MOLECULAR AND NANO-ELECTRONICS

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Contents

Summary

Molecular and nano-electronics using single molecules or nano-structures as active components are promising technological concepts with fast growing interest. It is the science and technology related to the understanding, design, and fabrication of electronics devices based on molecules or nano-structures. Molecular and nano-electronics will push advances in future computer technology far beyond the limits of silicon. "Single molecule electronics", which is the ultimate molecular nano-electronics, would make it possible to realize information systems of more than 1000 times higher performances using less than 1/1000 resources, which would satisfy

the social requirements for high performance information systems several decades from now.

Nano-electronics refer to the use of nanotechnology on electronic components, especially transistors. Although the term nanotechnology is generally defined as utilizing technology less than 100 nm in size, nano-electronics often refer to transistor devices that are so small that inter-atomic interactions and quantum mechanical properties need to be studied extensively. Unique materials and properties such as quantum electronic transports will be reviewed for various structures such as molecular switches, rectifiers, memories, transistors for next generation electronic devices and circuits.

Nano-materials electronics is an important route. Besides being small and allowing more transistors to be packed into a single chip, the uniform and symmetrical structure of nanotubes allows a higher electron mobility (faster electron movement in the material), a higher dielectric constant (faster frequency), and a symmetrical electron/hole characteristic. Also, nanoparticles can be used as quantum dots.
Single molecule devices are another possibility. Molecular electronics is a new technology which is still in its infancy, but also brings hope for truly atomic scale electronic systems in the future. These schemes would make heavy use of molecular self-assembly, designing the device components to construct a larger structure or even a complete system on their own. This can be very useful for reconfigurable computing, and may even completely replace present technology.

Also, there are other approaches and applications. For example, nano-materials have been proposed as a cost effective alternative for developing hybrid solar cells because of their excellent solution processing ability, well-suited optical properties, and compatibility with molecular materials. Molecularly-resolved bioelectronics is an extremely attractive for the development of molecular devices, in particular when a combination of information processing and chemo-mechanical tasks is desired. This chapter presents an in-depth discussion on molecular and nano-electronics in an easy-to-understand manner, aiming at chemists, computer scientists, surface scientists, physicists. Current status and prospects for molecular nano-electronics are reviewed, which are expected to supersede the present information technology paradigm based on "solid state electronics".

1. Introduction

It is well recognized that conventional lithography based very-large-scale integration (VLSI) technology is fast approaching the limits of its capabilities (Reichmanis et al., 1991). However, there is no doubt that the fundamental physical constraints will eventually limit the process of further miniaturization, even though the predictions for this final limit have continuously been adjusted towards smaller sizes. The underlying issues responsible are numerous: ultra-thin gate oxides (Varzgar, Kanoun et al. 2006), short channel effects (Tan, Buiu et al. 2008), doping fluctuations (Colinge, Xiong, et al. 2007), and last but not least increasingly difficult and expensive lithography. Nonetheless, devices with dimensions approaching the wavelength of free electrons cannot be described anymore by purely semi-classical theory. Rather, quantum mechanical effects like tunneling, coulomb blockade, and wave interference have to be taken into account (Tilke, Simmel, et al. 2001). To surmount these problems, molecular and nano-devices and circuits have been proposed for some time (Wada, 2001). Over the last two decades, demonstrations of many of these technologies have been accomplished. These include resonant tunneling diode (RTD) and resonant tunneling transistor (RTT) devices (Ando, Cappy, 1998) and circuits that promise compact multi-valued logic and memories; quantum dot (Asahi, 1997) and single electron devices(Bhattacharya, Ghosh, et al. 2004); and others.

An alternative is the bottom-up approach, where molecules are synthesized to possess some inherent function, then assembled with other components to build the electrical device. Recently, molecular electronics-based computation has attracted attention, because it addresses the ultimate in a dimensionally scaled system: ultra-dense and molecular scale (Jortner, 1997, Ratner, 1998). The significant scaling factor gained from molecular-scale devices implies eye-opening comparisons: a contemporary computer utilizes ~10^{10} silicon-based devices, whereas one could prepare ~10^{23} devices in a single beaker using routine chemical syntheses. An additional driving factor is the potential to utilize thermodynamically-driven directed self-assembly of components such as chemically synthesized interconnects, active devices, and circuits (Kato, Mizoshita, et al.2006). This is a novel technological approach for post-VLSI electronic systems, and can conceivably lead to a new era in ultra-dense electronic systems. This approach for spontaneously assembling atomic scale electronics attacks the interconnection and critical dimension control problems in one step, and is implicitly atomic scale.

