Nanofabrication for Molecular Scale Devices

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1. Introduction

The predicted 22-nm barrier which is seemingly going to put a final stop to Moore’s law (Fig. 1) is essentially related to the resolution limit of lithography. Consequently, finding suitable methods for fabricating and patterning nanodevices is the true challenge of tomorrow’s electronics. However, the pure matter of moulding devices and interconnections is interwoven with research on new materials, as well as architectural and computational paradigms. In fact, while the performance of any fabrication process is obviously related to the characteristic of the materials used, a particular fabrication technique can put constraints on the definable geometries and interconnection patterns, thus somehow biasing the upper levels of the computing machine. Further, novel technologies will have to account for heat dissipation, a particularly tricky problem at the nanoscale, which could in fact prevent the most performing nanodevice from being practically employed in complex networks. Finally, production costs – exponentially growing in the present Moore rush – will be a key factor in evaluating the feasibility of tomorrow technologies.

The possible approaches to nanofabrication are commonly classified into top-down and bottom-up. The former involves carving small features into a suitable bulk material; in the latter, small objects assemble to form more complex and articulated structures. While the present technology of silicon has a chiefly top-down approach, bottom-up approaches are typical of the nanoscale world, being directly inspired by nature where molecules are assembled into supramolecular structures, up to tissues and organs. As top-down approaches are resolution-limited, boosting bottom-up approaches seems to be a good strategy to future nanoelectronics; however, it is highly unlikely that no patterning will be required at all, since even with molecular-scale technologies there is the need of electrically contacting the single elements and this most often happens through patterned metal contacts, although all-molecular devices were also proposed. Here, we will give some insight into both top-down and bottom-up without the intention to be exhaustive, because of space limitations.
Fig. 1. Moore’s law, number of transistors as a function of time (points refer to the various processors introduced by Intel: 4004, 8008, 8080, 8086, 286, 386, 486, Pentium, Pentium II, Pentium III and Pentium 4, respectively). Some related milestones of nano/molecular electronics are also indicated (reprinted with permission from G. Maruccio et al., J. Mat. Chem., 14, 542 (2004). Copyright 2004 Royal Society of Chemistry).

2.2 Top-down processes

The top-down approach in building integrated circuits (ICs) usually involves some form of lithography to define the required pattern of features. Many other kinds of processes are required to build an IC, such as ion-implantation, metal evaporation and etching, which are used in several nanoscale devices too; however, here we will concentrate on the problems of lithography, since that is the side of technology directly related to resolution and, consequently, most innovative (and troublesome) in nanodevices. According to a common distinction, we will classify lithographic methods into hard and soft, where the former (often referred to simply as “lithography”) are the improved version of those already employed for present ICs, whereas the latter have been purposely developed for nanoscale fabrication (in particular when dealing with fragile molecules).

2.2.1 (Hard) lithography

By ‘hard lithography’ we mean all those techniques using resist layers and optical masks, derived from standard photolithography. The core-idea is to expose a sensitive material (the ‘resist’) to an activating agent (light or a particle beam) in order to harden (or soften) it in targeted areas. Subsequently, a developer solution will wash away the soft parts of the resist layer selectively, while the remaining hard parts mask the sample for subsequent processing (see the schematic in Figure 2a). Commonly, either the material is etched where unmasked by the layer (and the remaining resist is taken away after the etching); or a new layer of material is grown (e.g. metal by evaporation) so that it builds up upon the patterned resist, where this is present, or upon the underlying material in the resist’s voids; finally, the hardened resist will be removed, carrying away the material grown atop (lift-off) and leaving the material inside the patterned voids untouched.
Fig. 2. (a) Positive and negative photoresists; (b) Exposure methods: contact, proximity and projection; (c) Response curves for negative and positive photoresist after exposure and development. A threshold energy $E_T$ characterizes both the positive/negative resist solubilities in their developers.

The key issue is how, and how precisely the pattern can be drawn into the resist. Standard photolithography exposes a suitable type of resist to UV light passing through a mask featuring transparent and opaque zones, but is not suitable to fabricate nanoscale devices because of limited resolution. Actually, the minimum definable feature size, or half-pitch $p_{1/2}$ is related to the radiation wavelength by the Rayleigh criterion stating that

$$p_{1/2} \approx \frac{\kappa \lambda}{NA}$$

where $\lambda$ is the wavelength itself, $NA$ is the numerical aperture of the optical system and $\kappa$ summarizes other typical parameters of the system employed (such as the non-point-shaped light source) and typically lies between 0.25 and 1; at the UV wavelengths of photosensitive resists then the half-pitch is typically limited to hundreds of nanometres.

In order to realize sub-100 structures, a gradual shift from the more traditional mercury-based G- or I-Hg ultraviolet lamps as sources working at 436nm or 365nm respectively was deemed necessary. The requirement of the semiconductor industry for denser and faster chipsets in the 1980s drove the search for alternative sources able to meet this demand. In this respect, excimer lasers based on a combination of noble gases and reactive gases (mainly KrF 248 nm and ArF 193 nm) were the system of choice as deep-ultraviolet sources (Figure 3) (Jain et al., 1982).

Present technological trend spearheaded by technology behemoths like Intel, IBM and AMD have then seen a further gradual shift of focus from deep-ultraviolet sources for photolithography to manipulation of the wavevectors of the incident interfering laser light using novel forms of interferometric lithography (Figure 3) (Pfeiffer et al., 1999). Such novel forms take advantage by realizing an optically denser medium such as an index-matching...
liquid between the excimer source and the chemically amplified photoresist (immersion lithography for 22nm half-pitch). Extreme-ultraviolet lithography (EUVL) technology for now is prohibitively expensive due to cost of processing per wafer. However, extensive research is being carried out on EUVL-based technology as sub-22nm half-pitch structures would require choice of stable sub-193nm source, novel chemically amplified photoresists and understanding of photomask for EUV technology.

