Title: Nanoscience and Technology: An Interdisciplinary Initiative, Self-Assembling Nanoscale Quantum Devices

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Nanoscience and Technology: An Interdisciplinary Initiative,  
Self-Assembling Nanoscale Quantum Devices

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Abstract

This is the final report of a three-year Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). Our objective is to develop the devices, interconnection technologies, and self-assembling systems required for quantum-based information processing that permit ultra-dense integrated circuits and that allow continuation of the on-going silicon VLSI miniaturization process. That process is facing increasing difficulties related to switch performance, heat dissipation, interconnect failure, quantum effect complications, and rapidly escalating manufacturing costs. Our approach is intended to address these concerns and consists of the development of highly parallel stochastic computers utilizing quantum components and self-assembly methods; the development of self-assembling monolayers for use as resists and memory devices; and research on approaches to molecular self-assembly of the precursors to molecular transistors. The work will provide confirmation of principles, is intended to provide near-term results of potential relevance to the commercial sector, and has a range of applications that include high performance computing, biotechnology, and nanoscale chemistry.

1. Background and Research Objectives

Despite a strong desire for continued progress in microelectronics miniaturization, the means for achieving feature sizes below about 0.1 microns do not exist. Traditional

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VLSIC technologies are expected to dominate the market for the next 10-20 years, after which novel -- and presently undemonstrated -- techniques will be required. This project addresses the development and demonstration of certain nanometer scale components, circuits, techniques, and systems, -- that is, terascale integration (10^{12} components per chip) -- and the opportunities and limitations associated with their use. To achieve this level of integration with the precision necessary for computing, the circuits must be self-assembled. Since self-assembly takes place at the nanoscale, we focus our efforts on self-assembled nanoscale electronics, where device behavior and system performance is governed (and constrained) by quantum mechanics.

Our objectives are to pursue the self-assembly of wires, active gain devices, larger error-tolerant ensembles that memorize and compute, and more generally to explore self-assembly as a powerful alternative to technologies used currently by the semiconductor and micromachining industry. This new technology is clearly on the cusp of a revolution in how we make small devices. It will have global impact. Our specific objectives involve theoretical and experimental research in Coulomb blockade devices, resonant tunneling systems, and self-assembled systems.

2. **Importance To LANL's Science and Technology Base and National R&D Needs**

One of the goals of the laboratory is to develop and maintain world class projects in advanced technology, and to develop partnerships with universities and industries for national benefit. This project certainly fits those aims. Nanoscale self-assembly for circuits, computers, and machines is cutting-edge technology and cutting-edge science. Some of the members of our group are already recognized as world-class leaders in this subject. This project will enable the laboratory to create an enviable program in self-assembly that will have wide-ranging economic, technological and scientific impact. Additionally, the marriage of self-assembly to (nano)biology and genetic research in general is a very exciting current topic.

3. **Scientific Approach and Results**

A. **Semiconductor Coulomb Blockade Devices**

Our goal is a three-terminal room-temperature Coulomb blockade device best described as a quantum transistor. This basic structure represents the building block for more complex devices. The realization of such components poses three problems: fabrication of device sizes
in the range of 1 - 10 nm (required for room temperature operation); control of the device
dimensions (electron tunneling is exponentially sensitive to atomic-scale thickness fluctuations
in tunneling barriers); and achievement of interconnects between quantum elements.

Our efforts represent a multifaceted approach to the problem incorporating synthesis
and characterization, surface derivatization, assembly of complex structures, physical
characterization of these structures, and theory. We work with GaP and GaAs because of their
ease of synthesis and applicability to both resonant tunneling and Coulomb blockade devices.
We prepare nanometer scale nanoparticles by arrested precipitation and characterize them with
high resolution x-ray diffraction and transmission electron microscopy to determine the shape,
size, and size distribution of the particles; optical absorption to probe the quantum confinement
energy; and time resolved photoluminescence and pulse-probe optical absorption experiments
to assess carrier dynamics. Additionally, we assembled these species in some ordered
manner, e. g., by surface derivatization of the cluster and assembly on a two-dimensional (2-
D) substrate. Understanding the nature of the surface is necessary for the surface derivatization
chemistry required to functionalize these materials for the assembly strategies. This
coordinated approach gives us a thorough understanding of the basic properties of
nanoclusters, which provides in turn the bases for the exploration of quantum effect devices.

