Nanofabrication techniques using self-assembled molecular rulers

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Outline of presentation

- Motivation
- Metal-organic self-assembled multilayers
- Molecular ruler assisted lithography
- Applications of the technique
- Limitations
- Summary and conclusions

Motivation

- Demand for smaller feature sizes
- Parallel processing speed and compatibility with industry
- Precision hierarchical structures with 10nm – 100nm features over micron level ranges
- Flexibility in nanofabrication, patterned and unpatterned structures
- Top down approach to fabrication has fundamental limits
- Bottom up approaches using self-assembly

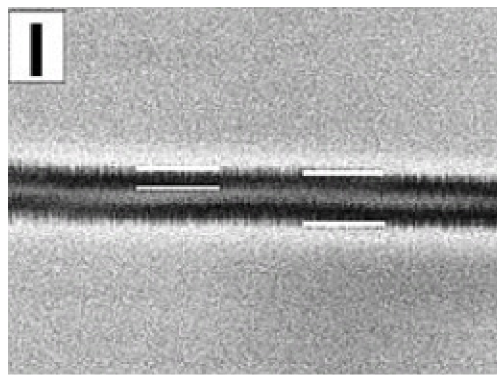
10nm-100nm features using Top-down

Scanning probe microscopy

Serial, limits construction of macroscopic arrays

Nanoimprint

Sub-100nm but hard to maintain pattern consistency/alignment



[2] 48nm parent gap.
16nm daughter gap

E-beam lithography

Expensive, tedious, slow

Nanotubes, membrane tube rods

Limited to predetermined widths and properties

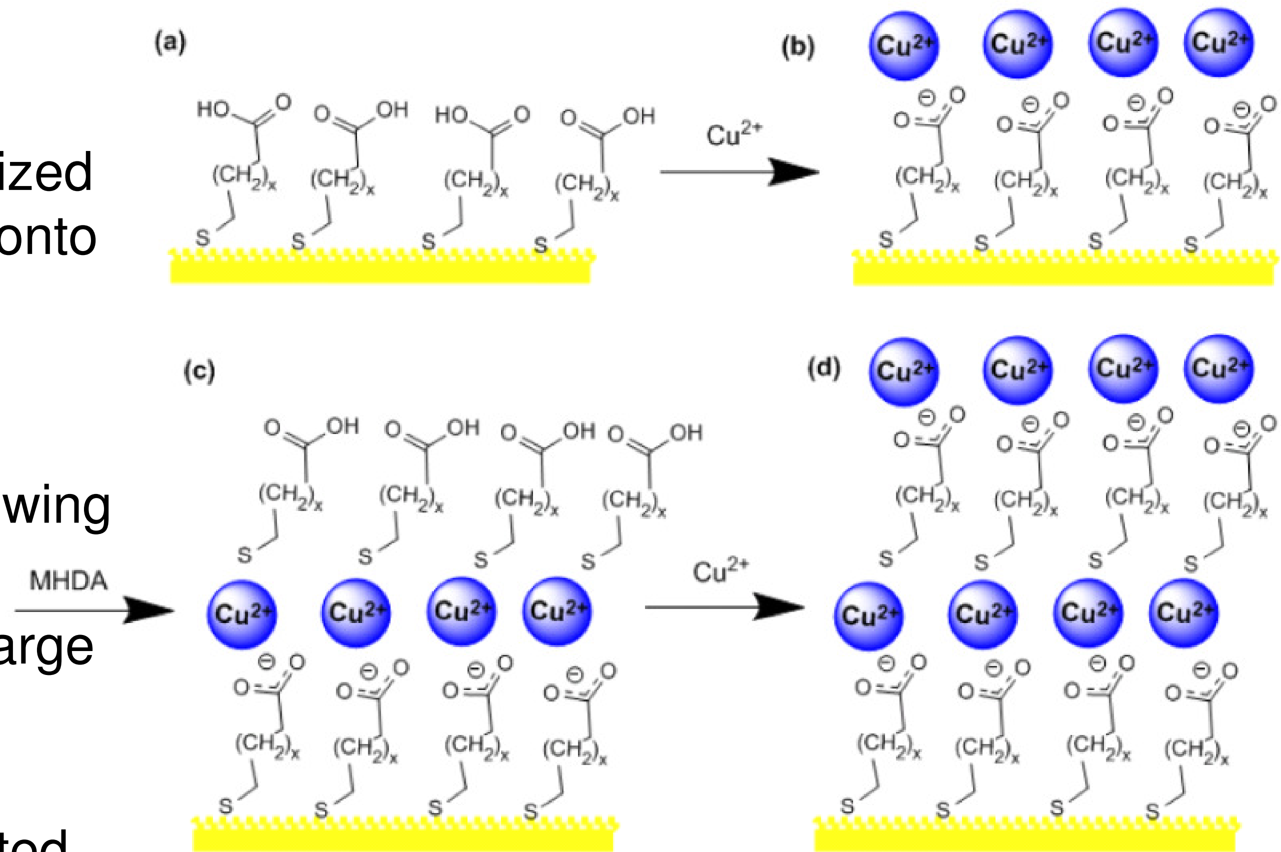
[2] A. Hatzor et al , Science, 291, 1019 (2001)

