

Molecular Nanoelectronics: A future perspective

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Abstract: The conventional VLSI technology based on lithography is reaching its limits and the extension of Moore's Law for small-scale conventional silicon based integrated circuits is gaining significance. Developments in the area of molecular electronics devices offer an alternative approach to overcome this problem and have the potential to miniaturize the computational devices down to few nm. This is a vast subject of research presently and this paper will review two main issues in this area which include multilayer edge molecular electronics devices (MEMED) and the self assembly monolayer (SAM's) approach.

Keywords: molecular electronics, multilayer edge molecular electronics devices (MEMED), nanoelectronics, self assembly monolayer (SAMs).

INTRODUCTION

As the size of the transistor has shrunk, computers have become more powerful. However, due to the minimum size of today's bulk-effect semiconductor transistors, limitations of materials and fabrication techniques and the laws of quantum mechanics, all together are likely to inhibit further reduction. The topic of nanoelectronic devices have been broadly subdivides into two which are solid-state quantum-effect nanoelectronic devices and molecular electronic devices. To increase the density and speed of information processing the nearest alternative is offered by solid-state quantum-effect nanoelectronic devices which can produce devices down to 25 nm in length and extend Moore's Law of electronics miniaturization without changing the solid fabrication medium for integrated circuits beyond the domain of the bulk-effect transistor. Commercial integrated circuits have field effect transistors (FETs) of approximately 1 micron or 1000 nm across, and it is predicted that they will cease to function effectively when their gate lengths dip below 25nm, which corresponds to an overall device length of approximately 100 nm. On the other hand, quantum-effect switching devices function better when they are made smaller. It is believed that solid state quantum-effect nanoelectronic devices will function effectively if they are fabricated reliably and uniformly having size as small as approximately 12 to 25 nanometers across. Presently, it is a challenge to undertake the mass fabrication on this small scale regardless of the device design. However, few prototype solid-state nanoelectronic processors are operational and solid-state nanoelectronic switching devices have been fabricated and demonstrated as well. Ultra-fast, low power integrated circuits with as many as 100 billion or even 1 trillion switching devices on a single CPU chip could result due to drastic decrease in size in the nanoelectronic devices, however, reliable, uniform mass fabrication of features which are 5 to 10 nanometers wide in solids is required and is at least twenty-five times as small as is achievable using UV lithography which is currently being used.

In the field of molecular electronics there has been hectic activity due to limitations of silicon technology and scaling of classical CMOS device architecture. However, in the nanoelectronics era, the technology scaling has become nontrivial due to fundamental limits imposed by device physics and materials technology [1]. Whether and how we can go along the Moore's law curve will be dictated by the innovations in novel materials and our ability to architect the systems using non-classical device architectures [2-5]. In light of this two important approaches are reviewed from literature with examples which include the multilayer edge molecular electronics device (MEMED) approach and the self-assembled monolayers (SAMs) approach which will in future address the issue of miniaturisation in nanoelectronic devices.

Multilayer Edge Molecular Electronics Device (MEMEDs) Approach

The methods for connecting functional molecule(s) to electrical leads are critical for the realization of any molecular electronics device. The recently developed multilayer edge molecular electronics device (MEMED) approach to produce MEMEDs molecular conduction channels are bridged across the ultrathin insulator, along the exposed vertical edges of a tunnel junction. The MEMED approach effectively addresses the major roadblocks encountered in the realization of practical molecular electronics devices. A number of research groups have produced various configurations of tunnel junctions to realize MEMEDs [6]. The first MEMED was realized with semiconductor-insulator-semiconductor junction [7]. Conventional CMOS fabrication steps were performed to produce a ~7 nm thick silicon dioxide (SiO₂) between two conducting silicon (Si) electrodes. The SiO₂ insulating layer was chemically etched for producing exposed side edges for hosting molecular channels. Along the exposed sides the minimum gap between two silicon electrodes was equal to SiO₂ thickness (Fig. 1). The ~7 nm thickness of SiO₂ was significantly more than

the physical length of the individual molecules used in this study. Hence, a multi-step chemistry was performed to chemically bond the molecules with nanoparticles to produce > 7 nm long hybrid conduction channels. Here, a conduction bridge was composed of short molecules with diazonium functional group, and a 5 nm gold particle. Current-voltage (I-V) studies revealed that hybrid conduction channels increased the current by several orders over the background level. This study clearly established that overlap of metallic wave functions via conduction channels, along the junction edge, is much stronger than that via planar SiO₂ tunnel barrier.

