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Room temperature negative differential resistance in molecular nanowires

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Electric-field assisted assembly has been used to place rod-shaped metal nanowires containing 4-{[2-nitro-4-(phenylethynyl)phenyl]ethynyl}benzenethiol molecules onto lithographically defined metal pads. In these systems the current–voltage characteristics exhibited negative differential resistance at room temperature with on–off peak-to-valley ratios of 1.80 to 2.21.

Introduction

There is an ambitious but realistic goal for molecular electronics: the use of synthesis, assembly and miniaturization on the molecular level to achieve huge densities of devices such as molecular wires, rectifiers, switches, transistors and memories. At very small dimensions characteristic quantum effects become prominent, which can be exploited to create a new class of quantum effect devices. Remarkable progress has been made in recent years in identifying candidate molecules with interesting electronic properties such as molecular conduction, rectification, negative differential resistance (*i.e.* increased resistance with increasing voltage) and configurable switching.[1–12] Such molecules can be used to perform logic and memory functions in electronic circuits, in a fashion analogous to the one currently performed by transistors. The broad variety of electronic functions available by synthetic modification of these molecules suggests many ways in which they may be used in hybrid or "post-silicon" applications. Recently significant advances in the demonstration and fabrication of molecular-scale systems have been made due to advanced nanofabrication and self-assembly techniques.[13–15] In the nanoscale device area the number of self-assembled molecules is small, so that the likelihood of defects is reduced. Investigations into electronic conduction through conjugated molecules that are end-bound onto surfaces are now possible and have been demonstrated with scanning tunneling microscopy and proximal probes. Here we report on the observation of large negative differential resistance behavior at room temperature in an electronic device that utilizes organic molecules as the active component.

Our electronic measurements were performed on circuits containing gold nanowires as supporters of the electronically active molecules. Nanowires were nanoscopic in diameter but macroscopic in length. Therefore, it was relatively easy to configure composites of nanowires and conducting molecules (molecular wires or electronically active molecules) in electronic circuits compared to wiring individual molecules. Similar experiments have already been made using metal nanoparticles.[12]

Experimental

We prepared nanowires using replication inside the pores of 70 nm diameter polycarbonate track etched membranes. Au was electrochemically deposited half way through the 6 μm long pores. Prior to electrodeposition of the nanowires, one side of a polycarbonate membrane was first coated with a 100 nm layer of Au by thermal evaporation. This conductive layer seals the pores on one side of the membrane and serves as a cathode on which to electroplate metal. The membrane was then placed on a conductive Ag plate or an Au coated glass slide, such that the Au coated side was in contact with the conductive surface.

The electrochemical cell, which consisted of a glass tube that terminated in an "O" ring seal, was placed on top of the membrane and held in place with a clamp. The electroplating solution was then added to the cell, and Au plated at a constant potential. A saturated calomel electrode served as the reference electrode and a Pt wire as the counter electrode.

A self-assembled monolayer (SAM) of organic molecules was adsorbed on top of the electrochemically deposited Au layer. Active molecules of 4-{[2-nitro-4-(phenylethynyl)phenyl]ethynyl}benzenethiol (referred to below as NDR molecules) were integrated into a matrix of 16-mercaptohexadecanoic acid molecules of composition $HS(CH_2)_{15}COOH$ (referred to below as C_{16} molecules), see Fig. 1. The high affinity of Au to thiol groups results in specifically oriented organic molecules.

Electroless plating was done to introduce metal caps on top of the SAM.[14] Sn was first adsorbed on top of the monolayer from a 50 : 50 mixture of methanol and water acidified with 0.007 M trifluoroacetic acid. This adsorbed Sn was then used to generate nanoparticles of Ag by adding ammoniacal $AgNO_3$ after thorough rinsing with methanol. To ensure the formation of a complete layer of metal on top of the monolayer, Au was electrolessly plated from a solution that was 0.04 M in Au and contained formaldehyde as a reducing agent. The remaining empty portion of the pores was then filled by electrolessly plated Au. A more detailed description of nanowire formation (containing a metal top contact C_{16} SAM as the active region, and a metal bottom contact) has already been published elsewhere.[13] The length of the NDR molecules extends above the alkanethiol film. The tops of the NDR molecules are adsorbed on gold deposited on a C_{16} SAM. The whole nanowire (Au–SAM–Au) is approximately 7 μm long and 70 nm thick.