Bottom up fabrication

- Use atomic and molecular building blocks as a self assembled template for precision lithography
  - Ultra-low tolerance
  - Unit-based, repeatability
  - High throughput and parallel by using organic, inorganic and hybrid molecules
- Goal → Combine conventional process technology with self assembly chemical processes
- Result → Flexibility of existing lithography techniques (ebeam, etc…) extended to higher resolution through molecular self assembly

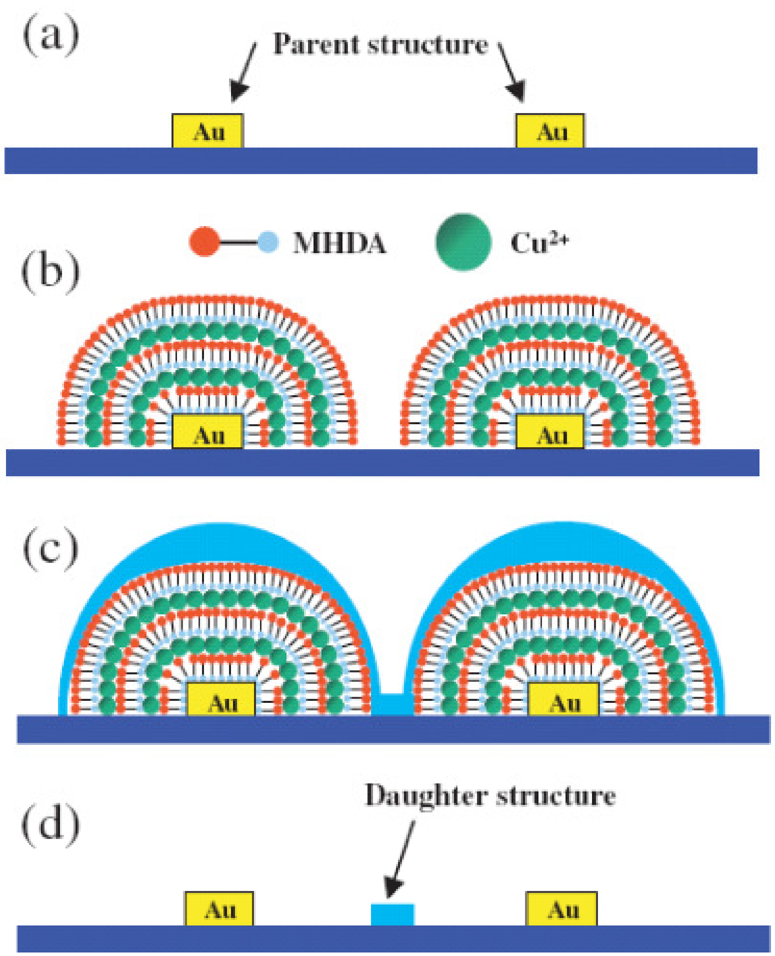
Organic multilayers

- Self assembled monolayer (SAM) of terminally-functionalized molecule deposited onto parent structure
- Cu^{2+} bind to the molecule serving as interface for the following SAM.
- Linear growth over large number of layers
- Can be exploited as precision length coated resist built from unit layers



[7] C. Srinivasan et al, Proc. SPIE 6517, 65171I (2007)

Molecular Ruler Assisted Fabrication



- Generate parent structures of metal via conventional lithography
- Selectively deposit molecular ruler onto parent in alternating exposures of α,ω-mercaptoalkanoic acids (MHDA) and copper perchlorate until desire thickness achieved
- Evaporate gold over the resist and onto substrate between resist
- Chemically lift off resist leaving daughter structures with well-defined spacing from parent

[5] H. Tanaka et al, Jpn. J. Appl. Phys., 43, L950 (2004)