MEMEDs can be produced by widely available micro fabrication tools. The tunnel junction used in a MEMED can have any combination of metallic electrodes. Additionally, the tunnel junction's insulator thickness can be precisely tailored to utilize a vast variety of molecules as a device element. A MEMED approach enables an unprecedented number of control experiments to reveal the true behaviour of molecular conduction channels. The tunnel junction used in a MEMED can be characterized before establishing molecular conduction channels. The MEMED approach makes it straightforward to reverse the molecule's effect and then retrieve characteristic of the parent device. This design offers a unique opportunity to transform highly matured magnetic tunnel junctions into futuristic molecular spintronics devices, a potential candidate device for quantum computation. Besides the application in computational devices, MEMED design can also be used for biosensing by enabling the interaction between MEMED's active molecular channels with the target bio-analytes [8].

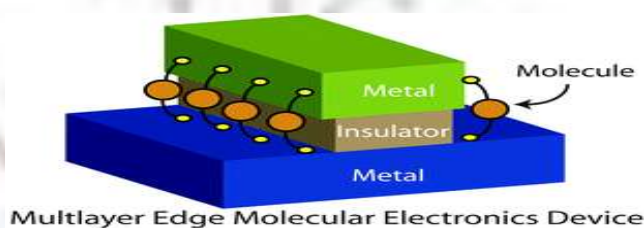


Fig.1: Setup of a MEMED device

Self -Assembled Monolayers (Sams) Approach

Functionalized molecules that organize to self-assembled monolayers (SAMs) are gaining importance in organic electronic devices. They are fully compatible with flexible substrates, are amenable to low-cost processing, and show reliable film-forming behaviour. Highly integrated devices, such as sensor arrays or memories, have also been demonstrated. Starting from auxiliary layers, which improve and modify surfaces and interfaces in traditional thin-film devices, the applications of SAMs develop towards molecular scale electronics, including active molecular device layers and multifunctional SAMs, which fulfill several layer functions of a device within one monolayer. Mixed SAMs make new and tunable device features possible, by stoichiometric control of the composition of different SAM-forming molecules. Organic molecules can be synthesized with unique properties that could be used to promote their self-assembly with one another and on specific surfaces, and to perform functions that could allow electronic-device operations.

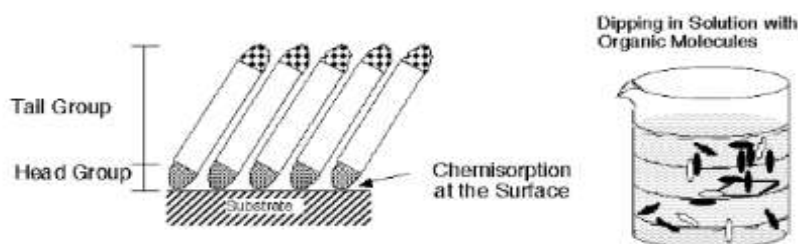


Figure 2. Schematic drawing of SAMs

New conductive conjugated molecular wires have been found or synthesized for the purpose of constructing molecular devices. Self-assembled monolayers (SAMs) provide a convenient technique to fix the functional organic molecules on the surface of metals or semiconductor materials. In particular, SAMs made from organosulfur compounds on an Au surface have been utilized for demonstration of nanomolecular electronics devices, because of the ease of formation of Au-S chemical bonds. For future application in nanoscale molecular devices, it is essential to explore new methods of using self-organization to obtain smaller nanoscale patterns and control the nanoscale structure. Manipulating and controlling the self-organisation of small collections of molecules, as an alternative to investigating individual molecules, has motivated researchers for processing and storing information in molecular electronic devices (MEDs). Although numerous ingenious examples of single-molecule devices have provided fundamental insights into their molecular electronic properties, MEDs incorporating hundreds to thousands of

molecules trapped between wires in two-dimensional arrays within crossbar architectures offer a glimmer of hope for molecular memory applications [9].

Self-assembled monolayers (SAM) that has the potential of fine structure tunability in molecular diodes from isolated molecular wires to two dimensional (2D) aggregates; this approach should be useful for studying dimensionality transition in molecular diodes. Using this technique, we have fabricated a variety of molecular diodes with structure tenability of two-component solid-state mixtures. These are molecular wires (1, 4-methane-benzene-dithiol; Me-BDT) and molecular insulator spacers (1-pentanethiol; PT). SAM-based two-terminal devices were prepared at various concentration ratios (r) of wires/spacers, sandwiched between two gold electrodes. The transport properties of molecular diodes at low r values ($r < 10^{-3}$) are dominated by the isolated molecular wires dispersed in the dielectric spacer matrix; we conclude that these are one-dimensional (1D)-type devices. At high r values ($r > 10^{-3}$), aggregates of molecular wires are formed in the PT matrix that show additional in-plane order; we conjecture that these are 2D-type devices [10].