Electric-field assisted assembly[14,15] was used to assemble nanowires on lithographically defined arrays for testing the electrical properties of rods containing organic molecules.

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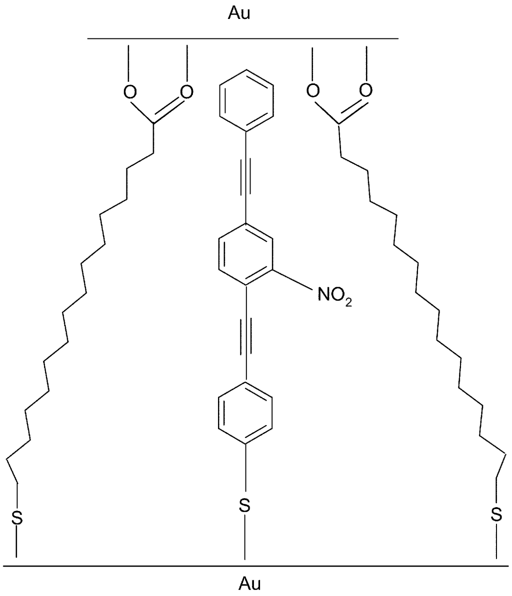

Fig. 1 Schematic representation of active molecules 4-{[2-nitro-4-(phenylethynyl)phenyl]ethynyl}benzenethiol integrated into a matrix of 16-mercaptohexadecanoic acid molecules of composition $HS(CH_2)_{15}COOH$. The height of the 4-{[2-nitro-4-(phenylethynyl)-phenyl]ethynyl}benzenethiol molecules extends above the alkanethiol film so the tops of the molecules are in physical contact with the gold deposited on the $HS(CH_2)_{15}COOH$ self-assembled monolayer.

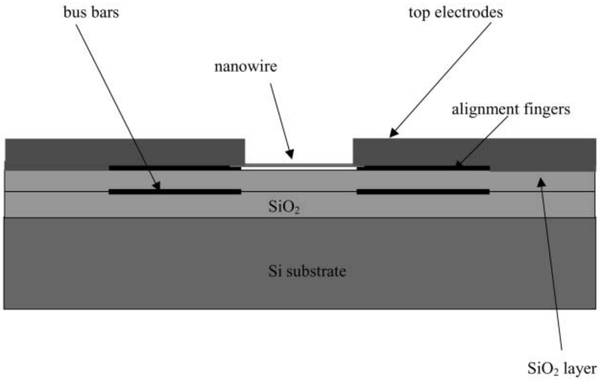

Fig. 2 Schematics of device fabrication. The bottom electrodes, the Ti/Au busbars, were isolated from the next level by a 2 μm thick SiO_2 layer. On top of the dielectric layer, upper electrodes were defined by Ti/Au liftoff. This level was an array of alignment fingers with separation distances varying from 2 μm to 6 μm. In order to investigate the electrical properties of the aligned rods, large Ti/Au contact pads were deposited after nanowire alignment to allow mechanical probing.

Lithographically defined arrays were prepared using a 3-mask process, see Fig. 2. An N-type Si wafer of <111> orientation with an approximately 2 μm thick SiO_2 layer was used as a base for the whole device. The bottom electrodes,Ti/Au busbars, were isolated from the next level by a 2 μm thick SiO_2 layer. On top of the dielectric layer, the upper electrodes were defined by Ti/Au liftoff (Fig. 2). This level was an array of alignment fingers with separation distances varying from 2 μm to 6 μm. To drive the alignment, a 35 V, 1 kHz voltage was applied to the busbars. After that a few microliters of a solution containing functionalized rods was dispensed on the sample surface. The nanowires polarize in the electric field due to charge separation and, consequently are pulled towards regions of strong field. Capacitive coupling between the busbars and the top electrodes produces a stronger electric field between the alignment pads than in the areas around it, and large near field forces place the nanowires between the alignment pads. In order to investigate the electrical properties of the aligned rods, large Ti/Au contact pads were deposited after nanowire alignment to allow mechanical probing. The scanning electron micrograph (SEM) of an aligned rod between two electrodes is shown in Fig. 3. Current–voltage (*I–V*) characterization of nanowires containing molecules was done at room temperature by a two-point probe method using a HP 4155 semiconductor parameter analyzer.

