Assembly

ESS5855 Lecture
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Contents

• Micro-assembly
• Self-assembly
  – In a general sense, might be defined as the spontaneous formation of complex hierarchical structures from pre-designed building blocks, typically involving multiple energy scales and multiple degrees of freedom
Microassembly Technologies for MEMS

R.T. Howe’s Group, U.C. Berkeley
SPIE, 1998

Abstract

Microassembly promises to extend MEMS beyond the confines of silicon micromachining. This paper surveys research in both serial and parallel microassembly. The former extends conventional “pick and place” assembly into the micro-domain, where surface forces play a dominant role. Parallel assembly involves the simultaneous precise organization of an ensemble of micro components. This can be achieved by microstructure transfer between aligned wafers or arrays of binding sites that trap an initially random collection of parts. Binding sites can be micromachined cavities or electrostatic traps; short-range attractive forces and random agitation of the parts serve to fill the sites. Microassembly strategies should furnish reliable mechanical bonds and electrical interconnection between the micropart and the target substrate or subassembly.
Serial Micro-Assembly

- Requiring an infrastructure of micro-tools and micro-parts designed to interface with each other and the macroscopic world
Hexsil Tweezers for Teleoperated Micro-Assembly

R.T. Howe’s Group, U.C. Berkeley
MEMS 1997

Abstract

This paper describes essential components of a prototype system for teleoperated microassembly. High aspect ratio molded polysilicon (hexsil) tweezers with integrated in-situ phosphorous doped thermal expansion actuator beams and piezoresistive polysilicon strain gauges for tactile feedback are described. The tweezers are normally closed, and require 75 mW to open 35 um. Piezoresistor performance remains to be measured. Metal lines on surface polysilicon flexible electrical interconnects bridge between rotating rigid hexsil beams. Surface polysilicon tweezer tips provide compliance suitable for force-controlled micromanipulation. The task demonstrated is the pick and placement of a 1 um x 4 um x 40 um peg in a 4 um x 4 um hole. The test parts used were surface micromachined SiO$_2$ and polysilicon beams held in organized arrays on the silicon wafer by break-away photoresist tethers.
Assembly of Hinged Structures

- Out-of-plane structures
- Manual assembly
- On-chip MEMS actuation
- Fluidic agitation
- Parallel external methods
Single-Step Assembly of Complex 3-D Microstructures

R.T. Howe’s Group, U.C. Berkeley
MEMS 2000

Abstract

This paper describes three-dimensional microstructures fabricated in a planar process and assembled in a single step. Multiple plates are constrained by hinges in such a way as to reduce the assembly process to a single degree-of-freedom of motion. Serial micro-assembly of these structures is simpler; moreover, self-assembly using hydrodynamic forces during release is much more feasible than with earlier, multiple degree-of-freedom hinged structures. A 250-um corner cube reflector, a 6-sided closed box, and a 3-D model of the Berkeley Campanile clock tower have been demonstrated in the 4-level polysilicon SUMMiT MEMS foundry.
Surface Tension-Powered Self-Assembly of Microstructures - The State-of-the-Art

G.M. Whitesides, et al., Harvard U.
J. MEMS, 2003
Abstract

Because of the low dimensional power of its force scaling law, surface tension is appropriate for carrying out reshaping and assembly in the microstructure size domain. This paper reviews work on surface tension powered self-assembly of microstructures. The existing theoretical approaches for rotational assembly are unified. The demonstrated fabrication processes are compared. Mechanisms for accurately determining the assembled shape are discussed, and the limits on accuracy and structural distortion are considered. Applications in optics, electronics and mechanics are described. More complex operations (including the combination of self-assembly and self-organization) are also reviewed.

Surface Tension Powered Rotation

[Diagrams showing the process of surface tension powered rotation]
Sacrificial Layer Process with Laser-Driven Release for Batch Assembly Operations

A.S. Holmes’s Group, Imperial College, U.K.
J. MEMS, 1998
Abstract

A dry sacrificial layer process is presented in which microstructures fabricated on UV-transparent substrates are released by excimer laser ablation of a polymer sacrificial material using laser light incident from the reverse side of the substrate. We investigate the application of this technique to the batch assembly of hybrid microelectro-mechanical systems (MEMS) built from parts fabricated on different substrates. Preliminary measurements of initial velocity are presented for nickel test structures released from polyimide sacrificial layers using a KrF excimer laser. At fluences in the range 50–250 mJ/cm² (i.e., close to the ablation threshold), structures with heights of 100 um are shown to exhibit initial velocities in the range 1–5 ms⁻¹, allowing controlled transfer of parts between substrates. Application of the new assembly method to a MEMS device is demonstrated by assembling arrays of electrostatic wobble motors from component parts fabricated on separate substrates by UV-LIGA processing.
Stochastic Parallel Assembly

- Mediated by thermal motion and interfacial forces
- Evolving toward a state of minimal potential energy

