# Review

Yong Chen Anne Pépin

Laboratoire de Microstructures et de Microélectronique (L2M), CNRS Bagneux, France

# Nanofabrication: Conventional and nonconventional methods

Nanofabrication is playing an ever increasing role in science and technology on the nanometer scale and will soon allow us to build systems of the same complexity as found in nature. Conventional methods that emerged from microelectronics are now used for the fabrication of structures for integrated circuits, microelectro-mechanical systems, microoptics and microanalytical devices. Nonconventional or alternative approaches have changed the way we pattern very fine structures and have brought about a new appreciation of simple and low-cost techniques. We present an overview of some of these methods, paying particular attention to those which enable large-scale production of lithographic patterns. We preface the review with a brief primer on lithography and pattern transfer concepts. After reviewing the various patterning techniques, we discuss some recent application issues in the fields of microelectronics, optoelectronics, magnetism as well as in biology and biochemistry.

Keywords: Nanofabrication / Lithography / Biosystems / Review

EL 4239

# Contents

1		187
2	Preliminary concepts	188
3	Conventional lithographic methods	189
3.1	Electron beam lithography	189
3.2	Focused ion beam lithography	190
3.3	Optical projection lithography	191
3.4	Extreme UV lithography	191
3.5	X-ray lithography	192
3.6	Electron and ion projection lithography	192
4	Nonconventional methods	193
4.1	Nanoimprint lithography	193
4.2	Soft-lithography	194
4.3	Near-field optical lithography	195
4.4	Proximity probe lithography	195
4.5	Other lithographic methods	196
4.6	Chemical and biological approaches	196
5	Other nanofabrication issues	197

Correspondence: Dr. Yong Chen, Laboratoire de Microstructures et de Microélectronique, CNRS, 196 Avenue Henri-Ravéra, F-92225 Bagneux, France E-mail: yong.chen@l2m.cnrs.fr Fax: +33-1-4231-7378

Abbreviations: AFM, atomic force microscope; CMOS, complementary metal oxide semiconductor field effect transistor; MEMS, microelectromechanical systems; PDMS, polydimethylsiloxane; PMMA, polymethylmethacrylate; SEM, scanning electron micrograph

5.1 Thin-film deposition	
5.2 Wet and dry etching techniques	197
5.3 Micromachining	198
6 Applications in information technology	199
6.1 Microelectronics	199
6.2 Optoelectronics and optics	199
6.3 Magnetism 2	200
7 Applications in biology 2	200
7.1 Microfluidics and analysis systems 2	200
7.2 Microarrays and gene chips 2	201
7.3 Nano-MEMS 2	201
7.4 Nanobiochemistry 2	201
7.5 Nanomaterials for biological applications 2	202
7.6 Bioelectronics 2	202
8 Conclusions 2	202
9 References	202

# 1 Introduction

Nanofabrication commonly refers to an ensemble of technologies used to fabricate very small structures (at scales ranging from 1 to 100 nm) which can be integrated into complex hierarchic systems. Sophisticated lithographic methods have origins in the microelectronics world [1]. For several decades, the semiconductor industry has been able to maintain a continuous increase of the integration rate with the number of transistors on a chip being doubled every 18 months [2]. Today, it is possible to integrate more than 100 million transistors on one square inch of a silicon wafer, which corresponds to a miniaturi-

0173-0835/01/0202-187 \$17.50+.50/0

zation level of making 100 nm structures and integrating them into complex circuits. To extend the current CMOS (complementary metal oxide semiconductor field effect transistor) technology to the generation of 30 nm and below, new lithographic techniques are under extensive investigation [2, 3]. Beyond this limit, quantum effects will most likely be used, and ultimately, electronic circuits working at molecular levels will be possible [3].

Nanofabrication is also a technological driver for other research and industry segments. Modern telecommunication systems, for example, employ enormous optoelectronic devices based on semiconductor processing. Even though these devices rely on similar technologies, they do not follow the integrated-circuit paradigm of size downscaling. Chemical and biological chips are other examples of areas which are in rapid progress toward a high degree of functionality and integration [4–7]. The challenges of applying nanofabrication technology to these and other new areas are formidable from the point of view of both basic and applied researches.

The standard fabrication process used by the semiconductor industry involves electron beam lithography for the formation of designed patterns on a set of masks and next optical projection lithography for the reproduction of the mask patterns at a high throughput level, combined to various material pattern transfer techniques. For applications in biology, new technological ingredients must be added to meet requirements such as size, power and biocompatibility. The design and engineering of micro- and nanostructures are specific to a given application, and we will concentrate in this review article on more generic issues such as pattern formation. We provide an outlook on various lithography methods, including both conventional and nonconventional techniques as well as nonlithographic pattern formation. Pattern transfer techniques are briefly discussed, together with a number of microsystem issues. Finally, application examples and current trends in information technology and biosystems are presented.

# 2 Preliminary concepts

A typical lithographic process consists of three successive steps: (i) coating a substrate with irradiation-sensitive polymer layer (resist), (ii) exposing the resist with light, electron or ion beams, (iii) developing the resist image with a suitable chemical. Exposures can be done by either scanning a focused beam pixel by pixel from a designed pattern, or exposing through a mask for parallel replication. Serial beam scanning is used for mask fabrication and single component fabrication, but it does not supply adequate throughput for manufacturing. Industrial techniques must be fast, reliable and cost-effective. Optical projection lithography with deep UV light is now used for large-scale fabrication. As next generation lithographies, several nonoptical techniques have been developed, including extreme UV lithography, X-ray lithography and projection lithography with either electrons or ions [2, 8, 9]. These methods, generally referred to as top-down methods, are very expensive but insufficiently flexible for new development out of the traditional microelectronic industry. In contrast, a number of new and nonconventional lithographic techniques such as nanoimprint, softlithography, near-field optical lithography and a number of proximity probe techniques are low cost and much more accessible [3]. In particular, these techniques not only conserve the lithographic printing strategy but also allow pattern processing at molecular levels. More generally, the so-called bottom up approaches involve self-assembly and self-organization in which molecular building blocks will automatically link together to form desired nanostructures. Much effort is currently being devoted to these new and exciting areas because they are very promising for the fabrication of future electronic devices [10, 11].

Conventional lithographic exposures involve the interaction of an incident beam with a solid substrate. Absorption of light or inelastic scattering of particles can affect the chemical structure of the resist by changing its solubility. The response of the resist to image-wise exposure can be either positive or negative, depending on whether the exposed or unexposed portions will be removed from the substrate after development. The next step after lithography is the pattern transfer from the resist to the substrate (Fig. 1). There are a number of pattern transfer techniques: selective growth of materials in the trenches of the resist, etching of the unprotected areas, and doping through the open areas of the resist by diffusion or implantation [12]. Both wet chemical etching and dry plasma etching can be used. For a high-resolution pattern transfer, dry etching is more suitable, and often requires a



Figure 1. Schematic representation of lithography and pattern transfer techniques.

metallic layer as a mask. This metal mask is obtained by lift-off, *i.e.*, by first depositing a thin metallic layer over the developed resist pattern and then dissolving the resist in order to leave only the metal portions that are directly in contact with the substrate [1].

For multilevel fabrication, lithography and pattern transfer are used for each level. To increase productivity, optical projection lithography is performed on a large wafer in a step-and-repeat fashion by accurately controlling the sample stage with laser interferometry. The performance of lithography for production thus depends on a number of factors: resolution, throughput, pattern placement, overlay alignment accuracy, etc. However, the control of critical dimensions and, in turn, the microscopic properties of individual nanostructures, are the most important issues. Fabrication of semiconductor integrated circuits is a wellestablished technology. More specialized topics on nanofabrication are collected in recent books [13-15] and some dedicated issues [16, 17]. Discussion on general concepts of nanotechnology and molecular engineering can be found in [18-20]. Moreover, a number of conferences and workshops are dedicated every year to lithography and nanofabrication technologies [21-23].

# 3 Conventional lithographic methods

## 3.1 Electron beam lithography

Electron beam (e-beam) lithography is used for primary patterning directly from a computer-designed pattern [1, 24]. It is the essential basis for nanofabrication in addition to mask and prototype device manufacturing. The scanning technique is, however, not suitable for mass production because of the limited writing speed. A typical ebeam system consists of a column of electron optics for forming and controlling the electron beam, a sample stage, and control electronics. The column includes principally an electron source, magnetic lenses, a beam blanker and a mechanism for deflecting the beam [24]. The electron source can be either a thermoionic emitter or thermal field emission. Depending on the design, ebeam energy varies in the range of 1-200 keV with a spot size down to a few nanometers. The beam current and the scanning field size are determined according to the experimental requirements. The sample position is precisely controlled with a laser interferometer feedback and thus a large area pattern can be exposed by decomposing the whole pattern into a number of scanning fields.

The resolution of e-beam lithography depends on the beam size and several factors related to the electron-solid interaction [24, 25]. In a resist, electrons undergo small angle forward scattering and some back-scattering

events coming from the substrate. The forward scattering tends to broaden the initial beam diameter, whereas the back-scattering can spread over a large volume (proximity effects). During this process, the electrons are continuously slowing down, providing a cascade of low-energy electrons (secondary electrons) which are responsible for the resist reaction. Finally, the dose distribution looks like a sharp peak of the forward contribution superimposed with a back-scattered fog. The secondary electroninduced resist reaction can be polymerization, polymer cross-linking or chain scission as well as more complex processes such as chemical amplification involving acidbase reaction. The proximity effects can be corrected by dose variation and/or sophisticated software. In principle, low energy electrons (~1 keV) yield very limited proximity effects because of their short penetration depths. Correspondingly, thin resist layers or surface imaging techniques have to be used. Another advantage of using low energy electrons is the possibility of high-speed writing, because of the increased resist sensitivity.

The resolution of electron beam lithography is essentially defined by the e-beam spot size and the forward-scattering range of the electrons. The higher the energies, the smaller the minimum feature size obtainable. Commercial systems generally work at 50-100 keV energy, and are routinely used to produce sub-100 nm features [26]. Smaller feature sizes can be obtained with even higher electron energies [27]. Figure 2 shows scanning electron micrographs (SEM) of patterns defined by (a) 50 keV and (b) 200 keV electrons, followed by lift-off and subsequent reactive ion etching of SiO<sub>2</sub>. Figure 3 shows two other examples of patterns equally defined by (a) 50 keV and (b) 200 keV electrons, but followed by reactive ion etching of tungsten (50 nm linewidth) or electroplating of gold (30 nm linewidth), respectively. These features were fabricated as nanoimprint molds (Fig. 2) and X-ray masks (Fig. 3) for one-by-one pattern replications (see below). Under optimal conditions, 10 nm [28] and sub-10 nm features [29, 30] can be obtained but particular attention has to be paid to the resist development and the pattern transfer processes (Fig. 4). Moreover, it is not possible to produce continuous metal lines at sub-10 nm scale by lift-off due to grain formation [30].

Electron beam lithography has also been used for hole drilling [31], contamination-induced growth [32], surface modification of inorganic materials (SiO<sub>2</sub>, AIF<sub>3</sub>, *etc.*) as well as Langmuir-Blodgett or self-assembled films [33, 34]. Finally, miniaturized electron beam systems have been prepared by microfabrication. Here, electrostatic lenses constructed from a series of parallel planar electrodes, each with a precision circular bore in the center, are used for the electron beam manipulation. The system





**Figure 2.** SEM of imprint molds obtained by e-beam lithography and reactive ion etching of  $SiO_2$ ; minimum pitch size in (a) 120 nm; (b) 40 nm, respectively.

also includes an electron source consisting of a cathode with one or more electrodes to extract and accelerate the emitted electrons to the desired energy (1 keV), an objective lens, and a deflector unit for beam scanning. Large arrays of such microcolumns were fabricated, showing a parallel writing feasibility [35–37].

## 3.2 Focused ion beam lithography

Focused ion beam lithography is analogous to e-beam lithography [38, 39], but here magnetic lenses are replaced by electrostatic lenses because of the much heavier ion masses. The ion source is typically made of a sharp W-tip coated with liquid metal, Ga for example. In addition, a mass separator is used as an aperture to select one type of ion. Focused ion beams operate in the range of 10–200 keV. As the ions penetrate the material, they loose their energy at a rate several orders of magni-



**Figure 3.** Absorber features for X-ray lithography. (a) Reactive ion etched tungsten (50 nm linewidth); (b) electroplated gold (50 nm linewidth).



