# LES DÉFIS TECHNIQUES DE LA MICROÉLECTRONIQUE CHALLENGES IN MICROELECTRONICS

# CMOS and beyond

Ray TSUI, Laura SIRAGUSA, Herb GORONKIN

Physical Sciences Research Laboratories, Motorola Labs, 2100 East Elliot Road, MD-EL508, Tempe, AZ 85284, USA E-mail: Ray\_Tsui@email.mot.com

(Reçu le 29 mai 2000)

**Abstract.** Lithography has played a key role in the scaling of CMOS-based integrated circuits. To fabricate sub-70 nm features, new techniques based on electron projection and extreme ultraviolet radiation are being developed. These and other lithographic solutions are discussed. For the ultimate in scaling, an alternate approach would be to start with objects that are inherently nano-scale in size, and use chemical techniques to have these objects self-assemble into units that provide electronic functionality. Several classes of molecules, including carbon nanotubes, deoxyribonucleic acid (DNA) and custom-synthesized organic molecules, are potentially suitable for this approach. Some recent advances in their research will be reviewed. © 2000 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

electron projection lithography / SCALPEL / extreme ultraviolet lithography / molecular electronics / carbon nanotubes / DNA / custom molecules

**Résumé.** Pour fabriquer des structures de géométries inférieures à 70 nm, de nouvelles techniques de lithographie basées sur la projection d'électrons ou les UV extrêmes sont développées. Leurs caractéristiques principales sont discutées dans cet article. Au-delà de ces géométries, pour l'intégration ultime, une approche alternative pourrait consister à partir d'objets intrinsèquement nano-métriques auto-assemblés par des techniques chimiques pour former les composants ayant les fonctionnalités électroniques voulues. Plusieurs classes de nano-structures présentant un potentiel intéressant en ce sens sont analysées dans cet article : les nano-tubes de carbone, l'acide déoxyribonucléique et certaines molécules organiques synthétiques. © 2000 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

lithographie électronique / SCALPEL / lithographie en ultraviolet extrême / électronique moléculaire / nanotubes de carbone / DNA / ingénierie moléculaire

# 1. Introduction

Since the early days of the semiconductor industry, lithography has played the role of a key enabler and technology driver. The growth of the industry has been the direct result of improved lithographic resolution and overlay. High volume factories at the leading edge of CMOS technology are currently using 180 nm design rules, though the need for faster and higher performance circuitry continues to accelerate. International SEMATECH, with the help of its industrial partners, has published in the 1999 Technology Roadmap describing in detail the targeted design rules for CMOS circuitry for the next fifteen years [1]. As shown in the *table* below, gate lengths of less than 25 nm will be needed in 2014.

Note présentée par Guy LAVAL.

### R. Tsui et al.

# CHALLENGES IN MICROELECTRONICS

Table. Ethography requirements from the 1999 International Technology Roadinap for Semiconductors [1].							
Year	1999	2001	2003	2005	2008	2011	2014
Technology node							
DRAM: half pitch (nm)	180	150	120	100	70	50	35
DRAM: contacts (nm)	200	170	145	130	100	70	50
MPU: gate length (nm)	140	100	80	65	45	30	20
ASIC: gate length (nm)	180	150	120	100	70	50	35

Table. Lithography requirements from the 1999 International Technology Roadmap for Semiconductors [1]

The means for printing these future geometries in a manufacturing environment is far from being a certainty. As gate lengths approach 70 nm, changes in the optical properties of quartz will require major changes to both mask and lens technology. In addition, the decrease in exposure wavelength is not significant enough to make the technology applicable to sub-50 nm circuitry. As a result, future lithographic solutions are being considered. While the choices include techniques based on X-ray (XRL), ion projection (IPL), electron projection (EPL) and extreme ultraviolet (EUVL), the two that are currently in favor are EPL and EUVL. The need to minimize the choices is based primarily on economics: the development of a technology along with the supporting infrastructure is estimated to cost close to one billion dollars. In this paper, aspects regarding EPL and EUVL will be discussed.