Thermokinetic Actuation for Batch Assembly of Microscale Hinged Structures

A. Lal’s Group, Cornell U.
J. MEMS, 2003
Abstract

This paper reports on surface micromachined hinged structure assembly using thermokinetic forces in the molecular flow regime. Ultrasonic vibration energy is used to reduce the static friction making the thermokinetic force comparatively significant. The thermokinetic force, resulting from the more energetic gas molecules emanating from the heated substrate, increases with pressure and substrate temperature in the molecular flow regime. The transition from viscous to molecular regime occurs as the molecular mean-free-path approximately equals the flap length, making the pressure threshold for thermokinetic flap actuation size dependent. In addition to the experimental results, one-dimensional (1-D) and two-dimensional (2-D) force models are presented. Examples of assembled structures are shown and assembly jig suitable for automated MEMS batch assembly is demonstrated.

Principles

• In the viscous regime, the gas molecules leaving the substrate equilibrate with ambient before impacting the flap and there is no net force
• As the pressure is decreased, the mean-free path increases and becomes comparable to the flap dimensions
• The molecules impacting the flap result in a net force perpendicular to the substrate
• Short flaps are expected to lift up at a higher pressure than tall flaps
• The flaps stabilize perpendicular to substrate, as momentum from impacting molecules is equal on both sides of the flaps
Thermokinetic Force
Abstract

We have demonstrated the fluidic self-assembly of micromachined silicon parts onto silicon and quartz substrates in a preconfigured pattern with submicrometer positioning precision. Self-assembly is accomplished using photolithographically defined part and substrate binding sites that are complementary shapes of hydrophobic self-assembled monolayers. The patterned substrate is passed through a film of hydrophobic adhesive on water, causing the adhesive to selectively coat the binding sites. Next, the microscopic parts, fabricated from silicon-on-insulator wafers and ranging in size from 150x150x15 μm³ to 400x400x50 μm³, are directed toward the substrate surface under water using a pipette. Once the hydrophobic pattern on a part comes into contact with an adhesive-coated substrate binding site, shape matching occurs spontaneously due to interfacial free energy minimization. In water, capillary forces of the adhesive hold the parts in place with an alignment precision of less than 0.2 μm. Permanent bonding of the parts onto quartz and silicon is accomplished by activating the adhesive with heat or ultraviolet light. The resulting rotational misalignment is within 0.3°. Using square sites, 98-part arrays have been assembled in less than 1 min with 100% yield. The general microassembly approach described here may be applied to parts ranging in size from the nano- to milliscale, and part and substrate materials including semiconductors, glass, plastics, and metals.
Capillary Forces

- Oxidize and glass surfaces: hydrophilic
- Self-assemble monolayer on gold: hydrophobic

\[ \gamma_{12} \cos \theta = \gamma_{23} - \gamma_{13} \]

Capillary Forces

- Patterned substrate is passed through hydrocarbon adhesive-water interface

H. Biebuyck et al., Langmuir, 1994
Capillary Forces

• Separate surfaces into hydrophobic and hydrophilic regions
• Coat substrate sites selectively with hydrophobic liquid
• Match hydrophobic binding sites

Capillary Forces

• The adhesive layer acts as a lubricant, facilitating movement of the part so the amount of SAM and adhesive surface area in contact with water is cooperatively minimized, thereby minimizing the interfacial free energy of the system
• This spontaneous shape matching occurs within 1 second; increasing the viscosity of the adhesive has been shown to slow the self-alignment step
Capillary Forces

- Once assembled, a part does not become unstuck at the level of agitation required to move the unbound parts over the substrate or when the substrate is turned upside down.

- For a self-assembled disk with binding site of diameter 200 um, we have estimated that a force on the order of $10^{-4}$ N is required to overcome the capillary “bond” in the z-direction.

- This is compared to drag force ($10^{-7}$ N) and gravitational force ($10^{-8}$ N).

- With a constant supply of parts, it should be possible to rapidly assemble large arrays with high yield.

Fabrication of a Cylindrical Display by Patterned Assembly

Abstract

We demonstrate the patterned assembly of integrated semiconductor devices onto planar, flexible, and curved substrates on the basis of capillary interactions involving liquid solder. The substrates presented patterned, solder-coated areas that acted both as receptors for the components of the device during its assembly and as electrical connections during its operation. The components were suspended in water and agitated gently. Minimization of the free energy of the solder-water interface provided the driving force for the assembly. One hundred and thirteen GaAlAs light-emitting diodes with a chip size of 280 micrometers were fabricated into a prototype cylindrical display. It was also possible to assemble 1500 silicon cubes, on an area of 5 square centimeters, in less than 3 minutes, with a defect rate of ~2%.
Sequential Self-Assembly by Controlling Interactive Forces between Microparticles

