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Semiconductor Nanowire Fabrication by Bottom-Up and Top-Down Paradigms

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ABSTRACT: Semiconductor nanowires have been the subject of intensive research investment over the past few decades. Their physical properties afford them applications in a vast network of active microelectronic research fields, including logic device scaling in very large scale integrated circuits, sensor devices and energy harvesting. A range of routes to semiconductor nanowire production have opened up due to advances in nanowire fabrication techniques over the last number of decades. These nanowire fabrication routes can usually be categorized into one of two paradigms, bottom-up or top-down. Microelectronic systems typically rely on integrated device platforms, where each device and component thereof can be individually addressed. This requirement for precise addressability places significant demands on the mode of fabrication, specifically with regard to device definition, placement and density, which have typically been strengths of top-down fabrication processes. However, in recent years advances in bottom-up fabrication processes have opened up the possibility of a synergy between bottom-up and top-down processes to achieve the benefits of both. This review article highlights the important considerations required for the continued advancement of semiconductor nanowire fabrication with a focus on the application of semiconductor nanowire fabrication for next-generation field-effect transistor devices.

1 Semiconductor Nanowires

Semiconductor nanowires are pseudo 1-D structures where the magnitude of the semiconducting material is confined to a length of less than 100 nm in two dimensions. Semiconductor nanowires have a vast range of potential applications¹, including electronic (logic devices, diodes)², photonic (laser, photodetector)³⁻⁵, biological (sensors, drug delivery)⁶, energy (batteries, solar cells, thermoelectric generators)^{7,8}, and magnetic (spintronic, memory)⁹⁻¹¹ devices. Semiconductor nanowires can be fabricated by a range of methods which can be categorized into one of two paradigms, bottom-up or top-down. Bottom-up processes can be defined as those where structures are assembled from their sub-components in an additive fashion. Top-down fabrication strategies use sculpting or etching to carve structures from a larger piece of material in a subtractive fashion. The challenge of continuous microelectronic device scaling to meet industry targets, e.g. ‘Moore’s Law’¹², and the diversification of the microelectronics industry into new materials for specialized applications (‘More than Moore’)¹², has motivated research in semiconductor nanowires for the past number of decades. The massive competition for a share of the global 304 billion USD semiconductor market¹³, has driven the expansion of the semiconductor nanowire research area, resulting in the evolution of, new fabrication techniques, innovative processes, new materials and creative advancements in semiconductor nanowire device design.

Nanowire materials offer a number of benefits over conventional planar materials for FET applications. Firstly, nanowires offer the option of creating gate-all-around (GAA) architectures, which allow for more efficient control over charge carriers in the channel of FET devices, thus reducing short channel effects caused by drain induced barrier lowering (DIBL).¹⁴⁻¹⁶ The use of multi-gate architectures such as the GAA architecture, facilitates the formation of shorter channel devices, and thus allows for increased device density to be achieved on a given chip. Additionally, fabrication of nanowires of a wide range of materials has been demonstrated which may not be readily produced in wafer form.^{1,17-22}

This review aims to summarize and compartmentalize the various approaches taken by both the bottom-up and top-down paradigms in this field, whilst identifying potential spaces in which both top-down and bottom-up approaches may be used in tandem. Primarily, this review will focus on Si and promising high charge carrier mobility materials for logic device applications, although, as mentioned previously the nanowire fabrication routes highlighted herein are also relevant to a wide host of potential device applications.

Firstly, the major fabrication routes to produce semiconductor nanowires in both paradigms will be discussed, whilst identifying recent advances and highlighting the benefits and drawbacks of these routes. The synergistic use of both top-down and bottom-up approaches to produce structures unattainable by either route alone will also be considered. Next, the most promising materials for high mobility logic device fabrication

1 will be considered. The current issues with processing these
2 materials within each fabrication paradigm will also be ad-
3 dressed.

4

5 2. Bottom-Up Semiconductor Nanowire Fabrication

6 2.1. Semiconductor Nanowire Growth Methods

7 Numerous routes exist to the bottom-up fabrication of semi-
8 conductor nanowires. The vapor-liquid-solid (VLS) mecha-
9 nism and analogues thereof, is the most commonly used route
10 to semiconductor nanowire production.^{1,23,24} The VLS mecha-
11 nism relies on a vapor phase precursor of the nanowire materi-
12 al which impinges on a liquid phase seed particle, from which
13 unidirectional nanowire growth proceeds. The choice of an
14 appropriate seed material has the benefit of allowing control
15 over the diameter of the nanowires produced, whilst the seed
16 material can also significantly affect the crystalline quality of
17 the nanowire.^{25,26} At this point, the importance of selection of
18 an appropriate precursor material should be highlighted.
19 Within a given precursor, MR_x , where 'M' represents the semi-
20 conductor element, or elemental component of a compound
21 semiconductor, and 'R', represents a ligand. The M-R bond
22 should be sufficiently labile under nanowire synthesis condi-
23 tions to directly liberate reactive M species for nanowire
24 growth, or to disproportionate forming reactive M species
25 indirectly.^{27,28} Furthermore, the R group liberated upon pre-
26 cursor decomposition should ideally exist as a gas phase speci-
27 es to prevent contamination of the nanowire product with
28 liquid or solid phase by-product. Consequently, metal hy-
29 drides are often used as precursor compounds for nanowire
30 growth, as H_2 gas is an especially clean by-product which has
31 the benefit of inhibiting undesirable oxide formation for non-
32 oxide semiconductor nanowire growth. Metal hydride precur-
33 sors are commonly used in the growth of nanowires by chemi-
34 cal vapor deposition (CVD), given that metal hydrides such as
35 SiH_4 and GeH_4 generally exist as gas phase compounds.²⁹
36 Metal-organic precursors, such as diphenylsilane and diphe-
37 nylgermane, often used in solution phase and supercritical
38 fluid phase nanowire synthesis can produce carbonaceous by-
39 products which may be difficult to completely separate from
40 the nanowire product.^{30,31} Semiconductor nanowire synthesis
41 conditions often encourage the formation of reactive radical
42 species which can initiate polymerisation reactions resulting in
43 unwanted contaminating by-products,³² and as such, precursor
44 design should always be considered when designing an exper-
45 iment for semiconductor nanowire synthesis. Analogues of
46 the VLS mechanism include supercritical fluid-liquid-solid
47 (SFLS)²⁴, supercritical fluid-solid-solid (SFSS),^{33,34} solution-
48 liquid-solid (SLS)³⁵, vapor-solid-solid (VSS)^{36,37} and oxide
49 assisted growth (OAG)³⁸ mechanisms. Common to all of the-
50 se analogues is the existence of a collector or seed particle
51 which acts as a sink for the nanowire material, and from which
52 unidirectional growth proceeds.³⁹ Conventionally, the seed
53 particle is a metal with which the nanowire material or com-
54 ponent thereof forms an alloy. However, autocatalytic or self-
55 seeded semiconductor growth has also been demonstrated.⁴⁰⁻⁴⁶
56 Self-seeded VLS-type nanowire growth is most commonly
57 observed for compound materials such as InP, GaN and SnO_2
58 whereby the metallic component of the material, In, Ga and Sn
59 for InP, GaN and SnO_2 respectively, forms seed particles for
60 nanowire growth of the compound material.⁴⁵⁻⁴⁷ However,

61 there have also been reports of self-seeded nanowire growth
62 for elemental materials where a VLS-type mechanism has
63 been invoked.⁴⁸ The most commonly used metal catalyst for
64 VLS-type nanowire growth is Au, prepared either as colloidal
65 Au nanoparticles or as an evaporated or sputtered thin film.
66 However, Au is inherently incompatible with semiconductor
67 device manufacturing. Au has a high diffusivity in Si and also
68 acts as a deep level acceptor and thus has detrimental effects
69 on device performance.⁴⁹⁻⁵¹ Furthermore, Au is a highly inert
70 material which makes cleaning of instrumentation contaminat-
71 ed with Au extremely difficult. For example, traditional Au
72 etchants include aqua regia (concentrated nitric acid and hy-
73 drochloric acid solution), KI/I_2 solution and alkali cyanide
74 solutions, all of which would corrode stainless steel equipment
75 and in the case of alkali solutions result in detrimental effects
76 on semiconductor device performance, such as shifting of
77 threshold voltage (V_t).^{52,53} Consequently, there has been sig-
78 nificant research into alternative, complementary metal-oxide-
79 semiconductor (CMOS) production compatible, metal seeds
80 for catalyzed VLS semiconductor nanowire growth.⁵⁴⁻⁵⁶ Ac-
81 ceptable metals should have ionization energies far from the
82 mid band-gap region of the semiconductor material. Si nan-
83 owire growth has been demonstrated using a number of Si
84 CMOS compatible metals including Bi³⁵ and Al.⁵⁷ Great care
85 must be applied even when using CMOS compatible metals
86 for nanowire growth, as these metals can still act as active
87 dopants in the nanowire material. Al, for example can readily
88 migrate through Si via interstitial sites in the Si lattice, thus
89 acting as an n-type dopant in Si.^{58,59} Furthermore, Si migration
90 through the Al metal is also possible and may dramatically
91 affect the electrical performance of the nanowire material.⁶⁰ A
92 seed metal, such as Al may also be beneficial for preparation
93 of an Ohmic contact to the nanowire tip, thus facilitating nan-
94 owire FET device formation.

95 One benefit of bottom-up nanowire growth over top-down
96 processing is that nanowires grown by bottom-up methods
97 may be doped in-situ during crystal growth by incorporating
98 dopant precursors in the nanowire synthesis procedure. Con-
99 sequently, bottom-up grown nanowires may not require de-
100 structive techniques such as ion implanting to generate addi-
101 tional charge carriers. Ion implanting can destroy atomic or-
102 dering in the implanted region of the semiconductor crystal
103 and requires subsequent thermal annealing steps to restore
104 crystal ordering.⁶¹

105 In addition to VLS-type nanowire growth mechanisms there
106 exists a range of other routes to produce bottom-up grown
107 nanowires. These routes, which do not invoke the VLS
108 growth mechanism include, oriented attachment,^{62,63} metal
109 organic vapor phase epitaxy (MOVPE),^{64,65} molecular beam
110 epitaxy (MBE),⁶⁶ soft templating,^{22,67,68} dislocation driven uni-
111 directional growth⁴² and crystal habit modification.⁶⁹⁻⁷¹

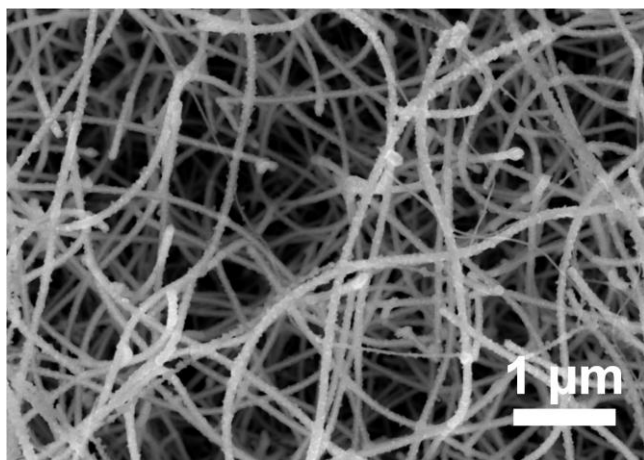
112 2.2. Nanowire Alignment Techniques

113 Bottom-up grown semiconductor nanowires fabricated by the
114 methods outlined above are typically produced as entangled
115 meshes of nanowires and as a result lack the periodic ordering
116 and placement required for large-scale semiconductor device
117 processing. Figure 1 displays an SEM image of an entangled
118 mesh of SiO_2 -coated Ge nanowires.