The collective behaviour of switchable mechanically interlocked molecules (MIMs)—specifically, bistable rotaxanes and catenanes—which exhibit reset lifetimes between their ON and OFF states ranging from seconds in solution to hours in crossbar devices. When these switchable MIMs are introduced into high viscosity polymer matrices, or self-assembled as monolayers onto metal surfaces, both in the form of nanoparticles and flat electrodes, or organised as tightly packed islands of hundreds and thousands of molecules sandwiched between two electrodes, the thermodynamics which characterise their switching remain approximately constant while the kinetics associated with their reset follow an intuitively predictable trend—that is, fast when they are free in solution and sluggish when they are constrained within closely packed monolayers. The importance of seamless interactions and constant feedback between the makers, the measurers and the modellers in establishing the structure-property relationships in these integrated functioning systems cannot be stressed enough as rationalising the many different factors that impact device performance becomes more and more demanding [11].

Although numerous ingenious examples of single-molecule devices have provided fundamental insights into their molecular electronic properties, MEDs incorporating hundreds to thousands of molecules trapped between wires in two-dimensional arrays within crossbar architectures offer a glimmer of hope for molecular memory applications. In this critical review, we focus attention on the collective behaviour of switchable mechanically interlocked molecules (MIMs)—specifically, bistable rotaxanes and catenanes—which exhibit reset lifetimes between their ON and OFF states ranging from seconds in solution to hours in crossbar devices. When these switchable MIMs are introduced into high viscosity polymer matrices, or self-assembled as monolayers onto metal surfaces, both in the form of nanoparticles and flat electrodes, or organised as tightly packed islands of hundreds and thousands of molecules sandwiched between two electrodes, the thermodynamics which characterise their switching remain approximately constant while the kinetics associated with their reset follow an intuitively predictable trend—that is, fast when they are free in solution and sluggish when they are constrained within closely packed monolayers. The importance of seamless interactions and constant feedback between the makers, the measurers and the modellers in establishing the structure-property relationships in these integrated functioning systems cannot be stressed enough as rationalising the many different factors that impact device performance becomes more and more demanding [12].

The choice of electrodes, as well as the self-organised superstructures of the monolayers of switchable MIMs employed in the molecular switch tunnel junctions (MSTJs) associated with the crossbars of these MEDs, has a profound influence on device operation and performance. It is now clear, after much investigation, that a distinction should be drawn between two types of switching that can be elicited from MSTJs. One affords small ON/OFF ratios and is a direct consequence of the switching in bistable MIMs that leads to a relatively small remnant molecular signature—an activated chemical process. The other leads to a very much larger signature and ON/OFF ratios resulting from physical or chemical changes in the electrodes themselves. Control experiments with various compounds, including degenerate catenanes and free dumbbells, which cannot and do not switch, are crucial in establishing the authenticity of the small ON/OFF ratios and remnant molecular signatures produced by bistable MIMs. Moreover, experiments conducted on monolayers in MSTJs of molecules designed to switch and molecules designed not to switch have been probed directly by spectroscopic and other means in support of MEDs that store information through switching collections of bistable MIMs contained in arrays of MSTJs. In the quest for the next generation of MEDs, it is likely that monolayers of bistable MIMs will be replaced by robust crystalline extended structures wherein the switchable components, derived from bistable MIMs, are organised precisely in a periodic manner [13].

Conclusion

Ultimately, it will be desirable to build ultra dense, low-power nanoelectronic circuits made from purely nanometer-scale switching devices and wires. Molecular electronics--using individual covalently bonded molecules to act as wires and switching devices--is the longer-term alternative for achieving this increase in density and for continuing Moore's Law down to the nanometer scale. Individual molecular switching devices could be as small as 1.5 nanometers across,

with densities of approximately 10¹² devices per sq. cm. This decrease in size could result in Terabyte memories on a chip and in excess of one trillion switching-devices on a single CPU chip. A primary advantage of molecular electronics is that molecules are natural nanometer-scale structures that can be made absolutely identical in vast quantities (approximately 10²³ at one time). This is the future of electronic devices and if successfully implemented based on the novel materials will revolutionise the field of computers and all electronic devices

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