I. Shimoyama’s Group, U. Tokyo
MEMS 2004

Abstract

This paper describes binding-sequence control in self-assembly of micro-particle by changing interactive forces from the outside. We demonstrated a sequential self-assembly with two binding steps. At the 1st step, the microparticles start to bind to each other on their hydrophobic surfaces in aqueous solution. By changing the pH of the solution, the particles subsequently connect on their hydrophilic surfaces at the 2nd step. We confirmed that this sequential process increases the yield of the assembled structure, and concluded that pH control is effective to achieve a sequential self-assembly.
Principles
Abstract

A technique is described for assembly of multiple batches of micro components onto a single substrate. The substrate is prepared with hydrophobic alkanethiol-coated gold binding sites. To perform assembly, a hydrocarbon oil, which is applied to the substrate, wets exclusively the hydrophobic binding sites in water. Micro components are then added to the water, and assembled on the oil-wetted binding sites. Moreover, assembly can be controlled to take place on desired binding sites by using an electrochemical method to deactivate specific substrate binding sites. By repeatedly applying this technique, different batches of micro components can be sequentially assembled to a single substrate. As a post assembly procedure, electroplating is incorporated into the technique to establish electrical connections for assembled components. Important issues presented are: substrate fabrication techniques, electrochemical modulation by using a suitable alkanethiol (dodecanethiol), electroplating of tin and lead alloy and binding site design simulations. Finally, we demonstrate a two-batch assembly of silicon square parts, and establishing electrical connectivity for assembled surface-mount light emitting diodes (LEDs) by electroplating.
Procedure

(c) **Electrochemical SAM desorption** from selected binding site (the right site) is used to de-activate it.

Towards Optimal Designs for Self-Alignment in Surface Tension Driven Micro-Assembly

K.F. Böhringer’s Group, U. Washington
MEMS 2004
Abstract

Fluidic self-assembly driven by surface tension force has demonstrated the capability of assembling micro parts to binding sites in parallel with high efficiency and accuracy. In this paper, we focus on the binding site design for this technique, as it is a critical factor not only for accurate assembly, but also to achieve unique alignment position and orientation. To find optimal designs, we use a first-order approximation model to evaluate a series of patterns including disks, rings and offset rings. From this analysis, optimal patterns assuring unique alignment are determined to be offset rings with specific geometric constraints. For comparison, experiments with different shapes are performed, and results matching with the simulations are observed.
Self-Assembly at All Scales (1)

Abstract

Self-assembly is the autonomous organization of components into patterns or structures without human intervention. Self-assembling processes are common throughout nature and technology. They involve components from the molecular (crystals) to the planetary (weather systems) scale and many different kinds of interactions. The concept of self-assembly is used increasingly in many disciplines, with a different flavor and emphasis in each.

In a general sense, self-assembly might be defined as the spontaneous formation of complex hierarchical structures from pre-designed building blocks, typically involving multiple energy scales and multiple degrees of freedom.
Reasons for Interest

• Appearance of order from disorder
• Living cells self-assemble, and understanding life will therefore require understanding self-assembly
• A practical strategy for making ensembles of nanostructures
• Manufacturing and robotics will benefit from applications of self-assembly
• Common to many dynamic, multi-component systems
• Bridges the study of distinct components and the study of systems with many interacting components

Common Features

• Components must be able to move with respect to one another (usually takes place in fluid phases or on smooth surfaces)
• Equilibration is usually required to reach ordered structures
• Molecular self-assembly involves non-covalent or weak covalent interactions (van der Waals, electrostatic, and hydrophobic interactions, hydrogen and coordination bonds)
• For larger components, interactions can often be selected and tailored, and can include interactions such as gravitational attraction, external electro-magnetic fields, and magnetic, capillary, and entropic interactions
Common Features

• The environment can modify the interactions between the components
• Use of boundaries and other templates to reduce defects and control structures
• Self-assembly requires that the components either equilibrate between aggregated and non-aggregated states, or adjust their positions relative to one another once in an aggregate
• Design of components with coded information that organize themselves into desired patterns and functions

Soft Lithography (2)