**Figure 4.** Typical Coulomb blockade device made by liftoff of a monogranular line between two metallic electrodes [30].

tude higher than that of electrons because of their masses. As a consequence, the penetration of ions, and thus the back-scattering-caused proximity effects, are much reduced compared to that of electrons. The heavier the ions, the smaller the penetration depth. Very thin layer resists are generally required for heavy ions. In practice,

#### Electrophoresis 2001, 22, 187-207

light ions such as  $H^+$ ,  $He^{++}$ ,  $Li^+$  and  $Be^{++}$  are employed for lithography. The drawback of the focused ion beam lithography is its limited writing speed, due to the fact that the ion beam current density is 1 or 2 orders of magnitude smaller than that of the electron beams, although resists are generally more sensitive to ions.

On the other hand, focused ion beams have proven to be an essential tool for highly localized implantation doping, mixing, micromachining, controlled damage as well as ion-induced deposition [38]. Figure 5 displays two examples of ion beam micromachined structures on (a) GaAs and (b) a multilayer sample of 50 nm thick AIF<sub>3</sub> on GaAs [40, 41]. A large number of experiments have been performed to demonstrate the viability of the technique, including optical and X-ray msk repairing, quantum devices fabrication, scanning probe tip modification and, more recently, biomolecule microsurgery and analysis [42].

## 3.3 Optical projection lithography

Optical projection lithography is used for mass production of integrated circuits [43, 44]. Deep UV light is applied to expose a photoresist through a mask containing alternating opaque and clear features, made of a chromium absorber on a glass substrate. Current projection systems used by the semiconductor industry work with a glass lens system with a demagnification factor of 5 or 6 and a stepand-repeat exposure capability over 8 inch silicon wafers. The resolution of optical projection lithography is defined by the Rayleigh criterion  $R = k_1 \lambda / NA$ , where  $\lambda$  is the wavelength, NA the numerical aperture of the optical system, and  $k_1$  an empirical factor depending on the details of the experimental conditions. In practice, the image contrast goes to zero rapidly for  $k_1 < 0.5$  [1, 44]. The depth of focus,  $DOF = k_2 \lambda / NA^2$ , is an important parameter to define the process latitude in optical lithography. A large NA provides a better resolution but the corresponding DOF decreases rapidly as NA increases. Sophisticated masks (e.g., phase-shifting, optical proximity correction), off-axial illumination and top surface image techniques are used but reducing the exposure wavelength appears to be the main issue for the improvement of the resolution [2, 43, 44]. The previous projection systems worked with mercury-rare gas discharge lamps with radiation between 350- and 450 nm. Now, the production systems employ the 248 or 193 nm radiation produced by krypton fluoride (KeF) or argon fluoride (ArF) excimer lasers, respectively. The research efforts are being shifted to the 157 nm radiation produced by F<sub>2</sub> laser [45]. For this short wavelength, the quartz optics now in use are no longer transparent so that new optical materials such as calcium fluorine  $(CaF_2)$ have to be used for the lens and mask fabrication [45].



**Figure 5.** (a) Micromachined GaAs membrane and (b) fine lines on a multilayer  $AIF_3$  (50 nm thick)/GaAs, obtained by direct focused ion beam lithography [40, 41].

Other issues including mask fabrication and repair, sensitive high resolution resists, overlay, *etc.*, are also under investigation.

# 3.4 Extreme UV lithography

Extreme UV lithography refers to the exposure technique developed with 13.4 nm radiation and a reflective reduction system [46]. For this selective wavelength, the radiation is obtained from laser-induced plasmas or synchrotron radiation. For instance, it can be produced with a supersonic jet of xenon gas as the target, converting a few percent of laser energy into required radiation. The projection system can operate with a 4  $\times$  reduction by means of a set of high quality multilayer mirrors and a reflective mask. The radiation is first projected on the reflective mask with a couple of mirrors acting as the condenser. Then, it is focused with another mirror system onto the wafer. All mirrors are made of alternating molybdenum and silicon or beryllium multilayers that provide constructive interference in the direction of reflection.

#### 192 Y. Chen and A. Pépin

The advantage of extreme UV lithography relies on its projection configuration and its high potentiality for several generation manufacturing. Fabrication of 100 nm line-and-space and 70 nm isolated lines has already been demonstrated [47]. In principle, the reflective masks are robust and the mask pattern can be made easily because the minimum feature size required is four times larger than that on a chip. However, there are still many technological challenges to be overcome, including mask optimization, fabrication of high precision optical elements as well as engineering issues such as alignment, system metrology and feedback control [2, 46]. In particular, the roughness of the surface and the interfaces of the mirrors and the reflective masks has to be minimized with an accuracy better than 0.25 nm. They must also be zerostress and show robustness to thermal effects.

#### 3.5 X-ray lithography

For smaller wavelengths ranging from 0.5 to 4 nm (soft-X rays), no material can be used for the construction of a projection system but a shadow technique is relevant [48–50]. A typical X-ray mask consists of 2 µm thick membrane of silicon carbide and absorber features of heavy metals such as Au, W, or Ta. Exposures can be done at a mask-to-wafer distance of ~10 µm with synchrotron radiation or laser-induced plasma source. The resolution of proximity X-ray lithography is defined by the Fresnel diffraction and the diffusion of photoelectrons in the resist. Increasing the X-ray wavelength decreases the diffusion range of the photoelectrons but increases the diffraction limited linewidth, estimated by  $W_{\rm D} = k_{\rm x} \sqrt{\lambda g}$ , g being the mask-to-wafer gap. It has been shown that the photoelectron scattering in polymethylmethacrylate (PMMA) is limited to a few nanometers [49] and the  $k_x$  factor is approximately 0.6 [51]. Experimentally, 50 nm lines were reproduced at a typical gap of 5 µm [51], and sub-30 nm structures were obtained at smaller gaps [52]. Figure 6 shows examples of the replicated resist patterns at very small gaps.

The X-ray lithography is nearly ready for industrial use [53–55], but some technical issues remain open, such as the mechanical and radiation stability of the masks, the availability of high throughput e-beam systems for mask making, and the reliability of high accuracy alignment. Soft X-rays can be also used to expose relatively thick resist. High aspect ratio features were thus obtained. Figure 7 shows one example of the fabrication of a 1.3  $\mu$ m period and 6  $\mu$ m thick photonic crystal template by three consecutive exposures of PMMA resist through a mask consisting of triangular lattice of holes [56]. Deep X-rays ( $\lambda$ ~0.1 nm) are used to expose much thicker resist for micromachining with the LIGA (lithography, electroform-

ing and molding) process [57]. Figure 8 shows one example of the fabricated 100  $\mu m$  thick PMMA resist structures.

# 3.6 Electron and ion projection lithography

Electron and ion projection lithography techniques are similar to optical projection lithography. A step-and-scan



**Figure 6.** PMMA resist profiles of (a) a 20 nm linewidth and (b) 60 nm linewidth (aspect ratio >10), produced by proximity X-ray lithography.



**Figure 7.** Sub- $\mu$ m resolution three-dimensional photonic crystal fabricated high-resolution X-ray exposures.





exposing strategy is generally used for high-throughput production. A recent version of the electron projection lithography is the so-called scattering with angular limitation projection electron-beam lithography, referred to as Scalpel [58]. A comparable method called Prevail (projection reduction exposure with variable axis immersion lenses) has also been investigated, showing an 80 nm resolution ability [59]. By Scalpel, high-energy electrons (~100 keV) are projected onto a substrate passing successively through a scattering mask and two focusing lenses. A back-focal plane aperture is placed between the two lenses, allowing only nonscattered electrons to pass through. The Scalpel mask consists of heavy metal structures (Cr/W) for strong scattering and a very thin SiN membrane for weak scattering, all supported by a framework of silicon struts. The advantage of Scalpel relies on its  $4 \times$  image reduction enabling an easy mask technology. The problem is that the energetic electrons significantly heat the wafer, possible leading to expansion and some distortion of the pattern. In addition, the interaction among the scattered electrons themselves can cause a blurring of the image. This limits the maximum achievable current and thus the rate of production.

Ion projection lithography uses accelerated hydrogen or helium ions at energies in the 70–150 keV range [60–62]. Now, ions are projected onto the wafer through a stencil mask and electrostatic lenses with a  $4 \times$  reduction. The ion stencil mask consists of an ion absorbing layer on a 2–3 µm thick silicon membrane in which ions are either stopped or pass through holes. Two complementary masks are generally required with extremely tight alignment to produce, for example, line arrays. Although a sub-100 nm resolution has been demonstrated [61], problems such as source uniformity, space charge, wafer heating, and energy deposition in stencil masks remain to be studied. Ion beam lithography can also be performed

as for shadow printing. The approach is similar to proximity X-ray lithography except that ion source and stencil masks are now used as described above.

# 4 Nonconventional methods

## 4.1 Nanoimprint lithography

Nanoimprint is a nonconventional and low-cost technique for high resolution pattern replication [63, 64]. A rigid mold is used to physically deform a heated polymer layer coated on a substrate. The imprint mold can be made of metal or thermal silicon dioxide produced on a silicon substrate. The imprint can be done by applying a typical pressure of 50 bar in the temperature range of 100°C-200°C depending on the polymer in use. After imprinting, the resist pattern is followed by reactive ion etching in order to produce a useful profile for the subsequent hard material pattern transfer. The mold can be re-used many times without damage. The imprint temperature for PMMA is typically 170°C and the resist thickness can vary in the range of 50-200 nm. Structures as small as 6 nm could be produced [64]. For PMMA, the lower the molecular weight, the easier the polymer flow because of the reduced viscosity. Other types of polymers such as standard optical resist S1805 [65] and newly developed hybrane, and hydrogen-bonded polymers were studied at lower imprint temperatures. In particular, the hybrane polymer shows a better etching resistance than PMMA and thus an easier process control [66].

Features with high aspect ratios can be obtained using trilayer techniques [67]. Now, the pattern is first imprinted into the top layer and then transferred to the middle and the bottom layers by sequential reactive ion etching with O<sub>2</sub> and SF<sub>6</sub> gases. Because of the high aspect ratio, liftoff and other techniques such as electroplating and direct etching can be applied for hard material pattern transfer. Trilayer nanoimprint lithography can have a large process latitude, an easy control of critical dimensions, and a good pattern homogeneity over large areas. Pattern placement accuracy is also acceptable, showing no significant thermal derivation. Until now, the problem of fine alignment has not yet been resolved. The fabrication of ultrahigh resolution molds is also a difficult task. Moreover, the whole process duration is still too long for mass production. Fabrication of reliable and cheap imprint devices is clearly another challenge. A wide range of applications has been studied, including GaAs photodetectors [68], waveguide polarizers [69], high-density magnetic structures [70, 71], silicon field-effect transistors [72], GaAs quantum devices [73], etc. Figure 9 shows SEM images of (a) a 60 nm pitch magnetic dot array and (b) a pattern of Fresnel zone plate obtained by a trilayer process and lift-off.





**Figure 9.** Magnetic dot array of (a) 60 nm period and (b) X-ray Fresnel zone plate fabricated by nanoimprint and lift-off.

There are several related techniques involving thermodynamic molding of polymers. Injection molding, for example, is now capable of replicating 100 nm features [74, 75]. Metallic molds for both nanoimprint and mold injection can be fabricated by first sputtering a thin Ni film on a patterned resist master and then increasing the metal thickness by electroplating, followed by a master and mold separation [76]. When a heated polymer thin film is in close proximity of the mold (<1  $\mu$ m), the electrostatic interaction between the two can result in a spatial redistribution of the quantity of the polymer. This phenomenon has been recently studied as a new patterning technique, referred to as lithographically induced self-construction of polymer [77, 78].