Synthesis. A range of cluster sizes, from 1 to 3 nm, have been prepared and x-ray
diffraction and transmission electron microscopy have been used to structurally characterize
them. We have made great strides in developing novel synthetic strategies to prepare
nanoclusters that are soluble in a number of organic solvents and that exhibit remarkable
solution stability. A number of solutions were prepared and provided to external collaborators
for STM experiments involving imaging, tunneling spectroscopy, and measurements of the
electron “addition spectrum” of the cluster.

Self-Assembled Monolayers (SAM). We have prepared and characterized a number of
SAMs. Crystalline thin films of gold have been reproducibly prepared that contain large (0.2
mm) crystals of gold. The large single crystals of gold are necessary to provide a substrate
surface smooth enough to image structures of 1 to 3 nm. Well ordered structures have been
obtained that are suitable for preparation of ordered nanocluster structures. A number of
attempts were made to attach the GaAs nanoclusters to the dithiol SAM with limited success.
Attempts to image these surfaces by AFM/STM were not successful.

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B. Resonant Tunneling Devices

We have studied resonant tunneling diodes because they offer near term applications, exemplify the quantum phenomena we are trying to understand, and may be developed into multi-value logic devices that could be used in terascale integrated circuits. We successfully predicted and measured many stress-induced and current-voltage properties of these devices.

(a) We showed that piezoelectric effects can give rise to internal electric fields that modify the current-voltage characteristics of double-barrier resonant tunneling devices if suitable stresses are applied. We measured current-voltage characteristics of (001)-oriented AlAs/GaAs/AlAs double-barrier structures as a function of uniaxial external stress applied parallel to the (110) and the (1-10) orientations, and found that stress shifts the resonant peak. We also calculated the current-voltage characteristics of resonant tunneling structures under uniaxial stress, taking into account stress effects on the band alignment and piezoelectric effects. We obtain satisfactory agreement between our calculations, which contain no adjustable parameters, and the measured data.

(b) We analyzed the effect of surface acoustic waves (SAW) on the optical properties of III-V semiconductor multiple quantum wells (MQW). The SAW modulates the optical properties of the MQW primarily by changing optical transition energies. The SAW generates both strains, which modulate the transition energies by deformation potential effects, and electric fields, which modulate the transition energies by the quantum confined Stark effect. We found that modulation of the transition energies by strain effects is usually more important than by electric field effects. Although we specifically considered GaInAs/GaAlAs MQWs grown on (100)- and (111)-oriented substrates, our general conclusions apply to other type I MQWs fabricated from III-V semiconductors.

(c) We calculated the effects of external stress on the current-voltage characteristics of double-barrier (001)- and (111)-oriented resonant tunneling devices. Crystal strains arising from the application of external pressure and, in pseudomorphic structures, lattice mismatch cause shifts in the conduction and valence bands of the well and barrier layers with respect to the unstrained alignment. For certain stress orientations piezoelectric effects give rise to internal electric fields parallel to the current direction. The combined piezoelectric and bandstructure effects modulate the transmission resonances that control the shape of the current-voltage characteristics of the structure.
C. Nanosystem Architectures

Our objective here has been to learn how to extend microelectronic component miniaturization to the nanometer scale in support of terascale integration. Yet, terascale circuits and systems built with nanoscale devices are very complex, operate in a different physical regime (quantum rather than classical), and pose a manifold of global and microscopic uncertainties. To explore their feasibility, we are approaching the problem from two different points of view; a bottom-up and a top-down approach. In the bottom-up approach we are developing an understanding of how devices can self-assemble into pre-described systems. We ask questions like, “What are the devices that we can self-assemble? What are their properties? How can we control and shape their growth? To what level of integration can we take self-assembly?” In the top-down approach, we assume that terascale systems can be assembled and we seek methods for programming them. We ask questions like, “What kinds of programs can be executed by such a system? What happens if there are small errors? What are the interactions within and between large ‘nanocomponent’ arrays?” It is comforting to note that the type of self assembly that we seek for electronic circuits is realized in nature, within the cell, in the formation of microtubule networks and in the construction of ATP motors. These provide a proof of principle. We do not plan to imitate biological methods; but we expect to use similar principles. It is our belief that much more efficient devices are possible than nature has built through trial-and-error.