Fig. 3. LEFT Immersion lithography uses beam splitters to split the laser beam in two which are then made incident on a beam coupling prism (inset) which focuses them. Once the beam leaves the coupling prism it enters a denser refractive-index matched liquid at an angle $\theta_2$ providing finer structures (for simplicity one of incident light beam is shown). RIGHT Over the years reduction in feature size has been possible due to the development of excimer laser sources. In order to realize sub-22nm half-pitch structures the use of extreme-ultraviolet sources is predicted to be necessary.

As Next Generation lithography (NGL), IBM is now focussing on using a modified version of immersion lithography technology for fabrication of 22nm nodes called projection reduction exposure with variable axis immersion lenses (Pfeiffer et al., 1999). Whereas, Intel in 2011 has launched its 22nm node transistors called the tri-gate transistor (Chau et al., 2003; Doyle et al., 2003) which uses conventional fabrication tools. Intel believes that it can further reduce the node size to 14nm using existing technology after which they believe that they would reach the Moore’s limit for conventional fabrication technologies. Extreme-ultraviolet lithography technology (EUVL) has not found centre stage as of 2011 in next generation lithographic processes due to the extremely high costs. Direct lithography and nanoimprint lithography (NIL) are also being considered as options for NGL techniques. Alternatively, for resolution enhancement and patterning on the nanometer scale, electron-beam lithography (EBL) can be employed due to resolution in the order of tens of nanometers and remarkable versatility especially when combined with other techniques, which make it the most widely employed method for patterning under-100 nm structures. Also, EBL is commonly employed to fabricate masks. At the core of this type of high resolution lithography there is the exposure of a sensitive resist to a thin beam of electrons, which is moved around the layer by deflecting electric fields and turned on and off to design the desired structure. The resist is usually made of polymers in a liquid solvent. High-energy electrons traveling across the resist can either break the main chain bonds (positive resist) thus making the resist removable upon exposition; or, they can promote the
formation of bonds making the resist irremovable (negative resist). A very common positive resist is poly methyl methacrylate (PMMA); an example of negative resist is SU-8.

The usual resolution of EBL (a few tens of nanometers) is larger than the spot of the electron paint-brush, due to the proximity effect, a result of the scattering of electrons passing through the resist up to the substrate. In a classical picture, the electrons experience elastic collisions which make them scatter either preserving the approximate direction of the momentum (forward scattering) or taking up the reverse direction (back-scattering), the latter especially when bouncing on the substrate. Besides, there are inelastic collisions producing secondary, lower energy electrons. The overall exposure results from adding up the three contributions from the forward and backward scattering and from the secondary electrons.

Fig. 4. LEFT (a) In a standard EBL process (e.g. on PMMA-SiO$_2$-Si$^+$ substrates), the electron beam experience both forward scattering (slightly in the PMMA and SiO$_2$ layers) and strong, broadly distributed back scattering (in the Si$^+$) resulting in the exposure of a wider PMMA region and a reduced resolution. On the contrary, using a PMMA-Si$_3$N$_4$ substrate, the proximity effect can be significantly reduced as illustrated in (b). Right TEM image of nanogaps with sizes 0.7 nm (a), 1.5 nm (b), 3 nm (c), 4 nm (d), 5 nm (e) and 6 nm (f). Insets: SEM and TEM images of electrodes on a suspended Si$_3$N$_4$ membrane (reprinted with permission from M. D. Fischbein et al., Appl. Phys. Lett. 88 (2006). Copyright 2006 American Institute of Physics).
The second and third terms obviously add supplementary exposure of the resist, causing the images to be larger than desired and very close structures (such as parallel lines) to experience unwanted ‘mutual’ exposure (the proximity effect). W. Hu et al. (Hu et al., 2005) improved the resolution of EBL by introducing cold development: the chemical developer is kept at a temperature down to 4-8 °C temperature obtaining substantially finer resolution, with definition smaller than 5 nanometres. In the cited work this approach was used to pattern the layout of a QCA adder. On the other hand, Fischbein et al. (Fischbein and Drndic, 2006) demonstrated how resolution close to the spot size can be achieved when EBL is carried out on a membrane due to the limited back scattering (see Figure 4).

If EBL is the most popular advanced lithographic technique, a bunch of other methods should be mentioned. Among them, ion-beam lithography (IBL) is the closest to EBL, since it substitutes ions to electrons in the writing beam. The principle and resolution are quite similar to those found in EBL but it presents some advantages for example concerning the backscattering; moreover ions can be used to directly build structures over a substrate.

In X-ray lithography (Silverman, 1997) collimated radiation with 0.1-10 nm wavelengths is used to expose a resist in a parallel replication process. The very short wavelength and remarkable penetration capability of X-rays are at the basis of the high resolution achieved.

The mask is usually made up of a thin, transparent layer covered with patterned, X-ray-opaque features of metals like gold or tungsten. Several drawbacks have been overcome, notably those concerning the relative weakness of the mask (Peckerar and Maldonado, 1993) which, due to the thinness of the transparent basis, tended to inflect upon stress, e.g. of thermal origin. Another lamented trouble was the lack of demagnification: in optical lithography lenses are commonly used to narrow the light cone by a scaling factor $n$, so that the mask features can be made $n$ times larger than those actually fabricated, easing the mask fabrication process. However, though X-ray lithography makes optical lenses useless, another kind of demagnification can be achieved by means of the so-called sweet-spot method or bias reduction (Vladimirsky et al., 1999). Basically, the metal absorber is narrowed at the sides by a controlled amount to compensate for the effects of diffraction, by which light propagates to some extent under the absorber in the nominally dark region. The entity of the required correction is dependent on the mask gap and exposure dose; in the cited work, demagnifications in the order of 3.5 were shown, comparable to those obtained in optical lithography, thanks to a combined optimization of exposure and diffraction. As of today, however, the most serious drawback to X-ray lithography is the need of a synchrotron as the source of radiation. Research is being carried out on small but reasonably powerful X-ray sources, which might make the difference in the success of this performing processes.

Other available fabrication techniques include:

- **Interference lithography**, exploiting the fringes naturally arising when two or more coherent (laser) light sources interfere (see for example (Solak et al., 2003)). This method is maskless, since the geometry is determined by the interference pattern and a comparatively large area can be exposed simultaneously, unlike in E- or IBL; the obvious drawback is that the patterns – and, so, the defined features – are severely bound as to geometry (typically, they must be symmetric).