Self-Assembled Monolayers

Table 4. Substrates and ligands that form SAMs.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Ligand or Precursor</th>
<th>Binding</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>RSH, ArSH (thiols)</td>
<td>RS−Au</td>
<td>[39, 46, 47]</td>
</tr>
<tr>
<td>Au</td>
<td>RSR' (disulfides)</td>
<td>RS−Au</td>
<td>[39, 46, 48]</td>
</tr>
<tr>
<td>Au</td>
<td>RSR (sulfides)</td>
<td>RS−Au</td>
<td>[39, 46, 49]</td>
</tr>
<tr>
<td>Au</td>
<td>RSO_{2}H</td>
<td>RSO_{2}−Au</td>
<td>[50]</td>
</tr>
<tr>
<td>Au</td>
<td>R_{3}P</td>
<td>R_{3}P−Au</td>
<td>[51]</td>
</tr>
<tr>
<td>Ag</td>
<td>RSH, ArSH</td>
<td>RS−Ag</td>
<td>[39, 52]</td>
</tr>
<tr>
<td>Cu</td>
<td>RSH, ArSH</td>
<td>RS−Cu</td>
<td>[39, 53]</td>
</tr>
<tr>
<td>Pd</td>
<td>RSH, ArSH</td>
<td>RS−Pd</td>
<td>[39, 54]</td>
</tr>
<tr>
<td>Pt</td>
<td>RNC</td>
<td>RNC−Pt</td>
<td>[39, 55]</td>
</tr>
<tr>
<td>GaAs</td>
<td>RSH</td>
<td>RS−GaAs</td>
<td>[56]</td>
</tr>
<tr>
<td>I$_{2}$P</td>
<td>RSH</td>
<td>RS−I$_{2}$P</td>
<td>[57]</td>
</tr>
<tr>
<td>SiO$_{2}$ glass</td>
<td>RSi(OR')$_{3}$</td>
<td>silane</td>
<td>[39, 46, 58]</td>
</tr>
<tr>
<td>Si$_{2}$H</td>
<td>(RCOOH) (neat)</td>
<td>R−Si</td>
<td>[59]</td>
</tr>
<tr>
<td>Si$_{2}$H</td>
<td>RCH=CH$_{2}$</td>
<td>RCH=CH$_{2}$Si</td>
<td>[60]</td>
</tr>
<tr>
<td>Si$_{2}$Cl</td>
<td>RLi, RMgX</td>
<td>R−Si</td>
<td>[61]</td>
</tr>
<tr>
<td>metal oxides</td>
<td>RCOOH</td>
<td>RCOO−...Mo$_{6}$</td>
<td>[62]</td>
</tr>
<tr>
<td>metal oxides</td>
<td>RCONH$_{2}$OH</td>
<td>RCONH$<em>{2}$OH−...Mo$</em>{6}$</td>
<td>[63]</td>
</tr>
<tr>
<td>ZrO$_{2}$</td>
<td>RPO$<em>{4}$H$</em>{3}$</td>
<td>RPO$_{4}$−...Zr$^{IV}$</td>
<td>[64]</td>
</tr>
<tr>
<td>In$<em>{2}$O$</em>{3}$/SnO$_{2}$ (ITO)</td>
<td>RPO$<em>{4}$H$</em>{3}$</td>
<td>RPO$_{4}$−...M$^{m+}$</td>
<td>[65]</td>
</tr>
</tbody>
</table>

Table 5. Techniques for characterizing SAMs of alkanethiolates on gold.

<table>
<thead>
<tr>
<th>Property of SAMs</th>
<th>Technique</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>structure and order</td>
<td>scanning probe microscopy</td>
<td>[66, 67]</td>
</tr>
<tr>
<td>STMs, AFMs, LFM</td>
<td>infrared spectroscopy</td>
<td>[39e, 68]</td>
</tr>
<tr>
<td>low-energy helium diffraction</td>
<td>X-ray diffraction</td>
<td>[69]</td>
</tr>
<tr>
<td>surface Raman scattering</td>
<td>transmission electron diffraction</td>
<td>[70]</td>
</tr>
<tr>
<td>sum frequency spectroscopy (SFS)</td>
<td>electron diffraction</td>
<td>[71]</td>
</tr>
<tr>
<td>composition</td>
<td>X-ray photoelectron spectroscopy (XPS)</td>
<td>[73]</td>
</tr>
<tr>
<td>temperature programmed desorption (TPD)</td>
<td>mass spectrometry (MS)</td>
<td>[74]</td>
</tr>
<tr>
<td>wettability</td>
<td>contact angle</td>
<td>[75]</td>
</tr>
<tr>
<td>thickness</td>
<td>ellipsometry</td>
<td>[76]</td>
</tr>
<tr>
<td>coverage and/or</td>
<td>quartz crystal microbalance (QCM)</td>
<td>[77]</td>
</tr>
<tr>
<td>degree of perfection</td>
<td>surface acoustic wave (SAW) device</td>
<td>[78]</td>
</tr>
<tr>
<td>defects</td>
<td>STM and AFM</td>
<td>[79]</td>
</tr>
<tr>
<td>wet etching</td>
<td>electrochemical methods</td>
<td>[80]</td>
</tr>
</tbody>
</table>

X(\mathrm{CH_{2}}\text{SH}) + Au^{n+} \rightarrow X(\mathrm{CH_{2}}\text{S})Au^{n+} + 1/2 \text{H}_2
Preparation of SAMs

• Langmuir films are formed by spreading amphiphilic molecules on liquid surface
• Langmuir-Blodgett (LB) films are prepared by transferring Langmuir films onto a solid substrate
• Growth of SAMs can be done either in solution or in UHV
• Organic molecular beam deposition (OMBD) or epitaxy (OMBE) is similar to evaporation techniques in UHV

Thermodynamics

• $\Delta E_{ads}$: adsorption energy
• $\Delta E_{corr}$: corrugation of substrate potential experienced by molecule
• $\Delta E_{hyd}$: van der Waals interaction of (hydrocarbon) tails
• $\Delta E_g$ energy of gauche defect (or, generally, deviation from fully stretched backbone)
Since the defining feature is the “pair” of the chemisorbing head-group of the molecule and the substrate (while the rest of the molecule can be almost freely chosen), this “chemisorption pair” is used to classify the specific system.