Features

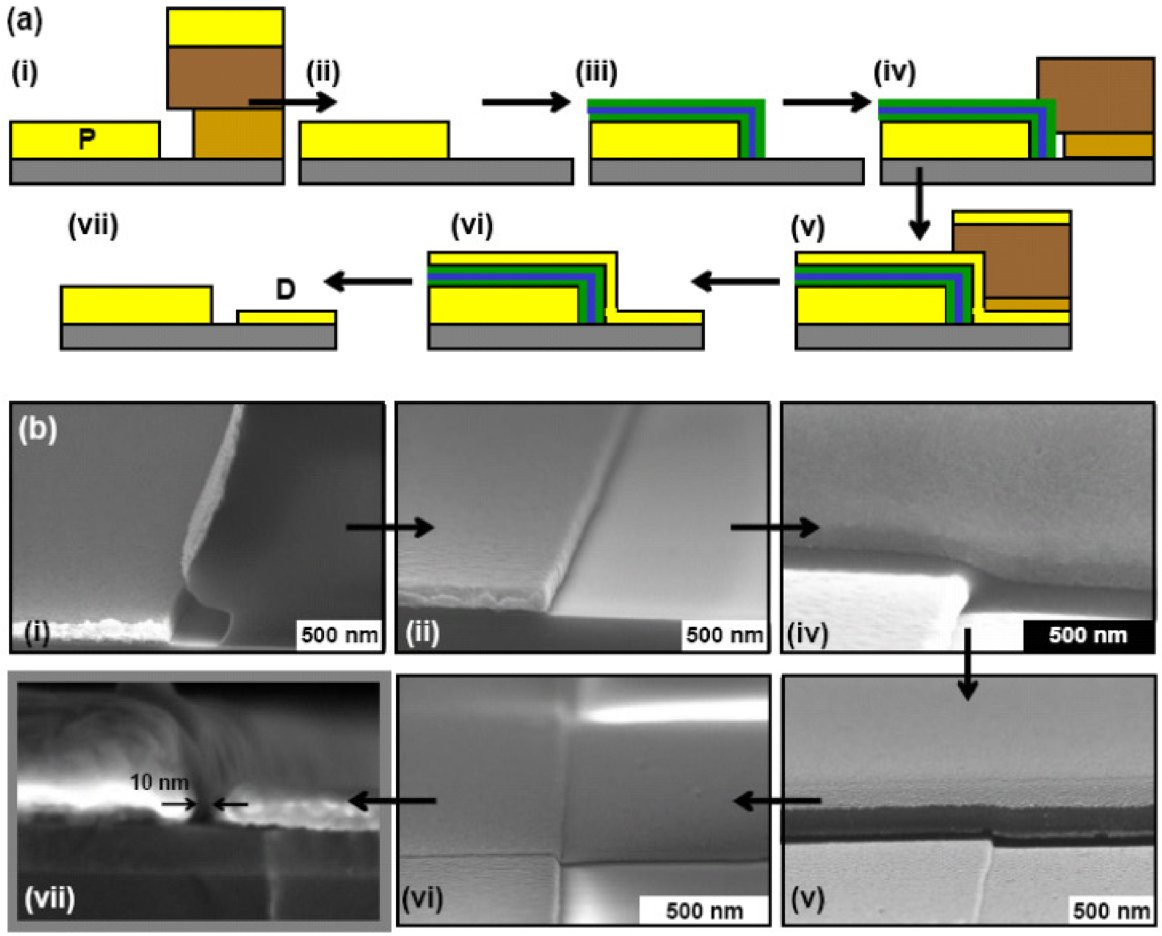
- Can achieve sub-10nm to 100nm spacings between parent and daughter.
- Molecular resist thickness determined by
  - length of organic component
  - number of layers
- Critical pinhole defects in monolayers self-healed by subsequent fluid multilayers
- Can be stored for weeks without degredation
- Stable in a variety of solvents

Table 1. FESEM measured gap width as a function of molecule length and layer count. The single molecule thicknesses calculated from ellipsometry are 1.5 ± 0.1 nm for $HS(CH_2)_{10}COOH$ and 2.0 ± 0.1 nm for $HS(CH_2)_{15}COOH$. Calculated multilayer thicknesses (Calc.) are from ellipsometry; measured gap widths (Expt.) are from FESEM and are averages of 3 to 13 different areas on the samples (*22*).