1 Recently there have been a number of techniques developed to
2 align semiconductor nanowires produced as entangled mesh-
3 es.⁷² Examples include alignment of polar nanowires within
4 strong electric fields,^{73,74} dielectrophoresis,^{75,76} microfluidic
5 alignment,⁷⁷ lubricant-assisted contact printing,^{78–80} and evapo-
6 ration-induced alignment.^{81–83} Electric field-based alignment
7 techniques, including dielectrophoresis, have been shown to
8 allow precise control over nanowire position with respect to
9 metallic contact pads, however, these techniques have not yet
10 demonstrated the high density of aligned nanowires required
11 for high volume manufacturing (HVM), which is currently
12 approaching a device half-pitch of 20 nm.¹² Figure 2 displays
13 images of nanowires aligned by dielectrophoresis at a pitch of
14 ~ 20 μm .

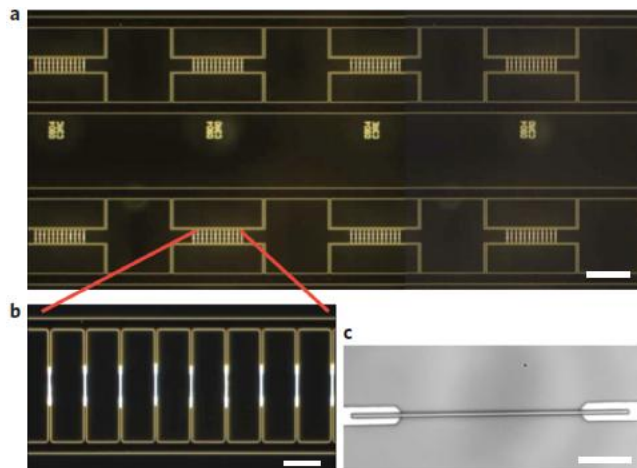
15 Microfluidic alignment, contact printing and evaporation in-
16 duced alignment techniques have all demonstrated the capabil-
17 ity to create parallel nanowire arrays, in some cases with high
18 areal density. Fan *et al.*, for example, have demonstrated
19 aligned nanowires at a density of ~10 nanowires/ μm .⁷⁸ How-
20 ever, these techniques lack the prerequisite precision of con-
21 trol over nanowire placement, required for individual nan-
22 owire addressability within very large scale integrated circuit
23 (VLSI) technology. Nevertheless, such techniques have been
24 used not only to demonstrate successful individual device
25 operation, but, also to demonstrate integrated devices in a fully
26 functioning nano-processor.⁷⁹

27



28

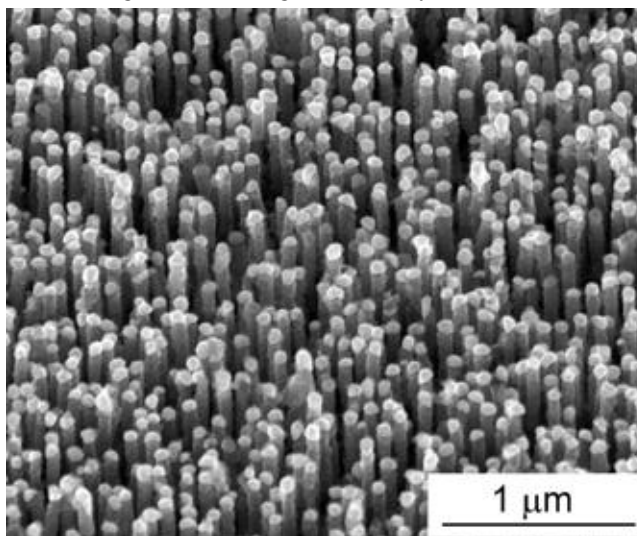
29 **Figure 1.** An SEM image of an entangled mesh of SiO_2 -coated Ge
30 nanowires grown from colloidal Au nanoparticles by the SFLS
31 method.



32
33 **Figure 2.** Optical dark-field and DUV images of nanowires as-
34 sembled onto electrodes by dielectrophoresis: (a) dark-field image
35 of defect-free nanowire assembly arranged on electrode arrays
36 (scale bar = 200 μm), (b) high magnification dark-field image of
37 nanowires aligned on 2 μm wide electrodes (scale bar = 20 μm)
38 and (c) DUV image of a single nanowire aligned on electrodes
39 separated by 12 μm .⁷⁶

40 A change of direction may be required for bottom-up ap-
41 proaches to achieve the requisite nanowire density, placement
42 control and alignment required for VLSI manufacturing. High
43 density vertical semiconductor nanowire films have been pro-
44 duced using a range of bottom-up techniques. These tech-
45 niques include, epitaxial nanowire growth,^{25,57,65,84–89} and hard-
46 templated nanowire growth.^{90,91} Figure 3 shows an SEM im-
47 age of vertically aligned epitaxially grown nanowires, where
48 the diameter was controlled by an anodized aluminium oxide
49 (AAO) template.

50 The epitaxial route to semiconductor nanowire synthesis has
51 the advantage of controlling nanowire crystal orientation



52

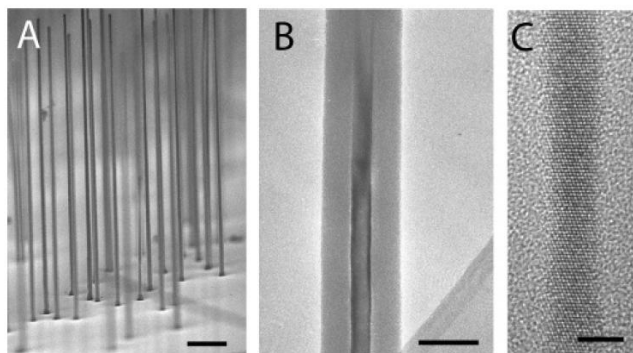
53 **Figure 3.** SEM image of epitaxial vertical Si nanowire arrays
54 grown within an AAO hard template (template removed in
55 image). Nanowire crystal orientation is controlled epitaxially
56 by the substrate, whilst diameter and placement of the nan-
57 owires is controlled by the template.⁹⁰

1 through the selection of an appropriate substrate crystal orien-
 2 tation. Wang *et al.* for example, have demonstrated the epi-
 3 taxial growth of vertically aligned <111> oriented Si nan-
 4 owires on a <111> Si substrate by CVD using an Al catalyst.
 5 Nanowires can also be produced epitaxially when there is a
 6 large lattice mismatch between the nanowire material and the
 7 substrate material. Tomioka *et al.* reported the growth of
 8 <111> oriented InAs nanowires on a Si <111> substrate, de-
 9 spite an 11.6 % lattice mismatch between the two crystals, by
 10 using a ‘selective area’ MOVPE technique whereby lattice
 11 mismatch strain was dissipated by limiting the interfacial area
 12 between the two crystals.⁶⁵ A patterned amorphous SiO₂ thin
 13 film, prepared by electron beam lithography and etching, acted
 14 as a mask for growth of the nanowires by vapor phase epitaxy.
 15 Shimizu *et al.* have shown that the combined use of epitaxial
 16 nanowire growth and an ordered template such as AAO to
 17 control the position of these nanowires, allows a route to or-
 18 dered arrays of vertically aligned, coaxial, Si nanowires suita-
 19 ble for use in vertical nanowire device fabrication (figure 3).⁹⁰
 20 Ordering of pores in AAO spontaneously occurs during AAO
 21 formation as a mechanism to reduce internal strain in the AAO
 22 film.⁹² The formation of AAO with hexagonally close packed
 23 (HCP) pores can be considered a bottom-up process, as the
 24 pores self-assemble into a HCP arrangement from an initial
 25 disordered state, pore by pore.⁹²

26 2.3. Vertical Nanowire Field Effect Transistors

27 There have been several reports of field effect transistor (FET)
 28 devices produced using vertically aligned, bottom-up grown
 29 semiconductor nanowires.^{93–100} Figure 4 shows electron mi-
 30 croscopy images of vertical Si nanowires used to create verti-
 31 cal nanowire FET devices. The reported devices showed rea-
 32 sonable performance characteristics with observed I_{ON}/I_{OFF}
 33 ratios $> 10^5$ and a sub-threshold slope of 120 mV/decade, alt-
 34 hough their performance was still significantly poorer than
 35 current state-of-the-art, top-down, strained Si devices.^{14,101}
 36 The vertical nanowire devices demonstrated significantly low-
 37 er on/off ratios and shallower sub-threshold slopes than their
 38 top-down counterparts. The reasons for their inferior perfor-
 39 mance can be attributed to a number of issues including, con-
 40 tact resistance at the source and drain interfaces, non-uniform
 41 dopant distribution within the nanowire channel, charge trap-
 42 ping at the

43



44
 45 **Figure 4.** Vertically aligned, epitaxial, Au seeded, Si nanowires
 46 with thermally grown SiO₂ shells. Scale bars represent lengths of
 47 1 μm, 75 nm and 4 nm in (a), (b) and (c) respectively.⁹⁹

48 gate dielectric interface, or charge carrier recombination due to
 49 Au incorporation within Au-seeded Si nanowires. Some of
 50 these issues may be rectified, for example, the choice of an
 51 appropriate seed metal for nanowire growth is important. Not
 52 only should the seed metal allow production of the desired
 53 nanowire structure, the metal should also have an appropriate
 54 work function to form an ohmic contact to the semiconductor
 55 nanowire.^{102,103} Au tends to form Schottky contacts to n-Si
 56 resulting in high contact resistance to the semiconductor nan-
 57 owire channel.¹⁰⁴ The choice of metal also depends strongly
 58 on the majority charge carrier and carrier concentration in the
 59 nanowire device, for example p-type devices require metals
 60 with increased work function values compared to n-type de-
 61 vices, and higher semiconductor charge carrier concentrations
 62 result in reduced depletion layer widths at the metal-
 63 semiconductor junction which facilitates carrier tunnelling and
 64 thus reduced contact resistance.¹⁰⁴ Alternatively, the option
 65 exists to use a seed metal which has an inappropriate work
 66 function to produce the nanowires and subsequently strip this
 67 metal away by chemical etching, followed by the deposition of
 68 a suitable electrical contact metal. However, this approach
 69 introduces additional device processing steps and complete
 70 removal of the seed metal after chemical etching is unlikely,
 71 especially when alloys may have formed with the semiconduc-
 72 tor during nanowire growth. The issue of dopant distribution
 73 is critical to device performance. A homogeneous, activated
 74 dopant distribution is desired within semiconductor devices in
 75 order to assure a stable threshold voltage (V_t).¹⁰⁵ Perea *et al.*
 76 have mapped the dopant distribution within an individual VLS
 77 grown Ge nanowire, and have shown the dopant distribution
 78 to be non-uniform along the nanowire growth axis and radially
 79 across the nanowire.¹⁰⁶ Techniques such as single ion implan-
 80 tation have been shown to improve the homogeneity of dopant
 81 incorporation in the nanowire structure resulting in improved
 82 V_t stability from device to device.¹⁰⁵ A number of approaches
 83 have been taken to improve semiconductor nanowire surface
 84 passivation to remove surface state charge trapping sites,
 85 which can have capacitive effects at the nanowire surface and
 86 hinder device performance. These approaches include organic
 87 passivation of the nanowire surface,^{107–110} deposition of dielec-
 88 tric materials such as SiO₂, and Al₂O₃ and nitridation or sulfi-
 89 dation of the nanowire surface.^{111,112} Finally, issues arising
 90 due to metal dopants from the catalyst metal particle can be
 91 negated through the use of an appropriate metal for the semi-
 92 conductor of choice. The metal should not have ionization
 93 energies at or near the centre of the band-gap of the semicon-
 94 ductor, *e.g.* Al or Bi for Si. Once the outstanding issues de-
 95 tailed above have been addressed, bottom-up grown vertical
 96 nanowire FETs may become a practical route toward contin-
 97 ued device footprint scaling within VLSI technology.