- **Shadow-mask** techniques where the deposition of a material on a substrate occurs through a holed mask, kept at little distance from the substrate itself, allowing features in the range of some hundreds of nanometres (see for examples the microtips shown in (Luthi et al., 1999)).
To obtain better resolutions or smaller inter-electrode gaps, it is possible to use **post-processing techniques**, by which large EBL-defined gaps are narrowed, or EBL-defined gapless junction are split. An example of the former technique is shown by Y.V. Kervennic and coworkers (Kervennic et al., 2002). The idea was to EBL-fabricate couples of free-standing contacts and subsequently to narrow the inter-electrode gap by electrodeposition, in a controllable way. In the cited work, platinum was electrodeposited from an aqueous solution of 0.1 mol of $\text{K}_2\text{PtCl}_4$ and 0.5 mol of $\text{H}_2\text{SO}_4$. During electrodeposition, the tunneling conductance between the two electrodes was constantly monitored, being obviously dependent on the gap size. The process was interrupted at predefined values, reproducibly obtaining gaps ranging from 20 to 3.5 nm (Figure 5 left).

The inverse pathway is breaking a narrow metal junction defined by EBL to create the gap *a posteriori*. Among the earliest experimented techniques there are electromigration and
mechanically controllable break. In the former case (see for example (Park et al., 2002; Heersche et al., 2006; Jo et al., 2006)), current is passed through the electrodes to reach electromigration densities (~10^6-10^7 J/cm^2) in the narrowest spot (Ho and Kwok, 1989). This gets the contact to break, an event easily revealed by the drop in conductivity within the contacts. Such junctions were employed for example for single molecule transistor measurements on magnetic molecules (Heersche et al., 2006; Jo et al., 2006). In mechanically controlled break junctions (Reed et al., 1997; Champagne et al., 2005), the substrate on which the thin junction is fabricated is flexed by the gentle push of a screw underneath, while firmly held at the ends, until the junction cracks (Figure 5 right). Again, the occurrence of this event is checked through constant measurement of the junction’s conductance. Obviously, all methods rely on not quite easily controlled nanoscale events – the growing of metal structures from electrodeposition, the dismantling of metal hillocks by electromigration, or the mechanical induction of nanoscale fissures – which can guarantee neither high reproducibility of the results nor their controllability a priori. In fact, the typical size of gaps fabricated in these ways has to be checked after the fabrication by scanning electron microscope (SEM) measurements.

Recently, Zandbergen et al. (Zandbergen et al., 2005) introduced a technique for sculpting couples of nanoelectrodes of given gap-size and shape by use of a Transmission Electron Microscope (TEM). A 300kV electron beam with a 2 to 10 nm spot size, carrying a current of 5 nA – corresponding to a flux of ~10^9 electrons/s – was scanned on a sample in which a metal bridge had been defined. By modulating the intensity of the beam, the shape and size of this bridge was finely-tuned, compatibly with the characteristics of the metal used for the contacts; to this respect more than one type of Au were tested, obtaining 1 to 5 nm separations. Pt lines were tested too, which, due to the comparatively low mobility of its atoms, required a much longer exposure time than Au (up to one hour vs. a few minutes) but also permitted the smaller gap obtained in this series of experiments (only 0.6 nm).

2.2.2 Soft lithography

Instead of creating a pattern by masking and exposure, soft lithography exploits an elastomeric stamp (Xia and Whitesides, 1997) (Figure 6). This approach includes different techniques, sharing this basic concept, which have undergone remarkable development in recent years. Here, we will briefly recall the main two techniques, listing only their main variants (Geissler and Xia, 2004).

In moulding techniques, structures are formed inside the voids of a master which is the 3D negative of the desired pattern. With replica moulding (REM), replicas of organic polymers are made against a polydimethylsiloxane (PDMS) mould, reaching feature sizes below 2 nm with some materials. In another variant known as microtransfer moulding (μTM, Figures 6a and 6b) the mould’s voids are filled with a liquid prepolymer and the mould is transferred onto the desired substrate. The prepolymer is subsequently cured to a solid and peeled off, exploiting the elasticity of the mould.

The printing techniques use the stamp to transfer an ink to the substrate. To this category belongs, among others, the microcontact printing technique (μCP, Figures 6c and 6d), also classified as a relief printing method, by which the stamp is first inked with a solution containing the molecules to be deposited (in the first and most classical example, alkanethiols), then dried and subsequently brought into contact with the surface of the substrate (in the cited case, gold).
Research is now ongoing on novel variants and materials (see for example (Choi and Rogers, 2003)). The main field of application of soft lithography remains microfluidics, particularly in the field of lab on a chip (Becker and Locascio, 2002; Pollack et al., 2002; Erickson and Li, 2004; Stone et al., 2004; Dittrich and Manz, 2006; Primiceri et al., 2010; Chiriacò et al., 2011). However, in a recent report (Briseno et al., 2006), soft lithography was, for example, employed also for the collective fabrication of organic single-crystal transistors, outperforming organic thin film transistors but requiring the growth and placing of one crystal per transistor separately, which is the bottle-neck of this technology. In the cited work, octadecyltriethoxysilane (OTS) films were printed by μCP in patterns on which the crystals were subsequently grown in a way pre-conditioned by the geometry of the soft-lithography-defined sites.

The range of applications of soft-lithography is widening, but it is of particular relevance for biomolecules. J. Damon Hoff et al. (Hoff et al., 2004) demonstrated protein patterning by imprint lithography, exploiting the binding specificity between biotin and streptadivin. J.P. Hulme et al. (Hulme et al., 2006) reported on a replica-moulding derived technique to pattern biological molecules, called biomolecular embossing, by which they were able to replica-mould DNA and then emboss it into poly(ethylene terephthalate). Similar approaches could prove very useful in tomorrow’s devices, because of the importance of biomolecules both in fabrication and in functional issues of nanoelectronic devices (hard lithography techniques typically can not be employed due to the fragility of these molecules).