#### 4.2 Soft-lithography

Soft-lithography, or microcontact printing, is based on the use of an elastomeric stamp to ink a solid substrate with the help of molecular self-assembly [79–82]. Stamps are

obtained by casting and curing of polydimethylsiloxane (PDMS) against a master patterned by electron beam lithography. Solutions of thiols in ethanol are used as inks for gold substrates [83, 84] and octadecyltrichlorosilane (OTS) in toluene for silicon substrates [85, 86]. A molecular transfer occurs when an inked stamp is in contact with the substrate, resulting in a self-assembled monolayer (SAM) deposited on the touched portions which then is used as a mask for wet etching. The resolution of soft-lithography is limited by the mold feature size and the diffusion of the ink molecules around the contact portions. In practice, the PDMS stamps provide a minimum feature size of ~200 nm. Smaller features can be obtained by using stamps of a higher stiffness such as a mixture of vinylmethyl-dimethylsiloxane copolymers, trimethylsiloxy terminated (VDT) and methylhydrosiloxane-dimethylsiloxane copolymers (HMS) polymer mixture [85, 86]. The commonly used thiol is hexadecanethiol (C<sub>16</sub>H<sub>33</sub>SH), but it can be replaced by eicosanethiol (C<sub>20</sub>H<sub>41</sub>SH) because of the reduced molecular diffusion [86].

A trilayer technique can be applied for an easier hard material pattern transfer including reactive ion etching, lift-off and ion implantation [87, 88]. A PMMA layer is first spin-coated on a substrate before gold deposition. Then, the etch-defined gold pattern serves as a mask for reactive ion etching of PMMA. Finally, the resulting PMMA pattern is used for lift-off or other hard material pattern transfer. Figure 10 shows patterns defined by (a) soft-lithography after wet etching of gold and (b) a trilayer process followed by lift-off of 40 nm thick Co.

Soft-lithography has been applied to the fabrication of field effect transistors [89, 90], magnetic structures [91] and optical devices [81]. Patterning on substrates such as  $SiO_2$ , glass, Ag, is also possible. More generally, SAMs were used as resists for lithography with UV light, X-rays,



**Figure 10.** (a) Soft-lithography-defined 0.4  $\mu$ m pitch dot array of gold after wet etching and (b) 1  $\mu$ m pitch dot array of cobalt after a trilayer process followed by lift-off.

electron or ion beam, proximity probes, for passivation of surfaces and for fabrication of colloids, *etc.* [81]. Similarly, modification of the surface hydrophobicity can be done in a precise way. Finally, biological species such as proteins can be printed directly [92]. Based on the use of PDMS stamps with relief patterns on their surface, other techniques such as molding in capillaries [93], microtransfer molding [94] and replica molding [95] were developed. In particular, molding of organic polymer was obtained by casting and curing an UV-curable polymer against an elastomeric PDMS master. Polymer waveguide [96], blazed diffraction gratings [97], waveguide interferometers/coupler [98], suspended carbon microresonator [99], and interdigitated carbon capacitors [100] have been fabricated as demonstration examples.

#### 4.3 Near-field optical lithography

Near-field optical lithography is derived from conventional optical contact printing. The commonly used contact printing is performed with a mask made of chromium as an absorber on thick glass plates. For ideal optical contact printing, optical flat and dust-free mask and wafer have to be used. In practice, this is not possible because of the nonflatness of both mask and wafer and/or the presence of defects between the two. For gratings, the transferable period is limited by  $p_{min} = \sqrt{\lambda(g + h)}$ , where *g* is the gap and *h* is the resist layer thickness. This gives rise to a minimum feature size of the order of 1 µm. In intimate contact, periods of 0.6 µm were achievable [101]. With a deep-UV F<sub>2</sub> excimer layer and a trilayer resist stack on a substrate, a linewidth of 0.15 µm has been obtained [102].

Conformable masks or substrates can be used to obtain a better contact. One solution is to use a thin flex glass mask coupled with a vacuum exposure device [103]. More recently, a conformable embedded-amplitude mask together with a trilayer resist stack on the substrate and 200 nm deep-UV radiation was used to replicate 100 nm features [104]. With highly flexible polymeric masks such as PDMS, a conformable contact can be easily made. With a PDMS phase mask (relief pattern without absorber), for example, 100 nm features could be produced over a large area [105, 106]. When the noncontact portions of such a PDMS mask are covered with a thin film of metal, the mask becomes a light-coupling mask, in which light is differentially guided by the structures from its backside towards the substrate [107]. Pattern replication with 100 nm minimum feature size could be achieved with a relatively thick resist layer and 256 nm light irradiation. Amplitude masks were also made from SiN membranes, which resulted in a replication in vacuum of 140 nm period gratings with a broadband light source (365-600 nm) [108].

Similarly, near-field optical lithography has been studied with mold-assisted polymerization. In this method, an etched silica plate is pressed into a light curable monomer and then UV light is used for photopolymerization [109]. After curing, the liquid monomer is solidified which provides a copy of the mold relief. Alternatively, an improved mask configuration was proposed to create a high contrast aerial image at the downstream of the mold. Here, the top portions of the mold are coated with a thin layer of absorber, which is sufficient to stop the light but allows optical tunneling through a small opening. Features as small as 50 nm could be obtained in addition to the possibility of a better resist 'profile' [110].

### 4.4 Proximity probe lithography

Proximal probe lithography refers to a new class of surface modification techniques, based on either scanning tunneling microscope (STM), atomic force microscope (AFM), or scanning near-field optical microscope (SNOM) [111–114]. All these techniques employ a sharp probe tip placed in the close proximity of the sample surface with a feedback loop for distance regulation. Tunneling current across the tip and the sample surface is used for STM whereas optical methods are employed to monitor the vertical movement of the AFM cantilever. For SNOM, either a tunneling current or a shear force monitor can be applied for the distance regulation.

A great diversity of material modification mechanisms can be involved in proximity probe lithography. In STM lithography, short current pulses are generated for atomic deposition, extraction or displacement. In AFM lithography, a metallized AFM tip can be used for current pulse generation, allowing selective oxidation, resist exposure, field ionization, field-induced evaporation, indentation, chemical etching, as well as precursor decomposition [114]. Individual atoms or molecules can also be displaced or repositioned [115, 116], thereby providing a way of building a true 'atomic circuit'.

Implementation of the probe techniques in actual device fabrication has motivated considerable efforts on Sibased technology [117]. With a metallized AFM tip, for example, an H-passivated Si-surface can be anodically oxidized selectively with a high spatial resolution. Although these oxide patterns are a few monolayers thick, they form a robust mask for selective etching. Finally, an AFM tip can be used as a pen to plot molecular ink for self-assembling over a surface [118, 119]. For highthroughput patterning, many scanning probes must operate simultaneously over a sample surface. Fabrication of probe arrays containing up to 50 tips have been recently demonstrated [120], but their applicability as a true parallel lithography tool remains to be proven.

#### 4.5 Other lithographic methods

A number of alternative methods can be used for the formation of more regular patterns. For example, holographic lithography produces periodic structures in a thin film resist. Typically, the optical standing waves used in holographic lithography are obtained by splitting a laser beam into two or more beams and then intersecting them via mirrors. With deep UV light, gratings of periods less than 200 nm were produced over large surface areas with a multilayer resist process [121]. More dense structures can be produced using an achromatic interferometric technique, with two-phase grating plates for the manipulation of the diffraction orders of a normal incident laser. By using two 200 nm period phase gratings for example, 100 nm period structures could be obtained [121, 122]. More recently, the interferometric technique has been used to pattern nonlinear optical polymers in order to create three-dimensional networks [123, 124].

Atom beam lithography is another example of the use of optical standing waves. When a coherent atom beam produced by laser cooling meets an optical standing wave just above a substrate, the atomic dipole interaction with the field gradient gives rise to a spatial redistribution of the atomic density, thereby producing a modulated atomic deposition on the substrate [125, 126]. Without using optical waves, atomic beam lithography can also be done through a mask [127].

In contrast, optical scanning lithography is a simple technique for direct patterning of a photo-resist film with a focused laser beam. Other kinds of material processing such as laser-induced polymerization [128] or etching and deposition [129] have also been demonstrated. The resolution of the optical scanning lithography is limited by diffraction [130]. If a laser beam is focused and a very short depth of focus is obtained, stereolithography can be performed [131, 132]. Moreover, by scanning an array of circular Fresnel zone plates (FZP) under UV light irradiation, parallel writing can be done [133]. An FZP is basically a diffractive grating consisting of concentric zones such that positive first order diffraction from all zones will add constructively at the focal point. The resolution of an FZPproduced light spot is determined by the smallest zone width of the FZP. Particularly interesting is that movable deflecting micromirrors can be used to address individual light beams [133]. A similar technique has also been proposed for X-rays, in which multiplexed micromechanical shutters should be used to turn individual X-ray beamlets on or off in response to commands from a control computer [134]. The first demonstration of this technique has been done with synchrotron radiation, without individual beam control, showing the possibility of parallel writing at large exposure gaps [135].

With more laser power, scanning optical lithography can be used as an ablation tool for micromachining with materials like polymer, glass, ceramics, and metals [136, 137]. Now hard and brittle materials can also be machined by ultrasonic impact grinding. Deep cavities with a feature size down to a hundred  $\mu$ m can be obtained [138]. Finally, for metal and alloys, electrochemical machining can be done with a fine electrolytic jet for scanning etching, a resist pattern for parallel dissolution, or ultrashort voltage pulses between a tool electrode and a work-piece in an electrochemical environment for three-dimensional fabrication [139, 140].

#### 4.6 Chemical and biological approaches

Numerous possibilities of nanostructure formation exist based on chemical and biological approaches relying on self-assembling and self-organization. The advantage of these techniques is to realize specific nanostructures without having to construct them atom by atom "by hand". Chemical processing in which self-assembly takes place in organic or inorganic materials can be used for forming aggregates and colloidal assemblies. For example, highquality semiconductor CdS and CdSe nanocrystals could be produced chemically with narrow size distribution [141]. Other nanocrystals such as ZnO, TiO<sub>2</sub> and porous Si films were also obtained, offering electronic and optical properties not present in bulk crystalline semiconductors [142]. Because of their very small sizes, tunable emission spectrum and good photochemical stability, semiconductor nanocrystals can be used as fluorescent biological labels [143, 144]. Another example is the regular periodic structure formation from colloids that can be used as new materials or templates. Many recent research works on the fabrication of three-dimensional photonic crystals were based on templates made of monodisperse opals and infiltration with silicon, metal, polymer and other materials [145-149]. Now, it is also possible to create particular patterns of colloidal crystals with the help of focused UV light [150]. More general application of nanoparticles can be found in metallurgy, catalyst, magnetic storage, drug delivery as well as in quantum device fabrication [142]. Another example is the self-organized growth of nanostructures on a strained substrate. By molecule beam epitaxy [151], InAs quantum dots were produced by depositing a fraction of InAs monolayer on a GaAs substrate, followed by another GaAs layer [152]. Metallic quantum particles were also obtained by depositing a Cu bilayer on a strain-relief pattern of the (111) Pt surfaces [153].

Carbon nanotubes are new quantum materials discovered recently [154, 155]. The electronic properties of these tiny and hollow cylinders show particular electronic properties which can be used for future nanoelectronics [156] or molecular computing [157]. Other physical properties of carbon nanotubes are also interesting because of their caged architecture which can receive various foreign atoms. The challenge is to integrate them into large structures in a controllable and efficient way. Organic nanostructure patterns can be obtained by interactive coupling of selectively activated monomers. Block copolymers, for example, were used to create honeycomb morphologies of star-polymer polystyrene films [158]. More recently, supramolecular networks could be created from nano-scale rods in binary, phase-separating mixtures [159]. Fabrication of more general organic nanostructures involves the association of individual molecular components into desired architectures by molecular and supramolecular assembly [160-164]. Many researchers are now turning to biocatalytic synthesis with templatedirected polymerization or more general genetic engineering [165]. For example, this approach is typically employed for the synthesis of artificial proteins, in which the template is a DNA sequence and the polypeptide chain is obtained through the intermediacy of a complementary mRNA sequence [166].

The integration of functional organic building blocks with the outside world can be done by assembling them on patterned inorganic structures with or without biomolecules and their recognition properties [167]. Based on silica surfactant self-assembling [168], several lithographic techniques such as pen-lithography, ink-jet printing and dip coating have been used to create hierarchically organized structures [169]. The selective binding of peptides to metal, metal-oxide and/or semiconductor structures can also be used to link inorganic building blocks [170].

# 5 Other nanofabrication issues

Conventional lithography methods result in patterned resist profiles serving as masks for subsequent material processing. Selective etching, doping, ion implantation or regrowth can then be performed [12]. Semiconductors, metals and dielectric materials are commonly used in microelectronics. Other materials such as polymers, glasses, ceramics, magnetic and superconducting materials now are used in nanofabrication. Selected pattern transfer methods are discussed in this section.