Single molecules as an active electronic unit have attracted huge attention both from the research community and industry. (Reed, 1999) Single molecules can offer several unique properties as an electronic unit. The size is within several nanometers for most simple molecules and hence the electronic spectrum is quantized with the typical energy scale of ~ eV. They also allow self-assembly, which is very useful in fabricating electronic devices at such a small length scale. Another huge advantage is their tremendous diversity and functionality. There exist an incredibly large number of chemicals and their different chemical and electrical functions can open up many new possibilities that have never been available.

2. Molecular and Nano-Electronics in General

2.1. The Electrodes

Once the molecules and nano-structures have been synthesized, a key problem is their attachment into a system in which it can be tested and eventually integrated into a circuit. This has proven to be difficult because, until recently, there has been no way of addressing individual molecules.

A good rule of thumb in single-molecule experiments is to be initially skeptical of any experiment which only measures a two-terminal conductance, because such a measurement is very dependent on the contacts, and short circuits (very common in gold electrodes due to weak bonding) can be easily misinterpreted (Wada, Tsukada, et al. 2000). More reliable measurements have at least one additional technique to distinguish transport through a single molecule from other artifacts. Such techniques include observing transport modulated by a gate electrode (Yu, Keane, et al. 2004), an optical probe (Wang, Zou, et al. 2007) or an applied magnetic field (Hod, Rabani, et al. 2006). Other approaches are to use a setup which will allow for thousands of identical experiments to be performed in rapid succession, so that averaging can be used to sort out random fluctuations from more reproducible effects, or to directly image the molecule during the measurement using scanning tunneling microscopy (STM). Another rule of thumb is to avoid experiments where voltages of more than 100 mV are dropped across a molecule during measurement because electric fields this strong often cause the electrodes to become unstable.

There is also a difference between the transfer of an electron and the conductance of a current, which the molecules and nano-structures would experience in an electrical circuit. It is not known if the molecules and nano-structures will carry the charge or simply decompose. This problem has become less of an issue with the design of molecular alligator clips and the use of STM.

2.2. The Molecules and Nano-Structures as Active Components

Several types of molecules have been suggested as ‘molecular wires’ and they all have the same key requirements (James and Tour, 2005). The most obvious fact is that they have to be electron or hole conducting in order to carry a current through the circuit. Thus the wire provides a pathway for transport of the electrons from one reservoir to another that is more efficient than electron transport through space. Quantification of the properties of a wire has been approached in different ways that generally depend on the technique used to analyze the wire properties. Measurements have been carried out of the rate of electron transfer across the wire using spectroscopic techniques and by techniques such as STM to obtain current-voltage characteristics and to classify wires as metallic or semiconducting (Zhang, He, et al. 2006). Conjugated molecules, comprising alternating single and double (or triple) carbon–carbon bonds, can conduct electrons through their π-system, and this has been the basis of many wires. The wire must also be linear and of a defined length in order to span the gap between two components in the circuit.

2.3. The Molecule–Electrode Interface

The attachment of ‘molecular alligator clips’ allows the wire to be attached to metal surfaces. One method of attachment is *via* thioacetates, which upon hydrolysis will form thiols (Nuzzo and Allara, 1983). The thiols then form gold–thiolates on exposure to gold surfaces. However thiols are oxidatively unstable and the optimal method is likely to be *via* an *in-situ* approach. Some research has been carried out with arylformamides, which after coupling to oligomers can be converted to isonitriles, providing good adhesion to tungsten surfaces (Schumm, Pearson, et al. 1996). These alligator clips allow the molecular wire to be attached to two electrodes so that a current can be passed.

In the previous examples, the contacts were made by the strong S–Au bonding. This served as a very good mechanical and chemical bonding for a single molecule device, which leads to a good electrical contact, too. If the thiol end group (–SH) was replaced by another end group (for example, $-CH_3$), it did not form a stable bond to gold any more and the conductance is predicted to change according to the exact placement of the end group relative to gold (Cui, Primak, et al. 2001).

3. Approaches to Nano-electronics

3.1. Nanofabrication

To perform conductance measurements on an object, one needs at least two electrodes contacting the object. However, conductance measurements on single molecules usually require a different experimental scheme, due to their exceedingly small size. Typically, two contact wires with a sub-10 nm gap are made first, and then single molecules are self-assembled between the contacts. People have thus developed various new experimental techniques for wiring up single molecules. They include scanning probe microscopy (SPM) techniques and unconventional fabrication techniques for making nano-electrodes. Current attempts to fabricate the contacts have included: break junctions (Osorio, Bjornholm, et al. 2008), vertical sandwich structures (Chou, Krauss, et al. 1996), electron beam lithography (EBL) and shadow evaporation (Dreyer, Fu, et al. 1993), electron beam deposition (Ellenbogen and Love, 2000), electrochemical growth (Klein, Roth, et al. 1997), and electromigration (Li, He, et al. 2000). Although successful, these processes are ill suited for large-scale integrations, as each gap must be fabricated individually in a time consuming fashion. Figure 1 summarizes some of the methods that have been used for studying electron transport in molecules.