Molecule	Layers adsorbed	Multilayer thickness (nm)	
		Calc.	Expt.
$HS(CH_2)_{10}COOH$	9	14	17
$HS(CH_2)_{10}COOH$	26	39	42
$HS(CH_2)_{15}COOH$	9	18	18
$HS(CH_2)_{15}COOH$	10	20	21
$HS(CH_2)_{15}COOH$	20	40	32

[2] A. Hatzor et al , Science, 291, 1019 (2001)

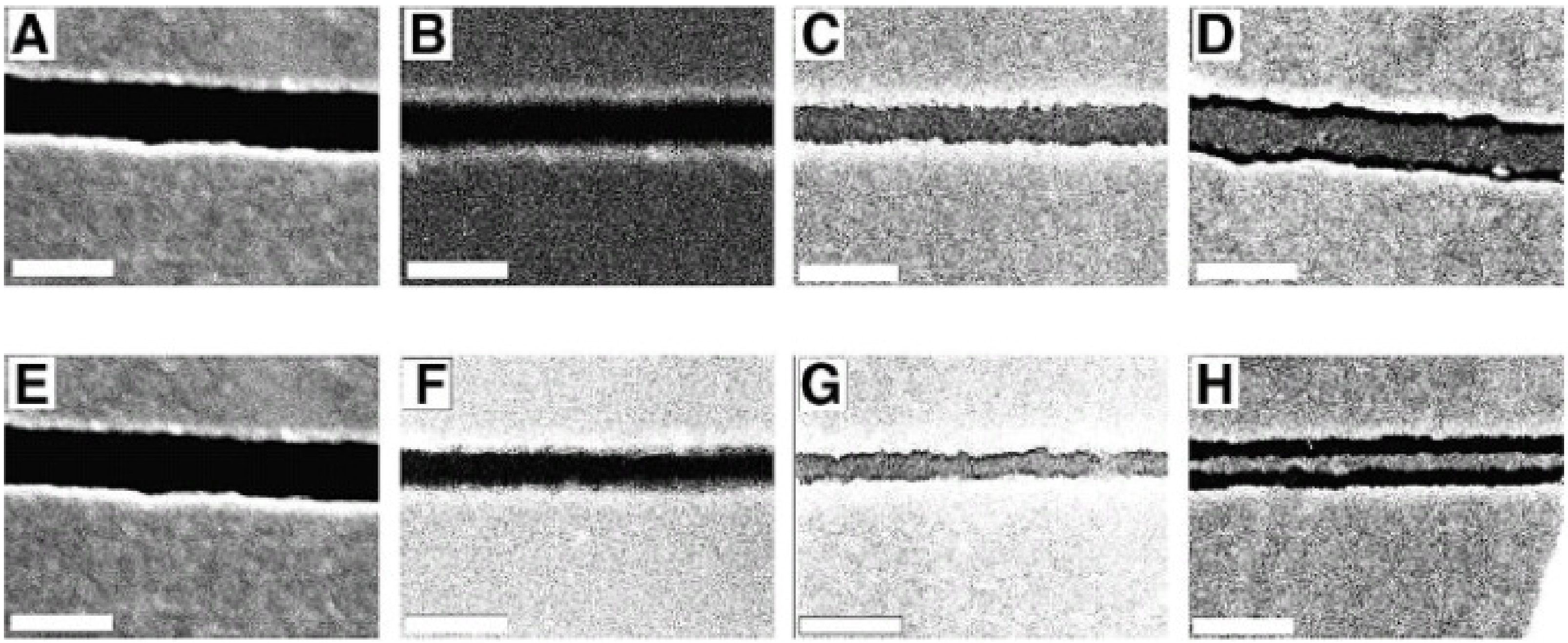
Nanogap fabrication



[7] 10nm gap from 5 layers of 16-mercaptohexadecanoic acids and Cu2+ ions

[7] C. Srinivasan et al, Proc. SPIE 6517, 65171I (2007)