# 5.1 Thin-film deposition

Basically, thin-film deposition is concerned with adhesion onto the substrate, stress, stoichiometry, defect, impurity, and homogeneity. A deposition method is chosen according to the material type and deposition characteristics [1]. Usually polymer thin films are deposited by spin-coating. Metallic thin films can be obtained by thermal deposition based on the Joule effect or electron-beam assisted evaporation, sputtering or electroplating. Dielectric layers are grown by gas or liquid phase epitaxy, chemical vapor deposition, molecular beam epitaxy, organometallic epitaxy, *etc.* In particular, thermal oxidation of silicon yields a thin film of silicon dioxide, which is used as an excellent dielectric layer.

Multilayers of alternative light (Si, C...) and heavy (W, Mo...) elements can be obtained for extreme UV and Xray reflection. In semiconductor physics, the association of III-V, II-VI, and IV-IV compounds results in various heterostructures such as quantum wells and super-lattices [171] which are now widely used for rapid electronic circuits and optoelectronic devices (laser diodes, modulators and receptors). More recently, multilayers of alternating magnetic (Fe, Co, etc.) and nonmagnetic (Au, Pt, Cu, Al<sub>2</sub>O<sub>3</sub>, etc.) metals is making a new generation of magnetic head and storage media possible for high-density magnetic recording [172]. Further exploration of different combinations will provide new structures with designed properties [173, 174]. Lateral structures are obtained by lithography and one of the pattern transfer techniques. For high-resolution fabrication, lift-off of a thin metallic layer is often used to produce dry etching masks. The quality of a lift-off is affected by resist profile, angle of deposition, and resist removal.

# 5.2 Wet and dry etching techniques

Wet chemical etching is often used for cleaning, polishing, and resist stripping. The etching performance through a mask of patterned resist is characterized by resist adhesion, minor contamination, and etching uniformity control [170]. Wet etching involves three steps: the transportation of the reactants to the reacting surfaces, the chemical reaction at the surface and the transportation of the products away from the surface. The chemical reactivity, *i.e.*, the etching rate, is affected by both agitation and the temperature of the etching solution [1, 175, 176]. In most cases, wet etch is isotropic, *i.e.*, the etching rate is the same in all directions. A notable exception is silicon etching, carried out with a hot solution of KOH and water, ethylenediaminepyrocatechol, or tetramethylammonium hydroxide. Typically, the etching rate is 0.6 µm/min in the (100)-plane, 0.1  $\mu$ m in the (110)-plane and 0.006  $\mu$ m in the (111)-plane. This can be understood by considering that the (111)-plane is more closely packed than the other planes. The silicon wet-etching is widely used for micromachining such objects as thin membranes as well as scanning proximity probes.

Dry etching utilizes fluxes of energetic particles to remove target materials [177, 178]. Ion beam etching (IBE), for example, is simply a sputtering etching technique in which atoms are ejected from a solid target as a result of ion bombardment. IBE can be applied to a large range of materials but the problems of surface damage and redeposition of the etched material on the resist side-walls make this technique less useful. IBE involving chemical species is referred to as reactive ion beam etching (RIBE) and chemical assisted ion-beam etching (CAIBE). Reactive ion etching is based on simultaneous exposure of the sample to chemical reaction species and fluxes of energetic particles. One or several types of reactive gases are introduced into an evacuated process chamber in which a radio-frequency-induced plasma is applied to create reactive ion species. Etching occurs by a chemical reaction between the substrate and atoms or radicals produced in the plasma, and etched materials are pumped away as volatile gaseous species. The dry etching performance is qualified by a number of factors: etch rate, etching directionality, etching selectivity, mask resistance, environment, cost, etc.

Particular attention also has to be paid to the damage at surfaces and side-walls, which may deteriorate the electrical and optical performances of the device. For polymers, silicon, silicon-based dieletric layers and some metals, SF<sub>6</sub>, CHF<sub>3</sub> O<sub>2</sub> gas mixtures are commonly used. Figure 11 shows examples of reactive ion-etched SiO<sub>2</sub> structures. For compound semiconductors such as GaAs, GaN, InP, etc., CI-based gases or a Ch<sub>4</sub>/H<sub>2</sub> gas mixture can be used. Several types of etching reactors are commercially available. They consist of two parallel plates (anode and cathode), an radio-frequency (RF) generator, impedance regulators, a vacuum pump, and a water cooling system. A few techniques are used for increasing the plasma density. In magnetron ion etching (MIE) reactors, a magnetic field is applied for electron confinement. In electron cyclotron resonance (ECR) reactors, power is fed by microwaves at cyclotron resonance condition and an electromagnet is used for electron confinement. Finally, in inductively coupled plasma (ICP) reactors highdensity plasmas are generated with an inductive coil, which provides an optimized etching speed for highaspect ratio experiments.

#### 5.3 Micromachining

Current efforts are devoted to the fabrication of so-called microelectro-mechanical systems (MEMS) [179–181]. The most essential elements of MEMS consist of miniaturized stationary and moving structures capable of realizing micromechanical actions with high precision and good repeatability. A capacitive microactuator, for example, is



**Figure 11.** Etched silicon dioxide structures of 30 nm linewidth and 450 nm thickness.

made of two chargeable plates, one of them being suspended. The electrostatic attractive force is used to move the structure by biasing one of the plates [180]. Various mechanical components such as micromotors, micropumps, microreactors, and microvalves can be produced on the same substrate. Micromachining techniques are currently used in the fabrication of accelerometers, ink jet printer heads, arrays of movable mirrors for color projection displays, and probes for atomic force imaging. Efforts are also made towards a full integration of microsensors, microactuators and microfluidic elements.

The fabrication of MEMS commonly involves bulk or surface machining. Bulk machining defines microstructures by etching directly into the bulk material such as single crystal silicon [182]. Both wet chemical etching or reactive ion etching can be applied to obtain suspended microstructures with a high-aspect ratio. The advantage of bulk machining is that it allows the integration of active devices and the use of integrated circuit technologies. Surface machining defines the release and movable structures in a polysilicon film on a sacrificial layer of silicon dioxide, both deposited on bulk silicon [183]. More complex microchips including multilayer interconnections can be obtained by bonding together and laser drilling of several layers of the components. Silicon, glasses and metals can be wet-etched. Oxides like alumina, quartz and rubidium molybdenum oxide can by machined by etching or ablation with electron, ion or laser beams. Polymers can be molded by imprint, injection molding or soft-lithography. LIGA process can be used for a large-scale production [184-186].

Elastomers can also be used in MEMS where rigidity is a drawback. The PDMS stamps are known for their low interfacial free energy, low reactivity and the possibility of conformal contacting and easy releasing. Moreover, they are optically transparent and mechanically compressible, which makes the PDMS structures very attractive as building blocks for micro-optical components. Photothermal detectors [187], devices for measuring displacement, strain, stress, force, torque, and acceleration [188], optical modulators and display devices [189] were fabricated. In these devices, the active optical elements are blocks of PDMS with a relief of a binary diffraction grating on their surface. Mechanical compression/extension can be used for controlling the relative optical path of light passing through the grating. Fabrication of light valves [190] has also been achieved. Other applications include phaseshifting masks for near-field optics [105], and threedimensional fabrication [191].

For biological applications, particular attention has to be paid to system stability, reliability, size, power, biocompatibility and also the functionality requirements. Microcomponents for biosystems are now mainly fabricated with the silicon technology. Remarkable efforts are also devoted to glass and polymers because of their optical and insulating properties. A typical microsystem for biology may contain a number of fluid control elements: microactuator, micropumps, microvalves and sensors [192, 193]. One may also include functional devices such as heat exchangers, mixers, separators and reaction units on the same chip [194]. Microactuators and active valves are based on electrostatic, electromagnetic, piezoelectric or thermopneumatic operation. Shape memory alloys and bias spring properties can also be used. Microfluidic pumping systems can be realized based on their electroosmotic, travelling wave (ultrasonic) and thermal capillary properties. Finally, microsensors are fabricated by miniaturizing mechanical, thermodynamic, electronic and optical devices. Electrochemical sensor arrays and gas sensor systems can also be included.

# 6 Applications in information technology

Information processing is based on electronic computing, optical communication and magnetic data storage. Therefore, the main concerns are the computing speed, the communication bandwidth and the storage capacity. Each of these subfields is undergoing rapid progress and all of them need nanofabrication for further development. Because of the growing interplay between these research and development areas, it should soon be possible to integrate electronic, optical as well as magnetic modules on the same chip and thus create optimal performance and functionality. In this section, the most important aspects of nanofabrication in information technology are presented.

# 6.1 Microelectronics

Microelectronics has been developed based on silicon technology. Since many years, the performance of electronic computing has been increased mainly by decreasing the size of circuit features. It is predicted that the minimum feature sizes of all involved critical components, including dynamic access memory, microprocessing units as well as application-specific integrated circuits will be continuously scaled down and that the current CMOS technology will be extended at least to a 50 nm generation by the year 2012 [2, 192-197]. New architectures such as massively parallel processing and three-dimensional transistor networks will probably further increase the CMOS capability. In the quantum regime, effects such as localization, electron wave-guide diffraction, coulomb blockade, resonant tunneling and many others can be used for data processing [3, 198, 199]. The fabrication efforts are now concentrated on single-electron transistors (SET) [200-202], resonant tunneling diodes (RTDs) [203, 204], and spin devices [205, 206]. Algorithms for quantum computer and artificial neural network computing are also under investigation [207-210]. Molecular electronics is still at a preliminary stage but has deserved vigorous investigation because of its huge potential. Molecular switching, for example, has recently been demonstrated, and may be used for memory elements [160, 211, 212]. The top down fabrication technologies described in previous sections can be equally applied to CMOS technology and quantum devices, whereas more elegant bottom-up approaches will be used for molecular electronics. It is clear that a total control over the emerging structures in terms of wiring and interconnections of the molecular devices will present enormous challenges.

# 6.2 Optoelectronics and optics

Optical communication is used for medium and long distance data transportation because of the ultimate light speed and the optical wavelength-broad bandwidths. Besides optical fibers, the most essential components for optical communication are optoelectronic and optical devices such as laser diodes, photodetectors, modulators, multiplexers, and demultiplexers. In addition to the medium and long-distance communication, optoelectronic devices will also be required for board-to-board or computer-to-computer connections. It is known that the performance of conventional laser diodes will be improved by using quantum wires and dots [213].

Semiconductor nanocrystals as well as organic materials can also be considered as the building blocks of new optoelectronic devices. More generally, nanoscale engineering of both optical and electronic waves will lead to important improvements of the all optoelectronic components [213]. For example, photonic band gap structures [213-216] can be designed and fabricated to fully control the spontaneous emission, thereby providing a way of realizing the so-called threshold-less semiconductor lasers [213]. In addition, the engineered waveguide channels and specified point defect through which light can flow will be realized precisely. In optics, much has to be done for system integration. The development of new sources, binary diffractive elements, as well as new spectroscopy methods is now in rapid progress. Finally, more conventional devices such as compact disks for information storage, CCD cameras, thin-film transistor (TFT)-LCDs, as well as plasma display panels will benefit from the nanofabrication developments [217]. Nanofabrication technology is clearly a key for the improvement of existing devices and the implementation of new optoelectronic devices. This particularly includes nonconventional lithographic methods such as soft-lithography and micromolding in capillaries for the fabrication of flexible light circuits.