Bottom-up Approach

Although many structures have been fabricated, there are no generally accepted models that provide a theoretical underpinning for experiments in self-assembled systems. We have pursued two theoretical developments in this area that will lead to better models: Laplacian growth and operator gases. Laplacian growth assumes that there is a growing interface that is self-assembling from parts that are in a gas or liquid medium. These particles are in random motion and have a certain probability of attaching themselves to the interface. Laplacian growth is the most fundamental form of self-assembly and one that is intrinsically immune to noise. Recently, several of us, notably Mark Mineev, who is one of the world experts on such systems, has been able to reduce Laplacian growth to a low-dimensional dynamical system. This allows us deep insight into the controlled growth problems associated with many nanoscale applications. His work indicates the presence of conserved quantities in these processes, even though they may not be in equilibrium, and indicate the possibility of growth control. The related inverse problem of reconstructing a shape from a low-dimensional
description is one we pursue, since it allows us to control the shape of structures made from molecules in a very accurate way. This will give us vital insight into the complex bundle growth processes we are seeing experimentally in all attempts to make self-assembled wires.

Operator gases offer a more detailed model for the growth process. Operator gases are a simplified form of molecular dynamics, in which the gas part is simulated by a lattice gas and the particles are generalized so that they can modify each other. This allows for the rapid simulation of self-assembly processes with many different species. There have been many proposals in the literature to use cellular automata to create self-organized structures. The difficulty with other approaches (and avoided by operator gases) is that they are too unconstrained. Cellular automata, when suitably averaged, can reproduce any dynamical process. This makes any blind search unproductive, as there are too many possibilities. Operator gases incorporate essential physics into the model right from the beginning (conservation of overall particle types and conservation of momentum). Operator gases are also central to the essential programming methodology to be discussed later.

**Top-down Approach**

We are trying to develop computer architectures that use error-prone nanocomponents but that yield reliable computers and machines. The central difficulty is trying to coordinate what can be built and how to program them in general. Therefore, we are developing a general scheme for compiling object-oriented programs into operator gases so that they are immune to defects and failures of the computer.

Generically, one can think of operator gases as abstract data structures and their operators. Then it becomes possible to compile logic programs (such as those written in Prolog) into an operator gas. Evolving the gas corresponds to executing the program. Once well-understood, the operator gas allows the rational design of novel architectures for massively parallel computers and their algorithms. It also provides a much-needed language for the Texas Instrument terabit computer now being designed.

Certain operator gases have a special property of hyperbolicity. When they have this property, their evolution is immune to errors. The evolution of the operator gas is equivalent to a flow on a hyperbolic surface, which makes it a mixing flow (in the ergodic sense). The strength of the error rate only affects the time it takes for the gas to reach a stationary state. It is known that mixing systems are immune to error. This makes operator gases an ideal concept to execute on a computer that will self-assemble and be error prone.

We have also analyzed several quantum computer approaches for their viability. These computers can support von Neumann style computation under ideal conditions. In particular,
these computers assume that excited quantum states have an infinite lifetime. When a finite lifetime is taken into account, we have concluded that their error rates are too large for traditional computation. We have also analyzed spin-based computers with dissipation (the dissipation coming from non-reversible error correction) and concluded that they also cannot support von Neumann style computing, again due to the large error rates. To overcome these difficulties we have proposed a stochastic computer that could be assembled from nanoscale components. This computer would not be a general purpose computer, but it would be immune to error and capable of simulating systems described by partial differential equations.

A quantum version of a general purpose cellular automaton was invented and its properties analyzed. This is the most realistic quantum computer proposed so far in the literature. It could be implemented by exciting the states of an idealized molecule with laser pulses that are precisely tuned for the calculation.

Several continuous logic circuits were analyzed. It was found that their error rates are smaller than equivalent binary logic circuits. If the loss of information through the circuit is defined, it is found to decay at some universal rate related to the loss of information per device. Even though this loss could be compensated by circuit replication, we have concluded that they do not constitute a viable alternative to stochastic algorithms.

