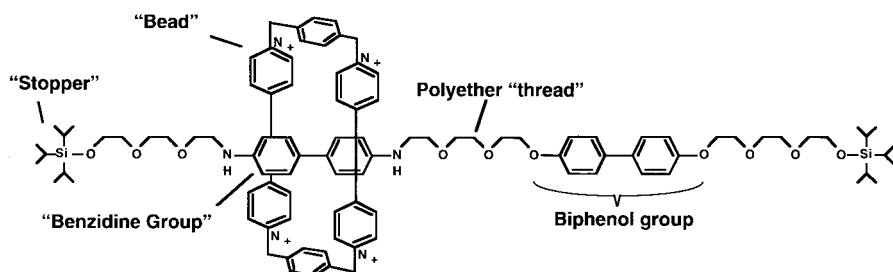
However, the designs for logic gates using atom relays could be limited to a two-dimensional plane. The Hitachi group did not demonstrate how two separate atom wires could cross. Without crossing wires, only a subset of all possible logic functions can be implemented with atom relays [147]. On the positive side, individual relays would have the advantage of being extremely small, on the order of 10 square nm. The speed of the relays would be limited only by the intrinsic vibrational frequency of atoms (approximately  $10^{14}$  cycles per second), which is several orders of magnitude faster than present-day semiconductor transistors. Energy requirements, while not reported by the authors, would be rather low, resulting mostly from frictional forces between a single atom and the substrate.

On the other hand, not much energy would be required to evaporate a switching atom off the substrate and out of the plane of the atom wires, thereby destroying the switch. For this reason, it seems likely that atom relays could only work at very low temperatures. While switching based on atom movement has the advantages of high speed and low power dissipation, incorporating this mechanism into a more reliable device would improve its chances for practical applications.

3) *Refined Molecular Relay:* A more reliable two-state device based on atom movement might use the rotation of a molecular group to affect an electric current. We suggest that the atom relay discussed in the last section might be refined and made more reliable by attaching the switching atom to a rotating group, or “rotamer.” This rotamer would be part of a larger molecule, perhaps affixed to the same surface as the atom wires. See Fig. 10 for a conceptual diagram of this arrangement (based upon a methyl-like group) and Takeda *et al.* [165] for a discussion of rotamers. The electric field of a nearby gate would force the switching atom to rotate in or out of the atom wire. When the switching atom is in the atom wire, the conductance of the atom wire is high—i.e., the switch is “on.” When the switching atom is rotated out of the wire, a second group takes its place. This replacement group hinders the flow of current through the atom wire, turning the switch “off.” A large third group on the rotamer could prevent it from rotating freely due to thermal energy. Alternatively, hydrogen bonding might provide a resistance to rotation just adequate to stop the rotamer in the conducting position, but not so much that reversing the gate voltage would be insufficient to turn the rotamer.

Use of such a rotamer to effect atom switching would prevent the evaporation of the mobile switching atom, alleviating one of the principal weaknesses of the atom relay discussed in the previous section. The refined molecular relay would operate somewhat similarly to the shuttle switch described below in Section IV-E4. The rotamer in the refined relay would likely be faster but also more sensitive to energetic perturbations than the molecular shuttle, because the rotamer would be lighter and would have a much smaller range of motion between switching positions. The molecular relays and the shuttle switch are a kind of hybrid between electronic switches and the molecular-scale mechanical devices suggested by Drexler [127], Merkle [149], and others.

One of the disadvantages of a rotating switch based upon a methyl-like rotamer group is that there are three different switch positions associated with the three groups attached to the rotamer. A more suitable molecule might be one that moves back and forth between only two distinct states. Cyclohexane, a simple example of this type of molecule, can bend into two different forms, commonly known as the “boat” and “chair” conformations [143], [163]. As shown in Fig. 11, a voltage on a nearby gate might force the cyclohexane switch into one of its two configurations, affecting the conductivity of a nearby atom wire. The cyclohexane-type molecule could link to a molecular framework while



**Fig. 12.** Reversible molecular switch synthesized by Bissel *et al.* [121]. Ring-like “bead” molecule slides along wire-like chain molecule to perform switching function as described in the text.

the remaining ring carbons would be replaced by groups tailored to use steric repulsions or chemical attractions to reduce undesired switching caused by thermal energy, while also sterically protecting the conducting atom from chemical attack.

These two designs should operate at speeds governed by molecular rotation, which typically occurs at frequencies in the vicinity of billions of cycles per second, or GHz. This is slower than the atom switch, but the operation could be much more reliable.

In contrast to the atom relay, these refined relays could be packed in three dimensions, attaining much higher packing density. This should not cause overheating since the energy dissipated in their operation ought to be very low, primarily arising from breaking weak van der Waals attractions and/or hydrogen bonds.