98 2.4. Bottom-Up Semiconductor Nanowire Outlook

99 There are a number of outstanding issues associated with the
 100 integration of bottom-up grown semiconductor nanowires into
 101 conventional integrated circuit (IC) design and processing.
 102 Conventional IC design is based on the active channel of the
 103 logic devices lying coplanar to the Si wafer substrate, and
 104 requires a very high degree of control over placement of the
 105 devices so that they may be individually addressed for suc-
 106 cessful IC operation. Traditionally, bottom-up grown semi-
 107 conductor nanowires are grown as entangled meshes and con-
 108 sequently lack the prerequisite ordering, and control of place-

1 ment required for IC manufacturing.^{24,40,113} Although there
2 have been recent advances in extracting nanowires from such
3 entangled meshes and aligning them on substrates, these ap-
4 proaches can produce neither the high density of nanowires
5 desired, nor the large scale areal coverage required, for
6 HVM.^{74–77,79,81,114} As such, industrial applications of entangled
7 meshes of semiconductor nanowires may be limited to the
8 production of nanowire composites, which may have applica-
9 tions in areas such as batteries, flexible electrodes and thermo-
10 electric generators.^{115–117} However, there still remains signifi-
11 cant value to be gained from the study of individual, novel,
12 nanoscale structures, from a conceptual standpoint. Given the
13 issues associated with the alignment of bottom-up grown sem-
14 iconductor nanowires in the substrate coplanar orientation, it
15 seems imperative that another route to IC fabrication be de-
16 vised. Perhaps the most promising route toward integration of
17 bottom-up grown semiconductor nanowires into an IC com-
18 patible arrangement is that of a vertically oriented active chan-
19 nel with respect to the substrate. Transferring to a vertical
20 orientation would be a huge change for a very mature technol-
21 ogy. However, recent developments in the industry with the
22 adoption of tri-gate and finFET structures have shown that
23 movement out of the plane of the Si substrate is possible and
24 as such presents an opportunity for the development of 3-D
25 device architectures.¹¹⁸ Advances in CVD techniques for nan-
26 owire growth have allowed the production of epitaxial nan-
27 owires whereby the crystalline orientation of the nanowires
28 with respect to a substrate is controlled at the epitaxial inter-
29 face. Operational vertically integrated nanowire field effect
30 transistors (VINFETs), produced using bottom-up grown sem-
31 iconductor nanowires have been reported by several
32 groups.^{96,99,100,119} The VINFET concept remains a viable op-
33 tion for future semiconductor device processing as it potential-
34 ly offers a route to high density stacks of GAA nanowire FET
35 devices. The vertical orientation with respect to the substrate
36 allows devices to be stacked on the substrate which ultimately
37 increases the density of devices and thus computing power per
38 chip area. A wrap around gate or GAA structure also offers
39 superior electrostatic control of the channel compared to cur-
40 rent devices in production, which may allow improved switch-
41 ing of the device. However, a great amount of work is still
42 required to individually contact each device within such a high
43 density, stacked architecture and consequently IC fabrication
44 using VINFET devices is still in its infancy. Furthermore, the
45 International Technology Roadmap for Semiconductors
46 (ITRS) has targeted a line width roughness (LWR) value of
47 1.4 nm 3σ for device structures by 2015.¹² LWR values in the
48 targeted range are not yet achievable in semiconductor nan-
49 owire fabrication by bottom-up means, where the narrowest
50 nanowire diameter distributions typically possess 3σ values of
51 approximately 3 nm.^{120,121} Consequently, further work is re-
52 quired in the areas of alloy engineering and nanowire catalyst
53 control to achieve the targeted control of nanowire diameter
54 for device components in future VLSI manufacturing. Bot-
55 tom-up grown nanowires are expected to possess fewer sur-
56 face dangling bonds than their top-down analogues, which are
57 fabricated by etching. A reduction in dangling bond density
58 for bottom-up grown nanowires can be attributed to nanowire

59 surface faceting during nanowire growth, which is driven by a
60 reduction in the surface chemical potential and atomic diffu-
61 sion during crystal growth.¹²² Surface dangling bonds can trap
62 charge carriers in the nanowire thus reducing carrier density,
63 and also inhibit effective gating of nanowire FETs by intro-
64 ducing interface states at the semiconductor-dielectric inter-
65 face.^{56,123} Additional annealing steps are typically employed in
66 top-down fabrication to reduce nanowire surface roughness
67 and dangling bond density to improve electrical performance
68 of top-down fabricated nanowires.^{123–125}

69 3. Top-Down Semiconductor Nanowire Fabrication

70 3.1. Optical Lithography

71 Optical lithography has been the industry standard for semi-
72 conductor device definition and placement for decades. In
73 that time there have been significant developments in optical
74 lithography, both in terms of resist technology and optics.^{126–}
75 ¹²⁹ There has been a general trend toward shorter wavelength
76 radiation sources to achieve higher image resolution as given
77 by the relationship in equation 1 derived from the Rayleigh
78 criterion.¹²⁹
79

$$80 \quad CD = \frac{k\lambda}{NA} \quad (1)$$

81 CD represents the minimum critical dimension that can be
82 imaged in a photoresist using a given process having a process
83 latitude factor of k , an emission wavelength λ (nm), and a nu-
84 merical aperture NA , where $NA = n\sin\theta$, where n represents the
85 refractive index of the medium in which the final projection
86 lens is operating and θ represents the half-angle of the maxi-
87 mum cone of light that exits the final lens of the system. In
88 the 1970s, Hg G-line emission, at a wavelength of 436 nm,
89 was the light-source of choice for optical lithography. Current
90 VLSI manufacturing employs an ArF laser with an emission
91 wavelength of 193 nm. In addition to reducing the wavelength
92 of the radiation source, other measures have also been taken to
93 improve image resolution. DUV scanners and steppers regu-
94 larly incorporate a reduction lens as the final projection lens of
95 the lithography system. Reduction lenses typically allow $4 \times$
96 or $5 \times$ reduction of features in the photomask.¹²⁸ The use of
97 reduction lenses in scanners and steppers results in a conse-
98 quent scaling of the image field, which translates as an in-
99 crease in the number of exposure fields per wafer and thus a
100 lower throughput of wafers. Consequently, $2 \times$ reduction
101 lenses are often used as a compromise between reduced fea-
102 ture size (CD) and wafer throughput. Although reduction
103 lenses do not increase the resolution of the lithography pro-
104 cess, they can be used to scale larger features in the photomask
105 to a fraction of that size in the image projected on the photore-
106 sist. This scaling reduces some of the demands placed on
107 mask manufacturing, as low density larger features are typical-
108 ly produced with fewer defects than high density, smaller fea-
109 tures in mask

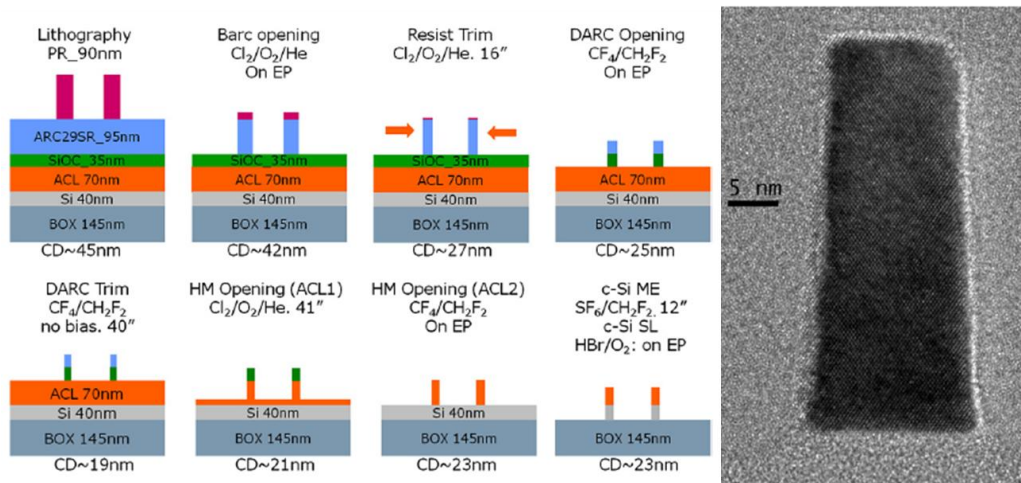


Figure 5. TEM image of a cross-section of a 10 nm × 40 nm Si nanowire produced from SOI using a 193 nm immersion lithography process incorporating resist trimming steps and overetching.¹³⁰