On the other hand, as the trend continues to achieve ever smaller devices and increasing circuit density, the use of individual molecules to fabricate device/circuit components (e.g., switches, wiring, etc.) becomes more and more attractive. Molecules are inherently nano-scale in size and highly uniform in nature. These two features could be very advantageous for the fabrication of ultra-dense, low-power ICs. Furthermore, organic and inorganic molecules can be synthesized with unique chemical, physical and biological properties that could be used to promote their self-assembly to one another and to specific surfaces, and to perform functions that can provide memory and logic operations. For these reasons, the field of 'molecular electronics' has generated considerable interest in recent years.

The concept of molecular electronics represents a very different paradigm to conventional semiconductor processing techniques. It comes from the 'bottom-up' in which the starting components are naturally nano-scale and are self-assembled into devices and circuits. The traditional semiconductor-based approach is from the 'top-down', starting with large wafers on which small components are fabricated and interconnected using lithography, metallization, etch, and other processing techniques. Such a bottom–up approach may offer significant economic advantage due to its inherent simplicity. Various details relating to molecular electronics will also be discussed here.

# 2. Lithography

# 2.1. Electron projection lithography

The approach taken in our laboratory in the development of EPL is termed SCALPEL (Scattering with Angular Limitation Projection Electron Lithography). It is designed to combine the attributes of resolution obtained via electron beam writing with the high throughput obtained by a parallel projection system [2]. The mask concept was originally conceived in 1989 at Bell Laboratories and the technology is targeted for production for integrated circuits with dimensions as small as 50 nm. The writing strategy used in EPL is shown in *figure 1*. The mask design uses a very thin membrane on which a thin metal scattering layer is patterned. Because the membrane is so thin (100–150 nm), electrons pass through without significant scattering. A 4 : 1 reduction lens projects the electrons through an aperture to a final lens and finally to the resist coated wafer. In the areas containing patterned metal features, electron scattering reduces the number of electrons passing through the aperture, providing the contrast necessary to satisfactorily expose the resist.

CMOS and beyond



Figure 1. Writing strategy employed for electron projection lithography.

In 1999, our laboratory completed the first ever SCALPEL mask to fabricate microprocessors with 180 nm minimum geometry on 200 mm wafers.

#### 2.2. Extreme ultraviolet lithography

As for EUVL, it is a technology that has been under development for more than 10 years [3]. It is attractive because of the short wavelength. Although the name suggests that the technology is simply an extension of the optical techniques used in production today, the actual application of EUVL will require many changes to be made. Eventual improvements in optics may make EUVL a possible choice for critical dimensions that are less than 50 nm. While wavelengths between 2 nm and 50 nm have been proposed, the current prototype systems have settled on 13.4 nm. This is actually a long X-ray and as such is easily absorbed in most material. As a result, refractive optics are no longer feasible. Instead, reflective optics are used. Since the radiation is so easily absorbed, a distributed reflector system consisting of multiple layer coatings must be deposited. The coatings are comprised of a significant number of alternating layers of materials with different optical constants. Resonant reflectivity is obtained when the period of the layers is half the wavelength (see *figure 2*). Our laboratory also demonstrated in 1999 an electron beam patterned EUVL mask for 200 mm wafers.

Mask defectivity is key to the success of these mask technologies. If a defect occurs during the multilayer deposition process, there is no means for going back for repairs. Significant efforts have therefore been focused on eliminating defects during the deposition process. While it is possible to deposit the multilayer with conventional systems such as dual-source RF or dc magnetron sputtering systems, motion within the chamber as well as electrostatic fields cause particulates to get trapped in the coating during deposition. As a result, an ion beam sputter deposition process is now used to deposit the multilayer. Extensive studies using this process on 150 mm silicon wafers have yielded multilayers with defect densities as low as 0.02 cm<sup>-2</sup>



Figure 2. Reflected intensities of two different multilayers developed for use in masks for extreme ultraviolet lithography.



Figure 3. Scanning electron microscope image showing 21 nm wide metal lines defined using PMMA resist and electron beam lithography.

and reflectance uniformity across the wafer of better than 0.5. By the year 2004, it will be necessary to routinely achieve defectivities of less than  $0.001 \text{ cm}^{-2}$  across 300 mm wafers.