4) *Molecular Shuttle Switch:* A research group at the University of Miami-Coral Gables reports the synthesis of a “shuttle switch” [121]. This switch consists of two interlocking molecules of the type developed and refined in the pioneering work of the British chemist Stoddart [111], [113]. As seen in Fig. 12, the “shuttle” is a ring shaped molecule that encircles and slides (i.e., “shuttles”) along a shaft-like chain molecule. Two large terminal groups at the end of the shaft prevent the shuttle ring from coming off the shaft. The shaft contains two other functional groups, a biphenol group and a benzidine group, which serve as natural “stations” between which the shuttle moves.

The shuttle molecule contains four positively charged functional groups, which cause it to be attracted to sites on the shaft molecule with extra negative charge. For this reason, the shuttle spends 84% of its time at the benzidine station, which is a better electron donor than the biphenol station. The shuttle spends the remaining 16% of its time at the biphenol station.

The shuttle can be forced to switch to the biphenol station by the removal of an electron from the benzidine station. This process is known as electrochemical oxidation. Since both the altered benzidine station and the functional groups on the ring are positively charged, they repel each other. In this state, the shuttle spends most of its time at the biphenol station. When the missing electron is added back to the benzidine station, the switch will return to its original state.

While this molecular device was designed to be electrochemically activated, as discussed above, this structure might lend itself to electromechanical switching. In that

case, a charged gate would be established at one or both ends of the molecule to force the shuttle to move between switching positions. This configuration might lend itself to use in nanoelectronic computers, if many such molecules were affixed to a substrate and switched individually. Thus, a two-piece molecular structure of this type could provide yet another mechanism for nanometer-scale electromechanical switching.

Such molecular electronic devices offer many attractive features. Large numbers of this type of device can be synthesized chemically at relatively low cost. Also, the small size of the device makes for extremely high packing density. However, the Miami group has not suggested any way of probing the state of individual switches. One possible way would be to arrange that the ring complete an electric circuit in one of its two positions. Then the rate of switching would be limited by two factors: the speed of electron transfer to and from the benzidine, and the sluggish motion of the ring, which is very heavy compared to an electron. Thus the switch would necessarily be slower than solid-state switches in which only electrons or electric fields move.

Although these switches would not be extremely fast, many would fit in a small area. In fact, these shuttle switches might pack into a three-dimensional lattice, creating an even larger space savings. Since this type of work is relatively new, there are many unresolved issues concerning the operation and application of such switches. However, the fabrication of a reliable molecular switch represents an important step forward toward molecular-scale computers.

## V. DISCUSSION AND CONCLUSIONS

In considering prospects for continuing the exponential rate of miniaturization of electronics well into the next century, one always must be cognizant of the obstacles. These include the fundamental limitations of thermodynamics and quantum mechanics [4], [5], [8], [79], [109], [133], as well as the practical limitations arising from the cost and difficulty of fabrication [9], [43], [80], [171]. However, as explained in this overview, progress is being made in harnessing the principles of quantum mechanics to design and to build solid-state and molecular devices that can function well on smaller and smaller scales, even after aggressive miniaturization of solid-state FET’s has ceased to be feasible and cost-effective.

This makes it possible to envision the stages of a natural evolution from microelectronic to nanoelectronic devices

and circuits. In parallel with the aggressive miniaturization of CMOS FET's, industry could begin to employ hybrid quantum-effect/bulk-effect devices similar to the one diagrammed in Fig. 6. This could permit the present technology for microelectronic digital circuitry to be leveraged to increase the logic density of two-dimensional digital circuitry by as much as 100 or 1000 times. After that, emerging methods of nanofabrication such as mechanosynthesis and chemosynthetic self-assembly may be used to manufacture purely quantum-effect, nanometer-scale solid-state circuitry or molecular electronics. This might achieve digital processing logic 10 000 or even 100 000 times as dense as is presently feasible. Memories, which are organized in more regular structures, might be made even more dense.

The problems of achieving such increases in computing power and information storage capacity still are formidable. As discussed elsewhere in this volume [88], [187], new architectures [81], [82], like cellular automata [84], [185], must be devised to reduce the amount of wire and number of interconnects on a circuit while accommodating billions or even trillions of devices in the same area now occupied by only a few million. These architectures also must compensate for the intrinsically lower reliability of very small quantum-effect devices [147]. Materials must be found to maximize device reliability, by better isolating the operation of closely spaced devices from each other, and by desensitizing individual devices to background charges. Less power must be used per device, and it must be used more efficiently, with less heat dissipation [5], [133].

Nonetheless, as described in this paper, there is already a range of design options and prototypes for next-generation nanoelectronic switching and amplification devices. These can be used to experiment with solutions to the fundamental problems outlined above. The exciting, world-wide enterprise of engineering nanometer-scale electronic computers is well under way and growing.

Nanocomputers will arrive as a result of breakthroughs on many fronts. The excitement of standing on the threshold of such an innovation is enhanced by the multidisciplinary nature of nanotechnology. It is impossible to predict from which traditional discipline will come the impetus or key breakthrough necessary to construct these new, much tinier computers with much greater speed and power. One only can be confident that such dramatically smaller computational engines, along with the methods devised to fabricate them, will transform electronic computing and our technological infrastructure as well.

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