1 fabrication. Interference lithography can be used to create 39
 2 arrays of features with CD values a fraction of the wavelength 40
 3 of the radiation source.^{128,131–133} Interference lithography re-41
 4 quires a number of coherent beams of radiation to be focused 42
 5 on a spot to create an interference pattern, where the period of 43
 6 the pattern is a fraction of the initial radiation wavelength. 44
 7 Typically interference lithography is only used to produce 45
 8 arrays of structures such as gratings. Immersion lithography is 46
 9 a technique whereby the final projection lens of the radiation 47
 10 source is immersed in a medium with a higher refractive index 48
 11 than air, *e.g.* water 1.436 at 193 nm. Increasing the refractive 49
 12 index of the medium in which the final lens operates, effec- 50
 13 tively increases the NA value of the system and as such reduc- 51
 14 es the minimum CD of features that can be imaged in the pho- 52
 15 toresist.¹²⁸ Media with higher refractive indices than water 53
 16 are also being investigated to further increase the process reso- 54
 17 lution.¹²⁸ The ‘ k -factor’ or process latitude factor given in 55
 18 equation 1, is a broad term which depends on a number of 56
 19 process dependant parameters. The ‘ k -factor’ accounts for 57
 20 photoresist effects, developer effects and reticle (photomask) 58
 21 effects, amongst others, and as such is a difficult term to pre- 59
 22 dict for a new process. In essence, a high ‘ k ’ value is repre- 60
 23 sentative of a lower resolution process, where process param- 61
 24 eters limit the achievable resolution. Typical ‘ k ’ values can be 62
 25 as low as 0.15, thus allowing features with dimensions a frac- 63
 26 tion of the wavelength of the incident light, to be imaged in 64
 27 the photoresist.^{128,134} Techniques that can be used to reduce 65
 28 ‘ k ’ values include the use of high resolution resists and resist 66
 29 trimming processes, as shown in figure 5.^{129,134} However, 67
 30 even with such low ‘ k ’ values, achieving the high feature den- 68
 31 sities desired for current semiconductor device production 69
 32 requires further process developments such as, optical proxim- 70
 33 ity correction (OPC),^{126,135} phase shift masks (PSM),¹³⁶ and 71
 34 double patterning (figure 6).^{16,130} Ultimately continued device 72
 35 scaling and increased device density may require extreme ul- 73
 36 tra-violet (EUV) or x-ray lithography (XRL) due to the dra- 74
 37 matically reduced wavelengths of these techniques, typically 75
 38 13.5 nm for EUV and < 1 nm for XRL, compared to current

UV lithography techniques. Whilst short wavelength tech-
 niques like EUV and XRL offer significant potential for nano-
 lithography, they do have drawbacks. EUV lithography tools
 have to operate in vacuum due to strong EUV absorption by
 air. Consequently, EUV resists should not be volatile or swell
 or under vacuum.¹³⁷ Additionally, the requirement for loading
 and unloading wafers from vacuum chambers puts significant
 time demands on the process. Furthermore, shot noise, prox-
 imity effects and flare issues remain outstanding, all of which
 will hinder the ultimate resolution of the lithography process.
 XRL too has a number of issues which may prove to be pro-
 hibitive for HVM. XRL requires synchrotron radiation
 sources which may prove to be too large an investment for an
 unproven manufacturing process with considerable associated
 risk. However, XRL does not demonstrate the significant,
 detrimental, radiation-material interactions observed for EUV
 and as such it remains a pursued and viable option for further
 technological development.¹²⁹

The significant technological advancements in the field of
 optical lithography outlined above demonstrate the suitability
 of these techniques to fabricate ordered arrays of semiconduc-
 tor nanowires with excellent control over placement and fea-
 ture-size. Lateral nanowires may be fabricated from layered
 substrates such as silicon-on-insulator (SOI), or epitaxial thin
 films, prepared by molecular beam epitaxy (MBE), or metal
 organic vapour phase epitaxy (MOVPE). Arrays of lateral
 nanowires can be prepared by fabricating gratings or line
 structures in the resist material and transferring the grating
 pattern to the substrate through the use of an appropriate etch
 process. Figure 5 displays a TEM image of a cross-section
 through a 10 nm wide Si nanowire fabricated from SOI using
 193 nm immersion lithography.

Similarly, vertical nanowires may be prepared from bulk or
 layered substrates by using a resist mask consisting of dot or
 polygonal structures with maximum lateral dimensions below
 100 nm and transfer of the mask pattern deep in to the sub-
 strate, again using an appropriate anisotropic etch process.¹³⁸

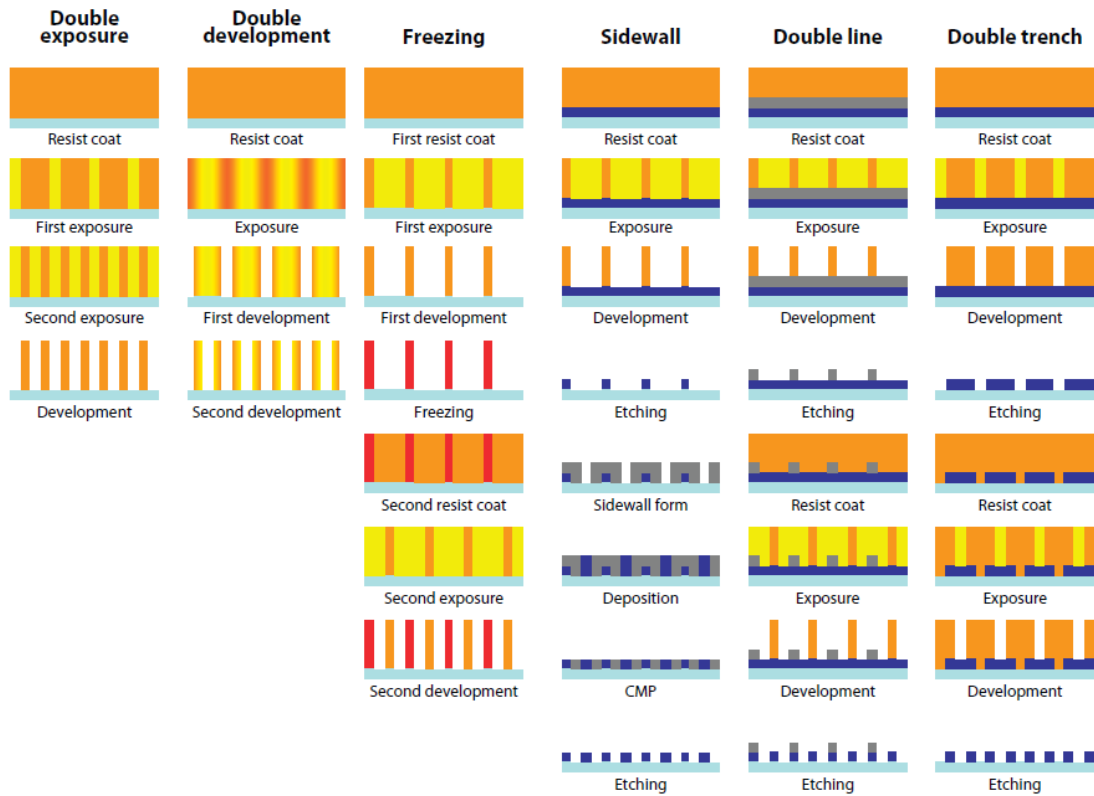


Figure 6. Schematic of a number of approaches for double-patterning lithography. CMP, refers to chemical mechanical planarisation.¹²⁸

1 Inductively coupled plasma (ICP) and reactive ion etch (RIE) 29
 2 techniques are most commonly used for pattern transfer, alt- 30
 3 hough anisotropic wet etch and metal assisted etch (MAE) 31
 4 procedures have also been used.^{138,139} 32

5 **3.2. Next Generation Lithography: Electron Beam Li-** 33
 6 **thography and Competing Techniques** 34

7 A number of lithography processes are being considered to 35
 8 extend lithography scaling beyond current UV lithography 36
 9 capabilities, for semiconductor device manufacturing. These 37
 10 techniques include, electron beam lithography (EBL),^{124,140,141} 38
 11 nanoimprint lithography (NIL),^{142,143} XRL,^{144,145} EUV lithog- 39
 12 raphy,^{146,147} scanning probe lithography (SPL),¹⁴⁸ ion beam 40
 13 lithography (IBL),^{149,150} and electron beam induced deposition 41
 14 (EBID) lithography.¹⁵¹⁻¹⁵³ EBL is at the heart of many of these 42
 15 techniques, including the optical lithography processes. EBL 43
 16 is generally used for the fabrication of high-resolution photo- 44
 17 masks for DUV, EUV and XRL. NIL stamps are also pro- 45
 18 duced using EBL direct-write processes. EBID lithography is 46
 19 essentially an EBL process that incorporates the use of a gas 47
 20 injection system which disperses a gaseous precursor that de- 48
 21 composes under the electron beam and directionally deposits 49
 22 on the substrate surface forming a mask. As such, current and 50
 23 future VLSI manufacturing is heavily dependent on the devel- 51
 24 opment of EBL processes and instrumentation. EBL has been 52
 25 shown to be capable of producing sub-10 nm features at sub- 53
 26 20 nm pitches.^{154,155} Figure 7 displays examples of high- 54
 27 resolution EBL processes used to produce line-widths as small 55
 28 as 4.5 nm at pitches as low as 9 nm.

However, the primary concern with the implementation of
 EBL techniques in HVM is the low throughput of wafers due
 to the exposure times required for full wafer layouts. Expo-
 sure times depend on several factors which include the tone of
 the resist, the area of the wafer to be exposed, the electron
 beam current, electron energy, and the sensitivity of the resist
 (electron dose required to completely chemically alter the res-
 ist).^{129,156} Resist technology may have a significant role to
 play in the reduction of EBL exposure times. Increasing the
 resist sensitivity will significantly reduce the required time for
 exposure; however, increased sensitivity should not compro-
 mise the ultimate resolution of the resist. Hydrogen silsesqui-
 oxane (HSQ), the smallest member of the polyhedral oligomeric
 silsesquioxane (POSS) family, is an example of one of the
 highest resolution negative-tone EBL resists. However, HSQ
 exposure doses are considered too high for use in HVM. Chemically
 amplified resists (CARs) have been developed with significantly
 increased sensitivity with respect to HSQ, but these resists offer
 lower ultimate resolution. The field of EBL resist research is an
 active one and recent demonstrations of EBL using analogues of
 HSQ with increased electron beam sensitivity are promising.¹⁵⁷

Multi-beam EBL systems are under development which will
 increase wafer throughput either through beam-splitting tech-
 niques, or through the use of instruments with multiple elec-
 tron sources, however, the technology is still not mature and
 as

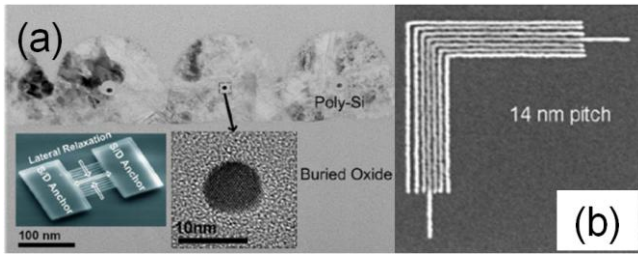


Figure 7. High resolution features produced by EBL: (a) 8 nm diameter strained n-Si nanowires produced using a hydrogen silsesquioxane (HSQ) EBL process for gate all-around FET devices and (b) nested lines at a pitch of 14 nm.^{124,155}

such has yet to be implemented on a HVM scale.¹⁵⁸ Lee *et al.*¹⁵⁹ have reported a particularly innovative example of multi-beam EBL using a Si crystal as an electron beam mask (figure 8). A transmission electron microscope (TEM) was used to create arrays of electron beams where the shape and separation of the beams was governed by the crystal structure and crystal orientation of the mask with respect to the incident electron beam. Atomic resolution images of the Si crystal lattice were magnified and projected onto HSQ films creating arrays of nanostructures in the resist. This technique shows promise for increased throughput where periodic arrays of simple nanoscale structures are desired.