### 2.3. Other lithographic solutions

As gate lengths decrease to 35 nm, new lithographic techniques will be needed to replace EPL and EUVL solutions. The semiconductor industry is just starting to examine multiple beam lithography [4] and X-ray zone plate lithography [5]. Electron beam lithography can provide the resolution necessary (see *figure 3*), but suffers from substantially long writing times. To improve throughput, one can imagine writing a pattern with a large array of electron beam sources all writing in parallel. Properly designed, space charge effects will not be an issue and good resolution is possible. Software concerns become predominant, however, as large amounts of data must now be processed error free. It is generally believed that these improvements will allow gate lengths down to 30 nm. Beyond this, a molecular approach may be appropriate for extending device technology to the 10 nm regime.

#### 3. Molecular electronics

The concept of molecular electronics dates back at least to 1974, when Aviram and Ratner proposed molecular rectifiers [6]. Since then, a wide variety of molecules and nanoparticles have been considered as candidates for use in molecular electronics, including custom-synthesized organic compounds, deoxyribonucleic acid (DNA), carbon nanotubes (CNTs), and metallic nanocrystals. These provide unique features such as negative differential resistance, molecular recognition, quantum transport, and ease of manipulation, respectively, but each has its own shortcomings as well. In the following sections, the strengths and limitations of some of these nano-scale components will be discussed.

#### 3.1. Carbon nanotubes

Carbon nanotubes (CNTs) are rolled-up graphite sheets that form multi-walled or single-walled (SW) tubes. They can be grown to lengths approaching the mm range but can have diameters of less than 1 nm in the case of SWCNTs. In late 1991, Iijima reported the first synthesis and characterization of CNTs [7]. The initial theoretical studies of their electronic structure soon followed [8]. It was predicted that changes

#### CMOS and beyond

in the winding angle of the hexagonal carbon lattice along the tube (i.e., the chirality) would have a strong effect on the conductive property, resulting in either semiconducting or metallic behavior. In the last few years, experimental data from several research groups including our laboratory [9] have confirmed the metallic nature and quantum-wire characteristics of SWCNTs through electron transport measurements at cryogenic temperatures. The correlation between chirality and conductive type has also been observed using scanning tunneling mircoscopy and spectroscopy [10]. Furthermore, characteristics similar to those of field-effect transistors have been measured in semiconducting tubes at room temperature [11]. *Figure 4A* shows an atomic force mircoscope image of a SWCNT on top of a pair of Au electrodes formed on a SiO<sub>2</sub>-covered Si substrate. The substrate serves as a back gate in the structure. Electrical transport data are obtained by applying a bias voltage to the electrodes and measuring the current. *Figure 4B* shows that a strong current modulation (of more than 5 orders of magnitude) can be obtained through the gate bias, suggesting that the tube is semiconducting in nature. Other tubes that do not exhibit this dependence on gate voltage are considered to be metallic. In those cases, the current–voltage (I-V) curves measured at 4.2 K show Coulomb blockade characteristics, with the conductance gap being a function of the gate voltage (see *figure 5*). More recently, coherent transport of electron spins and magnetoresistance have been observed



Figure 4. (A) Atomic force microscope image of a SWCNT spanning a pair of Au electrodes formed on a  $SiO_2$ -covered Si substrate which also serves as a back gate. Placement of the SWCNT was at random. A liquid suspension containing SWCNTs was deposited over the pre-patterned electrodes and then spun dried. (B) Room temperature current–voltage curves for a semiconducting SWCNT, showing more than 5 orders of magnitude of current modulation due to changes in gate voltage,  $V_g$ . These SWCNTs are grown by the laser ablation technique (see text).

**Figure 5.** Current–voltage curves at 4.2 K of a metallic SWCNT spanning a pair of Au electrodes as shown in *figure 4A*. A conductance gap centered about the zero point in source–drain bias is observed, and its magnitude changes with gate voltage, V<sub>g</sub>. Such characteristics are indicative of the Coulomb blockade effect, with the tunneling barriers in this case at the SWCNT/electrode junctions.