# 6.3 Magnetism

Micromagnetism is the main concern for high-density data storage. It is predicted that the bit size will be continuously scaled down from 1 to 0.1  $\mu$ m and smaller during the next fex years. Both the magnetic support (hard disk, magneto-optical bands and disks) and the recording head will be fabricated based on new technologies. In particular, ultrathin multilayers, in which the interface quality is controlled at the atomic level, and various lateral structures are fabricated for various applications [218–221]. Recording heads based on giant magneto-resistance and spin valves are used for compact disk recording. Proximity probe techniques are studied for ultimate high-density recording. In parallel, spin electronics are developed in such devices as magnetic random access memories (MRAM), *etc.* 

# 7 Applications in biology

The fabrication technologies, initially developed for microelectronics and MEMS, are now penetrating the biotechnology and biomedical industry. Compared to siliconbased electronic devices, the fabrication challenges are much more diverse in biochips, because of the large variety of biomaterials, fluids, and chemicals. On the other hand, the reduction in sizes and in volumes in miniaturized biosystems such as "labs-on-a-chip" can lead to drastic improvements in performance, throughput, and cost. These would be greatly helpful for biomedical applications, such as diagnostics and drug screening, and research on genomics and proteomics. The question of interest is how to meld the well-established nanofabrication technology with the required biological functionalities. The research frontiers in nanofabrication are on a scale that is much smaller than the size of a typical cell (~10  $\mu$ m). And without using powerful nanofabrication tools, micromachining has already resulted in a very exciting area [4–7]. Improvements are expected in many devices by either further scaling down dimensions or including nanostructured elements. Moreover, by addressing the molecular level, novel biodevices will be fabricated. The contribution of nanofabrication to biology covers a wide range of applications. In this section, we give selected examples in which nanofabrication has already allowed important progress, or is currently undergoing active research.

# 7.1 Microfluidics and analysis systems

Microfluidics is a fundamental research area which can be applied to advanced chemical and biological analysis. Large efforts are being devoted to the development of individual components for fluid injection, pumping, controlled delivery of samples and reagents, mixing, reaction, separation, and detection. The system integration should result in the so-called miniaturized total analysis systems (µTAS) that are capable of performing simple or multiple biochemical tasks. A large number of research laboratories around the world are developing such strategic activities [4, 5] and several companies are involved in a commercial exploration (Caliper, Agilent, Microcosm Technologies, Gamera Bioscience, Cepheid, etc.). µTAS devices are typically fabricated in silicon, glass or plastic, and often comprise a large variety of components including optical, electrical, and mechanical elements. Some areas can particularly benefit from the use of nanofabrication. Integrated separation systems, for instance, such as capillary electrophoresis, dielectrophoresis, and chromatography devices, are under intensive study.

The first effort on µTAS appeared almost a decade ago [222]. Since then, the development of chip-integrated capillary electrophoresis has received increasing interest [223]. Recently, size-dependent separation of long DNA molecules in a nanofluidic channel device consisting of a series of entropic traps was achieved [224]. This device was fabricated using standard photolithography and etching of silicon to create alternating deep and shallow (75-100 nm) regions in a 30 µm wide channel fixed over a flat glass substrate to allow fluorescence microscopy observation. Patterning the surface of electrophoresis microchannels with an array of posts in order to create stationary obstacles for DNA molecules, and thus improve separation, has been investigated for some years [225], and new improvements are expected for small biomolecules from reducing the size of the pillars down to the nano-scale range. Alternative approaches including soft material molding or porous composite materials are promising for large-scale manufacturing.

The detailed understanding of electrohydrodynamics phenomena on micro- and nano-structured surfaces of varying geometries and surface properties is important for bioanalysis and separation applications. A wide range of studies on electroosmotic flow have recently been launched. For example, measurement of electroosmotic flows in microchannels containing patterned surface charges was recently performed with the help of soft-lithography methods, *i.e.*, laminar flow patterning and micromolding [226]. Superpositions of patterned surface charge and periodic asymmetrical patterns have also been considered [227] but need experimental observation. Most of these studies deal with patterns in the range of one to a hundred  $\mu$ m, and the promising sub- $\mu$ m scale remains to be tackled.

In parallel, dielectrophoresis, or the use of AC electric fields *via* multiple electrodes is widely used. Separation of proteins was reported in electric fields created in micrometer-sized interdigitated electrodes [228]. Sub-µm particles, such as viruses and protein-covered latex spheres, could be manipulated and separated in castellated microelectrodes [229] and scaling down to achieve separation of smaller particles of biological relevance is now considered. The interdigitated micro- and nano-electrodes and asymmetrical patterns in sequential flow, in order to displace fluid droplets, is also very promising. The use of lithographically patterned stationary phase supports instead of bead-packed microchannels is also of great interest in chromatography for the separation of neutral analytes.

Of course, in all these integrated bioseparation techniques, proper detection systems are needed. Fluorescence is the main optical tool used by biologists and biochemists for characterization, and such techniques as confocal fluorescence detection now allow to probe volumes in the femtoliter range. Integration with optoelectronic or other detection components for high-throughput and high-resolution analysis is indeed highly desirable. Very recently, a microfluidic/integrated optics device was built in Cornell, allowing fluorescence correlation spectroscopy of sub-femtoliter volumes [230]. Other integrated detection systems such as laser-induced fluorescence detection with integrated vertical cavity surface emitting diode lasers as the light source are also considered [231]. Finally, a distinctive and expanding field, e.g., plastic CDbased centrifugal microfluidics, could also gain from the contribution of nanofabrication via such higher resolution and low cost techniques as nanoimprint.

#### 7.2 Microarrays and gene chips

One of the main contributions of microtechnologies to biology is of course the development of gene chips, e.g., DNA microarray chips for genetic sequence analysis [232]. These two-dimensional arrays of small reaction cells (each on the order of  $100 \times 100 \ \mu$ m), each containing a different set of bound known DNA sequences, are microfabricated on either silicon wafers, thin sheets of glass, plastic or a nylon membrane and are now revolutionizing such applications as diagnosis of genetic diseases, drug design and toxicology. A number of industrial companies are now commercializing gene chips (Affymetrix, Nanogen, Packard Instruments, Synteni, Motorola, etc.). Given that proper readout tools and data processing via bioinformatics can be developed, further reducing the sizes of the reaction cells to the sub-µm range via nanofabrication techniques like soft-lithography would therefore increase array density and be very beneficial by allowing a larger variety of probes and thus increasing parallel hybridization and speed of identification. Biomolecular assembly at the nanoscale, through polymer and supramolecular chemistry including self-assembled monolayers with a variety of functional groups are now areas in full bloom [141-146]. In particular, direct microcontact printing of proteins on solid substrates was recently carried out [233].

# 7.3 Nano-MEMS

Another area where impressive progress had been made in the past few years is nano-electromechanical systems. An example of nanomechanical achievement is the recent realization of microfabricated silicon cantilevers functionalized with a selection of biomolecules in order to provide molecular recognition [234]. Studies on nanomachines powered by molecular motors is another fascinating subject currently under study in several laboratories [235]. Biocompatible implantable nanodevices for in vivo operation, such as neural probes or multifunctional catheters containing microsensors and microactuators of a variety of types, have also opened a new future of medical applications [236]. In another area, sensitive analysis of proteins could recently be obtained through a nanomachined nanoelectrospray tip for mass spectrometry coupled to an integrated microchannel system [237].

# 7.4 Nanobiochemistry

Nanobiochemistry in picoliter volumes obtained by nanofabrication allows high concentration and increased throughput for combinatorial chemistry and diagnostics. Polymerase chain reaction (PCR) amplification in nanofabricated nanovials was recently achieved [238]. Specific nanorobotics tools such as piezoelectric fluid dispensers are necessary and under development.

# 7.5 Nanomaterials for biological applications

A large effort is also being dedicated to the engineering of nanomaterials, especially nanoparticles, nanotubes and colloids suitable for biological purposes, with again a wide range of applications: bioencapsulation, bioanalytical chemistry, bioseparation, bioimaging, etc. As an example, arrays of magnetic nanoparticles could be used for the electrophoresis of large DNA molecules [239]. Specific gold nanoparticles can also induce colorimetric DNA detection [240] or be used for staining in biological electron microscopy. More striking is the very recent demonstration of direct observation of single-nucleotide polymorphism in kilobase-sized DNA achieved via single-wall carbon nanotube capping of a conventional silicon AFM tip [241]. The use of an array of such nanotube tip AFMs could indeed allow unprecedented ultrafast genetic haplotyping.

# 7.6 Bioelectronics

Finally, the contribution of biology to nanofabrication for novel electronics is altogether a different field. So-called bioelectronics and molecular electronics are receiving ever growing attention from the physics and electronics scientific communities. Promising results have been obtained recently with DNA molecules, in particular on DNAtemplated assembly and electrode attachment of a conducting silver wire [242]. Arrays of nanoelectrodes have also been developed to examine the molecular basis for electron transport processes between redox proteins and metal surface, and biological molecules are being incorporated into conducting polymers during the polymerization process to provide a possible mechanism for localizing proteins at a microelectrode. If the correct polymers are used, there is the possibility of creating a bioelectronic interface by providing molecular wires between the electrode and the biomolecular material [243]. Another example of melding between biology and electronics is the use of semiconductor field-effect transistors to sense a charge change during DNA hybridization [244].

# 8 Conclusions

We have attempted to review some of the current topics in nanofabrication. The starting point was the pattern formation technology, including the most expensive but reliable industrial approaches and a number of nonconventional methods. Other fabrication issues have also been briefly discussed. It appears that all lithography methods presented are useful in enabling certain applications. The semiconductor industry will continue to use optical projection lithography for one or more CMOS generations. Then, one of the next generation lithographies will be employed to scale down further the CMOS critical dimensions. Following this, quantum devices as well as molecular computing will most likely be developed based on new fabrication technologies with the help of molecular selfassembling and self-organization. In parallel, nanofabrication techniques will be involved in many other research and industry segments.

Information processing and biological microsystems are two well-identified areas of top research priority. In particular, the challenges of fabricating nano-scaled biodevices are formidable from the point-of-views of system design, material choice, electric contacts, lithography and pattern transfer. An optimal strategy is to employ electrons, ions, X-rays or other nonconventional methods wherever they are most effective in solving the problem at hand. Nevertheless, nonconventional methods open more opportunities for engineering nanostructures and molecular systems. One should take care of the coming of new materials, algorithms, architectures and other innovative ways to overcome technological barriers in order to create designed functionalities. Due to the too many aspects of nanofabrication and the too rapid development of bioapplications today, it was not possible to cover the topic in an exhaustive manner, and a selection of the most important issues was thus chosen by the authors. Nevertheless, we hope that the stimulating conjunctures contained in this article will encourage new exploration of this exciting area.

Received August 1, 2000

# 9 References

- Sze, S. M., Semiconductor Devives: Physics and Technology, John Wiley, New York 1985.
- [2] The National Technology Roadmap for Semiconductor Industry Association, 1999.
- [3] The Technology Roadmap for Nanoelectronics, European Commission, 1999.
- [4] *Proceedings of Micro Total Analysis Systems 1998*, Kluwer Academic Publishers, Dordrecht 1998.
- [5] *Proceedings of Micro Total Analysis Systems 2000*, Kluwer Academic Publishers, Dordrecht 2000.
- [6] Hoch, H. C., Jelinski, L. W., Craighead, H. G. (Eds.), Nanofabrication and Biosystems: Integrating Materials Science, Engineering and Biology, Cambridge University Press, Cambridge 1996.
- [7] Manz, A., Becker, H. (Eds.), *Microsystem Technology in Chemistry and Life Sciences*, Springer Desktop Editions in Chemistry, Berlin 1999.

