Molecular and Polymer Nanodevices

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Over past years, the research and engineering community has been intensively looking for possibilities to extend of the information processing technologies into post-CMOS era. Recently, Nanotechnology Research Initiative formed by leading semiconductor companies has formulated a set of research vectors (Welser et al., 2008) to guide and to coordinate these efforts. Based on the analysis of the ultimate limitations of the present technology and on the observations of the research and development trends, one of the recommendations is the search of devices operating with the state variables different from an electronic charge. A solid-state switch where the computational state is defined by the spatial locations of heavy particles such as ions, atoms or molecular conformations is one of such possibilities.

Possible advantage of heavier information carriers can be easily illustrated (Cavin et al., 2006). Scaling of CMOS devices operating with electronic charge will eventually reach the limit when logic or memory state decays because of electron tunneling under the barriers. For a given barrier height and width that is limited by the material constraints and the device size and by the requirement of the minimal power dissipation, carriers such as ions or atom that are thousands time heavier than electron offer much greater stability to the computational state. Ironically, the use of heavy carriers is absolutely impractical in larger devices because of much lower mobility. However, in a device of a few nanometer size, the ion/atom transport can be fast enough for practical applications.

Short molecules and macromolecules can be used as active material for such switching devices. Devices built with short molecules have long been considered as promising candidates for post-CMOS era for a number of reasons. Organic molecules can be extremely small and at the same time exactly reproducible as a stand-alone units. There are numerous synthetic techniques and the variety of organic compounds is enormous. Some of well known approaches to molecular electronics relied on molecular conformation or oxidation for achieving electronic functionality. Examples (Chen et al., 1999; Collier at al., 2000)

However, the reliable fabrication of devices and the assembling of molecules into circuits turned out to be extremely challenging. I will illustrate some of the challenges of fabrication and characterization of molecular devices with examples from our research. Before starting to design a molecular switch or a transistor we have tested simpler building blocks of molecular “toolbox” such as molecular “wires” and molecular “barriers”.

The investigation of electronic properties of molecular devices is intimately related to research toward alternative fabrication routes that can better compatible with the new materials. First, the required feature size is often beyond the limits of the best lithography machines. Second, the properties of pristine material can be substantially altered by, e.g. exposure to high-energy electron beam encountered in e-beam lithography step, etching or contact deposition.

In our research, we have focused on the issue of non-invasive fabrication of nano- and mesoscale molecular devices and effects of fabrication on structural and electronic properties (Zhitenev et al., 2006). Metal-molecular monolayer-metal junctions have been made using three original techniques targeting different issues of fabrication and complementing each other. We have screened many possible candidates for molecular "wires" and molecular "barrier" and have selected representative molecules capable of forming dense self-assembled monolayer (SAM) with the most robust structural and electrical properties.

The first technique targets nearly single-molecule devices. The junctions are formed on the surface of the tips exploiting evaporation of contacts from different angles with assembly of the SAMs the middle. Device conductance is monitored during the final junction formation and the devices can be studied at multiple stages: from minimally detectable conductance that is below conductance of a single molecule junction to approximately single molecule device to multi-molecule device.

The shortcoming of the technique is its reliance on the conductance as a single feedback parameter characterizing the junction formation. The second technique was a planar evolution of the first one. In this case, we used nanoscale stencil mask pre-fabricated on chip surfaces and angled evaporations to fabricate the molecular junctions with well –defined areas from 30 nm x 30 nm to 1 μm x 2 μm.

The third technique, nanotransfer, was designed to avoid the evaporation on top of the SAM and hence to examine the potential damage of evaporation. A column pattern was fabricated on a flexible polymer (PDMS) stamp and thin metal (gold) was evaporated on the stamp. Functional groups at the top surface of the SAM bond to Au when the stamp is brought into proximity with the layer. Au dots with the diameters from 20 nm to 100 nm transferred on top of the SAM serve as the top contact to the molecular junction probed by conducting atomic force microscope.