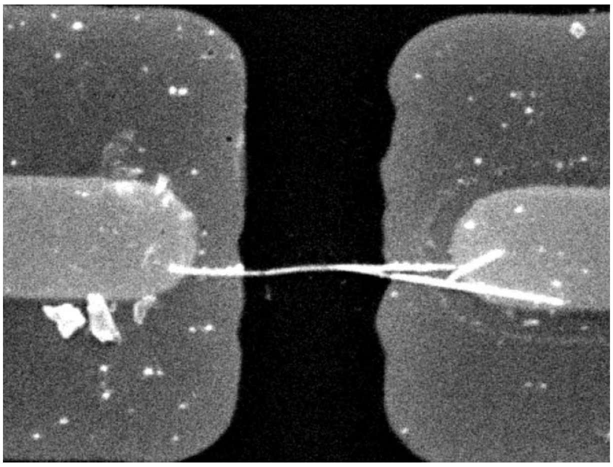

Fig. 3 SEM picture of a rod aligned between two electrodes covered by contact electrodes. Lithographically defined arrays were prepared using a 3-mask process. Au busbars were isolated from the next level by a SiO_2 layer. The next level was an interdigitated array of alignment fingers with separation distances varying from 2 μm to 6 μm. The third level consisted of contact pads that were vapor deposited on top of the aligned nanowires and could act as contacts for measurement probes.

Results and discussion

I–V characteristics of two different devices (labeled A, B) which exhibited NDR are presented in Figs. 4 and 5. Negative differential resistance was clearly seen when positive bias (from 0 to 2.0 V) had been applied to the system (Fig. 4). The *I–V* curve was reversible upon change of sweep direction—from 2.5 to 0 V. Standard diode behaviour was observed under negative bias (from 0 to −2.0 V), see Fig. 5. NDR molecules have great conductivity compared with that of C_{16} (which are known as good insulators[12,13,16]). Thus, when the Au–SAM–Au system works properly the current passing through C_{16} molecules is several orders of magnitude lower than current passing through the NDR molecules at the same voltage. The instrument current limit was typically set at the order of 10^{-8} A to prevent monolayer damage. We measured *I–V* characteristics of 800 nanowires (rods aligned between two electrodes prepared by the same procedure (described above) and measured at room temperature). For approximately 10% of the measured devices we obtained *I–V* characteristics which revealed negative differential resistance behaviour and had similar peak shapes and positions. Two examples of such *I–V* curves are presented in Figs. 4 and 5. The peak-to-valley ratios in the case of the positive bias *I–V* curves at room temperature were 1.80 (device A) and 2.21 (device B), the positions of the peaks were at 1.068 V (device A) and 1.12 V (device B), peak currents were 3.12×10^{-9} A (device A) and 3.26×10^{-9} A, (device B). The peak positions were close to the values previously obtained for similar systems (at room temperature) containing the same active component—the 4-{[2-nitro-4-(phenylethynyl)phenyl]-ethynyl}benzenethiol molecules.[17] The remaining portions of the tested devices (90%) exhibited faults. They gave ohmic *I–V* characteristics with either low (85%) or high (5%) resistances. We suppose that the faults are formed in the systems mainly during the rod preparation process, in particular top electrode electrodeposition should have a strong impact on the rods functionality. Epple *et al.*[18] studied molecular orientation in alkanethiolate SAMs on a gold surface during copper