Lessons From Nature

In light of the “proof-of-principle” example mentioned above, we have studied certain crucial biological self-assembly processes in order to better understand the yield on Nature’s investment.

One obvious example of self-assembly in the biological world is the cytoskeleton; here, proteins spontaneously assemble structures that perform many useful functions in the cell, including providing transport within the cell and maintaining structural integrity. Two principle constituents of the cytoskeleton are actin fibers and microtubules. We have investigated the formation of microtubule networks, which the cell can assemble and disassemble depending on the cell’s needs. We have developed a lattice gas code to simulate the assembly of microtubule networks, including the so-call “dynamic instability” observed in in-vitro experiments on tubulin self-assembly, and we intend to use this code to examine the observed behavior of tubulin network reconstruction in severed cell fragments.

A second activity involves self-assembly where the constituent particles are much more complex than proteins, namely bacteria. We have investigated the experimentally observed aggregation phenomenon observed by Budrene et. al. in colonies of Escherichia Coli, wherein the colonies, grown in an agar medium, exhibit remarkable patterning behavior when shocked.
with an oxidizing agent. We have had some success in modeling this process. We were able to qualitatively reproduce these patterns by assuming that the cells emit a chemoattractant in response to the oxidizing agent, causing them to aggregate, presumably to mitigate the damage caused by the agent. This mechanism, compounded with the cell's normal chemotactic motion up nutrient gradients, leads to the patterning behavior observed. The eventual dimming of the patterns interior structure is explained by the cells' eventually entering a dormant state after long exposure to the oxidizing agent.

Finally, we have studied the protein folding problem, one of the fundamental problems in self-assembly. We have principally been investigating the role of hydrogen bonding in the folding process. One problem we have been looking at is the interaction between hydrogen bonds on the protein chain and the solvent in the medium. It is our feeling that having a solvent competing for hydrogen bonds with the chain would provide a useful mechanism for rapidly getting a nascent protein into its globular state, since bonds forming on extended regions of the chain, exposed to the solvent, would be quickly broken. The only bonds that persist are those on the interior of a globular conformation which would be shielded from the surrounding solvent by the rest of the chain. In some sense, we suspect that this might lead to a physical process of “simulated annealing”. We have developed a code to simulate this process in two dimensions, and we are observing that indeed this behavior does take place.

D. Theory of Quantum Devices

We have developed a comprehensive model for the dynamic mechanism of electrons tunneling back and forth between a source and a nanostructure, leading to a quantized capacitance charging spectroscopy. Our model predicts that (1) lock-in voltages show a single peak structure at low AC excitation voltage amplitudes and a twin peak structure at high amplitudes for the tunneling of a single electron; and (2) the lock-in voltages show several peaks with different heights for multitunneling electrons within the AC voltage oscillation range. The peak height increases nonlinearly with increasing number of tunneling electrons. These predictions are in excellent agreement with experimental measurements at MIT and elsewhere.

We have calculated the tunneling properties of a resonantly-tunneling electron that interacts with phonons or other linear or nonlinear excitations. The method we use is based on mapping a many-body problem in a large variational space exactly onto a one-body problem. The method is conceptually simpler than previous Green's function approaches, and allows the essentially exact numerical solution of much more general problems than could be solved before. We solve tunneling problems with transverse channels, multiple sites coupled to
phonons, and multiple phonon degrees of freedom and excitations. This approach is being extended to calculate nonlinear quantum transport in microchannels from first principles. We are discussing the possibility of using this approach in a large resonant tunneling diode modeling program at Texas Instruments and the University of Texas--Dallas.

We have proposed a microscopic theory of Ohm's law for modeling conductance of electron tunneling through a quantum dot. We found that the conductance shows (a) an approximately periodic oscillation structure for a large number of electrons (typically 30) in the dot; and (b) a "shell" structure for a small number of electrons. In addition, we found even- and odd-occupation number effects in the conductance peak heights, line widths, and the separation between adjacent peaks of the oscillations. These findings are in excellent agreement with available experimental measurements.

Publications


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