Arrays of dot structures produced by EBL can be used to fabricate vertical nanowire arrays through the use of a deep anisotropic etch.¹⁶⁰⁻¹⁶² The use of an etch resistant material to form the dot structures is paramount to facilitate deep etching to form high aspect ratio nanowires. Typically, Al₂O₃, Al, and SiN_x, have been used as etch masks for vertical Si nanowire fabrication. Figure 9 shows an SEM image of arrays of vertical Si nanowires produced using an EBL process.¹⁶²

Commonly encountered issues for EBL processes include electron-substrate or electron-resist interactions and surface charging of insulating substrates. Electron-substrate and electron-resist effects can be grouped into three sub-classes, forward scattered electrons (scattering angle < 90°), backscattered electrons (scattering angle > 90°) and secondary electrons.¹²⁹ Forward scattered electron effects are most important within the resist as electrons which are forward scattered in the substrate have little contribution to resist exposure.

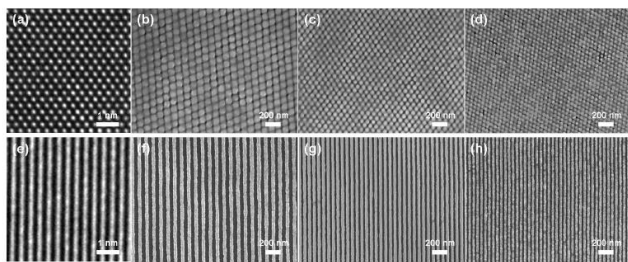


Figure 8. Arrays of HSQ nanostructures produced using projection of the atomic lattice of a Si crystal (a) and (e) in a TEM. SEM images (b-d) and (f-h) respectively show the critical dimension and pitch scaling of the structures with increasing TEM magnification, 160 × (b,f), 200 × (c,g) and 300 × (d,h).¹⁵⁹

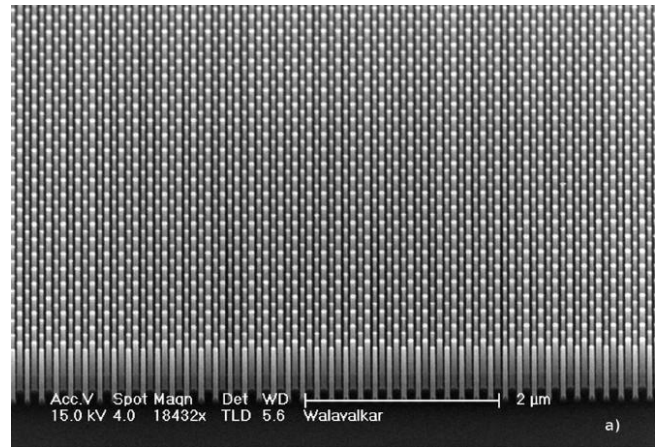


Figure 9. SEM image of an array of 50 nm diameter Si nanowires etched into a Si wafer. A sputtered Al₂O₃ hard mask, patterned by EBL was used as the Si etch mask.¹⁶²

Forward scattering can be minimised by using a high accelerating voltage (higher energy electrons) or a thinner resist layer. Backscattered electron exposure effects are more prominent for high atomic weight (Z) materials and as such are more commonly a consequence of electron-substrate interactions. Secondary electrons are the primary electron-solid interaction, and as such they make the largest contribution to resist exposure. Importantly, although secondary electrons are responsible for most of the resist exposure, their path length in the resist is short, typically < 10 nm, and as such these electrons do not have a significant contribution to proximity effects. Proximity effects can largely be attributed to backscattered electrons which experience large angle scattering and can commonly travel large distances laterally in the substrate and resist (~1 μm for 10 keV incident beam energy). Proximity effects due to electron-solid interactions can be corrected through careful modelling of electron scattering, typically as a point spread function (PSF) and the use of appropriate electron dose contour maps based on these models.^{158,163} Experimentally derived data can also be used to develop PSFs for use in proximity effect correction (PEC). PEC is particularly important for the exposure of high density features and large structures where electron scattering effects become prominent.

Charge accumulation at the surface of insulating substrates is another factor that can dramatically affect resolution and alignment in EBL. Surface charging results in an associated electric field at the substrate surface which acts to deflect the incident electron beam with detrimental effects on the EBL process. Surface charging effects can be avoided through a number of avenues. Deposition of a thin layer of conducting material (Au, Cr, Al or conducting polymers) atop the resist can remove surface charging effects, with the drawback of the introduction of an additional layer of material in the EBL process. Conducting polymers such as ESPACER (Showa-Denko), a member of the polythiophene family, are preferable to metals such as Au due to their superior process compatibility.¹²⁹ ESPACER is soluble in water and as such can be easily removed following electron beam exposure and prior to developing the resist, whereas complete removal of Au and similar metals requires harsh etching conditions which may alter

1 the resist, and the substrate. Much work has been performed 62
 2 in the field of electron-solid interactions and as such model- 63
 3 ling and correcting undesired electron-solid interactions is 64
 4 now possible.¹⁶³ However, until EBL sample throughput 65
 5 times are reduced to acceptable levels for HVM, EBL will 66
 6 remain confined to tasks such as quantum device demonstra- 67
 7 tion, NIL stamp fabrication and high-resolution photomask 68
 8 fabrication. Development of multiple beam EBL systems will 69
 9 improve the throughput of EBL tools, however such systems 70
 10 are still unproven and require further investment to compete 71
 11 with their optical counterparts for a role in next generation 72
 12 VLSI manufacturing.^{126,158,164,165} 73
 13 Electron beam induced deposition (EBID) can be used as a 74
 14 lithographic tool to produce sub-10 nm features.^{152,166} As stat- 75
 15 ed previously, EBID essentially involves introducing a gase- 76
 16 ous precursor species into the path of an electron beam in an 77
 17 EBL system. The precursor decomposes upon electron beam 78
 18 exposure and directionally deposits the solid decomposition 79
 19 product, typically a metal such as W, or Pt, on the substrate. 80
 20 EBID is a capable lithographic tool for the production of de- 81
 21 vices on a small scale.¹⁵¹ However, EBID suffers from inher- 82
 22 ent drawbacks such as metal contamination of device struc- 83
 23 tures and low throughput. Consequently, EBID is more suited 84
 24 to small-scale applications such as photomask defect repair. 85
 25 Lithography using focused beams of ions such as He⁺, Ga⁺ and 86
 26 Ne⁺ has been used to demonstrate structures with sub-10 nm 87
 27 critical dimensions.¹⁴⁹ Ions of He, Ga and Ne are significantly 88
 28 larger and heavier than electrons and as such travel shorter 89
 29 distances in resist materials than electrons. Consequently, ion 90
 30 beam lithography is a promising technique for generating a 91
 31 high-density of structures in a suitable resist material. Fur- 92
 32 thermore, Ne⁺ ions have been shown to transfer energy to HSQ 93
 33 resist more efficiently than electrons, thus facilitating high- 94
 34 resolution pattern generation at low exposure doses. In fact, 95
 35 Ne⁺ IBL has demonstrated exposure efficiencies ~1000× 96
 36 greater than electrons with equivalent landing energies.¹⁵⁰ 97
 37 Whilst Ga⁺ focused ion beam (FIB) systems are widely availa- 98
 38 ble and used for a range of applications such as TEM sample 99
 39 preparation, optical lithography mask repair and cross- 100
 40 sectional analysis, He⁺ and Ne⁺ ion beam system are far less 101
 41 common. He⁺ ion microscopy (HIM) has gained significant 42
 42 attention in recent years as it is not susceptible to surface 43
 43 charging effects commonly encountered in electron microscop- 44
 44 y, and as such may be used to acquire surface sensitive imag- 45
 45 es of insulating materials.¹⁶⁷ HIM may thus be particularly 46
 46 suited to lithography on insulating substrates. Although ion 47
 47 beam lithography techniques offer noticeable advantages over 48
 48 electron beam lithography in terms of reduced proximity ef- 49
 49 fect, increased energy transfer efficiency to the resist material 50
 50 and reduced charging effects, significant concerns still remain 51
 51 with regard to ion beam stability over the timescales required 52
 52 for full wafer exposures.^{167,168} Consequently, ion beam lithog- 53
 53 raphy is a very promising technique for next generation lithog- 54
 54 raphy, but requires significant investment for scalability of the 55
 55 technique for HVM and for techniques such as mask produc- 56
 56 tion where exposure times on the order of several hours will 57
 57 be required. 104
 58 Many of the issues associated with the implementation of 105
 59 EUV, and XRL techniques in HVM have been discussed in 106
 60 the previous section. NIL is a mechanical lithography tech- 107
 61 nique whereby a stamp or template created in a robust materi- 108

al, usually Ni or Si, for thermal NIL; PDMS for soft NIL; and quartz for step and flash NIL (S-FIL a trademark of Molecular Imprints Inc.), is pressed into a deformable resist on a substrate. The resist is then hardened so that when the template is removed the contours of the template are transferred to the resist. The patterned resist can then be used for subsequent pattern transfer procedures. NIL is a relatively inexpensive technique when compared to other nanolithography techniques and has demonstrated the production of very fine features at high areal densities.¹⁴² Feature sizes as small as 6 nm have been demonstrated, with half-pitches below 20 nm also readily achievable.¹⁶⁹ Furthermore, NIL can be used to directly pattern interlayer dielectric (ILD) materials such as low-*k* silsesquioxanes (SSQs) thus reducing the number of process steps required in the dual-damascene process typically used to form metallic interconnects.^{170,171} However, there are outstanding issues concerning overlay accuracy, defect density and throughput. Furthermore, NIL processes are mask specific and as such must be tuned to achieve the optimal resist volume for specific mask designs, which can limit the technique where large area patterns are required. Additionally, NIL may not be compatible with pattern transfer to porous low-*k* materials used as back-end-of-line (BEOL) insulators, which are inherently brittle and may be deformed by the pressure applied during NIL.¹⁴²

Scanning probe lithography (SPL) encompasses a range of lithography techniques including, dip-pen nanolithography (DPN), local oxidation nanolithography (LON), atomic force microscope (AFM) lithography and scanning tunnelling microscope (STM) lithography. Common to these techniques is the use of a scanning nanoscale probe, typically an AFM tip, to pattern a resist or substrate directly.^{172,173} In the case of DPN an AFM tip is used to transfer a material to the surface which can subsequently act as an etch mask or may act as an active device component itself. LON is used to locally oxidise a material thus forming a patterned surface oxide by applying a voltage bias between a conductive AFM tip and the substrate material in the presence of water vapour to induce localised oxidation of the substrate through electrochemical reaction with the water vapour.