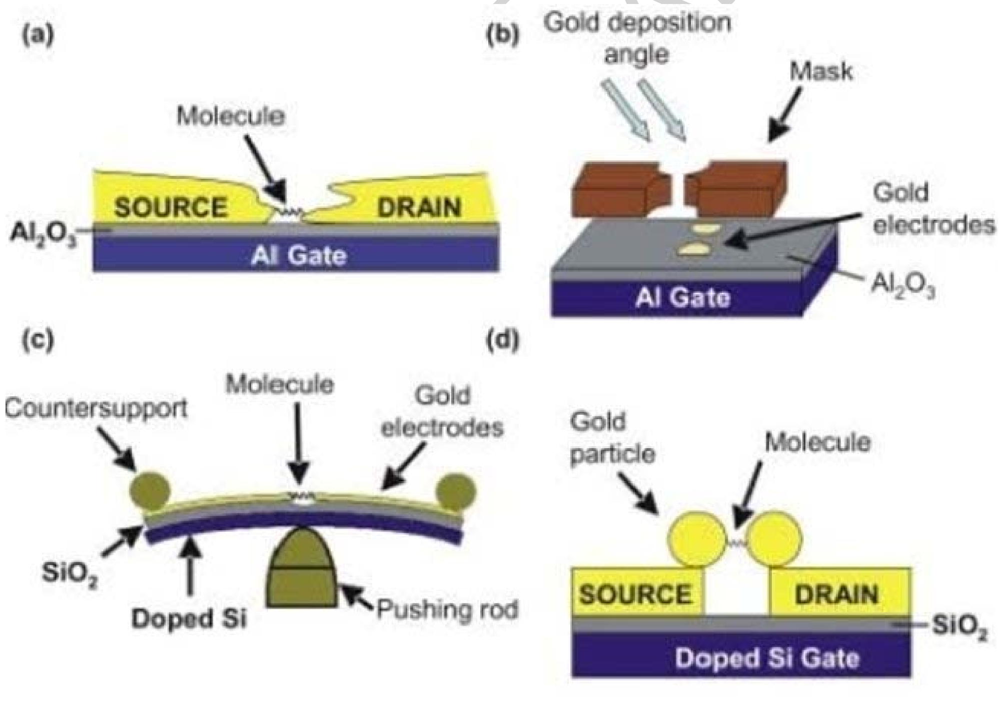

Figure 1. Schematic diagrams of different three-terminal device techniques. (a) Electromigrated thin metal wire on top of an Al/Al_2O_3 gate electrode. (b) Angle evaporation technique to fabricate planar electrodes with nanometer separation on top of an Al/Al_2O_3 gate electrode. (c) Gated mechanical break junction. (d) The dimmer contacting scheme.

Electron beam lithography (EBL) has long been established as the premier technique for defining structures at the nanoscale. Electron Beam Lithography (EBL) refers to a lithographic process that uses a focused beam of electrons to form the circuit patterns needed for material deposition on (or removal from) the wafer, in contrast with optical lithography which uses light for the same purpose. Electron lithography offers higher patterning resolution than optical lithography because of the shorter wavelength possessed by the 10–50 keV electrons that it employs. Given the availability of technology that allows a small-diameter focused beam of electrons to be scanned over a surface, an EBL system doesn't need masks anymore to perform its task (unlike optical lithography, which uses photo masks to project the patterns). An EBL system simply 'draws' the pattern over the resist wafer using the electron beam as its drawing pen. Thus, EBL systems produce the resist pattern in a 'serial' manner, making it slow compared to optical systems.

3.2. Nanomaterial Electronics

Nano-electronics refer to the use of nanotechnology on electronic components, especially transistors. Although the term nanotechnology is generally defined as utilizing technology less than 100 nm in size, nano-electronics often refer to transistor devices that are so small that inter-atomic interactions and quantum mechanical properties need to be studied extensively.

Nano-electronics are sometimes considered as disruptive technology because present candidates are significantly different from traditional transistors. Some of these candidates include: hybrid molecular/semiconductor electronics, one dimensional nanotubes/nanowires, or advanced molecular electronics. The sub-voltage and deep-sub-voltage nano-electronics are specific and important fields of R&D, and the appearance of new ICs operating almost near theoretical limit (fundamental, technological, design methodological, architectural, and algorithmic) on energy consumption per one bit processing is inevitable. The important case of fundamental ultimate limit for logic operation is reversible computing.