Nanowire fabrication

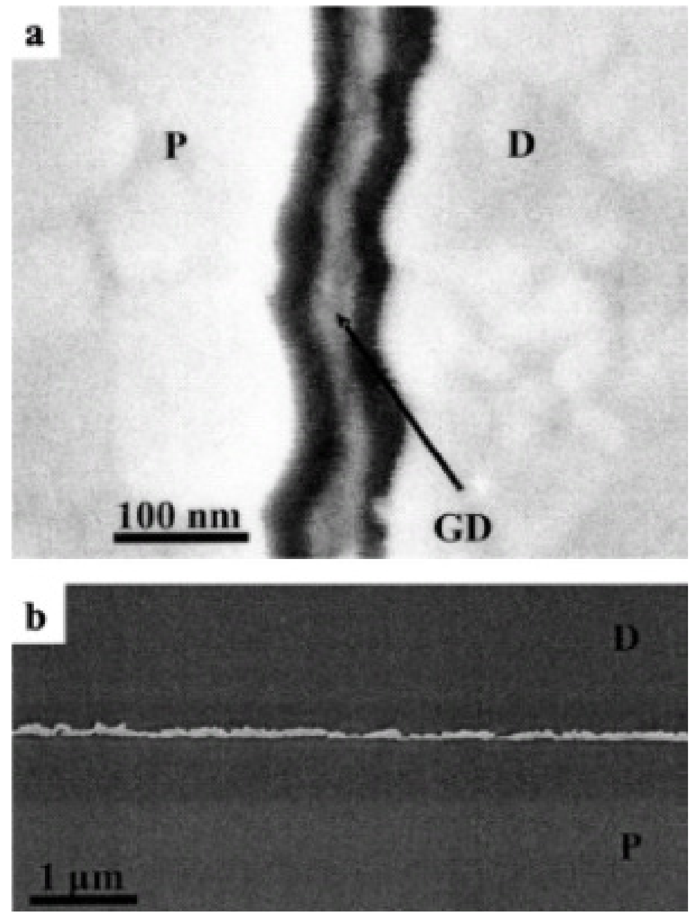


[2] (A) Parent gold traces on oxidized Si. Gap 110nm. (B) 10-layer molecular resist of mercaptoalkanoic acid with Cu2+ linker. Gap 80nm. (C) Thin Ti/Au layer deposited on resist. Gap 66nm. (D) Resist lift-off, 65nm wide, 1um long wire, 20nm gap both sides. (E) 20 layers molecular resist → 25nm wire.

[2] A. Hatzor et al , Science, 291, 1019 (2001)

