

Prospects for Molecular-Scale Electronics

Mark A. Reed

The following article is an edited transcript of the Symposium X: Frontiers of Materials Research address by Mark A. Reed, the Harold Hodgkinson Professor of Engineering and Applied Science and Chair of Electrical Engineering at Yale University, presented at the MRS Fall Meeting on December 1, 1999.

Introduction

Scientific consideration of how to scale electronics down to the molecular level started in the mid-1970s. Unfortunately, at the time, researchers did not have the adequate analytical tools to perform the experiments. That has changed drastically, and therefore interest in this field has been renewed, especially over the last few years.

I will be presenting a collection of results from a number of different studies, all of which were made possible by the availability of new analytical tools. The work presented here comes from the collaboration of a number of laboratories. My team is composed of researchers involved in the electrical-measurement aspect of this work. Others involved in this work are chemists.

Characterizing Nanoscale Materials

Researchers have been trying to scale systems down to the nanoscale level in various ways. They have explored semiconductors and metallic quantum dots and found various types of nanoscale phenomena. They have reported room-temperature, single-electron transistors and have observed some interesting quantization phenomena. The field of nanotubes and carbon systems, and the electronic properties of them, have been investigated. Researchers have also made tiny structures that look like abacuses and have developed molecular-scale organic systems. While many interesting developments are taking place in all of these various areas,

the one in which actual products are being made is in charge transport in bulk organic systems.

Quantizing Conductance in Single-Atom Systems

Let us go back to basics for a moment and talk about Ohm's law. About three decades ago, Rolf Landauer¹ at IBM proposed that the conductance of very small systems is, in fact, relatively well defined and that the conductance is quantized in units of the fundamental constant $2e^2/h$, where e is the electronic charge and h is Planck's constant (in this case, the inverse of approximately 12.9 k Ω) times the transmission coefficients (which tell us how electrons travel through a system); specifically,

$$G = (2e^2/h) \sum T_n, \quad (1)$$

where the sum is of the transmission probabilities (T_n) through the system, summed over all of the channels. This is a fundamental way to measure the conductance of small systems. If we examine a material, such as a hunk of copper, then we should be able to write down the appropriate Equation 1 and derive the resistance of that hunk of copper. Unfortunately, it is very difficult and complicated to sum all of the transmission coefficients. It is only when we examine something very small, where we can control the number of channels to a countable few, that we can actually see this effect. To fully understand some of the fundamentals, we have to limit the number of channels.

Let us consider the regime of *ballistic* transport, whereby an electron goes through a system without scattering into anything. The quantum mechanical transmission coefficient in a system like that is unity. Then, the conductance can actually be quantized in the most fundamental units.

This effect was first seen a number of years ago, when groups at Delft University of Technology and Cambridge University demonstrated the use of a *quantum point contact* in a two-dimensional electron gas.^{2,3} To be able to achieve conductance quantization, they realized that they had to cool the sample down to a very low temperature because of the relative length scales involved. Those length scales are determined by the Fermi wavelength. Imagine being able to examine a very small metallic system, where we might be able to actually see that effect. The length scales involved turn out to be atomic in length, since the Fermi energies are so high. We should easily be able to see those effects at room temperature.

Single Metal Atom Systems

Consider this experiment: take two single contacts and sandwich a single atom between them. Figure 1 shows an idealized illustration of the experiment. If we pull a wire apart like a piece of taffy, it will stretch and eventually break. But right before it breaks, how many atoms are between the two contacts? There might be just one. Figure 2 shows the experimental set-up devised by Muller et al.⁴ for conductance-quantization by means of a mechanically controllable break junction. The experiment is actually quite easy to do. The conductance of the metal wire as it is being pulled apart takes on very well-defined steps—a conductance of one times $2e^2/h$, which is the conductance of a single atom. It does not matter what kind of atom we use (gold, copper, etc.); we get the same result because this effect is material-independent now.

Single Semiconductor Atom Systems

To demonstrate that conductance can be quantized in any kind of system, I will de-

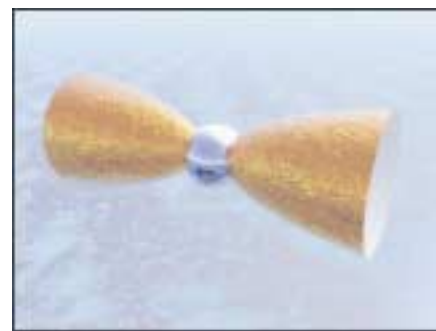


Figure 1. An idealized illustration of the experiment to measure conductance quantization in a single-atom metal system.