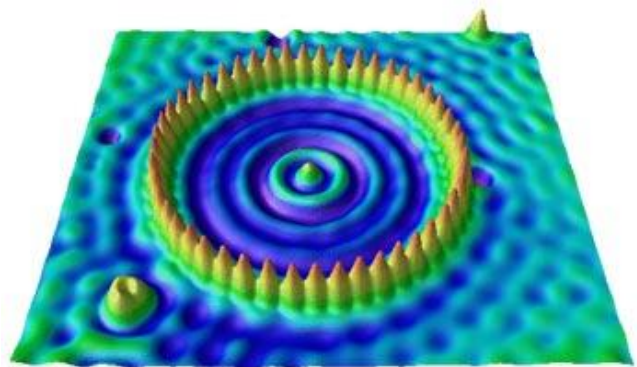


Figure 10. False colour STM image of a quantum corral structure created by the atomic manipulation of 48 Fe atoms on a Cu {111} surface. The Fe ring confines the surface electron wavefunction of the defect free Cu surface within.¹⁷⁴

AFM lithography can operate in contact mode or non-contact mode. Contact mode AFM lithography involves the mechan-

1 ical patterning of a substrate much like NIL. An AFM tip can 60
 2 be used to scratch or stamp a pattern into a resist material or 61
 3 into the substrate itself. Non-contact mode AFM can be used 62
 4 to pattern materials through local oxidation of the substrate 63
 5 surface as in the case of LON, through local heating of a resist 64
 6 material using a heated AFM tip, or through local electron 65
 7 exposure via a field emission AFM tip.^{172,173} STM lithography 66
 8 has been used to produce nanostructures by a variety of 67
 9 means. Scappucci *et al.* have reported the use of STM to se- 68
 10 lectively dope regions on a H-terminated Ge (100) surface 69
 11 where H atoms have been removed by STM, thus creating 70
 12 doped nanowire structures.¹⁴⁸ STM can also be used for the 71
 13 individual manipulation of atoms on a surface to produced 72
 14 quantum structures, such as the quantum corral reported by 73
 15 Crommie *et al.* in 1993 (figure 10).¹⁷⁴ SPM lithography tech- 74
 16 niques are inherently slow even when multiple probes are 75
 17 used.¹⁷⁵ As such, low throughput will prevent such techniques 76
 18 from being used in HVM.¹⁷⁵

19 3.3. Top-Down Semiconductor Nanowire Fabrication 78

20 Outlook 79

21 Top-down semiconductor lithography processes have domi- 81
 22 nated the area of semiconductor device definition and place- 82
 23 ment for decades. However, as the density of devices on a 83
 24 chip continues to scale significant difficulties are encountered. 84
 25 Techniques such as EBL and XRL with significantly reduced 85
 26 wavelengths, may readily achieve the high densities of devices 86
 27 desired by the semiconductor industry, however, there are a
 28 number of difficulties associated with the integration of these
 29 short wavelength techniques in VLSI manufacturing. Conse-
 30 quently, it seems increasingly likely that current top-down
 31 processes may have to 'reach out' to a bottom-up technology
 32 to achieve the future goals of the semiconductor industry.
 33 Integration of bottom-up fabricated VLS nanowires in VLSI
 34 manufacturing may be a step too far in the short term as the
 35 VLSI industry is geared toward device fabrication in the plane
 36 of the Si wafer, and integration of vertically oriented and
 37 stacked FETs will require extensive design and process recon-
 38 figuration. Consequently, a bottom-up technique that facili-
 39 tates continued scaling in the plane of the substrate may be a
 40 more likely first step toward the integration of a bottom-up
 41 technique in VLSI manufacturing. One such bottom-up tech-
 42 nique is that of directed self-assembly of block copolymers.

43 4. Integration of Bottom-Up and Top-Down Processes 87

44 for Nanowire Array Fabrication 88

45 4.1. Directed Self-Assembly 89

46 Directed self-assembly (DSA) is an advanced lithographic 88
 47 process based on the self-assembly of block copolymer (BCP) 89
 48 thin films. BCP self-assembly involves the bottom-up, mi- 90
 49 crophase separation of chemically different blocks within the 91
 50 BCP. Typically, A-B diblock copolymers are used for DSA, 92
 51 where an A-B diblock copolymer consists of a linear chain of
 52 a monomer A, joined at one end by a covalent bond, to a line-
 53 ar chain of monomer B. When the two blocks, A and B, are
 54 sufficiently chemically distinct from one another, they can
 55 microphase separate so as to minimise the interaction of
 56 blocks A and B, whilst maximising the interaction between
 57 similar blocks. The chemical interaction of the two blocks in
 58 a BCP is often quantised by the Flory-Huggins interaction
 59 parameter (χ) for that BCP system which is related to the en-

thalpy of mixing for that polymer system.¹⁷⁶ Self-consistent
 mean field theory has been used to generate theoretical phase
 diagrams for diblock copolymer melts (figure 11).¹⁷⁷ Mean
 field phase diagrams are presented as a plot of χN against f ,
 where N is the degree of polymerisation of the BCP and f is
 the volume fraction of a reference block in the BCP. χN is
 representative of the thermodynamic driving force for mi-
 crophase separation within the diblock copolymer melt. χ
 represents the enthalpic component and is inversely related to
 temperature and directly related to polymer chain length,
 whilst N represents the entropic component, which depends on
 the chain length dependent number of conformations that can
 be adopted by the polymer.

Figure 12 shows schematic examples of phase morphologies
 within a microphase separated A-B diblock copolymer with
 increasing number fraction of block A (f_A).¹⁷⁶ Lamellar and
 hexagonally close packed cylinder phases of BCPs are typical-
 ly used in DSA, where the phase of the BCP can be controlled
 through selection of appropriate polymer fractions in the BCP,
 and suitable polymer chain lengths. The microphase separa-
 tion of BCPs can be guided both chemically and physically
 through the use of careful templating techniques, *i.e.* directed
 self-assembly. Physically guided microphase separation of a
 BCP is often termed graphoepitaxy. DSA of lamella forming
 BCPs by graphoepitaxy, is generally achieved by creating
 trenches in a substrate where the trench width is an integer
 multiple of the block length.^{176,178}

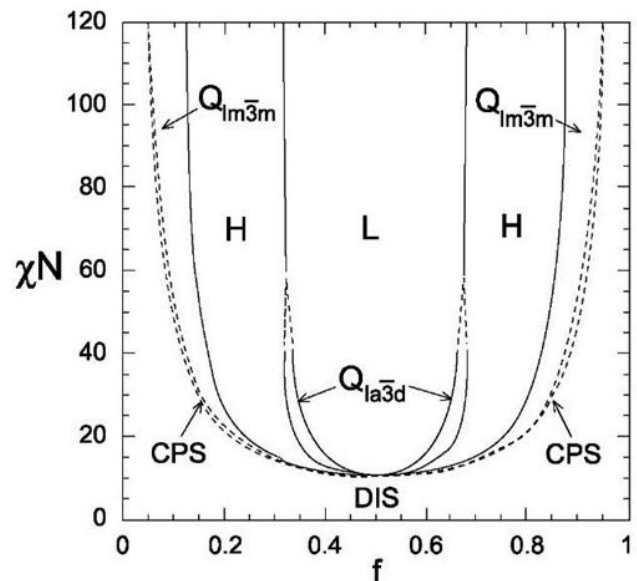


Figure 11. Phase diagram of a diblock copolymer as predicted by self-consistent mean field theory. Phases are labelled L (lamellar), H (hexagonally arranged cylinders), Q_{la3d} (bicontinuous I_{a3d} cubic), Q_{lm3m} (body centred cubic spheres), CPS (close packed spheres), and DIS (disordered).¹⁷⁷

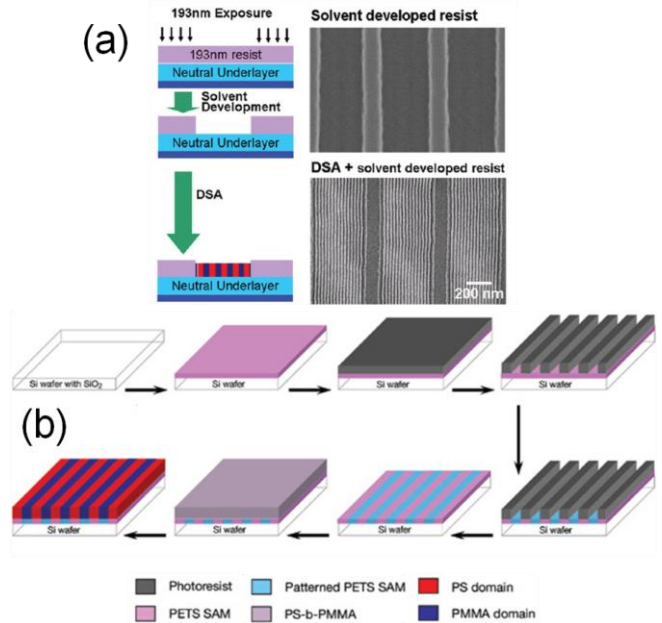
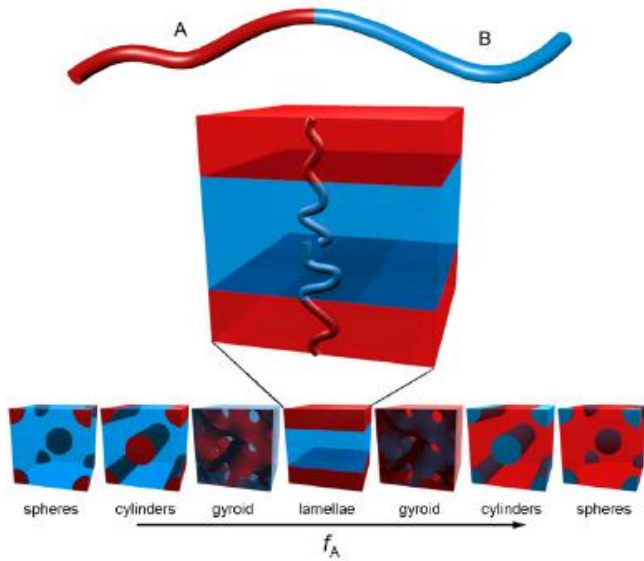


Figure 13. Typical process flows used to produce DSA of BCPs via (a) graphoepitaxy and (b) chemical epitaxy, respectively.^{180,188}

LER values as low as 1.95 nm (3σ) have been reported for lines produced by DSA of a lamella forming BCP.¹⁷⁹

However, there are a number of outstanding concerns associated with DSA as a lithographic technique. The primary concern with the process is high defect density, attributable to contamination, BCP purity, BCP molecular weight distribution, chemical uniformity of the substrate surface and defects within the DSA guiding template. Substrate surface uniformity is known to be a critical factor in achieving large areas of uniformly oriented microphases in BCP films. Consequently, there has been a large research investment in the study of self-assembled molecular monolayers and polymer brush layers to tailor the substrate surface energy, and BCP wetting, for BCP self-assembly.^{179,189–192} Additionally, BCP layers are often prepared as thin monolayers of the microphases *e.g.* a single layer of substrate coplanar cylinders in the case of PS-*b*-PDMS, and often have poor etch resistance, *e.g.* PMMA, PS.

Whilst the defect density in DSA masks is improving with increased research investment, DSA processes still require further optimisation before they can be integrated into a HVM landscape. Figure 14 shows an example of relatively large area patterning achieved via the graphoepitaxy of PS-*b*-PDMS.¹⁸² Chemical epitaxy DSA techniques can ‘heal’ defects present in the guiding template; however, chemical epitaxy has not yet demonstrated pattern multiplication to the extent of graphoepitaxy based techniques. Thus, it is likely that each approach, chemical epitaxy and graphoepitaxy, will find their own niche application within the semiconductor industry. Development of DSA masks with sufficient etch resistance will depend on the specific process requirements. PS-*b*-PDMS for example, is a promising material for DSA when a high etch resistance to Si etchants is required. PDMS has an inorganic Si-O backbone and as such offers superior etch resistance relative to organic polymers.