Fig. 6. Schematics of the microtransfer moulding (a and b) and microcontact printing; (c and d).
Finally, we mention an example of a cross-inspired technology, joining ideas from different approaches to overcome their inherent limits. S.Y. Chou et al. (Chou et al., 2002) used a stamp like in soft lithographies, but made of quartz instead of an elastomer, to imprint features on a crystal of silicon - not used with classical soft lithography - after melting its superficial layer by a single excimer laser pulse. The technique, called ‘laser-assisted direct imprint’ (LADI) was used to impress a 250 nm-periodic grating of parallel silicon wires, which could be used as a template for a crossbar structure. However, there are also 10 nm-wide, 15-nm tall silicon lines on the edges of the bigger wires which are just the negative of the notches created on the mould by the trenching effect during the reactive ion etching, meaning that the resolution of this technique is potentially much better than that of the first stamp.

### 2.2.3 Scanning probe nanolithography

Presently the highest fabrication precision is obtained by writing methods (most of them SPM-based), employing a stylus or pen with variable sharpness. Depending on the resolution of the writing instrument, macroscopic down to atomic-scale features can be defined according to virtually any topology, at the price of a low speed. Beyond the equivalent of a paper and a pen, ink may be required or not, depending whether the writing is additive (deposition of material on the substrate) or subtractive (removal of material from the substrate). Moreover, a local modification of the surface/layer can be achieved by means of an energy beam such as a laser or an electric/magnetic field.

The simplest subtractive solution employs a rigid stylus pressed against the substrate to dig channels that, at their best resolution, can be as slim as 0.1 nm. The choice of the stylus depends of course on the material: good results have been obtained with metals, oxides, and polymers.

Positive writing processes are also called add-on processes. By them, among others, resist-, etching- and development-incompatible materials can be patterned. A popular add-on method is dip-pen nanolithography (DPN) (Piner et al., 1999), developed by the Mirkin group, where an atomic force microscope (AFM) tip is coated with molecules and then drawn onto a surface. The water meniscus formed between the tip and the substrate by the condensation of humidity provides a transfer pathway by which the molecules are transferred from the tip to the substrate (Figure 7a). In (Hyun et al., 2002), the versatility of DPN was exploited in conjunction with other self-assembly methods. Specifically, 16-mercaptohexadecanoic acid was deposited onto gold by DPN and subsequently used as the grafting pattern for an amine-terminated biotin derivative. Subsequently, streptadivin structures were formed upon incubation and biotinylated proteins were deposited, always following the lithographed pattern. Biotin-tagged molecules being very common, this is a powerful molecular patterning method and shows that molecular mediation can be used to make the patterning method less dependent on the chemistry of the substance being patterned. The Mirkin group also used dip-pen nanolithography to construct proteins patterns with features in the range of 100 nm (Lee et al., 2002). Moreover, they also demonstrated a multiple-pen nano-plotter for multiple ink nanolithography in order to pattern different organic molecules down to a 5-nanometer separation (Hong et al., 1999; Hong and Mirkin, 2000).

Once the pattern is fabricated, replica processes can be also exploited to create duplicates as demonstrated by the Stellacci group at MIT (Yu et al., 2005).
The field is of course still in progress: among recent developments, a group at the ETH Zurich fabricated a four-terminal quantum dot and a double quantum dot system with integrated charge readout using a scanning force microscope to achieve a local, direct oxidation in a AlGaAs/GaAs heterostructure containing a two-dimensional electron gas. As a result of the local oxidation, the electron gas is locally depleted in the GaAs surface and the observed Coulomb blockade diamonds demonstrated the high quality of this fabrication process (Dorn et al., 2002). Let us also remember the variant of DPN called electro-pen lithography (Cai and Ocko, 2005) by which a conductive AFM probe coated with ink molecules and biased with a voltage oxidizes the substrate underneath and deposits the ink, all in a sweep. The lines drawn are as large as 50 nm with a writing speed larger than 10 μm/s. For a review on DPN see K. Salaita et al. (Salaita et al., 2007).

Ultradense atomic patterns can be also realized by atomic manipulation using a STM (Manoharan et al., 2000; Agam and Schiller, 2001; Fiete and Heller, 2003; Morr and Stavropoulos, 2004). Despite the advantage given by their ultimate resolutions, however, scanning probe nanolithography techniques are slow and appear too expensive for mass production, though a major performance leap cannot be excluded for these techniques in the future. Even if such dramatic improvement did not happen, however, tomorrow’s nanoelectronic circuits may turn to have critical parts requiring precise, very small-scale patterning without the intrinsic faultiness of other techniques (e.g. of self-assembly), for which the writing methods can turn out essential.

![Schematic representation of dip-pen nanolithography](image-url)
performance of the electric contacts can determine the behaviour of the device. Here, we present some non-conventional solutions for creating nanoscopic electrodes, addressing the problems of mass production and/or reproducibility.

Fig. 8. In the method for fabricating nanodevices proposed by R. Krahne et al. (Krahne et al., 2002) the MESA structure in (a) undergoes a GaAs-selective etching (b), so that the subsequent metal evaporation (c) leaves a gap in which a nanoparticle can be trapped electrostatically (d) and then measured in a three-terminal configuration (e). The method lends itself to one-step mass production of such SET arrays (f). Reprinted with permission from R. Krahne et al., Appl. Phys. Lett. 81, 730 (2002). Copyright 2002 American Institute of Physics. Schematics of the g) non-oxidized and h) oxidized mesa nanojunctions (reprinted with permission from G. Maruccio et al., Small 3, 1184 (2007). Copyright 2007 Wiley-VCH).