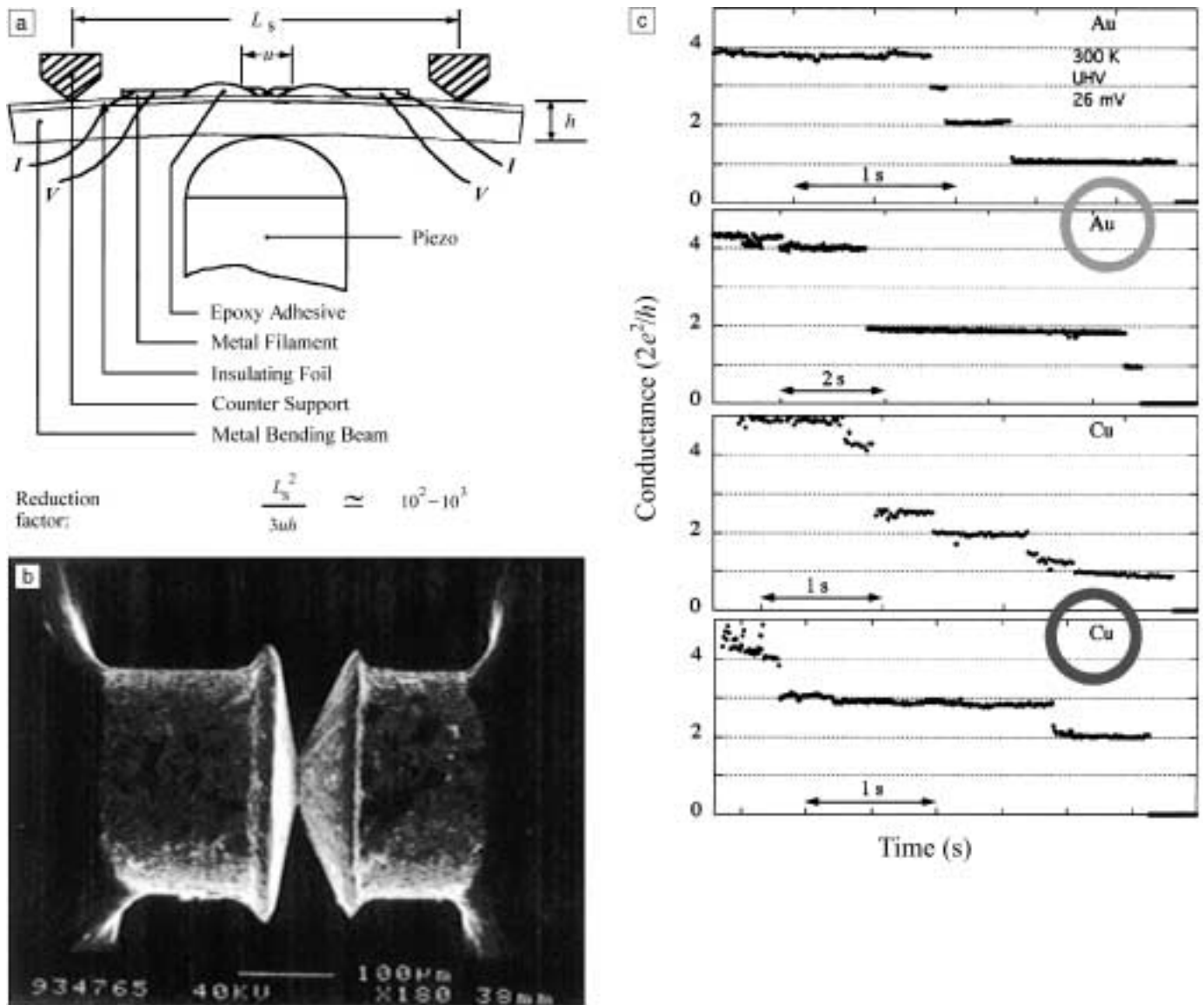


Figure 2. (a) The experimental set-up for conductance quantization by means of (b) a mechanically controllable break junction. (c) The conductance of the metal wire takes on very well-defined steps. (From Reference 4.)

scribe the process for measuring the conductance of a single semiconductor atom. First, we need to surround the atom with a semiconductor crystal field. Figure 3 is a schematic representation of what we did: we created a *quantum well* with tunneling barriers and added a single impurity atom into the structure. Then we determined the conductance through it. This process may be familiar to people studying transport physics at low temperatures. This is the semiconductor analogue of what I demonstrated earlier in the metallic system. In this case, we can work with materials that we can fabricate into a usable device. Figure 4 shows the *I-V* characteristics for a

semiconductor quantum well that has a single, unintentional Si impurity dropped right in the center of it. The peaks in the figure correspond to resonant tunneling through each of the bound states. What is interesting is that if we look about six orders of magnitude more closely at the current-voltage characteristics (in other words, with enough sensitivity), we see very small steps in the conductance, depending on how many impurities are there. Figure 4 illustrates the characteristic of a single impurity; the observed steps are due to transport through single impurities in a semiconductor system. If we change the barriers, we change the current

appropriately; this is all very understandable in light of the Landauer formulation (Equation 1).

But there is an interesting difference. In the metallic system, the conductance is equal to $2e^2/h$ multiplied by the transmission coefficient. As I explained earlier, we can create, in a metal system, a transmission coefficient of 1. In fact, being able to tune and control transmission coefficients is the key to these experiments. In the semiconductor system, we can tune the transmission coefficient to a high degree of precision. The tunneling barriers provide different transmission coefficients, which turn out to be of the order of

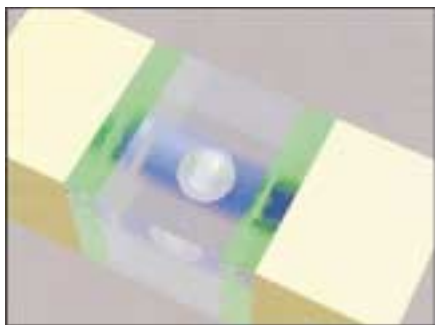


Figure 3. A schematic representation of a quantum well with tunneling barriers into which one impurity atom has been added, for measuring the conductance of a single semiconductor atom.

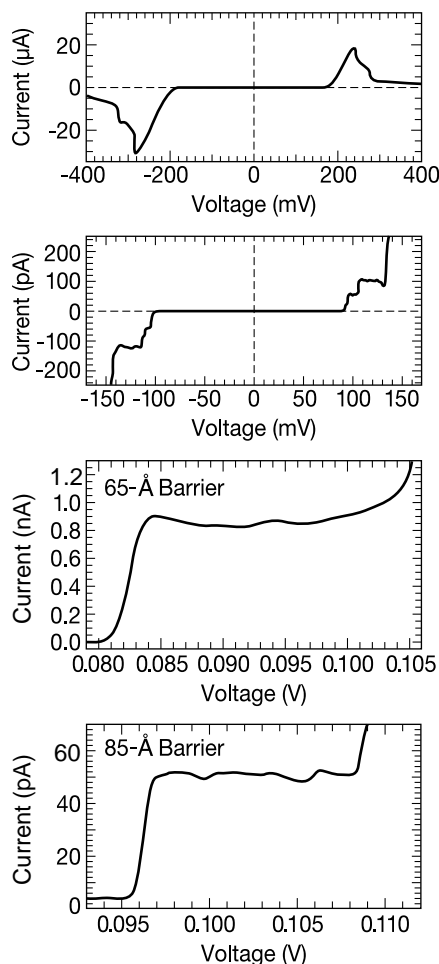


Figure 4. I-V characteristics of a semiconductor quantum well that has a single unintentional Si impurity; the observed steps are due to transport through single impurities in a semiconductor system.