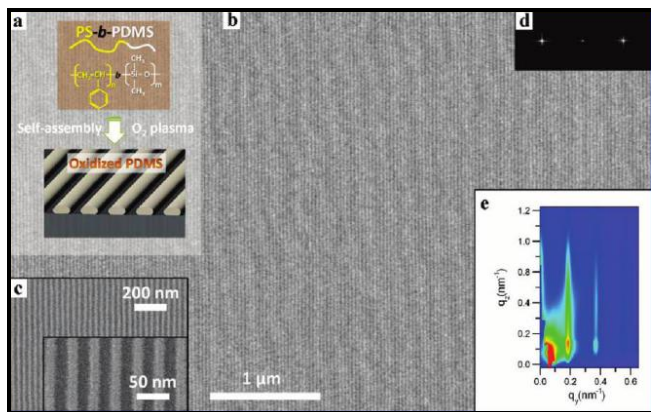


Figure 14. (a) A schematic of the structure of PS-*b*-PDMS and the structure formed by DSA. (b) SEM image showing large-scale alignment of PDMS lines produced by the graphoepitaxy of PS-*b*-PDMS within 10 μm wide, PDMS brush coated trenches etched in a Si wafer. (c) Higher magnification images of the aligned PDMS lines. (d) FFT of the image in (b) consistent with excellent long-range ordering. (e) Grazing incidence small angle x-ray scattering (GISAXS) pattern generated from a 1 cm^2 area of the PDMS line pattern.¹⁸²

The outlook for DSA is promising. DSA has already demonstrated the requisite resolution capabilities for continued device scaling outlined within the International Technology Roadmap for Semiconductors (ITRS), defect density levels are dropping with continued research investment and issues regarding production of device specific geometries appear to be resolvable using chemical epitaxy approaches.¹⁷⁹ LER and CD control issues also need to be addressed to meet ITRS specifications.¹⁷⁹ Theoretical models predict LER to be related to $\chi^{0.5}$, in which case, BCP systems with high χ values such as PS-*b*-PDMS ($\chi \sim 0.26$ at room temperature) are worthy of further investigation.¹⁸²

Self-assembly of cylinder and sphere forming BCPs has also been used to produce ordered arrays of metal nanoparticles by both additive¹⁹³ and subtractive¹⁹⁴ processes. These metal nanoparticles may then be used to produce epitaxial growth of semiconductor nanowires by means of the relevant techniques outlined in Section 2. Furthermore, the metal nanoparticles may be used as etch masks to produce ordered arrays of vertical nanowires by a top-down approach. The use of BCP films to template catalysts for epitaxial nanowire growth and to template hard masks for top-down vertical nanowire array formation is an example of a synergistic process, employing both bottom-up and top-down methods. This synergistic process is to date, a poorly explored application of BCP lithography which warrants further investigation.

DSA is a promising blend of top-down and bottom-up techniques for advanced lithography applications. DSA allows a route to increased pattern resolution and feature density relative to conventional optical lithographic means, and whilst concerns still exist over LER, CD control and reproducibility, these concerns are gradually being improved by continued advances in the field. DSA depends on conventional lithography techniques such as optical lithography, interference lithography and EBL to form guiding templates to direct the self-assembly of BCPs and as such it will remain a complementary

lithography technique. However, if and when the issues associated with DSA are resolved, this lithography technique may alleviate the growing demands on optical lithography and EUV for continued device scaling, thus extending the use of current optical lithography techniques in VLSI manufacturing.

4.2. Lithographic Catalyst Placement for Bottom-Up Nanowire Growth

EBL is a suitable tool for the preparation of ordered arrays of metal nanoparticles by subtractive or additive processes. Ordered arrays of metal nanoparticles can be readily prepared using a positive tone EBL process to generate a metal lift-off mask.^{25,88,97,195} This process can be used to produce epitaxial nanowire growth via a VLS-type mechanism through careful control of the metal substrate interface, and choice of an appropriate substrate material, using nanowire growth methods such as those outlined in section 2. Coupling EBL and self-assembly of BCPs allows the production of defect free high-density arrays of dot structures.¹⁹⁶

Similarly, phase shift lithography and interference lithography have been shown to be capable of producing very fine dot structures for the fabrication of metal nanoparticle arrays.^{197,198}

Metal nanoparticle arrays formed by these methods, too, could be used for the fabrication of nanowire arrays by bottom-up means.

4.3. Nanosphere Lithography

Nanosphere lithography (NSL) can be used to produce ordered arrays of vertical nanowires. NSL uses the bottom-up self assembly of spherical particles, such as polystyrene spheres, to create dot/anti-dot arrays on the surface of a substrate, which then may be used to transfer the pattern to the substrate creating structures such as vertically aligned nanowire arrays.^{21,199–201} NSL can be used to produce arrays of vertical Si nanowires using a metal-assisted etching approach as shown in figure 15 below. Combined use of NSL and metal-assisted etching (MAE) provides a route to forming arrays of long ($> 10 \mu\text{m}$) Si nanowires which have applications in fields such as vertical ICs and solar cells (figure 15).²¹ NSL can also be used to create an anti-dot array mask for the evaporation of arrays of metal nanoparticles for use as catalysts for epitaxial nanowire growth.¹⁹⁹

4.4. Miscellaneous Synergistic Nanowire Fabrication Processes

A range of processes exist which use both bottom-up and top-down techniques in tandem to produce semiconductor nanowires. One example of such a technique is the superlattice nanowire pattern transfer (SNAP) technique.²⁰² The SNAP technique is based on the formation of a stamp by selectively etching one of the layers in a superlattice material grown by a bottom-up epitaxy technique, such as MBE. Angular deposition of a metal on the etched superlattice then allows creation of a metal stamp which is pressed against the material of choice producing a metal grating which acts as an etch mask for the fabrication of nanowire arrays by pattern transfer.

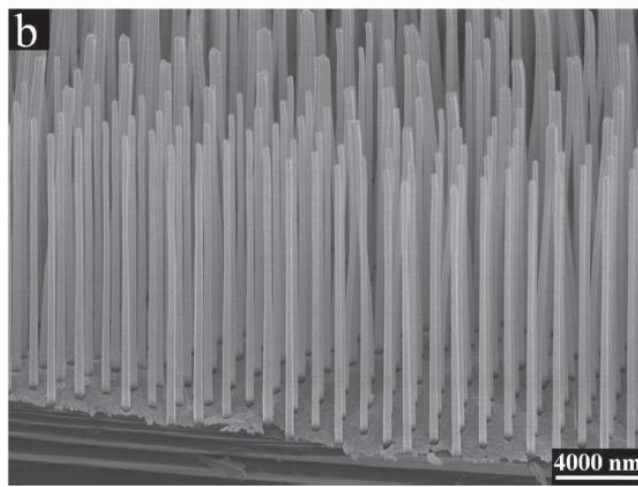
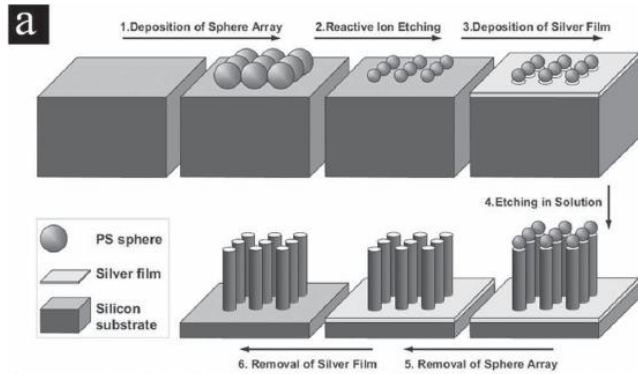


Figure 15. Schematic of NSL process for the fabrication of vertical Si nanowire arrays via MAE.^{201,203}

Figure 16, shows a schematic of the SNAP process. The SNAP process has been used successfully to produce arrays of Si nanowires from SOI, as well as metal nanowires formed directly from the stamp. However, the technique is limited in terms of the geometries of the structures that can be produced, and the complexity of the process for large-scale nanowire fabrication. Furthermore, the SNAP technique is susceptible to many of the pitfalls associated with NIL outlined in Section 3.2. NIL can be used to create arrays of metal nanoparticles for bottom-up nanowire growth.²⁰⁴ This process involves imprinting a bilayer positive-tone resist, developing the imprinted resist and evaporating a metal layer to produce arrays of metal nanoparticles by lift-off. The metal nanoparticles can subsequently be used as catalysts for nanowire array production by standard nanowire growth procedures.

AAO membranes with HCP pore arrangements are formed by a bottom-up process, as discussed in Section 2.2. When prepared as thin films, these ordered porous AAO membranes can be used as masks to produce patterned metal films on Si substrates for MAE of Si, producing ordered arrays of vertical Si nanowires.^{205,206} MAE techniques using patterned metal layers are successful at producing dense, ordered arrays of vertical nanowires with high aspect ratios. However, as with all MAE techniques, the nanowires produced have rough sidewalls thus inhibiting their use in logic applications where surface scattering of charge carriers is a significant drawback.^{201,207}

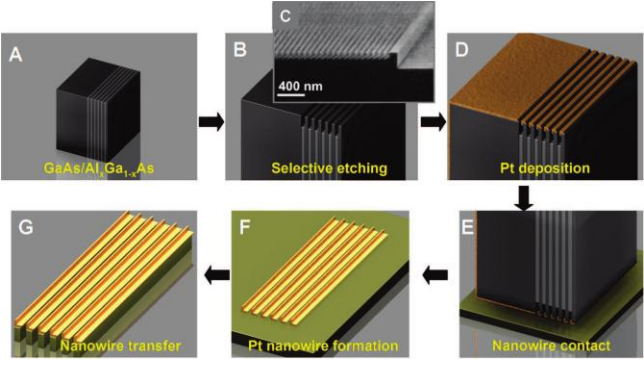


Figure 16. Schematic of the SNAP process for production of aligned nanowires.²⁰²

Nanowires produced by these methods are likely to find applications in solar cell, thermoelectric generator, sensor or battery anode applications where the increased surface area of nanowires with rough sidewalls may be beneficial to device performance.^{208,209}

Ion track etched membranes are an example of another nanowire template material. These membranes are formed in a top-down process by ion etching of a polymer material, producing cylindrical or tapered pores. Infilling ion track etched membranes by methods such as electrodeposition can produce arrays of nanowires.²¹⁰ Whilst this method can be used to produce some interesting network structures (figure 17), it is unlikely to find use in VLSI manufacturing due to the complexity of the process and the difficulty producing single-crystalline materials within these membranes.