Fig. 3. Some frequently used compounds for SAMs. For purpose of illustration, chain length is specified to $n = 10$ except for case of OTS ($n = 18$). (1) $n$-alkanethiol: $\text{HS}-(\text{CH}_2)_n-\text{CH}_3$; (2) $\omega$-alkanethiol: $\text{HS}-(\text{CH}_2)_n-\text{SH}$; (3) $\omega$-mercaptoalkanol: $\text{HS}-(\text{CH}_2)_n-\text{OH}$; (4) $\omega$-mercaptopalkane carboxylic acid: $\text{HS}-(\text{CH}_2)_{n-1}-\text{COOH}$; (5) 4-methyl-4'-mercaptopbiphenyl (MMB): $\text{HS}-(\text{C}_6\text{H}_4)_2-\text{CH}_3$; (6) 1, 1’dialkyl-disulfide: $\text{H}_2\text{C}-(\text{CH}_2)_{n-1}-\text{S-S}-(\text{CH}_2)_{n-1}-\text{CH}_3$; (7) alkylylchlorosilane: $\text{Cl}_3\text{Si}-(\text{CH}_2)_{n-1}-\text{CH}_3$ (shown here: octadecyltrichlorosilane (OTS) $\text{Cl}_3\text{Si}-(\text{CH}_2)_{17}-\text{CH}_3$).
Two complementary strategies can be used in the fabrication of molecular biomaterials. In the ‘top-down’ approach, biomaterials are generated by stripping down a complex entity into its component parts. This contrasts with the ‘bottom-up’ approach, in which materials are assembled molecule by molecule (and in some cases even atom by atom) to produce novel supramolecular architectures. The latter approach is likely to become an integral part of nanomaterials manufacture and requires a deep understanding of individual molecular building blocks and their structures, assembly properties and dynamic behaviors. Two key elements in molecular fabrication are chemical complementarity and structural compatibility, both of which confer the weak and noncovalent interactions that bind building blocks together during self-assembly. Using natural processes as a guide, substantial advances have been achieved at the interface of nanomaterials and biology, including the fabrication of nanofiber materials for three-dimensional cell culture and tissue engineering, the assembly of peptide or protein nanotubes and helical ribbons, the creation of living microlenses, the synthesis of metal nanowires on DNA templates, the fabrication of peptide, protein and lipid scaffolds, the assembly of electronic materials by bacterial phage selection, and the use of radiofrequency to regulate molecular behaviors.
Figure 1  Fabrication of various peptide materials. (a) The ionic self-complementary peptide has 16 amino acids, ~5 nm in size, with an alternating polar and nonpolar pattern. The peptides form stable β-strand and β-sheet structures; thus, the side chains partition into two sides, one polar and the other nonpolar. They undergo self-assembly to form nanofibers with the nonpolar residues inside (green), and + (blue) and − (red) charged residues form complementary ionic interactions, like a checkerboard. These nanofibers form interwoven matrices that further form a scaffold hydrogel with very high water content, >99.5%. This is similar to agarose gel and other hydrogels. (Images courtesy of H. Yokoi.) (b) A type of surfactant-like peptide, ~2 nm in size, that has a distinct head charged group, either positively charged or negatively charged, and a nonpolar tail consisting of six hydrophobic amino acids. The peptides can self-assemble into nanotubes and nanovesicles with a diameter of ~30–50 nm. These nanotubes go on to form an interconnected network similar to what has been observed in carbon nanotubes. (Image courtesy of S. Santoso.) (c) Surface nanocoating peptide. This type of peptide has three distinct segments: a functional segment, which interacts with other proteins and cells; a linker segment that not only can be either flexible or stiff, but also sets the distance from the surface; and an anchor for covalent attachment to the surface. These peptides can be used as ink for an inkjet printer to print directly on a surface, instantly creating any arbitrary pattern, as shown here. Neural cells from rat hippocampal tissue form defined patterns. (Images courtesy of S. Fuller and N. Sanjana.) (d) Molecular switch peptide, a type of peptide with strong dipoles that can undergo drastic conformation changes, between α-helix and β-strand or β-sheet, under external stimuli. It is conceivable that metal nanocrystals could be attached to these dipole peptides to fabricate them into tiny switches.