- [8] Canning, J., J. Vac. Sci. Technol. 1997, B15, 2109–2111.
- [9] Lerner, E. J., *The Industrial Physics*, New York 1999, June, 18–21.
- [10] Reed, M. A., Tour, J. M., *Sci. Amer.* 2000, *June*, 68–75.
- [11] Macilwain, C., Nature 2000, 405, 630-732.
- [12] Smith, H. I., Craighead, H. G., *Physics Today* 1990, *Feb*, 24–30.
- [13] Timp, G. (Ed.), Nanotechnology, Springer-Verlag, New York 1998.
- [14] Taniguchi, N. (Ed.), Nanotechnology: Integrated Proceecing Systems for Ultra-precision and Ultrafine Products, Oxford University Press, Oxford 1997.
- [15] Rai-Choudhury, P. (Ed.), Handbook of Microlithography, Microfabrication and Microsystems, Vol. 1, 2 SPEI Press, Washington 1997.
- [16] Vittiger, P., Staufer, U., Kern, D. P. (Eds), Nanotechnology, special issue of *Microelectron. Eng.* 1996, 32, (1–4).
- [17] Nanometer-Scale Science & Technology, special issue of Proceedings of the IEEE 1996, p. 85.
- [18] Ball, P., *Designing the Molecular World*, Princeton University Press, Princeton, New Jersey 1994.
- [19] Ball, P., Made to Measure, Princeton University Press, Princeton, New Jersey 1994.
- [20] Regis, E. D., Nano, Bantam Press, London 1995.
- [21] IEPBN: International Conference on Electron. Ion and Photon Beam Technology and Nanofabrication, held once a year in the USA.
- [22] MNE International Conference on Micro and Nanofabrication, held once a year in Europe.
- [23] MNC International Conference on Microprocesses and Nanotechnology, held once a year in Asia.
- [24] McCord, M. A., Rooks, M. J., in: Rai-Choudhury, P. (Ed.), Handbook of Microlithography, Microfabrication and Microsystems, SPEI Press, Washington 1997, pp. 139–250.
- [25] Chang, T. H. P., Kern, D. P., Kratscgmer, E., Lee, K. Y., Luhn, H. E., McCord, M. A., Rishton, S., Vladimirsky, Y., *IBM J. Res. Develop.* 1988, *32*, 462–492.
- [26] Chen, Y., Carcenac, F., Rousseaux, F., Launois, H., Jpn. J. Appl. Phys. 1994, 33, 6923–6927.
- [27] Carcenac, F., Vieu, C., Lebib, A., Chen, Y., Launois, H., *Microelectron. Engineer.* 2000, in press.
- [28] Craighead, H. G., Howard, R. E., Jackel, L. D., Mankievich, P. M., *Appl. Phys. Lett.* 1983, *42*, 3841–3843.
- [29] Chen, W., Ahmed, H., Appl. Phys. Lett. 1993, 62, 1499– 1503; J. Vac. Sci. Technol. 1993, B11, 2519–2522.
- [30] Chen, Y., Vieu, C., Launois, H., Condensed Matter Phys. 1998, 6, 22–30.
- [31] Broers, A. N., Cuomo, J. J., Harper, J., Molzen, W., Laibowitz, R. B., Pomerantz, M., in: Sturgess, J. M. (Ed.) *Electron Microscopy*, Vol. III, Microscopial Society of Canada, Toronto 1978, pp. 343–354.
- [32] Broers, A. N., Timbs, A. E., Roch, R., *Microelectron. Engineer.* 1989, 187–190.
- [33] Allee, D. R., Broers, A. N., Appl. Phys. Lett. 1990, 57, 2271–2274.
- [34] Kuan, S. W. J., Franck, C. W., Yen Lee, Y. H., Eimori, T., Allee, D. R., Pease, R. F. W., Browning, R., *J. Vac. Sci. Technol.* 1989, *B7*, 1745–1750.

- [35] Chang, T. H. P., Muray, L. P., Staufer, U., Kern, D. P., Jpn. J. Appl. Phys. 1992, 31, 4232–4240.
- [36] Chang, T. H. P., Thomson, M. G. R., Yu, M. L., Kratschmer, E., Kim, H. S., Lee, K. Y., Rishton, S. A., Zolgharnain, S., *Microelectron. Engineer.* 1996, *32*, 113–130.
- [37] Shimazu, N., Saito, K., Fujinami, M., Jpn. J. Appl. Phys. 1995, 34, 6689–6693.
- [38] Melngailis, J., Mondelli, A. A., Berry III I. L., Mohondro, R., J. Vac. Sci. Technol. 1989, B16, 927–957.
- [39] Gamo, K., Microelectron. Engineer. 1996, 32, 159-171.
- [40] Gierak, J., Vieu, C., Schneider, M., Launois, H., Ben Assayag, G., Septier, A., *J. Vac. Sci. Technol.* 1997, *B15*, 2373–2378.
- [41] Gierak, J., Vieu, C., Septier, A., Nucl. Ins. Methods Phys. Res. 1999 A427, 91–98.
- [42] Austin, R. H., Invited talk presented at the EIPBN 2000 Conference, Palm Springs CA, USA.
- [43] Bowden, M. J. in: Thompson, L. F., Willson, G. G., Bowden, M. J. (Eds.), *Introduction to Microlithography*, Americal Chemical Society, Washington, DC 1994, pp. 19–138.
- [44] Levinson, H. J., Arnold, W. H., 1997, in: Rai-Choudhury, P. (Ed.), Handbook of Microlithography, Microfabrication and Microsystems, SPEI Press, Washington 1997 pp. 10–138.
- [45] Bloomstein, T. M., Rothschild, M., Kunz, R. R., Hardy, D. E., Goddman, R. B., Palmacci, S. T., *J. Vac. Sci. Technol.* 1998, *B16*, 3154–3157.
- [46] Gwyn, C. W., Stulen, R., Sweeney, D., Attwood, D., J. Vac. Sci. Technol. 1998, B16, 3142–3149.
- [47] Cardinale, G. F., Henderson, C. C., Goldsmith, J. E. M., Mangat, P. J. S., Cobb, J., Hector, S. D., *J. Vac. Sci. Technol.* 1999, *B17*, 2970–2974.
- [48] Spear, D. L., Smith, H. I., Electron. Lett. 1972, 8, 102.
- [49] Smith, H. I., Schattenburg, M. L., Hector, S. D., Ferrera, J., Moon, E. E., Yang, I. Y., Burkhardt, M., *Microelectron. Engineer.* 1986, *32*, 143–158.
- [50] Cerrina, F., 1997, in: Rai-Choudhury, P. (Ed.), Handbook of Microlithography, Microfabrication and Microsystems, SPEI Press, Washington 1997 pp. 253–319.
- [51] Chen, Y., Kupka, R., Rousseaux, F., Carcenac, F., Decanini, D., Ravet, M., Launois, H., *J. Vac. Sci. Technol.* 1994, *B12*, 3959–3964.
- [52] Simon, G., Haghiri-Gosnet, A. M., Bourneix, J., Decanini, D., Chen, Y., Rousseaux, F., Launoiss, H., *J. Vac. Sci. Technol.* 1997, *B15*, 2489–2494.
- [53] Viswanathan, R., Seeger, D., Bright, A., Bucelot, T., Pomerene, A., Petrillo, K., Blauner, P., Agnello, P., Warlaumont, J., Conway, J., Patel, D., *J. Vac. Sci. Technol.* 1993, *B11*, 2910–2916.
- [54] Deguchi, K., Miyoshi, K., Oda, M., Matsuda, T., J. Vac. Sci. Technol. 1996, B14, 4294–4302.
- [55] Silverman, J. P., J. Vac. Sci. Technol. 1998, B16, 3137–3141.
- [56] Cuisin, C., Chelnokov, A., Decanini, D., Lourtioz, J. M., Chen, Y., *Appl. Phys. Lett.* 2000, *77*, 770–772.
- [57] Ehrfeld, W., Schmidt, A., J. Vac. Sci. Technol. 1988, B16, 3526–3534.
- [58] Harriot, L. R., J. Vac. Sci. Technol. 1997, B15, 2130-2135.
- [59] Pfeiffer, H. C., Dhaliwal, R. S., Golladay, S. D., Doran, S. K., Gordon, M. S., Groves, T. R., Kendall, R. A., Lieber-

man, J. E., Petric, P. F., Pinckney, D. J., Quickle, R. J., Robinson, C. F., Rockrohr, J. D., Senesi, J. J., Stickel, W., Tressler, E. V., Tanimoto, A., Yamaguchi, T., Okamoto, K., Suzuki, K., Okino, T., Kawata, S., Morita, K., Suziki, S. C., Shimizu, H., Kojima, S., Varnell, G., Novak, W. T., Stumbo, D. P., Sogard, M., *J. Vac. Sci. Technol.* 1999, *B17*, 2840–2846.

- [60] Melngailis, J., Mondelli, A. A., Berry III, I. L., Mohondro, R., J. Vac. Sci. Technol. 1998, B16, 927–957.
- [61] Bruenger, W. H., Torkler, M., Leung, K. N., Lee, Y., Williams, M. D., Leoschner, H., Stengl, G., Fallmann, W., Paschke, F., Stangl, G., Rangelow, I. W., Hudek, P., *Microelectron. Engineer*. 1999, *46*, 477–480.
- [62] Cross, G., Kaesmaier, R., Loschner, H., Stengl, G., J. Vac. Sci. Technol. 1998, B16, 3150–3153; J. Vac. Sci. Technol. 1999, B17, 3091–3097.
- [63] Chou, S. Y., Krauss, P. R., Renstrom, P. J., Appl. Phys. Lett. 1995, 76, 3114–3116.
- [64] Chou, S. Y., Krauss, P. R., Zhang, W., Guo, L., Zhang, L., J. Vac. Sci. Technol. 1997, B15, 2897–2904.
- [65] Lebib, A., Chen, Y., Carcenac, F., Cambril, E., Manin, L., Couraud, L., Launois, H., *Microelectron. Engineer.* 2000, *53*, 175–178.
- [66] Lebib, A., Chen, Y., Cambril, E., Manin, L., *MNE'2000*, Jena, Germany.
- [67] Lebib, A., Chen, Y., Bourneix, J., Carcenac, F., Cambril, Couraud, L., Launois, H., *Microelectron. Engineer.* 1999, 46, 319–323.
- [68] Yu, Z., Schablitsky, S. J., Chou, S. Y., Appl. Phys. Lett. 1999, 64, 2381–2383.
- [69] Wang, J., Schablitsky, S. J., Chou, S. Y., J. Vac. Sic. Technol. 1999, B17, 2957–2960.
- [70] Wu, W., Cui, B., Sun, X., Zhang, W., Zhuang, L., Kong, L., Chou, S. Y., *J. Vac. Sic. Technol.* 1998, *B17*, 3825–3829.
- [71] Chen, Y., Lebib, A., Li, S., Pépin, A., *EPJ-Appl. Phys.* 2000, in press.
- [72] Guo, L., Krauss, P., Chou, S. Y., Appl. Phys. Lett. 1997, 71, 1881–1883.
- [73] Martini, I., Eisert, D., Kamp, M., Worschech, L., Forcel, A., Keoth, J., *Appl. Phys. Lett.*, 2000, 77, 2237–2239.
- [74] Macintyre, D., Thomas, S., *Microelectron. Engineer.* 1988, 41/42, 211–215.
- [75] Emmelius, M., Pawlowski, G., Vollamann, H. W., Angew. Chem. Int. Ed. Engl. 1989, 28, 1445–1460.
- [76] Gale, M. T., Microelectron. Engineer. 1997, 34, 321–339.
- [77] Chou, S. Y., Zhuang, L., Guo, L., Appl. Phys. Lett. 1999, 75, 1004–1006.
- [78] Chou, S. Y., Zhuang, L., J. Vac. Sci. Technol. 1999, B17, 3197–3202.
- [79] Whitesides, G. M., Mathiqs, J. P., Seto, C. T., *Science* 1991, *254*, 1312–1319.
- [80] Xia, Y., Whitesides, G. M., Angew. Chem. Int. Ed. 1998, 37, 550–575.
- [81] Wilbur, J. J., Whitesides, G. M., in: Timp, G. (Ed.), Nanotechnology, Springer-Verlag, New York 1998, pp. 331–369.
- [82] Xia, Y., Zhao, X., Whitesides, G. M., *Microelectron. Engineer*. 1996, *32*, 255–268.
- [83] John, P. M., Graighead, H. G., Appl. Phys. Lett. 1996, 68, 1022–1024.