10^{-4} – 10^{-8} , depending on how we design the system. In fact, this is very easy to accomplish, simply by controlling the width of the tunneling barrier, which can be measured very precisely.

This process allows for a very interesting physics measurement: we can actually measure the Zeeman splitting of a single impurity.⁵ In Figure 5, we can see that the single step arising from the conductance of a single impurity splits with magnetic field, which corresponds very well to theory.

Quantizing Conductance in Molecular Systems

Let us move on to the greatest challenge of all. Once again, we create our miniature system, this time putting a molecule between the two metal contacts (Figure 6). Since we've done this with single metal and semiconductor atoms, can we do it with a molecule? This is a tough experiment. Being able to ball-bond a contact onto the end of a molecule is a challenging experimental task, but we have a method that helps us, and that is chemical-directed *self-assembly* (Figure 7). The technique is very simple: we place a substrate of a given metal into a beaker containing a solution of molecules with the appropriate end groups, and they self-assemble into very well-defined layers.

There are all sorts of metals, end groups, and molecules available that will work with this technique. Probably the

most well-defined system, although by no means the only one, is the gold-sulfur end-group system. In chemistry, this is called a *thiol end group* (we also know it as "tarnish"). Gold-sulfur works very well, as do silver, cyanide, and other types of end groups. Many researchers specifically work with alkane thiol systems, *alkane* meaning simply a saturated aliphatic chain.

We can obtain domains of the order of a fraction of a micrometer in these types of systems. The first conductivity measurements of this kind of self-assembled molecular system (Figure 8), done a few years ago,⁶ employed these saturated aliphatic chains. Although scanning tunneling microscope (STM) images show us that these self-assembled layers can be very perfectly made, the film in this case was made slightly defective so that the researchers could measure the types of interesting molecules that absorb into some of these defects. The alkane thiol-type system is a very good insulator, having very little conductivity along its length, which corresponds to the tunneling distance if measured by an STM tip. Think of this monolayer as the molecular equivalent to silicon dioxide. In Figure 8b, the two bright spots (indicated by arrows) are spots of high conductivity, which resulted from the absorption of molecules that were not insulating but in fact had some conductivity along their lengths. That conductivity is provided by the types of

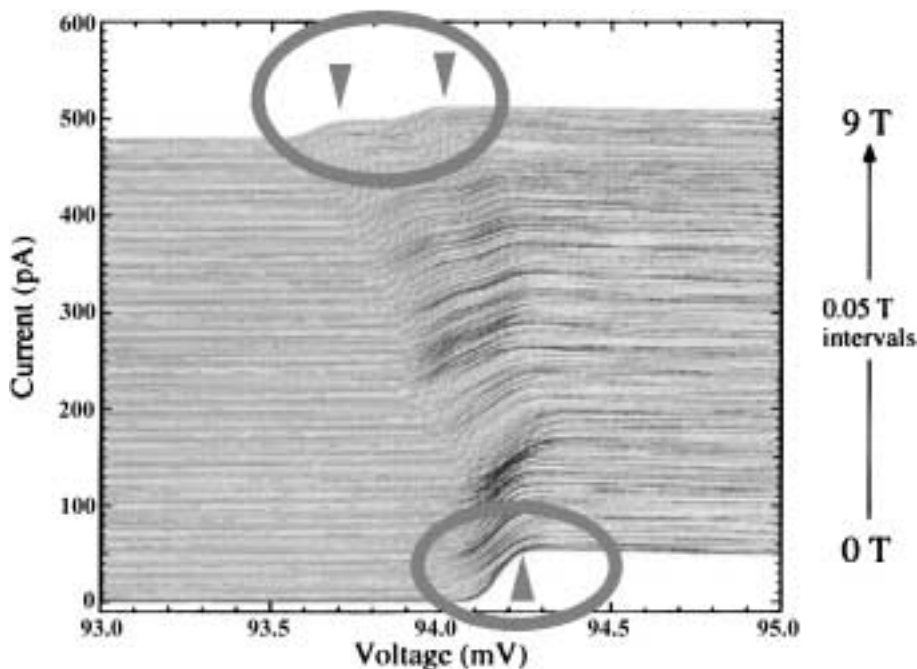


Figure 5. The step arising from the conductance of a single impurity splits with magnetic field, which corresponds to Zeeman splitting (from Reference 5).

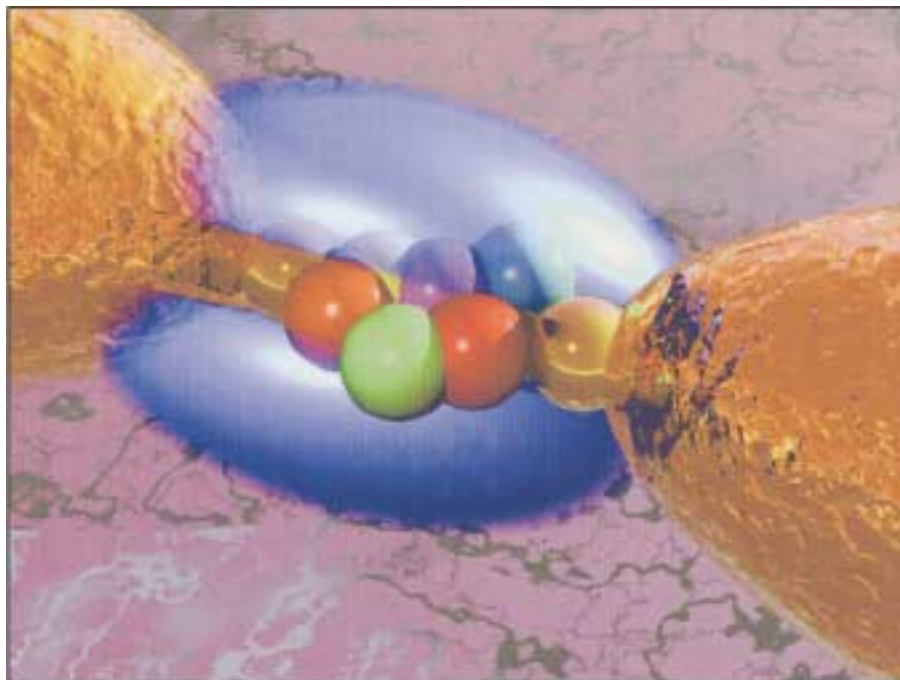


Figure 6. An idealized illustration of the experiment to measure conductance quantization in a single-molecule metal system.