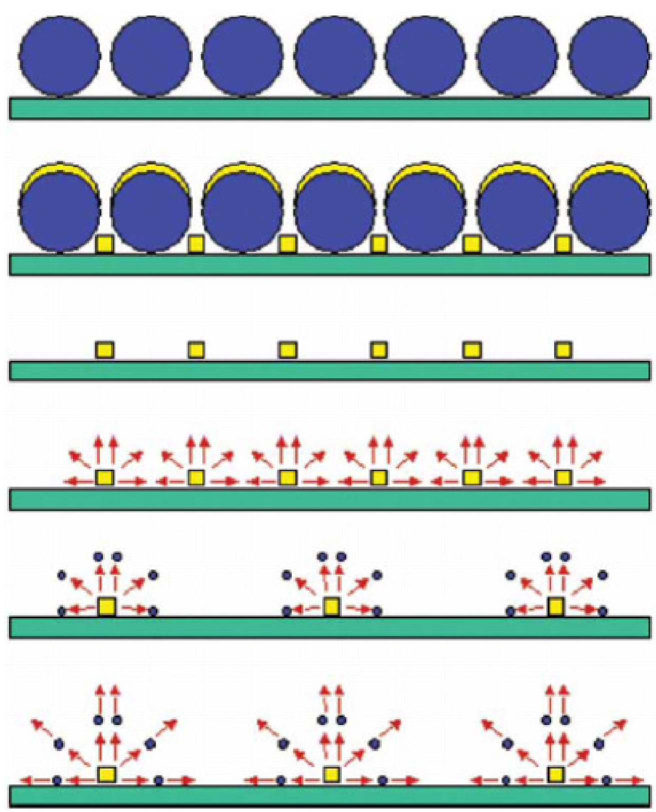
Granddaughter structures

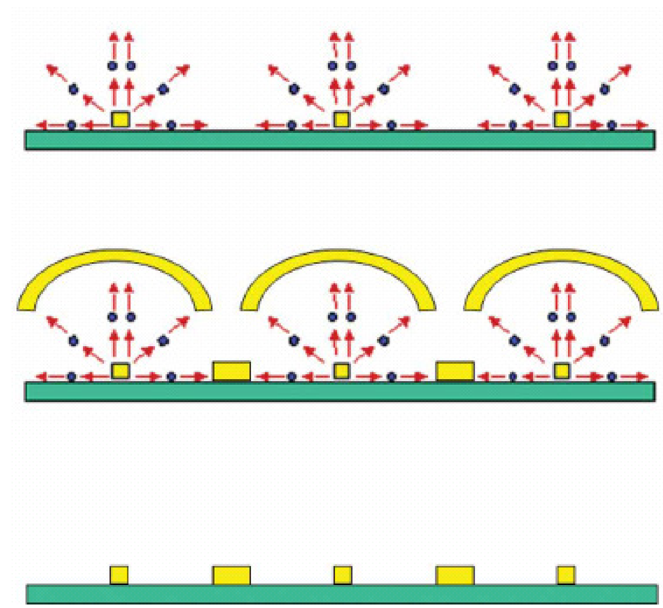
- Nanowire fabrication using granddaughter structures
- (a) Parent (P), daughter (D) and granddaughter (GD) structures. 15 MHDA/Cu2+ layers to create the gap between P and D then by five layers to create granddaughter structure.
- (b) Isolated granddaughter structure after the chemical removal of parent and daughter structures.



[4] M. E. Anderson et al, J. Vac. Sci. Tech. B, 21, 3116 (2003)

Nanosphere lithography using molecular ruler resist - 1

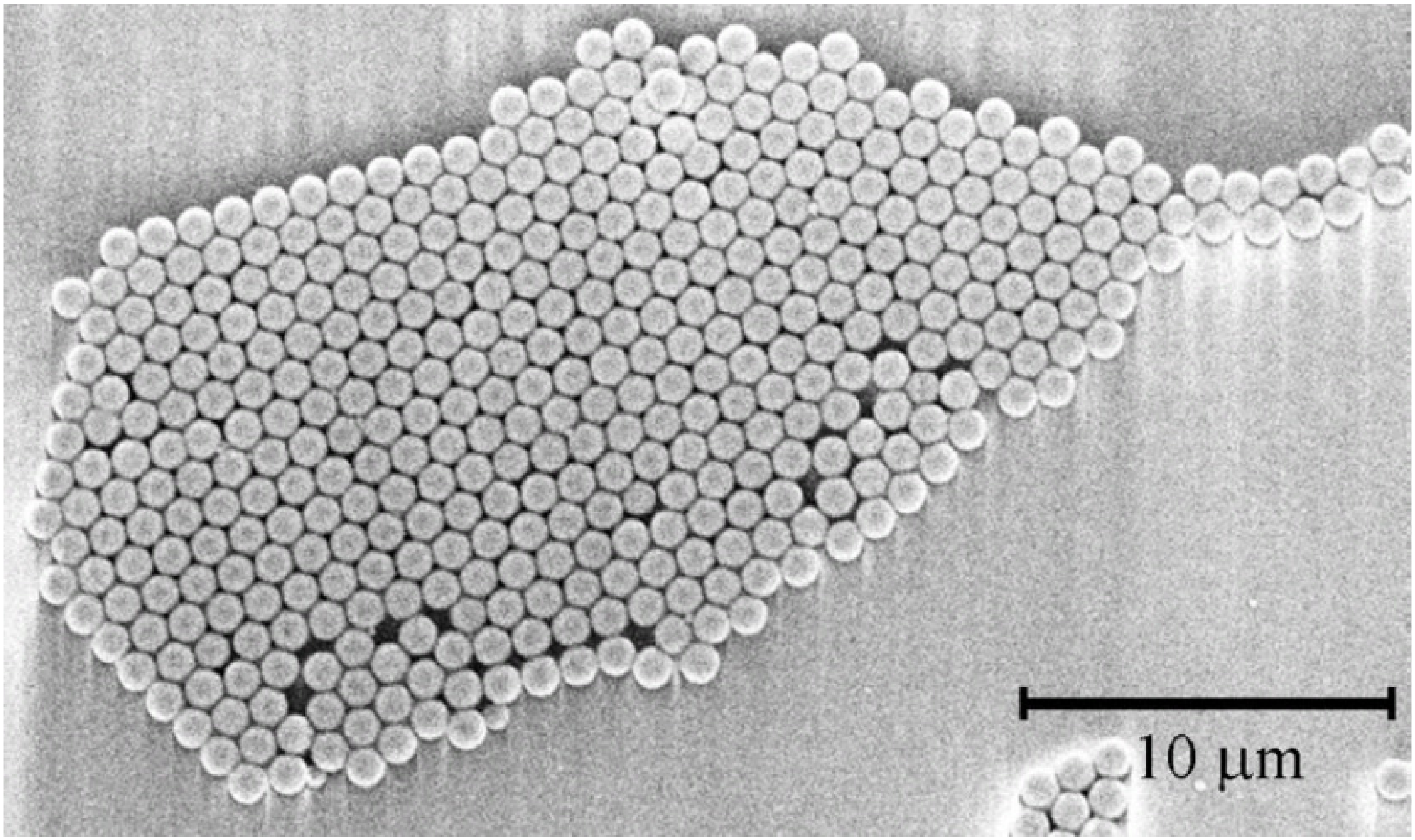




Can combination of nanosphere lithography with molecular ruler to make star-like patterns