- [84] Inoue, A., Ishida, T., Choi, N., Nizutani, W., Tokumoto, H., *Appl. Phys. Lett.* 1998, *73*, 1976–1978.
- [85] Schmid, H., Michel, B., *Macromolecules* 2000, *33*, 3042–3049.
- [86] Biebuyck, H. A., Larsen, N. B., Delamarche, E., Michel, B., *IBM J. Res. Develop.* 1997, *41*, 159–167.
- [87] Schmidt, G., Tormen, M., Muller, G., Molenkamp, L. W., Chen, Y., Lebib, A., Launois, H., *Electron. Lett.* 1999, *35*, 1731–1733.
- [88] Chen, Y., Lebib, A., Carcenac, F., Launois, H., Schmidt, G., Tormen, M., Müller, G., Molenkamp, L. W., Liebau, M., Huskens, J., Reinhoudt, S. N., *Microelectron. Engineer*. 2000, *53*, 253–256.
- [89] Hu, J., Reck, R. G., Deng, T., Westewdt, R. M., Maranorski, K. D., Gossard, A. C., Whitesides, G. M., *Appl. Phys. Lett.* 1997, *71*, 2020–2022.
- [90] Jeon, N. L., Hu, J., Whitesides, G. M., Erhardt, M. K., Nuzzo, R. G., Adv. Mater. 1998, 10, 1466–1472.
- [91] Li, S., Lebib, A., Pépin, A., Couraud, L., Lafosse, X., Chen, Y., to be published.
- [92] Libioulle, L., Bietsch, A., Schmid, H., Michel, B., Delamarche, E., *Langmuir* 1999, *15*, 300–304.
- [93] Kim, E., Xia, Y., Whitesides, G. M., *Nature* 1995, *376*, 581–584.
- [94] Zhao, Y. M., Xia, Y., Whitesides, G. M., Adv. Mater. 1996, 98, 837–842.
- [95] Xia, Y., Kim, E., Zhao, Y. M., Prentis, J. A., Whitesides, G. M., *Science* 1996, *273*, 345–349.
- [96] Zhao, Y. M., Stoddart, A., Smith, S. P., Kim, E., Xia, Y., Prentis, J. A., Whitesides, G. M., *Adv. Mater.* 1996, *8*, 420–425.
- [97] Xia, Y., McClelland, J. J., Gupta, R., Qin, D., Zhao, Y. M., Sohn, L. L., Celotta, R. J., Whitesides, G. M., *Adv. Mater.* 1997, *9*, 147–151.
- [98] Zhao, Y. M., Smith, S. P., Waldman, S. J., Prentis, J. A., Whitesides, G. M., *Appl. Phys. Lett.* 1997, *71*, 1017–1019.
- [99] Schueller, O. J. A., Marzolin, ST. T., Whitesides, G. M., *Chem. Mater.* 1997, *9*, 1399–1406.
- [100] Kim, E., Xia, Y., Whitesides, G. M., Adv. Mater. 1996, 8, 245–251.
- [101] Smith, H. I., Efremow, N., Kelley, P. L., J. Electrochem. Soc. 1974, 121, 1503–1508.
- [102] White, J. C., Craighead, H. C., Howard, R. E., Jackel, L., Behringer, R. E., Epworth, R. W., Henderson, D., Sweeney, J. E., *Appl. Phys. Lett.* 1984, 44, 22–25.
- [103] Melngailis, J., Efremow, N., Smith, H. I., *IEEE Trans. ED* 1975, *22*, 49–55.
- [104] Goodberlet, J. G., Appl. Phys. Lett. 2000, 76, 667–669.
- [105] Paul, K. E., Breen, T. L., Aizenberg, J., Whitesides, G. M., *Appl. Phys. Lett.* 1998, *73*, 2893–2895.
- [106] Aizenberg, J., Rogers, J. A., Paul, K. E., Whitesides, G. M., Appl. Opt. 1998, 37, 2145–2155; Appl. Phys. Lett. 1997, 70, 2658–2660.
- [107] Schmid, H., Biebuyck, H., Michel, B., Martin, O. J., Piller, N. B., J. Vac. Sci. Technol. 1998, B16, 3422–3425; Appl. Phys. Lett. 1998, 72, 2379–2381.
- [108] Alkaisi, M. M., Blaikie, R. J., McNab, S. J., *Microelectron. Engineer.* 2000, in press.

- [109] Haisma, J., Verheijen, M., van den Heuvel, K., van den Berg, J., J. Vac. Sci. Technol. 1996, 14, 4124–4129.
- [110] Chen, Y., Carcenac, F., Ecoffet, C., Lougnot, D. J., Launois, H., *Microelectron. Engineer.* 1999, 46, 69–73.
- [111] Binning, G., Rohrer, H., Gerber, C. H., Weibel, E., Appl. Phys. Lett. 1982, 40, 178–181; Physica 1982, B109/110, 2075–2083.
- [112] Avouris, P. (Ed.), Atomic and Nanometer Scale Modifications of Materials: Fundamentals and Applications, NATO ASI Series E, Vol. 239, 1993.
- [113] Marrian, C. R. K. (Ed.), The Technology of Proximity Probe Lithography, SPIE Press, Bellingham, WA 1993.
- [114] Marrian, C. R. K., Snow, E. S., *Microelectron. Engineer*. 1996, *32*, 173–189.
- [115] Eigler, D. M., *Nature* 1990, *344*, 524–528; Eigler, D. M., Lutz, C. P., Rudge, W. E., *Nature* 1991, *352*, 600–603.
- [116] Lyo, I.-W., Avouris, P., Science 1991, 253, 173-176.
- [117] Minne, S. C., Soh, H. T., Flueckiger, P., Quate, C. F., Appl. Phys. Lett. 1995, 66, 703–705.
- [118] Piner, R., Zhu, J., Xu, F., Hong, S., Mirkin, C. A., *Science* 1999, *283*, 661–663.
- [119] Hong, S., Mirkin, C. A., Science 2000, 288, 1808–1811.
- [120] Minne, S. C., Yaralioglu, G., Manalis, S. R., Adams, J. D., Zesch, J., Atalar, A., Quate, C. F., *Appl. Phys. Lett.* 1998, *71*, 2324–2326.
- [121] Anderson, E. H., Komtsu, K., Smith, H. I., J. Vac. Sci. Technol. 1988, B6, 216–221.
- [122] Yen, A., Schattenburg, M. L., Smith, H. I., Appl. Opt. 1992, 31, 2972–2976.
- [123] Cumpston, B. H., Ananthaval, S. P., Barlow, S., Dyer, D. L., Ehrlich, J. E., Erskine, L. L., Heikal, A. A., Kuebler, S. M., Lee, I.-Y. S., McCord-Maughon, D., Jinqui Qin, H., Rockel, H., Rumi, M., Wu, X.-L., Marder, S. R., Perry, J. W., *Nature* 1999, *398*, 51–54.
- [124] Campbell, M., Sharp, D. N., Harrison, M. T., Denning, R. G., Turberfield, A. J., *Nature* 2000, *404*, 53–56.
- [125] McClelland, J. J., Prentiss, M., *Microelectron. Engineer*. 1996, *32*, pp. 403–435.
- [126] Thywissen, J. H., Johnson, K. S., Yonkin, R., Fekker, N. H., Berggren, K. K., Cho, A. P., Prentiss, M., *J. Vac. Sci. Technol.* 1997, *B15*, 2093–2100.
- [127] Keller, C., Abfalterer, R., Bernet, S., Oberthaler, M. K., Schmiedmayer, J., Zeilinger, A., J. Vac. Sci. Technol. 1998, B16, 3850–3854.
- [128] Torres-Filho, A., Neckers, D. C., *Chem. Mater.* 1995, *7*, 744–753.
- [129] Hirsh, T. J., Miracky, R. F., Lin, C., Appl. Phys. Lett. 1990, 57, 1357–1360.
- [130] Lehmann, O., Stuke, M., Appl. Phys. Lett. 1992, 61, 2027–2029.
- [131] Wallenberger, F. T., Science 1995, 267, 1274–1275.
- [132] Lehmann, O., Stuke, M., Science 1995, 270, 1644-1646.
- [133] Carter, D. J. D., Gill, D., Menon, R., Mondol, M. K., Smith, H. I., *J. Vac. Sci. Technol.* 1998, *B17*, 3449–3452.
- [134] Smith, H. I., J. Vac. Sci. Technol. 1996, B14, 4318-4321.
- [135] Pépin, A., Decanini, D., Chen, Y., *J. Vac. Sci. Technol. B* 2000, in press.
- [136] Patel, R. S., Redmond, T. F., Tessler, C., Tudryn, D., Pulaski, D., *Laser Focus World* 1996, Jan. 71.

- [137] Lizotte, T., Ohar, O., O'Keefe, T., Solid Stat. Technol. 1996, 39, 120–128.
- [138] *Technical Report*, Bullen Ultrasonic Inc., Eaton, OH, USA 1995.
- [139] Datta, M., J. Electrochem. Soc. 1995, 142, 3801-3806.
- [140] Schuster, R., Kirchner, V., Allongue, P., Ertl, G., Science 2000, 289, 98–101.
- [141] Brus, L., Szajowski, P., Harris, W., Schuppler, S., Citrin, P. J., Am. Chem. Soc. 1995, 117, 2915–2922.
- [142] Brus, L., in: Timp, G. (Ed.), Nanotechnology, Springer-Verlag, New York 1998 pp. 255–283.
- [143] Bruchez, M., Moronne, M., Gin, P., Weiss, S., Alvisatos, A. P., *Science* 1998, *281*, 2013–2015.
- [144] Chan, W. C. W., Nie, S., Science 1998, 281, 2016-2018.
- [145] van Blaaderen, A., Ruel, R., Wiltzius, P., *Nature* 1997, *385*, 321–324.
- [146] Velev, O. D., Lenhoff, A. M., Kaler, E. W., *Science* 2000, 287, 2240–2243.
- [147] Wijnhoven, J. E. G. J., Vos, W. L., *Science* 1998, *281*, 802–804; Zakhidov, A. A., Baughman, R. H., Iqbal, Z., Cui, C., Khayrullin, I., Dantas, S. O., Marti, J., Ralchenko, V. G., *Science* 1998, *282*, 897–901.
- [148] Holland, B. T., Blandfor, C. F., Stein, A., Science 1998, 281, 538–540.
- [149] Hayward, R. C., Salville, D. A., Aksay, I. A., *Nature* 2000, 403, 56–59.
- [150] Edelstein, A. S., Cammarata, R. C. (Eds.), *Nanomaterials: Synthesis, Properties and Applications*, Institute of Physics Publishing, Bristol, Philadelphia 1996.
- [151] Cho, A. Y., Thin Solid Growth 1983, 100, 291-296.
- [152] Marzin, J. Y., Gérard, J. M., Izrael, A., Barrier, D., Bastard, G., *Phys. Rev. Lett.* 1994, *73*, 716–719.
- [153] Brune, H., Giovanni, M., Bromann, K., Kern, K., Nature 1998, 394, 451–453.
- [154] lijima, S., *Nature* 1991, *354*, 56–58; *Nature* 1993, *363*, 603–605.
- [155] Dresselhaus, M. S., Dresselhaus, G., Saito, R., in: Timp, G. (Ed.), *Nanotechnology*, Springer-Verlag, New York 1998 pp. 285–329.
- [156] Yao, Z., Pastma, H. W. C., Balents, L., Dekker, C., *Nature* 1999, 402, 273–276.
- [157] Rueckes, T., Kim, K., Joselevich, E., Tseng, G. Y., Cheung, C. L., Lieber, C. M., *Science* 2000, *289*, 94–97.
- [158] Widawskin, G., Rawiso, M., François, B., *Nature* 1994, 369, 387–389.
- [159] Peng, G., Qin, F., Ginzburg, V. V., Jasnow, D., Balazs, A. C., *Science* 2000, *288*, 1802–1804.
- [160] Reed, M. A., Zhou, C., Muller, C. J., Burgin, T. P., Tour, J. M., *Science* 1997, *286*, 252–254.
- [161] Chen, J., Reed, M. A., Rawlett, A. M., Tour, J. M., Science 1999, 286, 1550–1551.
- [162] Yang, P., Deng, T., Zhao, D., Feng, P., Pine, D., Chemelka, B., Whitesides, G. M., Stucky, G. D., *Science* 1998, 282, 2224–2226.
- [163] Boel, A. K., Iihan, F., DeRouchey, J. E., Thurn-Albrecht, T., Russell, T. P., Rotello, V. M., *Nature* 2000, 404, 746–748.
- [164] Hayward, R. C., Saville, D. A., Aksay, I. A., *Nature* 2000, 404, 56–59.