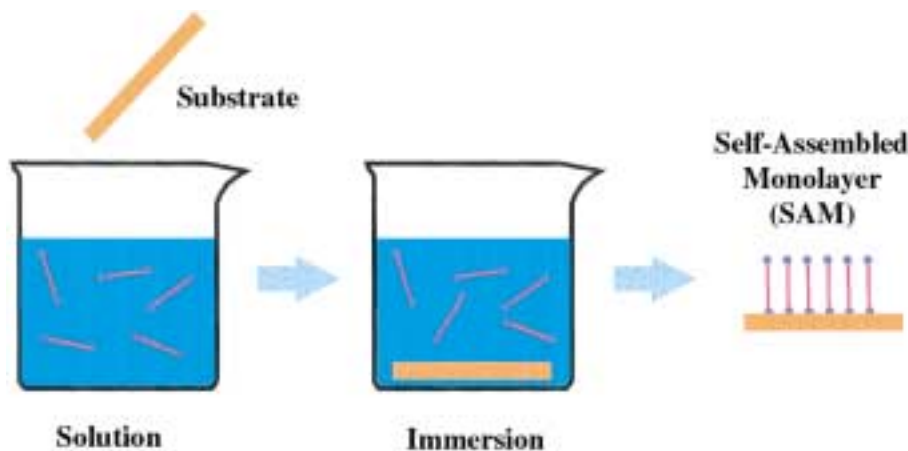


Figure 7. The technique of chemical-directed self-assembly. Illustration courtesy of P. Weiss.

bonds, in this case π bonds, that provide electron delocalization along the length of the molecule. The fact that researchers observed an enhanced conductivity is an indication of this phenomenon.

Figure 9 shows how, instead of using a film with defect sites, we can start with a perfect layer and actually create some holes in it with an STM tip. Reference 7 demonstrates how these more “conjugated” (i.e., more conductive) molecules can then be absorbed into those sites.

Although a number of groups are now doing these types of experiments, no one

has yet been able to determine the transmission coefficient, that is, the conductance, of a molecule. Figure 10 shows how we set out to accomplish this.⁸ We use metallic break junctions with an extreme dimensional sensitivity of 2 pm. For the molecule, we use one that has sulfur end groups, as they will adhere to a gold surface. We can adjust the break junction precisely to the dimension of the molecule we are using and then measure its conductivity. In fact, this set-up led to the first measurements and determination of the I - V characteristics of a single molecule. In

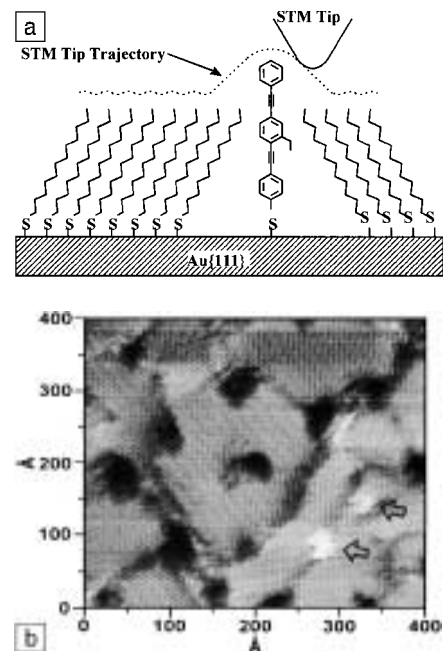


Figure 8. The first conductivity measurements of a self-assembled molecule system by scanning tunneling microscopy (STM). (a) Schematic illustration showing direct observation of conjugated (i.e., conductive) “wires” by means of an STM tip. (b) STM conductivity measurement of single, fully conjugated molecules into self-assembled films of alkane thiol. (From Reference 6.)

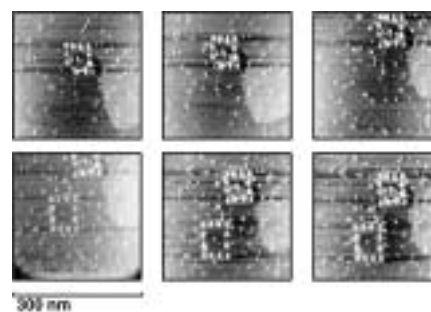


Figure 9. Controlled placement of “conjugated” (i.e., conductive) molecules in an inert alkane thiol matrix by means of an STM tip (from Reference 7).

Figure 11, the red curve shows the I - V characteristics we obtained, and the blue curve shows the conductance, which is useful in comparing these studies.

The transmission coefficient obtained is very poor. In fact, it is about 10^{-5} , and we only need to look at the conductance to measure this coefficient. Why? That is what some of the theoretical work is explaining.

We decided that we needed to undertake a very thorough investigation of what contacts were to molecular systems in order to determine why those transmission coefficients were so poor. We devel-

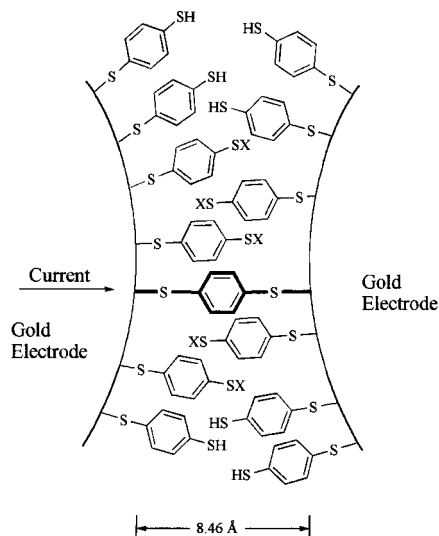


Figure 10. Schematic illustration of an experiment to determine the conductance of a single molecule, in this case, benzene-1,4-dithiol (from Reference 8).

oped a way to create very small tunnel junctions to make these measurements, such that we can determine the current-voltage and the temperature characteristics of the molecule. The previous system (the break junction) had incredible dimensional sensitivity. Unfortunately, it must be held at a fixed temperature; if we vary the temperature by even a fraction of a degree, the junction moves all over the place. Variable-temperature measurements in that system are not possible. Instead, we created very small packets of molecules—about 1000 molecules across—by using various types of electron-beam lithography. We can actually transfer our lithography pattern into the number of molecules that we can measure. We can do that in a stable device configuration and then measure the temperature-dependence of the transfer characteristics. That realization led to the true real beginnings of an understanding of transport in molecular systems. Figure 12 shows the experimental results. We prepare the substrate, place it in the beaker, and the molecules absorb onto the surface, as in Figure 7. Then we evaporate the top contact and create very small devices, where the active area is determined solely by the molecular-absorption layer.