Figure 2  Self-assembling peptides form a three-dimensional scaffold woven from nanofibers ~10 nm in diameter. The scaffolds have been applied in several three-dimensional cell culture studies and in tissue engineering applications. (a) Representation of self-assembling peptide. (b) Electron micrograph of three-dimensional scaffold formed in vitro. (c) Rat hippocampal neurons form active nerve connections; each green dot represents a single synapse. (d) Neural cells from a rat hippocampal tissue slide migrate on the three-dimensional peptide scaffold. Cells on the polymer membrane (left) and on the peptide scaffold (right) are shown. Both glial cells (green) and neural progenitors (red) migrate into the three-dimensional peptide scaffold. (Image courtesy of C. Semino.) (e) Brain damage repair in hamster. The peptide scaffold was injected into the optic nerve, which was first severed with a knife. The cut was sealed by the migrating cells after 2 days. A great number of neurons form synapses (R. Ellis-Behnke, personal communication). (Image courtesy of R. Ellis-Behnke.) (f) Chondrocytes from young and adult bovine encapsulated in the peptide scaffold. These cells not only produce a large amount of glycosaminoglycans (purple) and type II collagen (yellow), characteristic materials found in cartilage, but also a cartilage-like tissue in vitro. (Images courtesy of J. Kisiday and A. Grodzinsky.) (g) Adult rat liver progenitor cells encapsulated in the peptide scaffold. The cells on the two-dimensional dish did not produce cytochrome P450-type enzymes (left). However, cells in three-dimensional scaffolds showed cytochrome P450 activity (right). (Image courtesy of C. Semino.)
By studying the materials properties of nanoparticles functionalized with DNA, it is feasible to identify many novel structures, which are proving useful in new biodetection schemes.
A DNA-based Method for Rational Assembling Nanoparticles into Macroscopic Materials (24)


FIG. 1 Scheme showing the **DNA-based colloidal nanoparticle assembly** strategy (the hybridized 12-base-pair portion of the linking duplex is abbreviated as \[\text{TCGGA}\_5'\text{GCAGG}_3'\]). If a duplex with a 12-base-pair overlap but with 'sticky ends' with four base mismatches (5'-AAGTCAGTTAAGCAGCGCTAG and 3'-ATATGCAGCTACAAATCACAA) is used in the second step, no reversible particle aggregation is observed. The scheme is not meant to imply the formation of a crystalline lattice but rather an aggregate structure that can be reversibly annealed. Δ is the heating above the dissociation temperature of the duplex.
Selective Colorimetric Detection of Polynucleotides Based on the Distance-Dependent Optical Properties of Gold Nanoparticles

Robert Elghanian, James J. Storhoff, Robert C. Mucic, Robert L. Letsinger,* Chad A. Mirkin*

A highly selective, colorimetric polynucleotide detection method based on mercaptoalkyloligonucleotide-modified gold nanoparticle probes is reported. Introduction of a single-stranded target oligonucleotide (30 bases) into a solution containing the appropriate probes resulted in the formation of a polymeric network of nanoparticles with a concomitant red-to-pinkish/purple color change. Hybridization was facilitated by freezing and thawing of the solutions, and the denaturation of these hybrid materials showed transition temperatures over a narrow range that allowed differentiation of a variety of imperfect targets. Transfer of the hybridization mixture to a reverse-phase silica plate resulted in a blue color upon drying that could be detected visually. The unoptimized system can detect about 10 femtomoles of an oligonucleotide.
A “melting curve” obtained at a wavelength of 260 nm on a nanoparticle-DNA aggregate hybridized by the freeze-thaw cycle gave a “melting” temperature ($T_m$) of 57°C (black circles), as compared with $T_m = 56°C$ for a solution of free oligonucleotides hybridized in solution at room temperature in the absence of nanoparticles (red squares). The curve for the Au-nanoparticle/DNA complex is remarkably steep; the temperature range for melting is narrow compared with the temperature range for dissociation of the complex formed from the free oligonucleotides. Corresponding sharp transitions at the same temperature but with a drop in absorbance rather than an increase were obtained when the dissociation of the nanoparticle aggregates was observed at 620 and 700 nm.

Scanometric DNA Array Detection with Nanoparticle Probes

T. Andrew Taton, Chad A. Mirkin, Robert L. Letsinger

A method for analyzing combinatorial DNA arrays using oligonucleotide-modified gold nanoparticle probes and a conventional flatbed scanner is described here. Labeling oligonucleotide targets with nanoparticle rather than fluorophore probes substantially alters the melting profiles of the targets from an array substrate. This difference permits the discrimination of an oligonucleotide sequence from targets with single nucleotide mismatches with a selectivity that is over three times that observed for fluorophore-labeled targets. In addition, when coupled with a signal amplification method based on nanoparticle-promoted reduction of silver(I), the sensitivity of this scanometric array detection system exceeds that of the analogous fluorophore system by two orders of magnitude.
Array-Based Electrical Detection of DNA with Nanoparticle Probes
So-Jung Park, T. Andrew Taton,* Chad A. Mirkin†

A DNA array detection method is reported in which the binding of oligonucleotides functionalized with gold nanoparticles leads to conductivity changes associated with target-probe binding events. The binding events localize gold nanoparticles in an electrode gap; silver deposition facilitated by these nanoparticles bridges the gap and leads to readily measurable conductivity changes. An unusual salt concentration-dependent hybridization behavior associated with these nanoparticle probes was exploited to achieve selectivity without a thermal-stringency wash. Using this method, we have detected target DNA at concentrations as low as 500 femtomolar with a point mutation selectivity factor of ~ 100,000:1.