[1] A. Hatzor et al, J. Exp. Nanoscience, Vol. 2, Nos. 1-2, 3-11 (2007)

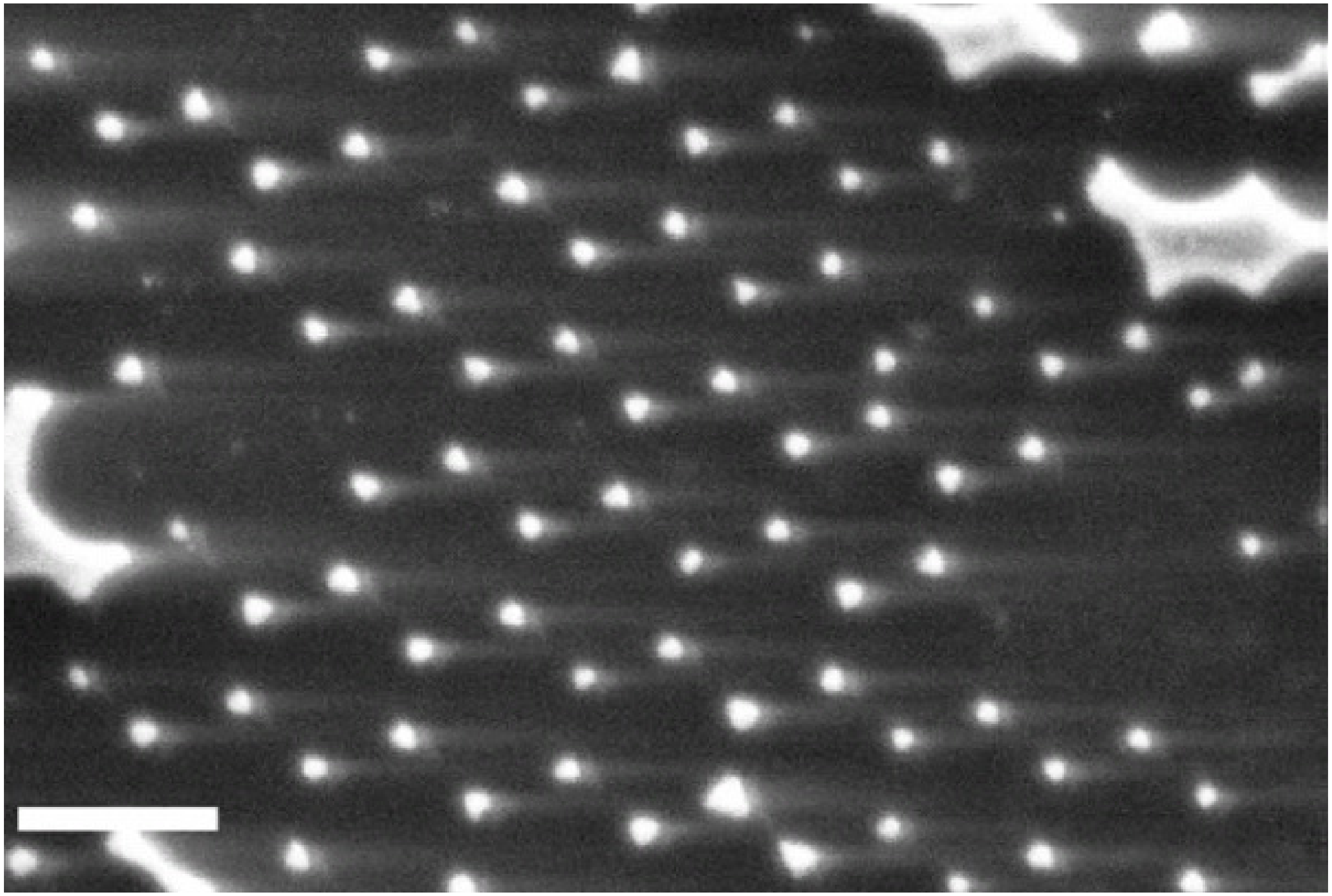
Nanosphere/molecular ruler - 2



[1] Array close-packed one-micron polystyrene nanospheres formed by spin-coating the nanosphere solution onto a SiO2 substrate.