In this respect an innovative approach is that proposed by R. Krahne et al. (Krahne et al., 2002) and then improved by G. Maruccio et al. (Maruccio et al., 2007) An AlGaAs/GaAs/AlGaAs quantum well structure is grown by molecular beam epitaxy (MBE) and subsequently carved to a slanted shape by wet-etching (Figure 8a), until reaching the bottom AlGaAs layer. Then the GaAs layer is removed to a few tens of nanometers by selective wet-etching with citric acid and $\text{H}_2\text{O}_2$ (Figure 8b) and a metal layer is evaporated perpendicular to the substrate to form the contacts (Figure 8c). In such a way, a contacted gap as large as a few nanometers is created where, for example, a gold particle can be immobilized by electrostatic trapping (Figure 8d) and provided with a gate electrode (Figure 8e) to form a SET. In order to reduce the leakage current at room temperature through the underneath semiconductor layer, a selective oxidation was used (Maruccio et al., 2007) to convert the AlGaAs barriers in insulating oxide layers. This approach allowed G. Maruccio et al to investigate electron transfer in individual proteins (Maruccio et al., 2007) and pave the way to applications in molecular electronics. Since only photolithography is used to define the electrode pattern and all processes are carried out at wafer scale, this improved mesa-gap technique enables the simultaneous, economic fabrication of large arrays of nanodevices working at ambient conditions, a crucial advance for the implementation of low-cost mass-production of nanoscale devices and the fabrication of complex circuits consisting of different nanodevices and arrays of sensors at reasonable cost.
(Maruccio et al., 2007; Maruccio et al., 2009) (Figure 8f). Similar approaches for parallel fabrication of nanodevices were also developed by other groups. For example Ray et al. reported a CMOS-compatible fabrication of room temperature single-electron devices having source and drain electrodes vertically separated by a thin dielectric film (Ray et al., 2008).

Concerning the problem of good and reproducible contacts, T. Dadosh et al. (Dadosh et al., 2005) proposed the use of two gold nanoparticles (NPs) to contact a conductive organic molecule in a controlled way (Figure 9). A NP dimer was assembled using the molecule as a bridge and a device was fabricated, in which the two nanoparticles were also exploited to electrostatically trap the dimers (thanks to their polarizability) within EBL-defined nanojunctions. Their results demonstrated that the transport through a conjugated molecule is quenched by localizing groups placed at its center or near the contacts (Figure 9). Metal nanoparticles were employed as means to probe molecular conduction also by other groups in order to create a bridge between organic monolayers formed on metallic electrodes. Most of these studies focused on conductance through conjugated molecules with thiol terminal groups linked to gold. For example, Amlani et al. (Amlani et al., 2002) demonstrated the particle bridge concept by measuring conductance through a monolayer of (1-nitro-2,5-diphenylethynyl-4¢-thioacetyl)benzene. Long et al. (Chu et al., 2007) demonstrated magnetic nanoparticle assembly by comparing conductance through undecanethiol, oligo(phenylene ethynylene)-dithiol, and oligo(phenylene vinylene)dithiol.

![Diagram](image.png)

**Fig. 9.** (a-b) Three organic molecules attached to two gold nanoparticles. (c) high-resolution SEM image of a dimer (d) I-V characteristics of the different molecules. Transport through a conjugated molecule (BPD) is quenched by localizing groups placed at its center (BPE) or near the contacts (BDMT). (reprinted with permission from T. Dadosh et al., Nature 436, 677 (2005). Copyright 2005 Macmillan Publishers Ltd.)
2.3 Bottom-up processes

In bottom-up processes, the capability of atomic or molecular building blocks of assembling into ordered, complex arrangements is exploited. Very common in living beings, especially with regeneration purposes, bottom-up processes are made up of the composition of many atomistic processes, on which no punctual control is required, in opposition to top-down processes where the degree of refinement of a defined structure is directly related to the precision employed. What is required in bottom-up processes is instead that the molecular constituents are apt to assemble and that the environment favors the process.

Following (Barth et al., 2005), we classify bottom-up phenomena as ‘self-assembly’ or ‘self-organized growth’ processes, where the first term refers to the spontaneous association of molecular constituents into supramolecular structures, while the second term is used to designate autonomous order phenomena guided by mesoscale force fields or kinetics limitations, such as those leading to the deposition of a monolayer of molecules on a substrate. The use of bottom-up processes in nanoelectronics is crucial to the construction of molecular devices, in which the ‘active’ part is a bunch of molecules (typically a monolayer) or consists of individual conductive molecules.

Bottom-up processes usually involve two main factors, namely a driving force and a recognition mechanism. The driving force is usually exerted by a gradient of concentration, or an electric field, and tends to bring some molecules, usually in solution, in contact with other molecules, often fixed to a substrate or another molecular or supramolecular structure. The recognition mechanism is the necessary chemical affinity between the two molecules, usually provided by two chemical groups playing the role of molecular-scale compatible ‘hooks’. Once the suitable conditions and environment have been created, the assembling goes on by itself without need of direct control on each elementary event (which would be impossible, on the other hand).

As in all physical processes and chemical reactions, bottom-up processes are driven by the goal of reaching a minimum of energy, but conditioned to the overcoming of activation energies, i.e. barriers which could get the process trapped into local minima. The accuracy of the final result and the speed of the process depend on the equilibrium between kinetics and thermodynamics.

Let us consider a crystalline substrate on whose surface an organized structure must be grown; for example an ordered monolayer of molecules. The involved atomistic phenomena are the deposition of the molecules from solution onto the surface and their surface diffusion kinetics. The former factor mainly depends on the solution concentration and the applied driving force (possibly just a concentration gradient and the Brownian motion) and can be summarized by the deposition rate $F$. The latter factor is dependent on the molecule-substrate interaction as well as on the reciprocal interaction between the deposited molecules. We then assume the diffusivity $D$ of the molecules on the surface as the representative parameter of thermodynamics. If an Arrhenius law is assumed, then

$$D = \exp(-E_a/RT) \tag{2}$$

where $E_a$ is the activation energy, $T$ is the absolute temperature and $R$ is the gas constant; now, the thermodynamics-to-kinetics $D/F$ ratio summarizes the overall character of the process. After molecules have ‘landed’ on the substrate, they generally undergo random hopping processes across the lattice, during which they can meet other similar species to enucleate a new one or join an already formed aggregate. The slowest is the deposition rate
F, the most likely is the settling of the newly deposited adsorbates onto an equilibrium condition, for they simply have time to move around the lattice until a minimum energy configuration is reached; hence, the largest is $D/F$, the closest is the process to the equilibrium condition. In such condition the individual processes are of little or virtually no importance, since the system evolves towards a minimum quite independently of the random walk followed by each constituent. Conversely, a large deposition rate with respect to diffusivity (small $D/F$) means that kinetics is prevailing on thermodynamics, i.e. the quick deposition of adsorbates on the substrate prevents the movement of the single adsorbate towards the overall minimum energy; in this case, rather, local energy minima are favored corresponding to metastable structures. The effect of the $D/F$ ratio is shown pictorially in Figure 10 from (Barth et al., 2005).