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將捕捉DNA序列（a）固定在電極中，再與含有標的DNA序列（ab）與帶有另一探針序列（b）的金奈米粒子（Au）的溶液混合。三種DNA序列間的配對結合，便可將金奈米粒子固定在電極之間並形成緊密排列，再以含硝酸銀的顯影液處理而使得銀沈積在上面，電子（e−）便可兩個間形成通路而產生傳導，電極間的電阻即大幅下降。

Nanoparticle-Based Bio–Bar Codes for the Ultrasensitive Detection of Proteins

Jwa-Min Nam,* C. Shad Thaxton,* Chad A. Mirkin†

An ultrasensitive method for detecting protein analytes has been developed. The system relies on magnetic microparticle probes with antibodies that specifically bind a target of interest [prostate-specific antigen (PSA) in this case] and nanoparticle probes that are encoded with DNA that is unique to the protein target of interest and antibodies that can sandwich the target captured by the microparticle probes. Magnetic separation of the complexed probes and target followed by dehybridization of the oligonucleotides on the nanoparticle probe surface allows the determination of the presence of the target protein by identifying the oligonucleotide sequence released from the nanoparticle probe. Because the nanoparticle probe carries with it a large number of oligonucleotides per protein binding event, there is substantial amplification and PSA can be detected at 30 attomolar concentration. Alternatively, a polymerase chain reaction on the oligonucleotide bar codes can boost the sensitivity to 3 attomolar. Comparable clinically accepted conventional assays for detecting the same target have sensitivity limits of ~3 picomolar, six orders of magnitude less sensitive than what is observed with this method.
**Photonic Band Gap Materials**

- 具有規律且週期性折射率變化的光學材料
- 電磁波經結構散射後，某些波段的電磁波強度會因破壞性干涉而呈指數衰減，無法在系統內傳遞
- 在介電係數呈規律且週期性排列的介質當中，電磁波的分佈也會有能帶結構

**Photonic Crystals**

- 在光子晶體中，能隙的存在使得某些波長範圍的光波無法在光子晶體中傳播
- 藉由在規律且週期性的結構中刻意造成某種程度的缺陷，可以在原本不容許傳播模態存在的能隙當中，產生一個得以傳播的缺陷模態
- 完全掌控光波的傳導
Natural Photonic band gaps occur in some butterfly wings. The band gap is incomplete - it is not effective in every direction - but it produces iridescent colors. A micrograph of a fractured iridescent green butterfly scale shows the sub-micron-size face-centered cubic structure inside.
Full Three-Dimensional Photonic Bandgap Crystals at Near-Infrared Wavelengths

Susumu Noda,¹* Katsuhiro Tomoda,¹ Noritsugu Yamamoto,² Alongkarn Chutinan¹

An artificial crystal structure has been fabricated exhibiting a full three-dimensional photonic bandgap effect at optical communication wavelengths. The photonic crystal was constructed by stacking 0.7-micrometer period semiconductor stripes with the accuracy of 30 nanometers by advanced wafer-fusion technique. A bandgap effect of more than 40 decibels (which corresponds to 99.99% reflection) was successfully achieved. The result encourages us to create an ultra-small optical integrated circuit including a three-dimensional photonic crystal waveguide with a sharp bend.

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Fig. 1. (A) Schematic drawing of one unit of woodpile-structure 3D photonic crystal, (B and C) SEM images of the stacked two stripes fabricated in a previous report (12) and here, respectively. (D) SEM image of 3D photonic crystal fabricated with advanced processing techniques.
On-chip natural assembly of silicon photonic bandgap crystals

Yurii A. Vlasov, Xiang-Zheng Bo, James C. Sturm & David J. Norris

Photonic bandgap crystals can reflect light for any direction of propagation in specific wavelength ranges. This property, which can be used to confine, manipulate and guide photons, should allow the creation of all-optical integrated circuits. To achieve this goal, conventional semiconductor nanofabrication techniques have been adapted to make photonic crystals. A potentially simpler and cheaper approach for creating three-dimensional periodic structures is the natural assembly of colloidal microspheres. However, this approach yields irregular, polycrystalline photonic crystals that are difficult to incorporate into a device. More importantly, it leads to many structural defects that can destroy the photonic bandgap. Here we show that by assembling a thin layer of colloidal spheres on a silicon substrate, we can obtain planar, single-crystalline silicon photonic crystals that have defect densities sufficiently low that the bandgap survives. As expected from theory, we observe unity reflectance in two crystalline directions of our photonic crystals around a wavelength of 1.3 micrometres. We also show that additional fabrication steps, intentional doping and patterning, can be performed, so demonstrating the potential for specific device applications.