#### R. Tsui et al.

### CHALLENGES IN MICROELECTRONICS



**Figure 6.** (A) Scanning electron microscope image of a substrate patterned with metal pads (for alignment) and regions covered with chemicals to which SWCNTs preferentially adhere (e.g., amine-terminated self-assembled monolayers). (B) A higher magnification view after the substrate has been exposed to a liquid suspension containing SWCNTs. The image shows a SWCNT selectively positioned at one of the 'high surface energy' regions while the surrounding areas are free of SWCNTs.

in ferromagnetically contacted CNTs [12]. Thus CNTs hold much potential for the fabrication of novel electronic and spin–electronic devices on a nanometer scale.

CNTs can be grown by the arc discharge method [13] or laser ablation of a graphite rod [14], as well as by chemical vapor deposition (CVD) [15]. The first two approaches result in an entangled web of CNTs intermixed with residual metallic impurities (from the catalysts used during growth) and amorphous carbon byproducts that require extensive wet chemical treatments to purify and untangle to obtain individual CNTs [16]. Even afterwards, isolated SWCNTs are insoluble in most solvents [17] unless a surfactant is used or chemical modifications to the tubes are carried out [18]. Such insolubility and the strong van der Waals attraction between tubes cause them to bundle together as ropes. This hinders the placement and manipulation of individual SWCNTs on a surface for electrical measurements. For device application it is important that CNTs can be positioned at pre-determined locations, preferably via self-assembly. Some studies have been carried out to pattern a surface with regions covered by an amine-terminated self-assembled monolayer to which SWCNTs preferentially adhere [19]. Figure 6 shows micrographs from our laboratory of one such patterned surface and a SWCNT selectively positioned via surface energy manipulation. In our work, the selectivity was enhanced by patterning with a resist layer prior to monolayer formation and, eventually, lifting-off the resist from regions where CNT placement is not desired. These initial results indicate that, with further development, a large number of CNT-based devices can be fabricated simultaneously via self-assembly.

An alternate approach is the selective area growth of SWCNTs by CVD [20]. By using lithographic techniques to obtain patterned islands containing nanoparticles of catalytic material (e.g., Fe, Mo, etc.), SWCNTs can be grown with methane as the source gas. These SWCNTs tend to bridge neighboring islands, on which metallic electrodes can be subsequently deposited to facilitate electrical measurements. In addition to the ability of positioning tubes at predetermined locations on a surface, this approach offers the added advantage of eliminating the bundling problem described above associated with tube manipulation after growth. This approach also seems to be able to provide SWCNT-to-metal electrode interfaces with low

contact resistance, with two-terminal values as low as 20 k $\Omega$  [20] compared to around 1 M $\Omega$  [9] in cases described above in which SWCNTs are physically placed in contact with electrodes. For optimal device performance, it is important that contact resistance not be a dominant effect. This last point highlights the fact that substantial work remains to be done to better understand the physics of CNT/metal interfaces. Furthermore, irrespective of the growth technique, the control of tube diameter and chirality still requires considerable development since those parameters determine the type and properties of the CNT, and are not well-controlled at the present time.

#### 3.2. DNA

Strands of DNA are extremely selective in terms of molecular recognition due to the complementary nature of the base-pair sequences. This property is ideally suited for self-assembly and for further integration with other nano-scale objects, leading to what might be envisioned as bio/nano devices. For example, one can imagine attaching short strands of DNA molecules to the ends of CNTs and complementary strands to electrodes to facilitate highly selective positioning of the tubes. However, DNA is highly sensitive to temperature, pH and other environmental factors. This has a strong bearing on its chemical compatibility with other processes and molecules. Furthermore, the fundamental question as to the nature of DNA electrical conductivity is still not totally resolved. Results from earlier studies of fluorescence quenching measurements have been widely different, ranging from basically insulating properties to claims that DNA is a molecular wire [21]. More recently, however, there have been two reports of direct measurement of electrical transport through DNA molecules [22]. Linear I-V characteristics were observed at low voltages in one case, while nonlinear I-V curves with a voltage gap which increases with temperature were measured in the other. These are encouraging results but a detailed understanding of the conduction mechanism remains as a key objective in researching the use of DNA as an active component in electronics.