Fig. 10. Atomic-scale view of growth processes at surfaces. The kind of assembled structures is chiefly determined by the $D/F$ diffusivity-to-flux ratio: a small $D$ compared with $F$ favours the aggregation in structures such as metal nanoislands, the reverse situation drives the reaction towards the global energy minimum and is the most suitable for supramolecular assembly (reprinted with permission from J. V. Barth et al., Nature 437, 671 (2005). Copyright 2005 Macmillan Publishers Ltd.)

Tuning the $D/F$ through control on the process parameters reflects, in turn, on the average geometric characteristics of the structures to build. For example, metal islands are thermodynamically sub-optimal with respect to a more uniform distribution of metal atoms; consequently, their construction is kinetics-driven, imposing small $D/F$. Intermediate $D/F$ values are used for building semiconductors, while supramolecular structures require a high degree of ordering of the constituents, or a close proximity to the equilibrium condition (large $D/F$) because the final, ordered structure just coincides with the global energy minimum.

Basing on the exposed principles one can build also complex multilayered structures (see the review (Hammond, 2004) and references therein) provided that the chemistry of the layers is chosen carefully according to the deposition sequence; a common way is depositing...
layers provided with charges of alternated signs (layer-by-layer electrostatic assembly). Varying the constituents during deposition one can tune the variation of the layers’ cross profile in a very fine way.

Other techniques can be employed to design the in-plane structures. One widely used is the employment of block copolymers, i.e. at least two variable polymer fragments, immiscible and joined by a covalent bond (Geissler and Xia, 2004). Once deposited, ensembles of block copolymer can form a variety of regular 2D patterns, in turn usable to template other molecules (binding with them) or to mask the deposition of other molecules (by letting them through nanoscale pores).

Before describing some significant examples of bottom-up patterning it is opportune to remind that these processes are intrinsically faulty due to their statistical nature. Their envisaged positive importance in nanoscale fabrication is also the main reason why fault-tolerance is predicted to become a ubiquitous problem in nanotechnology. In what ways and to what extent this will affect future systems depends on both the details of the process and the spatial resolution of the employed devices. In larger-than-molecular-scale devices, where charge transport can be modeled to happen inside a bulk of molecules, a not too high faultiness can be accounted for in statistical terms as a correction in the charge transport performance. Using single-molecule-scaled devices, even a single flawed molecular site – one where the molecule is wrongly oriented, structurally altered or lacking at all – will generally imply alteration of the local and possibly overall processing capabilities, a much more severe problem requiring specific countermeasures like redundancy and error correction mechanisms.

2.3.1 Biomolecules for patterning

The world of biological molecules offers a plethora of opportunities from nanoelectronics to biosensing, because of the complexity and richness of structures and functional properties. For space constraints, they can not be discussed here in detail. However, we want to introduce the biomolecules as instruments for patterning and device fabrication. To this aim biological molecules are ranked basing mainly on their mechanical characteristics and manipulability; this is where and why DNA plays a major role.

As is well known, DeoxyriboNucleic Acid has a double-helix structure supported by a sugar backbone and surrounded by counterions yielding global neutrality. The thermodynamical stability of the structure is based on the matching between compatible couples of bases, among four types (adenine, A, thymine T, guanine, G, and cytosine C). Stable links are A-T and C-G; each mismatch is a weak ring in the chain increasing the flexibility of the overall structure (Schallhorn et al., 2005) and decreasing its stability; couples of too mismatched (non-complementary) helices are expected not to bind at all.

Since its discovery in the 1950s by Watson and Crick, the progress in DNA manipulation proceeded at astonishing speed: nowadays it is possible to design and synthesize single or double helices with relative simplicity to create even very complicated structures. The main idea in using DNA as a template is to synthesize single helices and let them self-assemble. Intertwined assembling is possible, since a single helix (say 1) can contain a sequence complementary to that of single helix 2 adjacent to another complementary to 3, and 2 and 3 in turn can be bound to other complementary helices along other spots, and so on. Hence, careful design of the base sequences permits to synthesize true DNA
crystals, with complex patterns and structures (Winfree et al., 1998; Reif, 2002; Chelyapov et al., 2004; He et al., 2005; Liu et al., 2005; Mathieu et al., 2005; Reishus et al., 2005; Paukstelis, 2006; Rothemund, 2006).

Research is therefore ongoing on improving DNA modelling, to tune the base sequence according to the target characteristics, as well as on DNA synthesis. Regarding the latter, for instance, it was shown that the rolling circle amplification technique can be used to synthesize long periodic DNA sequences (Beyer et al., 2005) quickly and reliably, so representing a helpful method to produce relatively large amounts of DNA with repetitive structure to self-assemble into large patterns. J. Zhang et al. (Zhang et al., 2005) assembled straight filaments on DNA on a Si surface by combining the advantages of molecular combing – a technique for stretching and binding molecules on a surface by the force of a receding meniscus of liquid - and microcontact printing. D.C. Chow et al. (Chow et al., 2005) demonstrated a way to grow vertical filaments of DNA beginning from an oligonucleotide initiator nanopatterned on a surface. As a result, an ordinate layer of vertical DNA strands can be grown with controlled and variable lateral structures, to be used as scaffolding for various types of molecules, of biological origin or not. A.P.R. Johnston et al. (Johnston et al., 2005) demonstrated the assembly of a multilayer structure obtained alternating two-block homopolymeric nucleotides (polyA20G20/C20T20); A. Granéli et al. (Graneli et al., 2006) tethered DNA molecules on a lipid bilayers. Since the filamentary shape of DNA suggests that it be used as a template for nanowires, Park et al. (Park et al., 2005a) have proposed that DNA be synthesized in tiles, forming 1D and 2D-lattice structures and subsequently coated with silver to obtain a 20-nm diameter and ohmic current-voltage characteristics. H. Kudo et al. (Kudo and Fujihira, 2006) performed electroless metallization of DNA with copper, upon previous activation with palladium; heights from the substrate as large as some tens of nanometers were shown, depending on the metallization time. Other examples of DNA-based nanowire fabrication are found in G. Braun et al. (Braun et al., 2005) who ‘decorated’ DNA strands with gold nanoparticles obtaining grainy nanowires of different densities; and in L. Berti et al. (Berti et al., 2005) who photoinduced the reduction of charged silver nanoparticles on DNA and the subsequent formation of chains, possibly usable as seeds to further metallization. Extensive work on the characterization of variously metallised DNA nanowires is found in the literature (see for example (Hosogi et al., 2005)).