- [165] Deming, T. J., Conticello, V. P., Tirell, D. A. 1999, in: Timp, G. (Ed.), *Nanotechnology*, Springer-Verlag, New York 1998 pp. 371–401.
- [166] Alberts, B., Bray, D., Lewis, J., Raff, M., Roberts, K., Watson, J. D., *Molecular Biology in the Cell*, Garland Publishing Inc., New York 1994.
- [167] Mirkin, C. A., Taton, T. A., Nature 2000, 405, 626-627.
- [168] Trau, M., Yao, N., Kim, E., Xia, Y., Whitesides, G. M., Aksay, I. A.. *Nature* 1997, *390*, 674–676.
- [169] Fan, H., Lu, Y., Stump, A., Reed, S. T., Baer, T., Schunk, R., Perez-Luna, V., Lopez, G. P., Brinker, C. J., *Nature* 2000, 405, 56–60.
- [170] Whatley, S. R., English, D. S., Hu, E. L., Barbara, P. F., Belcher, A. M., *Nature* 2000, *405*, 665–668.
- [171] Sakaki, H., in: Davies, J. H., Long, A. R. (Eds.), *Physics of Nanostructures*, Cromwell Press Ltd. Wiltshire 1992, pp. 1–30.
- [172] Boeck, J., Science 1998, 281, 357-358.
- [173] Fiederling, R., Klein, M., Ossau, W., Schimidt, G., Wang, A., Molenkamp, L. W., *Nature* 1999, *402*, 787–790.
- [174] Ohno, Y., Young, D. K., Beschoten, B., Matsukura, F., Ohno, Y. A., Awshalom, D. D., *Nature* 1999, 402, 790–793.
- [175] Vossen, J. L., Kern, W., *Thin Film Processes*, Academic Press, New York 1978.
- [176] Kendall, D. L., Shoultz, R. A., in: Rai-Choudhury, P. (Ed.) Handbook of Microlithography, Microfabrication and Microsystems, SPEI Press, Washington 1997, pp. 41–97.
- [177] Newman, R. (Ed.), Maddox, R. L., Splinter, M. R., *Fine Line Lithography*, North-Holland Publisher, Amsterdam 1980, pp. 337–415.
- [178] Coburn, J. W. (Ed.), Steinbrüchel, C., Handbook of Thin Film Process Technology, IOP Publishing, London 1995, C1.1, C1.2, C1.3.
- [179] McWhorter, P. J., Fraizier, B., Rai-Choudhury, P., in: Rai-Choudhury, P. (Ed.), *Handbook of Microlithography, Microfabrication and Microsystems*, SPEI Press, Washington 1997, pp. 3–39.
- [180] MacDonald, N. C., in: Timp, G. (Ed.), *Nanotechnology*, Springer-Verlag, New York 1998 pp. 89–160.
- [181] Fukuda, T., Menz, W. (Eds.) Handbook of Sensors and Actuators: Micro Mechnical Systems - Principle and Technology, Elsevier Science B. V., Amsterdam 1998.
- [182] Vovacs, G. T., Maluf, N. I., Petersen, K. E., Proc. IEEE 1998, 86, pp. 1536–1551.
- [183] Sze, M., Semiconductor Sensors, John Wiley and Sons, New York 1994.
- [184] Lochel, A., Maciossek, A., Quenzer, H. J., Wagner, B., J. Electrochem. Soc. 1996, 143, 237–243.
- [185] White, V., Ghodssi, R., Herdev, C., Denton, D. D., McCaughan, L., Appl. Phys. Lett. 1995, 66, 2072–2074.
- [186] Ehrfeld, W., Lehr, H., *Rad. Phys. Chem.* 1995, *45*, 349–355.
- [187] Rogers, J. A., Meier, M., Dodabalaour, A., Appl. Phys. Lett. 1998, 73, 1766–1768.
- [188] Rogers, J. A., Qin, A., Schuller, O. J. A., Whitesides, G. M., *Rev. Sci. Instrum.* 1996, *67*, 3310–3317.
- [189] Rogers, J. A., Whitesides, G. M., Appl. Opt. 1997, 36, 5792–5798.

- [190] Qin, D., Xia, Y., Whitesides, G. M., Adv. Mater. 1997, 9, 407–412.
- [191] Jackman, R. J., Brittain, S. T., Adams, A., Prentiss, M. G., Whitesides, G. M., *Science* 1998, *280*, 2089–2091.
- [192] Shoji, S., 1999, in: Manz, A., Becker, H. (Eds.) *Microsystem Technology in Chemistry and Life Sciences*, Springer Desktop Editions in Chemistry, Berlin 1999, pp. 163–213.
- [193] Cheng, J., Kricka, L. J., Sheldon, E. L., Wilding, P., in: Manz, A., Becker, H. (Eds.), *Microsystem Technology in Chemistry and Life Sciences*, Springer Desktop Editions in Chemistry, Berlin 1999, pp. 215–231.
- [194] Ehrfeld, W., Hessel, V., Lehr, H., in: Manz, A., Becker, H. (Eds.), *Microsystem Technology in Chemistry and Life Sciences*, Springer Desktop Editions in Chemistry, Berlin 1999, pp. 234–252.
- [195] Asai, S., Wada, Y., Proc. IEEE 1997, 85, 505-520.
- [196] Kawaura, H., Sakamoto, T., Baba, T., Ochiai, Y., Fujita, J., Matsui, S., Sone, J., *IEEE Elec. Dev. Lett.* 1998, *19*, 74–76.
- [197] Wind, S. T., Franck, D. J., Wong, H. S., *Microelectron. Engineer*. 1996, *32*, 271–282.
- [198] Goldhaber-Gordon, D., Montemerlo, M. S., Love, J. C., Opiteck, G. J., Ellenbogen, J. C., *Proc. IEEE* 1997, *85*, 521–540.
- [199] Goser, K., Pacha, C., Kanstein, A., Rossmann, M. L., *Proc. IEEE* 1997, *85*, 558–573.
- [200] Kouwenhoven, L. P., Eurn, P. L. M., in: Rai-Choudhury, P. (Ed.), Handbook of Microlithography, Microfabrication and Microsystems, SPEI Press, Washington 1997 pp. 471– 536.
- [201] Ahmed, H., Nakazato, K., *Microelectr. Engineer.* 1996, *32*, 297–316.
- [202] Guo, L., Leobandung, E., Chou, S. Y., Science 1997, 275, 749–751.
- [203] Chen, K. J., Kaezawa, K., Yamamoto, M., *IEEE ED Letters* 1996, 17, 127–129.
- [204] Mazumder, P., Kulkarni, S., Bhattacharya, B., Sun, J. P., Haddad, G. I., *Proc. IEEE* 1998, *86*, 664–686.
- [205] Prinz, G. A., Science 1998, 282, 1660-1663.
- [206] Kane, B. E., Nature 1998, 393, 133-137.
- [207] Lent, C. S., Tougaw, P. D., Proc. IEEE 1997, 85, 541-557.
- [208] Orlov, A. O., Amlani, I., Bernstein, G. H., Lent, C. S., Snider, G. L., *Science* 1997, *277*, 928–930.
- [209] Heath, J. R., Kuekes, P. J., Snider, G. S., Williams, R. S., *Science* 1988, 280, 1716–1721.
- [210] Hahnloser, R. H. R., Sarpeshkar, R., Mahowald, M. A., Douglas, R. J., Seung, H. S., *Nature* 2000, 405, 947–951.
- [211] Braun, E., Eichen, Y., Sivan, U., Ben-Yoseph, G., Nature 1998, 391, 775–778.
- [212] Andes, R. P., Bein, T., Dorogi, M., Feng, S., Henderson, J. I., Kubiak, C. P., Mahoney, W., Osifchin, R. G., Reifenberger, R., *Science* 1996, *272*, 1323–1325.
- [213] Burstein, E., Weisbuch, C. (Eds.) Confined Electrons and Photons: New Physics and Application, NATO ASI Series B340, Plenum Press, New York 1995.
- [214] Yablonovitch, E., Phys. Rev. Lett. 1987, 58, 2059–2062.
- [215] Joannopoulos, J. D., Meade, R. D., Winn, J. N., *Photonic Crystals*, Princeton University Press, Princeton, NJ 1995.
- [216] Joannopoulos, J. D., Villeneuve, P. R., Fan, S., Nature 1997, 386, 143–149.

- [217] Iizuka, K., Manab, D., Sano, S., Seki, M., Komatsu, T., Matsumoto, T., Kawachi, M., in: Taniguchi, N. (Ed.), *Nanotechnology: Integrated Proceecing Systems for Ultra-precision and Ultrafine Products*, Oxford University Press, Oxford 1997 pp. 325–367.
- [218] Awshalom, D. D., Divincenzo, D. D., *Physics Today* 1995, 48, 43–48.
- [219] Awshalom, D. D., von Molnar, S., in: Rai-Choudhury, P. (Ed.), Handbook of Microlithography, Microfabrication and Microsystems, SPEI Press, Washington 1997 pp. 438– 470.
- [220] Gibbs, W. W., Sci. Amer. 1999, May, 9-10.
- [221] Toigo, J. W., Sci. Amer. 2000, May, 41-52.
- [222] Harrison, D. J., Manz, A., Fan, Z., Ludi, H., Widmer, H. M., *Anal. Chem.* 1992, *64*, 1926–1932.
- [223] Ueda, M., Oana, H., Baba, Y., Doi, M., Yoshikawa, K., *Biophys. Chem.* 1998, *71*, 113–123; Nishimura, A., Tsuhako, M., Baba, Y., *Chem. Pharm. Bull.* 1998, *46*, 1639–1942; Ueda, M., Tabata, O., Baba, Y., *T.IEE Jap.* 1999, *10*, 460–463.
- [224] Han, J., Craighead, H. G., Science 2000, 288, 1026–1029.
- [225] Volkmuth, W. D., Austin, R. H., *Nature* 1992, *358*, 600–602.
- [226] Stroock, A. D., Weck, M., Chiu, D. T., Huck, W. T. S., Kenis, P. J. A., Ismagilov, R. F., Whitesides, G. M., *Phys. Rev. Lett.* 2000, *84*, 3314–3317.
- [227] Adjari, A., Phys. Rev. E 1996, 53, 4996–5005.
- [228] Washizu, M., Suzuki, S., Kurosawa, O., Nishizaka, T., Shinohara, T., *IEEE Trans. Ind. Appl.* 1994, *30*, 835–843.
- [229] Morgan, H., Hughes, M. P., Green, M. G., Biophys. J. 1999, 77, 516–525.
- [230] Foquet, M. E., Turner, S. W., Korlach, J., Webb, W. W., Craighead, H. G., *Proceedings of Micro Total Analysis*

*Systems 2000*, Kluwer Academic Publishers, Dordrecht 2000 pp. 549–552.

- [231] Arnold, D. W., Bailey, C. G., Garguilo, M. G., Matzke, C. M., Wendt, J. R., Sweatt, W. C., Kravitz, S. H., Warren, M. E., Rakestraw, D. J., *Proceedings of Micro Total Analy*sis Systems 2000, Kluwer Academic Publishers, Dordrecht 2000 pp. 435–438.
- [232] Ramsey, G., Nature Biotechnol. 1998, 16, 40-44.
- [233] Bernard, A., Delamarche, E., Schmid, H., Michel, B., Bosshard, H. R., Biebuyck, H., *Langmuir* 1998, 14, 2225–2229.
- [234] Fritz, J., Baller, M. K., Lang, H. P., Rothuizen, H., Vettiger, P., Meyer, E., Guntherodt, H. J., Gerber, C., Gimzewski, J. K., *Science* 2000, *288*, 316–318.
- [235] Montemagno, A., Bachand, G., *Nanotechnology* 1999, *10*, 225–231.
- [236] Proceedings of the 13<sup>th</sup> IEEE International MEMS Conference, Miyazaki, Japan, 23–27 January 2000.
- [237] Lazar, I. M., Ramsey, R. S., Sundberg, S., Ramsey, J. M., *Anal. Chem.* 1999, 71, 3627–3631.
- [238] Litborn, E., Roeraade, J., J. Chromatogr. B 2000, in press.
- [239] Mayer, P., Mat. Res. Soc. Proc. 1997, 463, 57-61.
- [240] Elghanian, R., Storhoff, J. J., Mucic, R. C., Letsinger, R. L., Mirkin, C. A., *Science* 1997, *277*, 1078–1081.
- [241] Woolley, A. T., Guillemette, C., Cheung, C. L., Housman, D. E., Lieber, C. M., *Nature Biotechnol.* 2000, *18*, 760–763.
- [242] Braun, E., Eichen, Y., Sivan, U., Ben-Yoseph, G., Nature 1998, 391, 775–778.
- [243] Jiang, L., Glidle, A., McNeil, C. J., Cooper, J. M., Biosensors Bioelectr. 1997, 12, 1143–1155.
- [244] Souteyrand, E., J. Phys. Chem. B 1997, 101, 2980–2985.