The first thing we noticed was that at room temperature, an asymmetric structure has an asymmetric I - V characteristic,

with a rectification ratio of about 500:1 (Figure 12a). We can perform variable-temperature measurements and thereby observe all of the interesting transport physics. That was our real goal here and one of the real first advances in this area.

Figure 12b shows log current as a function of the inverse of temperature for various voltages. The results display a very nice thermionic emission, where we can discern the actual barrier heights of the metal contact to the molecule. For the first time, we are starting to gain a true understanding, on a molecular scale, of the role of the metal contact to a molecule.⁹ When we scale up to systems such as doped bulk systems, we can start to treat the transport in a real semiconductor sense.

Being able to realize a molecular-scale diode, in fact, was one of the first proposals ever made for these systems, back in 1974.¹⁰ Note the years it took to progress from that point to the present. We are starting to build a database, as are many in the field, in an effort to understand the relationships between the various types of molecule systems and their contacts.

Figure 13 shows something a bit different from the thiol system: isocyanide. This group, which connects to gold or palladium, is now showing relatively low barriers.¹¹ We hope, at some future stage, to reduce those barriers to zero. In some cases, we want a large barrier, as when we want to create the equivalent of a Schottky diode. In some cases, we want an ohmic contact.

All of these effects seemed to be contact-type phenomena until researchers started to actually see the internal workings of molecules. Thus came the first hints of something new—the observation of transitions that were different from what had been seen in any other molecular systems. This was due to adding another phenyl ring into the center of the system, giving it an internal rotational degree of freedom. Researchers noticed an insulating transition (albeit at a very low temperature, about 20 K) that had not been seen in any other system before, perhaps due to the actual internal rotation of this molecule.

Temperature is not the easiest thing to control in an actual device; we would like to be able to control it with voltage. Figure 14 provides recent results that show the realization of one of the first genuine molecular-scale switches. Here we have changed the internal structure of the molecule to have what is called a *redox* center, that is, something that can be oxidized and reduced. By employing our SAM (self-assembled monolayer) device process, we can actually measure the I - V characteristics of the molecule. If we were to remove the redox center, an essentially

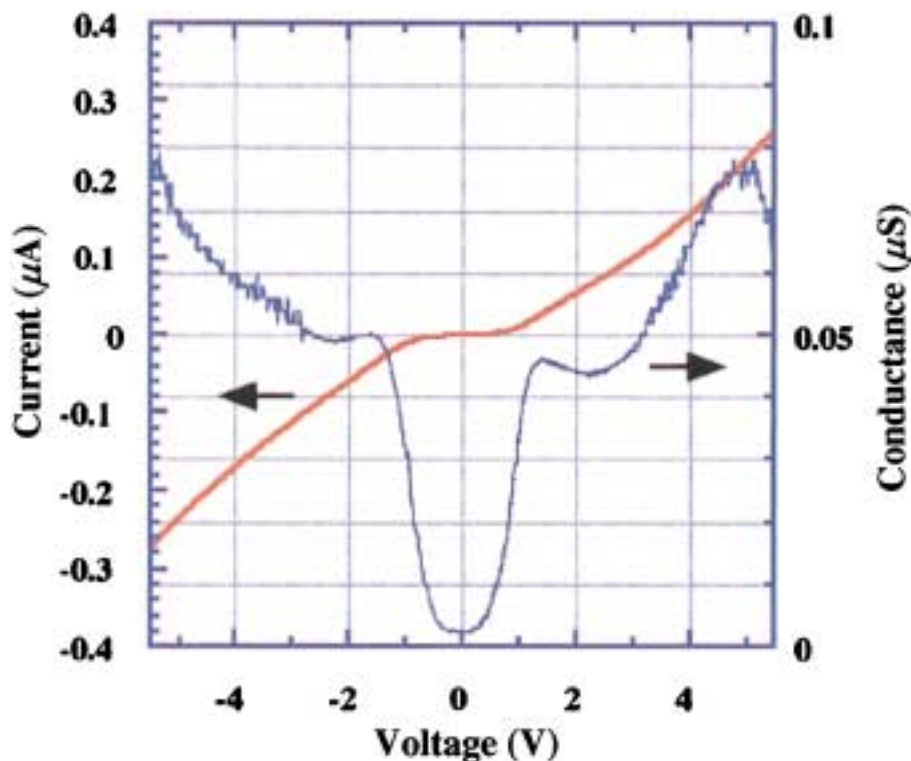


Figure 11. The I - V (red) and G - V (blue) characteristics of a single molecule.