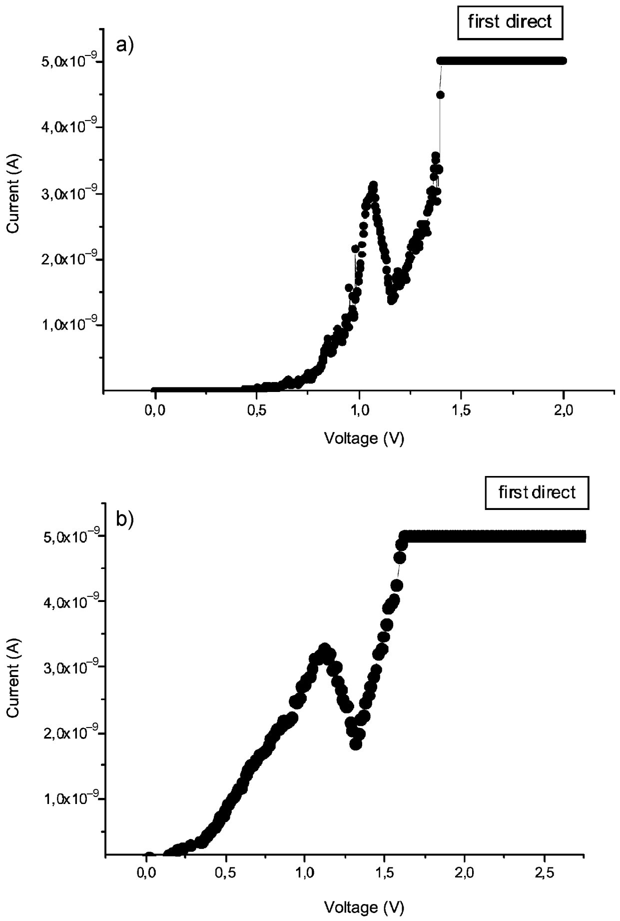

Fig. 4 a) Current *vs.* voltage characteristics for the Ag–NDR–Au structure on a linear scale for device A; first measurement, measured from 0 to 2.0 V. b) Current *vs.* voltage characteristics for Ag–NDR–Au on a linear scale for device B; first measurement, measured from 0 to 2.0 V.

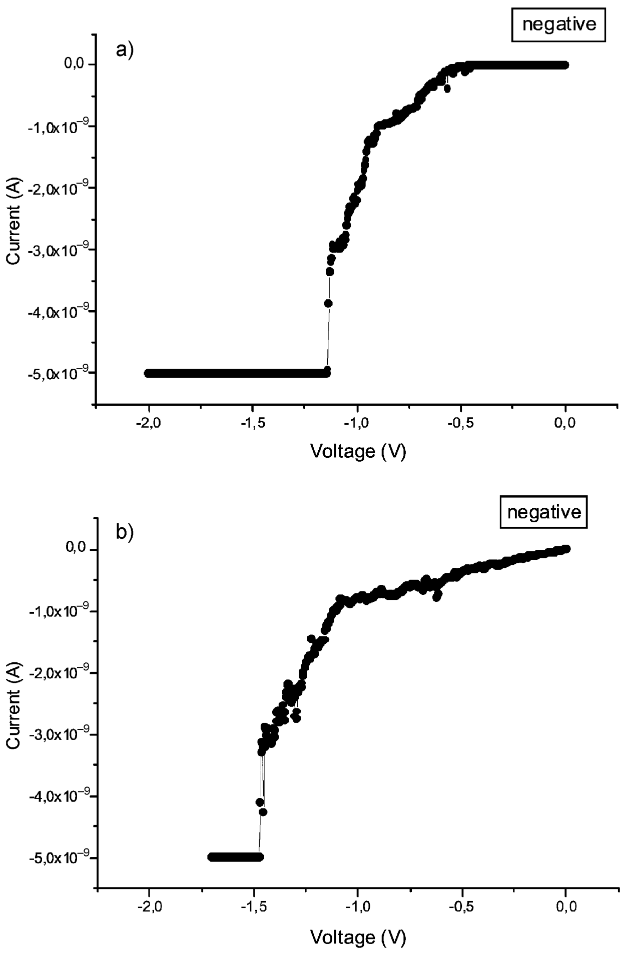

Fig. 5 a) Current *vs.* voltage characteristics of the Au–NDR–Au structure on a linear scale for device A, measured from 0 to −2.0 V. b) Current *vs.* voltage characteristics for Ag–NDR–Au on a linear scale for device B, measured from 0 to −20 V.