In the meantime, others have used the molecular recognition properties of DNA to facilitate the selfassembly of micro- and nano-scale structures. The hybridization of a DNA molecule with surface-bound oligonucleotides was used to bridge it across two Au electrodes, and allows it to be used as a template for the deposition of a 12  $\mu$ m long, 100 nm wide Ag wire [23]. Another example is the self-assembly of wires into two- and three-dimensional networks. The Au regions of Au–Pt–Au segmented wires (35–200 nm in diameter) can be derivatized selectively relative to the Pt with single-strand DNA molecules. Then a combination of field- and chemical-assisted assembly techniques can be used to align and attach segmented wires with good uniformity and reproducibility onto templated SiO<sub>2</sub> substrates [24]. In other studies, the binding of DNA onto surfaces of CdSe quantum dots (QDs) allows these nanoparticles to be used in combination with complementary oligonucleotides and other DNA-functionalized particles to form pure QD or mixed Au/QD nanostructures [25]. With further development, such approaches will lead to the formation of complex nano-scale structures that can be used as scaffolding for the assembly of molecular electronic components as well as provide unique properties of their own.

#### 3.3. Custom molecules

Since the original proposal of molecular rectification in the mid-1970's [6], a tremendous amount of theoretical and experimental work has been done to understand how to make use of individual molecules as components in electronic applications [26]. Much of this work has been focused on molecular wires and switches. With advances in chemical synthesis, self-assembly procedures and scanning probe microscopy, it became possible to demonstrate conductance in molecules such as  $C_{60}$  [27] and linear conjugated oligomers [28]. For example, in the latter case, conjugated organic thiolates were synthesized and inserted from dilute solutions into the domain boundaries of insulating *n*-alkanethiolate monolayers self-assembled on Au(111) surfaces. The tip of a scanning tunneling microscope was then used to image and to measure the conductivity of the conjugated organic thiolates. The interest in using these custom synthesized molecules as wires, however, has waned somewhat with the recent emergence of the CNT since the metallic variety of the latter has much higher current carrying capability.



Figure 7. (A) Schematic view of molecules of 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'nitro-1-benzenethiol positioned between Au electrodes in the nanopore structure. The molecules were self-assembled onto the bottom Au surface while the top Au contact was formed by evaporation. (B) I-V curve of the structure measured at 60 K, showing a peak-to-valley current ratio of 1030 : 1. The value for the valley current is instrument limited. (Figures courtesy of Mark Reed, Yale University.)

The research of molecular switches, on the other hand, has made significant advances in the last few years. Molecules of benzene-1,4-dithiol were self-assembled onto two closely-spaced Au electrodes of a mechanically controllable break junction [29]. The electrodes were then slowly moved towards each other until the onset of conductance is observed. At room temperature, the I-V measurements yielded a conductance gap of 0.7 V centered about zero bias that could be attributed to the mismatch between the Fermi level of the contact and the lowest unoccupied molecular orbital of the dithiol [30]. More recently, the I-V characteristics of a molecule synthesized with a nitroamine redox center were measured [31]. Molecules of 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'nitro-1-benzenethiol were self-assembled onto the Au surface of lithographically defined nanopore structure. At 60 K a peak-to-valley current ratio as high as 1030 : 1 was observed, as shown in *figure 7*. A negative differential resistance behavior of this large magnitude is not observed even in much more extensively studied semiconductor tunneling devices. These results suggest that molecules with unique electronic characteristics can be designed and synthesized to act as active components in the fabrication of ultra-high density circuits.

#### 4. Conclusions

With further development of EPL, EUVL and electron beam source arrays, lithography will continue to drive the scaling of CMOS circuits during the next decade. However, for feature sizes less than 30 nm, a new approach may become necessary for technical and/or economical reasons. Molecular electronics could well be this alternate approach. For that to happen, it is likely that research in molecular electronics will evolve in a manner in which the various classes of molecules are used in combination to make use of their respective strengths. By developing techniques to customize and control properties such as charge transport, molecular recognition, and self-assembly, and by developing novel architectures that can fully utilize the benefits of nano-scale devices and circuits, a revolutionary approach to ultra-large-scale integration can be realized. Development of these methods is challenging and will require coordinated multi-disciplinary research in the fields of physics, chemistry, molecular biology, material science and nano-scale engineering. Many opportunities for scientific and technological discovery can be expected from long-term inter-disciplinary research in molecular electronics.