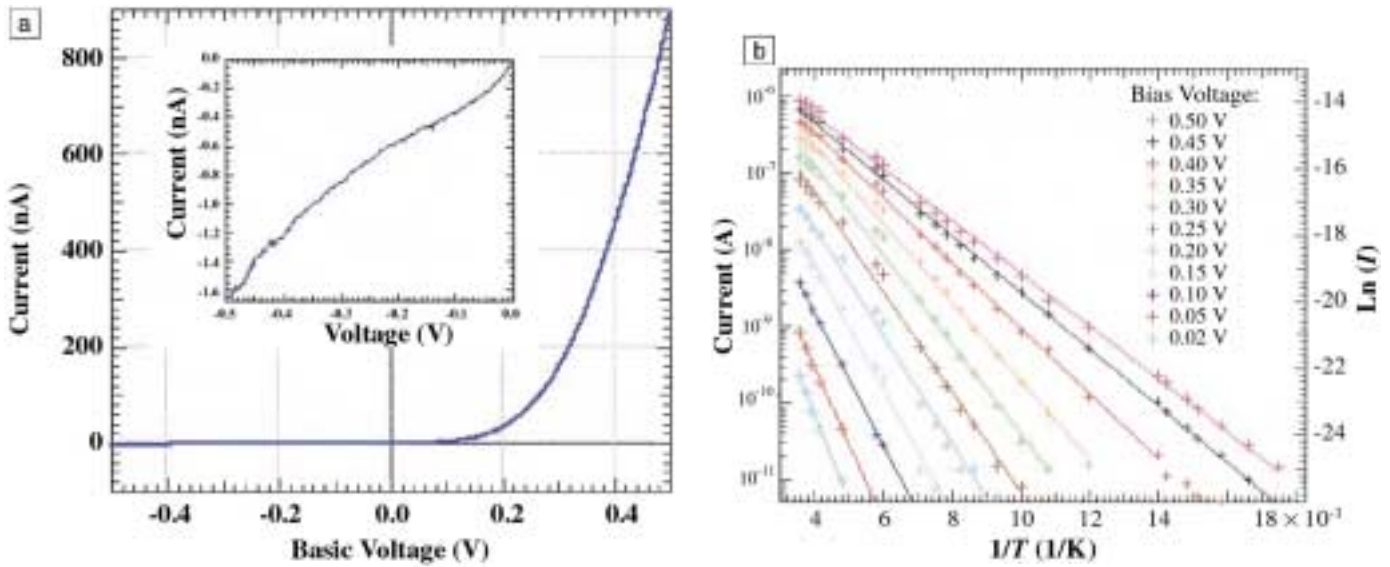


Figure 12. Experimental I-V characteristics of a molecule/metal device. (a) The linear characteristics exhibit a rectification ratio of about 500:1 (300 K). (b) The log current as a function of 1/T demonstrates thermionic emission. (From Reference 9.)

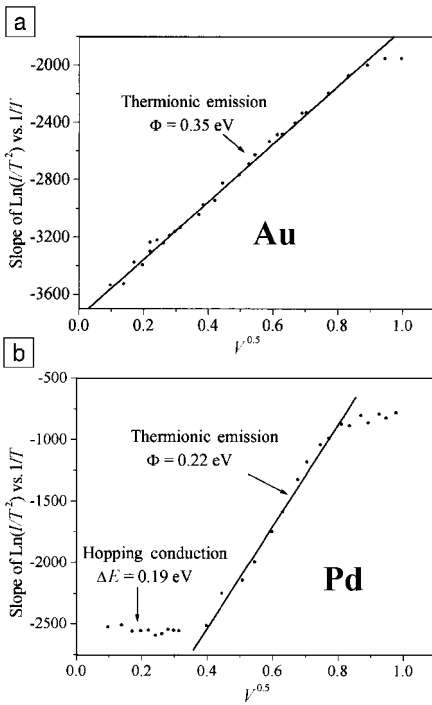


Figure 13. Barrier heights of the isocyanide system (from Reference 11).

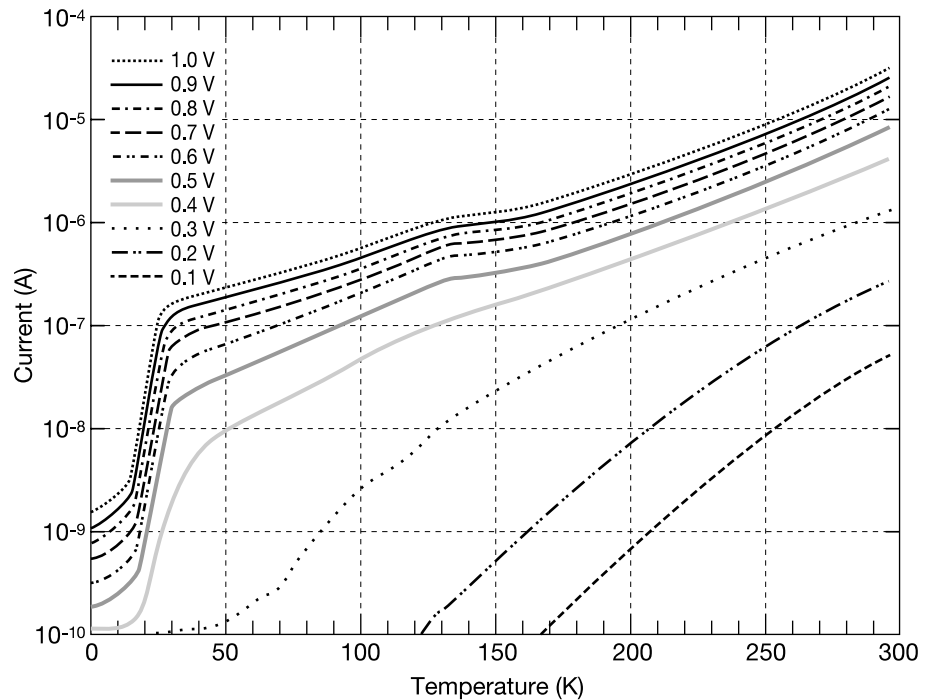


Figure 14. A low-temperature transition in a multiphenyl system.

featureless I-V characteristic (except for the low-temperature transition phenomenon) would be observed.

In this case, we saw something dramatically different. At a certain voltage, we observed a turn-on of the conductivity and, very quickly afterward, a shut-off.

In solid-state language, this looks like a resonant tumbling diode (RTD), although it is not. It has the same type of I-V characteristics, that is, it exhibits negative differential resistance (NDR). Figure 15 shows the device parameters at 60 K. A figure of merit often used to quantify this is the

peak-to-valley ratio (PVR), which is an expression of how well the current shuts off. The peak turns out to be a little greater than 1 nA, while the valley current is roughly at the limit of the electrical apparatus on which this was measured. The PVR here is in excess of 1000:1, and it very

well could be greater, since we start experiencing noise limitation at that temperature. This phenomenon is fully repeatable, meaning that we can switch back and forth between these states.