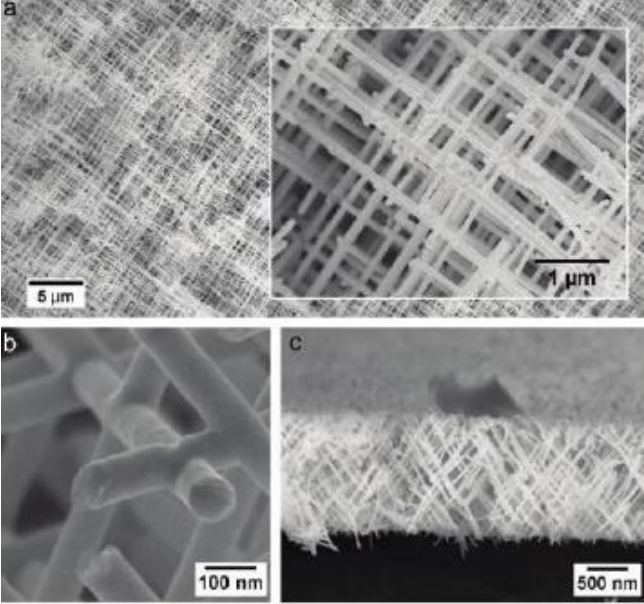


Figure 17. SEM images of polycrystalline Pt nanowire networks produced within ion track etched membranes: (a) low magnification SEM images of Pt nanowire networks, (b) high magnification SEM image of nanowire junctions and (c) cross-section of a nanowire network composed of 35 nm diameter nanowires.

5. Emerging Semiconductor Nanowire Materials

5.1. High Mobility Materials for Next Generation CMOS Devices

High charge carrier mobility materials have been subject to significant research investigation in the past few decades. These materials offer increased transconductance relative to Si, and as such, devices constructed from these materials may achieve similar drive current at lower power, or operate as high performance devices at equivalent power, to current Si devices.²¹¹ Many materials are under consideration for integration in future CMOS devices due to their increased charge carrier mobility relative to Si.^{12,211–213} Ge, for example, exhibits hole mobility over four times that of Si, and as such is a strong contender for use in future p-FET devices. Likewise, InSb, InAs and graphene demonstrate massively increased electron mobility relative to Si.^{212,214} However, these high mobility materials are not without their drawbacks. Often, Ge and III-V materials possess complex native oxides with poor chemical or electrical properties for device fabrication.¹¹² GeO₂, a component of the complex native oxide on Ge crystals, is water soluble and as such must be removed or capped with a more suitable material to facilitate processing steps involved in device manufacturing. Additionally, GeO, another component of the native oxide on Ge, desorbs at temperatures above 400 °C, which may result in detrimental effects on overlying layers during annealing steps in device manufacturing. Similar difficulties have been reported for III-V materials such as GaAs and In_{1-x}Ga_xAs, whose complex native oxides prevent the formation of a stable semiconductor-insulator interface. The result is a high density of interface states at the semiconductor-insulator interface in the gate stack.^{111,215} Interface states often lie near the mid band-gap of the semiconductor and can lead to Fermi-level pinning at the semiconductor surface. Fermi-level pinning can result in a number of detrimental effects on device performance, including, rectifying characteristics in metal-semiconductor contacts, and depletion of free charge carriers in the device channel at the semiconductor-insulator interface.^{104,216} Interface states result from unsaturated surface atoms, which act as charge acceptors and donors at the semiconductor surface. Consequently, reduction of the density of interface states is dependent on the formation of a stable and saturated semiconductor surface. There have been significant investigations into improvement of the electrical and chemical interfaces with these materials to facilitate their integration within next generation CMOS devices. The use of a capping Si layer of the order of a few monolayers thickness has been successful in reducing the density of interface states (D_{it}) in GaAs from 10^{13} cm⁻² eV⁻¹ to 10^{11} cm⁻² eV⁻¹.¹²¹⁵ Similarly, deposition of SiO₂ directly on an untreated Ge surface results in a relatively high D_{it} of 10^{13} cm⁻² eV⁻¹, whilst formation of a Ge₍₁₀₀₎/GeO_xN_y/HfO₂/Pt gate stack produced a D_{it} of 3×10^{11} cm⁻² eV⁻¹.^{111,112} A further promising route toward improving the interface of inorganic semiconductor materials with gate-dielectric layers may be through the use of appropriate organic dielectric material chemically tethered to the semiconductor. Extensive research has been pursued in the field of chemical functionalisation of Ge and III-V surfaces with high coverage of organic ligands.^{217–219} High- k organic gate-dielectrics have been investigated primarily for use with organic FET devices, and have demonstrated competitive lev-

els of performance when compared with current VLSI devices.²²⁰ Consequently, the molecular tethering of high- k organic molecules directly to these surfaces may allow a route to high- k insulating layers with low D_{it} , thus improving device performance.

Graphene has demonstrated impressive electrical performance in reported device applications with charge carrier mobilities as high as 230000 cm²V⁻¹s⁻¹.²²¹ However, there are a number of outstanding concerns with regard to the integration of graphene in VLSI manufacturing. Firstly, pristine graphene is a zero-gap semi-metal and as such exhibits poor switching behaviour in logic device applications. Significant efforts have been made to introduce a large and reproducible band-gap into graphene. These efforts have included quantum confinement of graphene within graphene nanoribbon (GNR) structures, doping, edge functionalisation and use of bilayer graphene.²²¹ Additionally, there are serious concerns regarding graphene processing for device fabrication. Production of large area, single layer graphene is a challenging task, and handling such a delicate material has associated difficulties. Metals and gate-oxides exhibit poor adhesion to graphene and graphene layers are extremely vulnerable to plasma induced damage.²²² Despite the many concerns regarding implementation of graphene in CMOS manufacturing, it maintains a massive research impetus and is firmly implanted on the ITRS for continued investigation.¹²

Similarly, carbon nanotube (CNT) structures have been investigated heavily for use as FET semiconductor channels and as metallic interconnect materials.²²³ The primary difficulty with CNT material preparation for FET and interconnect applications is controlling the electronic band structure of the material, which is dependent on CNT growth direction, and diameter.²²⁴ Furthermore, CNTs are subject to alignment and integration issues inherent to bottom-up nanowire and nanotube synthesis techniques as outlined in section 2.2.

The introduction of high- k dielectric materials in the gate stack of the active devices in VLSI manufacturing in recent years has paved the way for the introduction of high mobility, non-Si materials for FET applications. Materials such as Ge and III-Vs have long been held back by issues associated with their complex native oxides. However, the transition of the semiconductor industry from a SiO₂ gate dielectric to materials such as HfO₂, Al₂O₃ and ZrO₂,⁵⁹ has reignited interest in these high mobility materials. Consequently, there has been heavy research investment in the preparation of high- k materials on high mobility materials in recent years.^{111,112}

6. Nanowire Fabrication Outlook

The continued scaling of semiconductor devices in the VLSI industry has created a landscape where the introduction of nanowire or nanoribbon devices into mass production seems increasingly likely. As the density of semiconductor devices in VLSI architectures increases there has been an associated shift of the semiconductor channel from a planar orientation, to the recently developed fin structure where the semiconductor channel is raised above the surface of the Si wafer. A natural progression from the finFET or tri-gate structure would appear to be a nanowire structure, be it lateral – parallel to the substrate – or vertical. The benefits of nanowires have been highlighted for a number of years now. Semiconductor nan-

1 owires allow production of GAA devices which offer superior 60
 2 control of the device channel and thus improved switching
 3 speed and on/off ratios. A nanowire structure can also be used
 4 to create quantum well, core-shell structures with improved
 5 electrical transport properties relative to standard structures.
 6 Nanowires may also incorporate strain, a prerequisite in current
 7 VLSI devices^{16,225,226}, through the incorporation of dopants
 8 or a lattice mismatched shell material.^{227,228}

9 The exact fabrication route to future semiconductor nanowire-
 10 based integrated circuits is as yet, unclear; however, it is quite
 11 probable that the route will incorporate both top-down and
 12 bottom-up techniques in tandem to allow a scalable path to
 13 nanowire integrated circuit fabrication. Bottom-up nanowire
 14 growth processes allow routes to structures that may not be
 15 produced by top-down means, and also may allow production
 16 of exotic channel materials that may not be accessible in the
 17 bulk wafer form. Bottom-up grown semiconductor nanowires
 18 often exhibit faceted surfaces that may not be achieved by top-
 19 down fabrication. Control of the crystal surface facets formed
 20 during nanowire growth, may allow control over the density of
 21 interface states formed at nanowire surfaces, which is particu-
 22 larly important for Ge and III-V materials to develop improved
 23 device performance. Top-down processes such as optical and
 24 electron beam lithography consistently demonstrate their supe-
 25 riority in the nanometre control of device definition and
 26 placement. DSA of BCP films is an example of the synergistic
 27 cooperation of a bottom-up self-assembly process and tradi-
 28 tional top-down lithography, allowing routes to aligned pat-
 29 tern multiplication, which is not feasible by either technique
 30 alone. As such, a conservative prediction would be that future
 31 nanowire-based electronics will be fabricated by a cooperative
 32 mix of both bottom-up and top-down processes.

33 Table 1, summarizes the achievable minimum feature sizes,
 34 and potential feature pitch, using a number of top-down and
 35 synergistic fabrication processes. All of the techniques listed
 36 in table 1 are suitable for the fabrication of nanowire arrays.
 37 However, the choice of a suitable technique for the fabrication
 38 of a particular nanowire system requires the consideration of
 39 all aspects of the fabrication technique, and not merely the
 40 ultimate resolution. AAO for example is usually used to pre-
 41 pare arrays of nanowires oriented vertically with respect to a
 42 substrate. Interference lithography is suited to the fabrication
 43 of linear arrays of nanowire structures and does not typically
 44 allow routes to arbitrary shapes and nanowire layouts such as
 45 those achievable via top-down optical lithography or direct-
 46 write charged particle lithography. Consequently, considera-
 47 tion of a number of fabrication techniques may be required
 48 when developing a nanowire fabrication process, and the ben-
 49 efits and drawbacks of each technique should be carefully
 50 weighed against one another so as to identify the technique
 51 best suited to the fabrication of the desired product.

Fabrication Technique	Minimum Feature Size	Linear Feature Pitch
Top-Down Optical Lithography	< 10 nm	< 40 nm ¹⁴⁶
Interference Li-thography	< 15	< 25 nm ^{133,198}
Direct-Write Charged Particle Lithography	< 5 nm	< 10 nm ¹⁵⁵
NIL	< 10 nm	< 20 nm ¹⁴²
SPL	< 1 nm	< 2 nm ¹⁷²
DSA	< 5nm	< 20 nm ^{179,229}
AAO	< 20 nm	< 50 nm ²³⁰
Bottom-Up EBL Synergy	< 30 nm ²⁵	< 500 nm
NSL	< 15 nm	~ 200 nm ²³¹

Table 1. Minimum feature sizes and potential minimum linear feature pitch achievable by a number of top-down and synergistic lithography techniques.

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Table of Contents Figure

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Semiconductor
Nanowire Fabrication by
Bottom-Up and
Top-Down Paradigms

This review article highlights the important considerations required for the continued advancement of semiconductor nanowire fabrication for next-generation field-effect transistor devices.