This suite of the techniques allowed us to examine various fabrication issues, materials properties and transformation affecting the apparent electrical behavior of molecular devices. We found that it is extremely hard to fabricate the junctions without defects. The defects can broadly vary in their origin and their effect on device performance. Metal electrodes in general have surface topography features comparable or exceeding the length of the molecules. The order of molecular assembly is disrupted at the grain boundaries making this location “defective” in structural and electronic sense. The nucleation of metal films from the evaporation stream, the resulting surface morphology, the penetration of metal atoms and particles into molecular layer, chemical reaction between metal, molecules and/or oxygen and water is very specific for every particular combination of metal and molecular species. For example, junctions with molecular “wires” can appear more resistive that the junctions with molecular “barrier” because of deeper penetration penetrating of gold clusters from top electrode into the film in the second case. Or, if top electrode is Ti, Ni or other reactive metal, any distinction between “wires” and “insulators” is lost as the whole molecular firm is converted into metal carbides or oxycarbides.

In general case, the electronic levels of molecules are strongly shifted from the Fermi level of metal electrodes, typically by 1 to 5 eV. Tunneling conductance of such mis-matched systems is very low for practical applications. Defects that create electronic states within 50-200meV off the Fermi energy contribute significantly to the electronic transport and define the overall behavior. The reliance on precise atomic positions of device constituents generally fails because the defects take over.

Do we really need the atomic precision to build the functional devices? Latest research and engineering results (Scott and Bozano, 2007; Waser and Aono, 2007) illustrate that the traditional "statistical" approach when the overall properties are defined by the self-averaging of multiple non-precise events can be extended to very small devices.

As an example, we found useful switching functionality in polymer films or monolayer of macromolecules (Zhitenev et al., 2007) that are just a little bit thicker (5-12 nm) than the thickness of molecular monolayers (1-2.5 nm). The resistive switching is caused by the shift of electronic levels in the device caused by ionic motion. There is nothing precise about a single ion position or motion, but the total number of ions in the nanoscale device is large enough to statistically result in a reproducible switching.

Initially, the devices are non-conducting. When applied voltage exceeds some critical voltage the devices switch to conducting state. This conducting state is stable at small applied voltages. Large applied voltage of opposite polarity switches device back to non-conductive state. The switching voltage is scales linearly with the film thickness and depends on the concentration of ionic groups in the film. Further, it is rather straightforward to modify ionic groups by partly or fully replacing protons with other ions. Many of these substitutions are reversible allowing us to examine multiple chemical compositions within the same mesoscopic devices. We found that these chemical modifications have major effect on the switching behavior. A simple physical model that captures the most essential experimental finding is the following.

In “off”-state, all molecular energy levels are at a few eV from the electrode Fermi level. Switching electric field is strong enough to break ionic bonds. The ion separation acts as an internal “chemical gating” and shifts some energy levels into better alignment with the Fermi energy of electrodes. These electronic states with energies within 100-300 meV off the Fermi level form the conducting channels. Strong electric field of opposite polarity pushes the separated cations back facilitating the recombination with anions at the polymer backbone and eliminating the conductive electronic levels. The electric field required for the ion separation depends on the ions size and properties. For example, larger monovalent cations have smaller bond strength and, respectively, the devices can be switched at smaller fields. Multivalent ions substitution result in significant increase of the switching field.

These polymer switches is just one example of material systems displaying resistive bistability. There are many other candidates based on various organic and inorganic compositions (Scott and Bozano, 2007; Waser and Aono, 2007). For all dissimilar materials, there is a common theme for the switching behavior of such devices. The switching functionality is caused by the movement or displacement of heavy particles such as ions or atoms over distances ranging from elementary cell to the size of devices. The breadth of the materials capable of displaying the switching leads to believe that the devices based on atom/ion motion can be eventually used in practical circuits.

The application of the switching devices in memory and storage has been the main driver for the development of such switches by most of major semiconductor companies. However, if the switching phenomenon can be reliably engineered in devices of sufficiently small size, this will lead to the emergence of new hybrid logic circuits based on novel architectural concepts (Strukov and Likharev, 2007). Some of these concepts go after mimicking the “architecture” and the well-developed connectivity of human brain intimately combining the memory, the connectivity and the computational elements.

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