We are starting to get the first glimpses of what is happening in these devices. Figure 16a shows a curve of the I - V characteristics; Figure 16b shows a curve of what happens when we place this into an electrochemical cell. The first reduction peak in the electrochemical cell, in fact, correlates to the turn-on. It appears that for the first charging effect, we obtain the turn-on, and for the second charging effect, the turn-off. How this affects the transport,

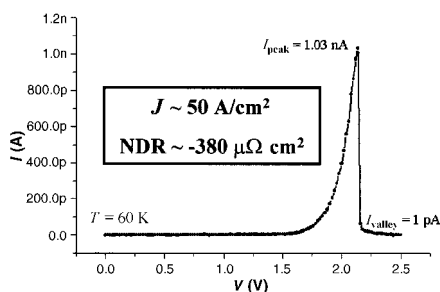


Figure 15. Negative differential resistance (NDR) with 1000:1 peak-to-valley ratio (PVR) in a molecular junction.

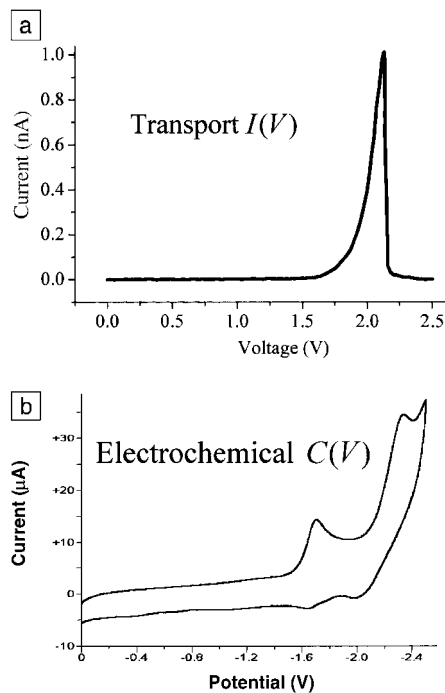


Figure 16. (a) I - V characteristics and (b) cyclic voltammetry of the NDR molecular device.

though, we still do not know, although the correlation is excellent.

Figure 17 shows the temperature characteristics of the device. Its PVR is reasonably good at a low temperature of about 60 K. As we increase temperature, we notice a bit of a shift. There are some similarities and some differences between these devices and resonant tunneling diodes that are interesting. There is a 31-meV activation barrier that we are in the process of trying to explain, but outside of those details, what we see is that performance disappears at high temperatures. It would be nice to get high-temperature characteristics; in fact, those exist now (see Figure 18 and Reference 12).

Interestingly, researchers observed these negative resistance effects in semiconductor systems back in the 1970s, and it took over a decade before anyone was able to create these effects at room temperature. Yet this was done in about three months. That is why these advances are really exciting; now that we have the analytical tools, we can do much more detailed tailoring and synthesis of the in-

ternal workings of these structures and thereby characterize them.

The Future of Molecular-Scale Electronics

“Electronics” means not just devices, but also materials. We are still at the materials stage in this field, working to under-

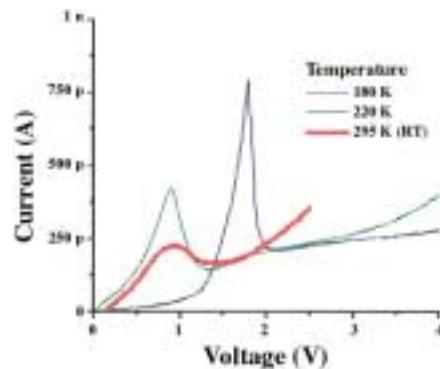


Figure 18. Room-temperature NDR molecular device.

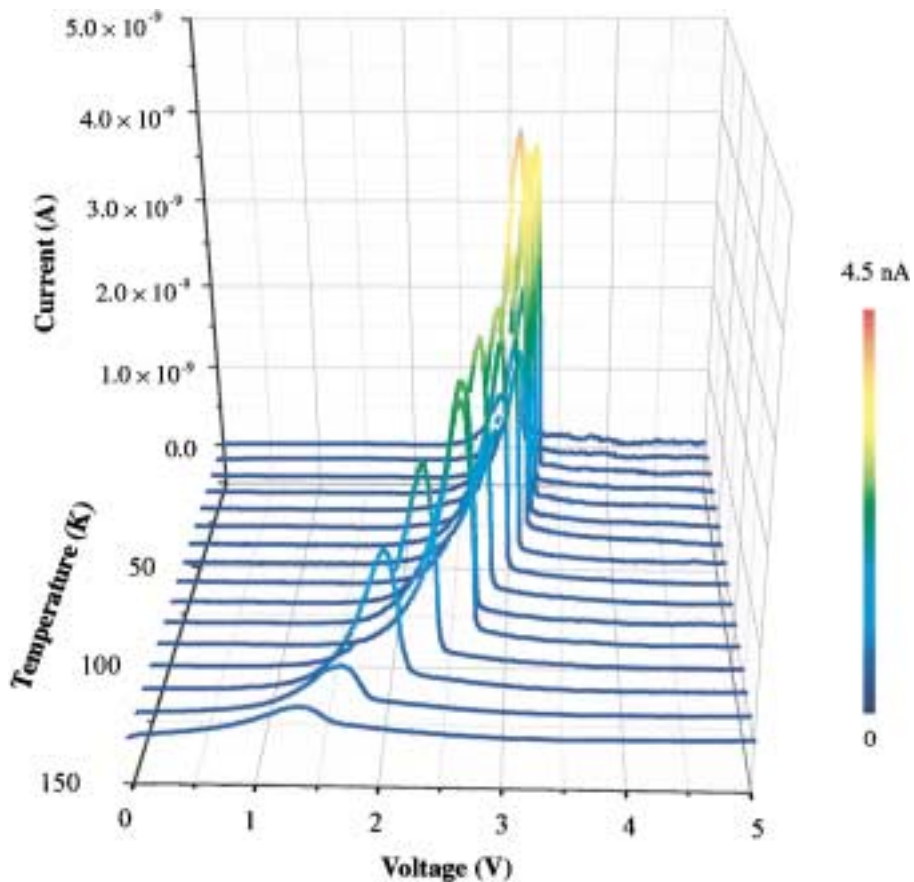


Figure 17. The temperature dependence of the NDR device.

stand fundamentally what is going on in the materials by measuring their transport characteristics. Electronics has to go one step further, to a point where we can actually interconnect all of the devices. How we are actually going to progress technologically to the point where we can connect molecules is still not clear, although many ideas are being investigated. It will take a number of years to understand which of these ideas really work. Learning how we can connect all of these structures at the molecular scale is the next stage in understanding these systems. We can prototype many circuits, for example, using other molecules.