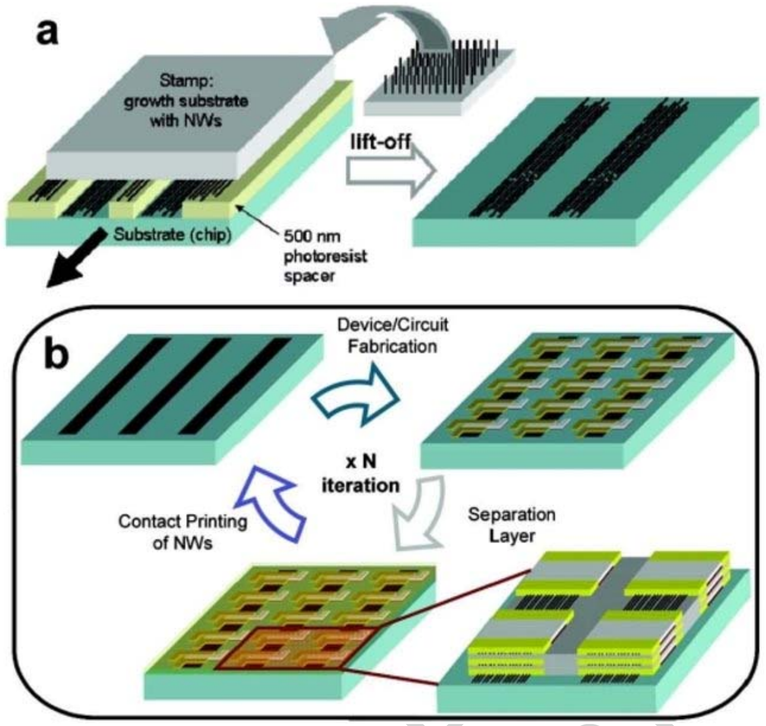

Figure 2. Overview of 3D NW circuit integration. (a) Contact printing of NWs from growth substrate to prepatterned substrate. In general, NWs are grown with random (nonepitaxial) orientation and are well-aligned by sheer forces during the printing process. (b) Three-dimensional NW circuit is fabricated by the iteration of the contact printing, device fabrication, and separation layer deposition steps N times. (Javey, Nam, et al. 2007)

Recently, a general approach for three-dimensional (3D) multifunctional electronics based on the layer-by-layer assembly of nanowire (NW) building blocks was developed as shown in Figure 2.[29] Using germanium/silicon (Ge/Si) core/shell NWs as a representative example, ten vertically stacked layers of multi-NW field-effect transistors (FETs) were fabricated. Transport measurements demonstrate that the Ge/Si NW FETs have reproducible high-performance device characteristics within a given device layer, that the FET characteristics are not affected by sequential stacking, and importantly, that uniform performance is achieved in sequential layers 1 through 10 of the 3D structure. Five-layer single-NW FET structures were also prepared by printing Ge/Si NWs from lower density growth substrates, and transport measurements showed similar high-performance characteristics for the FETs in layers 1 and 5. In addition, 3D multifunctional circuitry was demonstrated on plastic substrates with sequential layers of inverter logical gates and floating gate memory elements. Notably, electrical characterization studies show stable writing and erasing of the NW floating gate memory elements and demonstrate signal inversion with larger than unity gain for frequencies up to at least 50 MHz. The ability to assemble reproducibly sequential layers of distinct types of NW-based devices coupled with the breadth of NW building blocks should enable the assembly of increasing complex multilayer and multifunctional 3D electronics in the future.

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Biographical Sketches

Weiping Wu born on August 1, 1981, received the B.S. degree in Material Science from Shanghai Jiaotong University, Shanghai, China in 2004, where he carried out research on electrorheological and magnetorheological materials. He is currently working toward the Ph.D. degree in physical chemistry from Institute of Chemistry, Chinese Academy of Sciences, Beijing, China. His interests include organic semiconductors and conjugated polymers for transistors, solar cells and memory devices, including novel materials, fundamentals of device physics and their application in printed and transparent electronics.

Yunqi Liu, born on April 1, 1949, graduated from the Department of Chemistry, Nanjing University in 1975, received a doctorate from Tokyo Institute of Technology, Japan in 1991. Presently, he is a professor of the Institute of Chemistry, CAS. His research interests include molecular materials and devices.

Daoben Zhu, born on August 20, 1942, finished his graduate courses at the East China University of Science and Technology in 1968. Currently, he is a professor and Director of the Organic Solids Laboratory of the Institute of Chemistry, CAS. He was selected as an academician of CAS in 1997. His research interests include molecular materials and devices.