In 2002, K. Keren et al. (Keren et al., 2002) demonstrated DNA-based molecular lithography (Figure 11a-e) by which a substrate of possibly patterned single strands of DNA can be selectively metallized or, alternatively, tagged with molecules grafted in specific sites. The two main ideas underlying molecular lithography just point out the analogy to traditional lithographic methods. First, spots of immobilized DNA single strands can be selectively masked by attaching complementary sequences marked with an enzyme, the RecA protein. Upon DNA hybridization (homologous recombination) the proteins polymerize on the substrate making DNA inert, for instance, to metallization (see the sequences in the images of Figure 11b-e and the schematic of Figure 11a). Secondarily, molecules can be tagged with short strands bearing selected base sequences, complementary to deposited spots in specific positions. Unspecific binding is negligible, provided that the reaction is assisted by RecA. In principle, molecular lithography permits remarkable topology flexibility, limited only by the complexity of the patterned structure of DNA and the selectivity of the homologous recombination processes. Selective metallization and coating with selected molecules can
prove the basis to build a topologically complex network of ‘processing’ molecules, interconnected or insulated depending on the metallization (Keren et al., 2003).

Fig. 11. (a) Molecular lithography permits selective metallisation of DNA with gold after masking some parts of the strand with the RecA protein. The deposition of gold is enhanced by Ag as a catalyst. AFM images of the process are shown, in particular: (b) RecA bound to a sequence of DNA; (c) the sample after exposing to Ag; (d) the metallisation with Au; in the inset, the gap is zoomed in. (e) is a SEM image of the sample in (d). The height of the metallisation is around 50 nm; the scale bars in (b) through (e) are 0.5 μm, except in the inset of (c) where it is 0.25 μm. (Reprinted with permission from K. Keren et al., Science 297, 72 (2002). Copyright 2005 American Association for the Advancement of Science).

Other simpler though less general processes have been devised, such as that by Park et al. (Park et al., 2005b) who built a scaffold assembling two types of DNA tiles (A and B) in a chessboard manner (Figure 12a-f) and got proteins bind at the crossings. Four types of scaffolds (or nanotracks) are shown in the cartoon schematic: the first two form are 2D, i.e. thanks to mutually sticky ends (marked with n and n’) they can assemble into planes of indefinite extension. They differ in that in one case only A tiles are modified in the center to carry biotin, by which streptadivin is subsequently bound, while in the other case both A and B are biotinylated. In the other two cases, intentional non-stickiness allows assembling of a 1D nanotrack. The AFM images in Figure 12g-j are significant as to the effectiveness of the method in building large, regular and functionalized structures. To assess the potential importance of such methods, suffice it to think of the possibility of building large, regular component matrices for memories. It should be pointed out that the DNA-protein interaction may be of general importance in fabricating molecular electronic devices (not just applications like biosensors as might be expected) because of the patterning function briefly illustrated here. Binding and interaction between DNA and proteins are being more and more elucidated by ongoing research (Dixit et al., 2005; Yang and Schepartz, 2005; Hu and Shklovskii, 2006; Sun et al., 2006).
Fig. 12. (a) Geometry of two cross-shaped DNA tiles capable of assembling into lattices; coupled of sticky ends are labelled with $n$ and $n'$. (b) These version of the tiles are sticky only along one axis. In (c) and (d) there are the cartoon images of the lattices formed by (a) and (b) respectively, where only tile A is tagged with biotin; due to the differences in stickiness, lattice (c) is 2D while lattice (d) is 1D. In the lattices (e) and (f) both tiles are biotinylated. (g) and (i) are AFM images of lattices (c) and (e) before the attachment of streptadivin; (h) and (i) are the images of the same, respectively, after the streptadivin has been grafted (reprinted with permission from S. H. Park et al., Nano Lett. 5, 729 (2005). Copyright 2005 American Chemical Society).

Application of similar techniques to pattern nanoparticles was also reported, for example by G.H. Woehrle et al. (Woehrle et al., 2004), who attached gold nanoparticles on DNA with fine-controlled separation thanks to molecular lithography, and L. Dillenback et al. (Dillenback et al., 2006) who employed temperature control to direct nanoparticles assembly by tuning the thermal stability of the DNA sequences used as hooks. A somewhat close use of DNA as linker between floating objects – i.e. without needing a substrate – is found in (Goux-Capes et al., 2006) by L. Goux-Capes et al., who linked different single-walled carbon nanotubes coated with streptadivin through biotin- or bis-biotin-terminated DNA links. Future nanoelectronic components might be assembled in similar fashions and then patterned in larger grids or templates.

As another example, we recall the work by Y.Y. Pinto et al. (Pinto et al., 2005) who assembled gold nanoparticles of two different sizes (5 and 10 nm in diameter) on a same self-assembled DNA scaffolding (Figure 13). The DNA tiles were designed in order to let two types of sticky ends prong out of the scaffold in alternate rows. Two groups of nanoparticles where functionalized with thiol-modified DNA, each bearing strands complementary to one type of sticky end; the final result is shown in the AFM image of Figure 13c. Assemblies of photocrosslinked proteins bound to nanoparticles are used in (Hill et al., 2005) to build a scaffolding for a bioelectronic 3D architecture. The recognition properties of DNA can also be used for computation (Adleman, 1994; Braich et al., 2002).
Fig. 13. (a) Three types of DNA tiles; each possesses sticky ends to bind with other tiles; the ‘red’ and ‘yellow’ tiles also have other sticky ends pronging outwards and different from each other. In (b) the cartoon image of the assembly sequence: the tiles assemble in a predefined sequence to form a lattice; gold nanoparticles are grafting to the pronging sticky ends, after being functionalized with the complementary strands; thanks to the diversity in the sticky ends, two types of nanoparticles (with diameters 5 and 10 nm) can be made assemble in ordinate, alternate rows. The AFM image in (c) shows the result of this process (reprinted with permission from Y. Y. Pinto et al., Nano Lett. 5, 2399 (2005). Copyright 2005 American Chemical Society).