#### References

- [1] The 1999 International Technology Roadmap for Semiconductors (http://www.itrs.net/ntrs/publntrs.nsf).
- [2] Harriott L.R., Berger S.D., Liddle J.A., Watson G.P., Mkrtchyan M.M., J. Vac. Sci. Technol. B 13 (1995) 2404.
- [3] Jewell T.E. et al., SPIE Proc. 1263 (1990) 80.
- [4] McCord M., J. Vac. Sci. Technol. B 15 (1997) 2125.
- [5] Smith H.I., J. Vac. Sci. Technol. B 14 (1996) 4318.
- [6] Aviram A., Ratner M., Chem. Phys. Lett. 29 (1974) 277.
- [7] Iijima S., Nature 354 (1991) 56.
- [8] Mintmire J.W., Dunlap B.I., White C.T., Phys. Rev. Lett. 68 (1992) 631; Dresselhaus M.S., Dresselhaus G., Saito R., Phys. Rev. B 45 (1992) 6234; Hamada N., Sawada S.I., Oshiyama A., Phys. Rev. Lett. 68 (1992) 579.
- [9] Bockrath M. et al., Science 275 (1997) 1922; Tans S.J. et al., Nature 386 (1997) 474; Shieh C.L. et al. (unpublished).
- [10] Wildöer J.W.G. et al., Nature 391 (1998) 59; Odom T.W. et al., Nature 391 (1998) 62; Venema L.C. et al., Science 283 (1999) 52.
- [11] Tans S.J. et al., Nature 393 (1998) 49; Martel R. et al., Appl. Phys. Lett. 73 (1998) 2447; Shieh C.L. et al. (unpublished).
- [12] Tsukagoshi K., Alphenaar B.W., Ago H., Nature 401 (1999) 572.
- [13] Ebbesen T.W., Ajayan P.M., Nature 358 (1992) 220.
- [14] Thess A. et al., Science 273 (1996) 483.
- [15] Cassell A.M., Raymakers J.A., Kong J., Dai H., J. Phys. Chem. B 103 (1999) 6484, and references therein.
- [16] Lui J. et al., Science 280 (1998) 1253.
- [17] Journet C. et al., Nature 388 (1997) 756.
- [18] Chen J. et al., Science 282 (1998) 95; Boul P.J. et al., Chem. Phys. Lett. 310 (1999) 367.
- [19] Liu J. et al., Chem. Phys. Lett. 303 (1999) 125; Burgin T.P. et al. (unpublished).
- [20] Soh H.T. et al., Appl. Phys. Lett. 75 (1999) 627.
- [21] Beratan D.N., Priyadarshy S., Risser S.M., Chem. Biol. 4 (1997) 3; Wilson E.K., Chem. Eng. News (August 23, 1999) 43.
- [22] Fink H.-W., Schönenberger C., Nature 398 (1999) 407; Porath D. et al., Nature 403 (2000) 635.
- [23] Braun E., Eichen Y., Sivan U., Ben-Yoseph G., Nature 391 (1998) 775.
- [24] Mayer T.S., Jackson T.N., Natan M.J., Mallouk T.E., in: Materials Research Society Fall Meeting, Paper H9.3, November 1999.
- [25] Mucic R.C. et al., J. Am. Chem. Soc. 120 (1998) 12674; Mitchell G.P. et al., J. Am. Chem. Soc. 121 (1999) 8122.
- [26] Aviram A. (Ed.), Molecular Electronics: Science and Technology, AIP Press, New York, 1992; Jortner J., Ratner M. (Eds.), Molecular Electronics, Blackwell, Oxford, 1997.
- [27] Joachim C., Gimzewski J.K., Europhys. Lett. 33 (1996) 635.
- [28] Bumm L.A. et al., Science 271 (1996) 1705; Cygan M.T. et al., J. Am. Chem. Soc. 120 (1998) 2721.
- [29] Reed M.A., Zhou C., Muller C.J., Burgin T.P., Tour J.M., Science 278 (1997) 252.
- [30] Datta S. et al., Phys Rev. Lett. 79 (1997) 2530; Tian W. et al., J. Chem. Phys. 109 (1998) 2874.
- [31] Chen J., Reed M.A., Rawlett A.M., Tour J.M., Science 286 (1999) 1550.