Figure 1 Characterization of thin planar opal templates assembled directly on a Si wafer from 855-nm spheres. a, Cross-sectional SEM image. b, Large-scale optical photograph, looking down on the wafer. The opal is formed as the meniscus is swept from right to left. The horizontal lines represent monolayer steps in the crystal (lighter shades of blue represent single-layer increases in thickness). c, Optical diffraction pattern obtained from the sample in b. Under normal incidence, a characteristic 6-spot diffraction pattern with weak Kossel rings (enhanced in the photo) remained unchanged while scanning a 100-μm-diameter laser spot over centimetre-scale regions of the opal. These 6 spots arise from diffraction off (110) planes of a single-crystal f.c.c. lattice with 1% stacking faults.
Figure 2: SEM images of planar Si photonic crystals. Cross-sectional SEM images are shown as a function of the thickness of the initial opal template for 2 (a), 4 (b), and 16 (c) layers. The Si substrate is snapped, and the fracture propagates up through the photonic crystal. Close examination of the lowest layer reveals that the photonic crystals are completely integrated into the wafer. Apparent defects in c are due to a ripple in the fracture surface that occurs in thicker photonic crystals. d, Sample edge showing the (100) surface, confirming that the crystals are f.c.c. e, A planar (111) surface exposed by RIE. From this image, parameters such as the radius of the Si coating sphere (0.41) and the radius of the air sphere (0.55), both in units of the lattice constant, were estimated. f, A planar (100) surface exposed by RIE. The sphere diameters are 670 nm (c and e), 855 nm (d and f), and 1 μm (a and b).

APPLICATIONS FOR PHOTONIC CRYSTALS

<table>
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<tr>
<th>DEVICE</th>
<th>DESCRIPTION</th>
<th>STATUS</th>
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<tr>
<td>OPTICAL FIBERS</td>
<td>2-D band-gap material stretched along the third dimension</td>
<td>Early versions already commercialized</td>
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<tr>
<td>NANOSCOPIC LASERS</td>
<td>World’s tiniest optical cavities and tiniest lasers; formed in a thin-film 2-D band-gap material</td>
<td>Demonstrated in the lab</td>
</tr>
<tr>
<td>ULTRAWHITE PIGMENT</td>
<td>Incomplete 3-D band-gap material, usually patterned as opal structure</td>
<td>Demonstrated; low-cost manufacturing methods under development</td>
</tr>
<tr>
<td>RADIO-FREQUENCY ANTENNAS, REFLECTORS</td>
<td>Uses inductors and capacitors in place of ordinary dielectric materials</td>
<td>Demonstrated, far magnetic resonance imaging and antennas</td>
</tr>
<tr>
<td>LIGHT-EMITTING DIODES</td>
<td>Photonic band-gap structure can extract light very efficiently (better than 50%)</td>
<td>Demonstrated, but must compete with other methods of achieving the same goal</td>
</tr>
<tr>
<td>PHOTONIC INTEGRATED CIRCUITS</td>
<td>2-D thin films can be patterned like conventional integrated circuits to make channel filters, modulators, couplers and so on</td>
<td>Under development</td>
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Enabling Nanotechnology with Self Assembled Block Copolymer Patterns

Edwin L. Thomas, MIT
Polymer, 2003

- Block copolymers (BCPs) have received great attention for the past 40 years
- Their applicability to nanotechnology stems from the scale of the microdomains and the convenient tunability of size, shape, and periodicity afforded by changing their molecular parameters
- The use of the tensorial physical properties of BCPs in such areas as transport, mechanical, electrical, and optical properties will provide substantial benefits in the future
- In this review article, we first focus on the current efforts to utilize BCPs in nanotechnologies including nanostructured membranes, BCP templates for nanoparticle synthesis, photonic crystals, and high-density information storage media
- In order to realize these applications, control over microdomain spatial and orientational order is paramount
- This article reviews various methods to control BCP microdomain structures in the bulk state as well as in thin films
- A variety of biases such as mechanical flow fields, electric fields, temperature gradients, and surface interactions can manipulate the microstructures of BCPs
- A particular emphasis is made on two approaches, epitaxy and graphoepitaxy, and their combinations
Schematic of morphologies for linear ABC tri-block copolymer

Nanotechnologies Enabled with BCPs

- Photonic band gap BCPs
  - Selective etching
  - Sequestering high index nanoparticle
  - 1,2 and 3D PBG [70-73, 75-77]
  - Metallodielectric PBG [74]
  - Tunable PBG [80]

- Nanostructured Network
  - Selective etching and heating
  - Nanoporous Polymer/Ceramic membrane [43]

- Nanocomposite
  - Electroless deposition
  - Nanoporous synthesis [62-63]
  - BCP/semiconductor [56-57]
  - BCP/oxide/metal [68]

- Nanolithographic Template
  - Structure directing sol-gel
  - Electroplating
  - Dry etching
  - Thermal evaporation
  - Nanoporous membrane [45-49]
  - Nano-object [49]
  - Nanoporous waveguides [50]
  - High density magnetic storage media [91]
  - High aspect ratio magnetic storage [93]
Various applications of BCPs in nanotechnologies