Besides DNA, other affine molecules can be used like Peptide Nucleic Acid (PNA) (Nielsen et al., 1991). Its main difference to DNA is that it is uncharged, bearing a polyamide backbone. Its binding properties and selectivity are even better than those of DNA, to some respect. K.A. Williams et al. (Williams et al., 2002) coupled carbon nanotubes with single-strand PNA covalently and tested hybridization with single-strand complementary DNA: there resulted that DNA-PNA grafted to nanotubes, especially near the cut ends. The preference for the extremities of the nanotubes ensues from the higher reactivity there, at
least in the lack of side-wall defects along the nanotubes themselves, and is a useful feature; moreover, DNA does bind to PNA through specific interaction, rather than with nanotubes through unspecific binding. Such processes could might be envisaged as a future opportunity to exploit molecular lithography for handling nanotubes (as done also by Keren et al. (Keren et al., 2003)), considered among the most promising objects for nanoelectronics, as well as to build more complex objects for computation.

At the end of this overlook of biomolecules in patterning we want to cite the work by L. Riemenschneider et al. (Riemenschneider et al., 2005), a ‘hybrid’ technique joining the advantages of scanning probe lithography with the use of an enzyme. First, an AFM tip was functionalized with a molecule of substrate of alkaline phosphatase, by a technique ensuring that it was grafted exactly at the apex of the tip. The tip was then moved across a mica substrate in a solution of 5-bromo-4-chloro-3-indolyl phosphate (BCIP) and nitro blue tetrazolium (NBT); since alkaline phosphatase dephosphorylates BCIP, making it precipitate in the presence of NBT, the resulting precipitate layer follows the tips’ path. For instance, keeping the tip standing for some tens of seconds produces a spot of precipitate whose large size is proportional to time, and moving it across the substrate at proper speed causes different patterns to form.

In addition to DNA and its derivatives, also other specific interaction (antigen-antibody, ligand-receptor, etc) can be exploited for patterning. Recognition between biotin and streptadivin, as well as between bovine serum albumin (BSA) and the corresponding anti-BSA antibody, were used by Y. Wang et al. (Wang et al., 2005) to assemble CdTe nanowires into branched structures, representing prototypes of nanoscale circuits. Diode-like characteristics were found in the single nanowires, while the junctions were found to be non-conductive, presumably due to the large tunnelling barriers placed by the proteins themselves, creating a ~ 5 nm gap. The authors suggested that the existence of such gap could be viewed as an opportunity to build single-electron devices or, on the other hand, could be reduced by using DNA oligomers in place of proteins. Moreover, scaffolds of nanoparticles were built by McMillan et al. (McMillan et al., 2002) assembling engineered chaperonins (i.e. protein complexes assisting proteins in their folding phase) into regular patterns of units of variable diameter.

2.3.2 Other patterning methods based on self assembly

Wiring is essential in any electronic architecture; that is why patterning specific networks of nanowires to connect devices is one of the most debated - and trickiest - tasks in nanoelectronics. In many cases, nanowires are grown from nanoparticles assembled on a suitable pattern by using biomolecules or other methods like those involving force fields (see for instance (Cohen, 2005)). Actually, S.O. Lumsdon et al. (Lumsdon and Scott, 2005) assembled gold and carbon black colloids, as well as carbon nanotubes, into wires thinner than 1 μm. The growth was triggered by ac electric fields exerting electrophoretic forces on the objects and this technique may be helpful in growing nanowires, provided that the electrodes are capable of shaping the electric field with the due precision. Finally, as carbon nanotubes and nanorods become increasingly important, methods are being studied to get them assembled in ordered geometries (Harnack et al., 2003; Gupta et al., 2006; Hu et al., 2006; Ryan et al., 2006; Nobile et al., 2007; Yan et al., 2007).

Another interesting way of patterning might be that of exploiting the natural periodicity of crystals, which can be tuned to some extent by cutting the crystal to expose a particular face.
Let us cite in this respect the work by A. Kirakosian et al. (Kirakosian et al., 2001) who demonstrated an atom-accurate silicon grating with period 5.73 nm, or exactly 17 atoms, by means of a Si(577) surface: notice that a grating of parallel lines is one of the most frequent test for patterning methods and an insidious one for lithography, since chemical etching suffers from capillarity when it comes to penetrating nanometer-narrow channels.

Finally, the self-assembly properties of monodisperse spheres were also exploited to demonstrate shadow nanosphere lithography (NSL) that allow the fabrication of periodic arrays with morphologies ranging from cups to rods and wires by simply changing the substrate position with respect to the evaporation source (Kosiorek et al., 2005; Imperia et al., 2008; Gwinner et al., 2009).

3. Conclusions

In conclusion, many nanofabrication methods are today available and the choice among them is typically dictated by the materials employed and the specific application targeted. In general, however, they allow modern researchers and IC companies an unprecedented control on processes and open the way to the fabrication of completely new classes of devices.

4. References


We face many challenges in the 21st century, such as sustainably meeting the world's growing demand for energy and consumer goods. I believe that new developments in science and technology will help solve many of these problems. Nanofabrication is one of the keys to the development of novel materials, devices and systems. Precise control of nanomaterials, nanostructures, nanodevices and their performances is essential for future innovations in technology. The book "Nanofabrication" provides the latest research developments in nanofabrication of organic and inorganic materials, biomaterials and hybrid materials. I hope that "Nanofabrication" will contribute to creating a brighter future for the next generation.

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