electrodeposition. The study demonstrates that slow metal deposition in the submonolayer range can have an influence on the structure of short chain thiolates (for the shortest molecule—hexanethiol, C_6—an increase in the methyl group tilt angle from 22° to 83° during copper deposition has been observed). Top layer electrodeposition in our systems can not only cause a change in the molecular structure but also other defects in the systems as well as the insertion of metallic contacts into the SAMs. It is also possible that other faults in the systems arose during subsequent manipulations and processes (electric-field assisted assembly, photolithography, Ti/Au contact pads deposition, *etc.*). Nevertheless it should be emphasized again that we were able to obtain a relatively good yield—approximately 10%—of measured devices that exhibited negative differential resistance behavior comparable to other teams' results.[6,17] The negative differential resistance was absent in the control samples (containing just C_{16} molecules molecules, not NDR molecules).

Present understanding of the negative differential resistance in molecular systems is not definitely clear. Several models have been found in the literature.[6,8,17,19–22] The mechanism proposed to explain the negative differential resistance behavior for short phenylene–ethynylene oligomer molecules (substituted asymmetrically by π-active groups)[6] sandwitched between two gold contacts was based on density functional theory calculations.[10,20] These calculations have been used to analyze the electronic structure of molecules in the neutral, singly, and doubly reduced states. The results have been interpreted to suggest that the high current peak is associated with full electronic delocalization of the lowest unoccupied molecular orbital in the singly reduced state; according to this interpretation, the peak profile results from the absence of delocalization in the neutral and doubly reduced states, such delocalization being required to ensure conductance across the molecular junctions. The current–voltage characteristics of the molecular systems are frequently proposed to be sensitive to the electronic structure of the molecule and contacts,[19] which depends on the spatial arrangement (conformation) of the atoms that make up the system and the distribution of the electronic charge along the system. It has also been proposed[20] that conductance switching of 4-{[2-nitro-4-(phenylethynyl)phenyl]ethynyl}benzenethiol molecules is a result of conformational changes in the molecules or bundles, rather than the electrostatic effects of charge transfer. In ref. 21 the molecular systems have been observed to switch between the conducting and nonconducting state due to a voltage-induced redox reaction, *i.e.*, to a change in the charge distribution in the wire and also in response to bias-driven conformational change. These experiments indicate that transport nonlinearities, conformational changes, and charging in molecular systems are coupled phenomena that can strongly influence each other. Recent theoretical work[22] suggests that in the nonlinear transport regime the molecular wires acquire an excess electronic charge. This charge resides in molecular orbitals which, being partly occupied, lies at the Fermi level and therefore controls electron transport through the molecule. As the bias increases, the partly occupied orbital acquires more charge and the electrostatic contribution to its energy rises, together with electrochemical potential of the source electrode. When this electrostatic contribution to orbital energy rises well above the electrochemical potential of the drain electrode, the electron flux that transmits from drain to source approaches zero and ceases to decline with increasing bias, while the flux that transmits from source to drain cannot increase significantly. Thus, the net current through the molecule is saturated. At the same time the current density wave grows along the wire and atomic displacement occurs, *i.e.* lengthening and thus weakening certain molecular bonds. In summary, the effects of charging and conformational change can be understood together in terms of a robust physical mechanism of negative differential resistance.

Conclusions

In conclusion, the formation of a metal–SAM–metal junction was established inside nanowires through combined electroplating–electroless plating and template replication. This has been demonstrated using an alkanethiol SAM containing NDR molecules. For these molecular wires the current–voltage characteristics exhibited negative differential resistance at room temperature with on–off peak-to-valley ratios of 1.80 to 2.21. Thus, a novel method with which to prepare nanostructures containing organic molecules with negative differential resistance properties has been devised. We have also demonstrated a simple method for inserting an organic molecule into an electronic circuit. We have developed a method to form junctions containing SAMs of organic molecules using electric field self-assembly to place rod-shaped metal–SAM–metal nanowires in colloidal suspensions onto lithographically defined metal pads. In this way we have constructed electrical devices containing monolayers with negative differential resistance.

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