Getting to the field of true electronics means massively connecting many of these systems, and that is a challenge that will require some novel ideas. Our view of what circuits are may change quite dramatically. We might imagine a circuit in which some of these molecular components are connected to metallic or semiconductor spheres that are connected by perhaps carbon nanotubes that are interfaced to the real world. The actual system might be significantly more complex than we currently realize. That is our challenge for the future: to gain a greater understanding of these structures.

The first lesson lies almost completely in the contacts. Contacts always have been the problem with any new materials system—a problem that has always been solved by alchemy. To understand this better, we are starting to build the experimental database and examine what the contacts are to molecular-scale systems. These studies involve less of what is going on in the device and more of what is going on in the contacts.

If we are going to progress to molecular-scale systems, we cannot use systems that

are as large as depletion layers. Depletion layers do not work when the system size shrinks significantly below 100 Å because their electron densities are simply not high enough. We have to think of switching to different mechanisms. The example I discussed of resonant tumbling diode behavior is one of several that we need to develop in order to explore electronics on this scale.

Circuit implementations will have to be dramatically different, and we have yet to figure out how to get there. It is not going to happen as a step function. But at some stage, we will learn how to change our circuit architectures to take advantage of self-assembly-type processes.

References

1. R. Landauer, *IBM J. Res. Dev.* **1** (1957) p. 223.
2. B.J. van Wees, H. van Houten, C.W. J. Beenakker, J.G. Williamson, L.P. Kouwenhoven, D. van der Marel, and C.T. Foxon, *Phys. Rev. Lett.* **60** (1988) p. 848; B.J. van Wees, H. van Houten, C.W.J. Beenakker, J.G. Williamson, L.P. Kouwenhoven, D. van der Marel, and C.T. Foxon, *Phys. Rev. B* **43** (1991) p. 12431.
3. D.A. Wharam, T.J. Thornton, R. Newbury, M. Pepper, H. Ahmed, J.E.F. Frost, D.G. Hasko, D.C. Peacock, D.A. Ritchie, and G.A.C. Jones, *J. Phys. C* **21** (1988) p. L209.
4. C.J. Muller, J.M. Krans, T.N. Todorov, and M. A. Reed, *Phys. Rev. B* **53** (1996) p. 1022.
5. M.R. Deshpande, J.W. Sleight, M.A. Reed, R.G. Wheeler, and R.J. Matyi, *Phys. Rev. Lett.* **76** (1996) p. 1328.
6. L.A. Bumm, J.J. Arnold, M.T. Cygan, T.D. Dunbar, T.P. Burgin, L. Jones II, D.L. Allara, J.M. Tour, and P.S. Weiss, *Science* **271** (1996) p. 1705.
7. J. Chen, M.A. Reed, C.L. Asplund, A.M. Cassell, A.M. Rawlett, J.M. Tour, and P.G. Van Patten, *Appl. Phys. Lett.* **75** (1999) p. 624.
8. M.A. Reed, C. Zhou, C.J. Muller, T.P. Burgin, and J.M. Tour, *Science* **278** (1997) p. 252.
9. C. Zhou, M.R. Deshpande, M.A. Reed, and J.M. Tour, *Applied Phys. Lett.* **71** (1997) p. 611.
10. A. Aviram and M.A. Ratner, *Chem. Phys. Lett.* **29** (1974) p. 277; R.M. Metzger, B. Chen, U. Höpfner, M.V. Lakshminantham, D. Vuillaume, T. Kawai, X. Wu, H. Tachibana, T. Hughes, H. Sakurai, J.W. Baldwin, C. Hosch, M.P. Cava, L. Brehmer, and G.J. Ashwell, *J. Am. Chem. Soc.* **119** (1997) p. 10455.
11. J. Chen, L.C. Calvet, M.A. Reed, D.W. Carr, D.S. Grubisha, and D.W. Bennett, *Chem Phys. Lett.* **313** (1999) p. 741.
12. J. Chen, W. Wang, M.A. Reed, M. Rawlett, D.W. Price, and J.M. Tour, "Room-Temperature Negative Differential Resistance in Nanoscale Molecular Junctions," *Appl. Phys. Lett.* **22** (2000) p. 1224.

Mark A. Reed received his BS (1977), MS (1979), and PhD (1983) degrees in physics from Syracuse University in New York. From 1983 to 1990, he was at Texas Instruments, and in 1990, he joined Yale University and holds the Harold Hodgkinson Chair in Engineering and Applied Science. Since 1995, Reed has been the Chair of Electrical Engineering at Yale. His research activities include nanoscale and mesoscopic systems, tunneling and transport in heterojunction systems, artificially structured materials and devices, microelectromechanical systems (MEMS), nanotechnology, and molecular electronics. Reed is the author of more than 100 professional publications and three books, and he holds 17 U.S. and foreign patents on quantum-effect, heterojunction, and molecular devices. He has given numerous plenary and invited talks. His awards include Fortune's "Most Promising Young Scientist" (1990), the Kilby Young Innovator Award (1994), the DARPA ULTRA Most Significant Achievement Award (1997), and the Syracuse University Distinguished Alumni Award (2000). In 1999, Reed co-founded the Molecular Electronics Corp. in Chicago, for which he serves as Director and Chief Technical Officer.

ICNS-4
FOURTH INTERNATIONAL CONGRESS
ON NITRIDE SEMICONDUCTORS
DENVER, COLORADO USA • 2001

Abstract Deadline: March 31, 2001

July 16-20, 2001 • Denver, Colorado

Chair: Jacques Pankove, Astralux, Inc.

Sponsored by the
Materials Research Society and the Electron Devices Society of IEEE



Networking the World™

E-mail: info@mrs.org • www.mrs.org/meetings/icns-4/