[1] A. Hatzor et al, J. Exp. Nanoscience, Vol. 2, Nos. 1-2, 3-11 (2007)

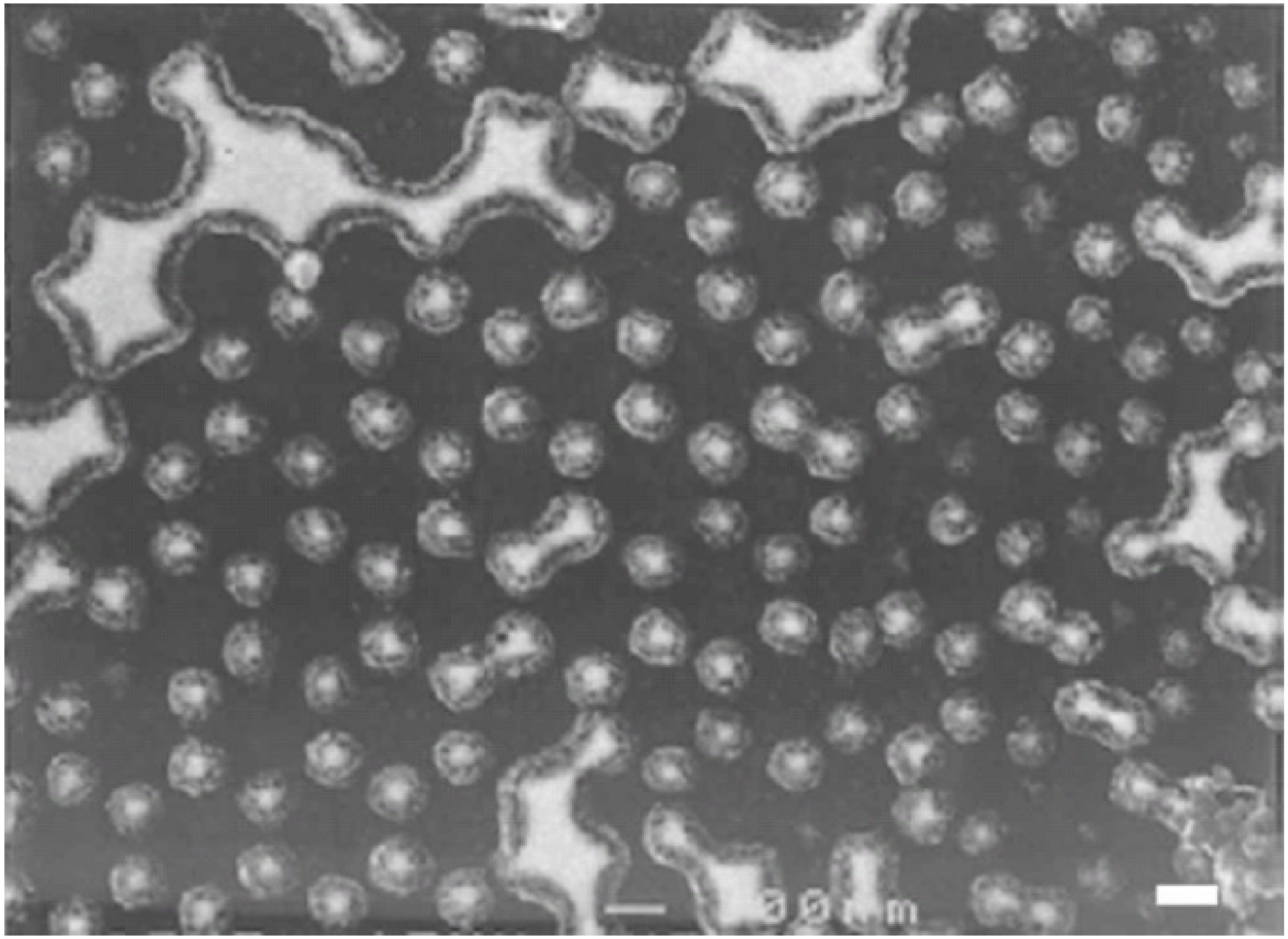
Nanosphere/molecular ruler - 3



[1] Array of Au/Ti particles formed by evaporating the metals through holes in a hexagonally packed 240nm nanosphere mask. Particle shadow is formed by the FESEM detector position and is not inherent to the sample. Scale bar = 250nm.

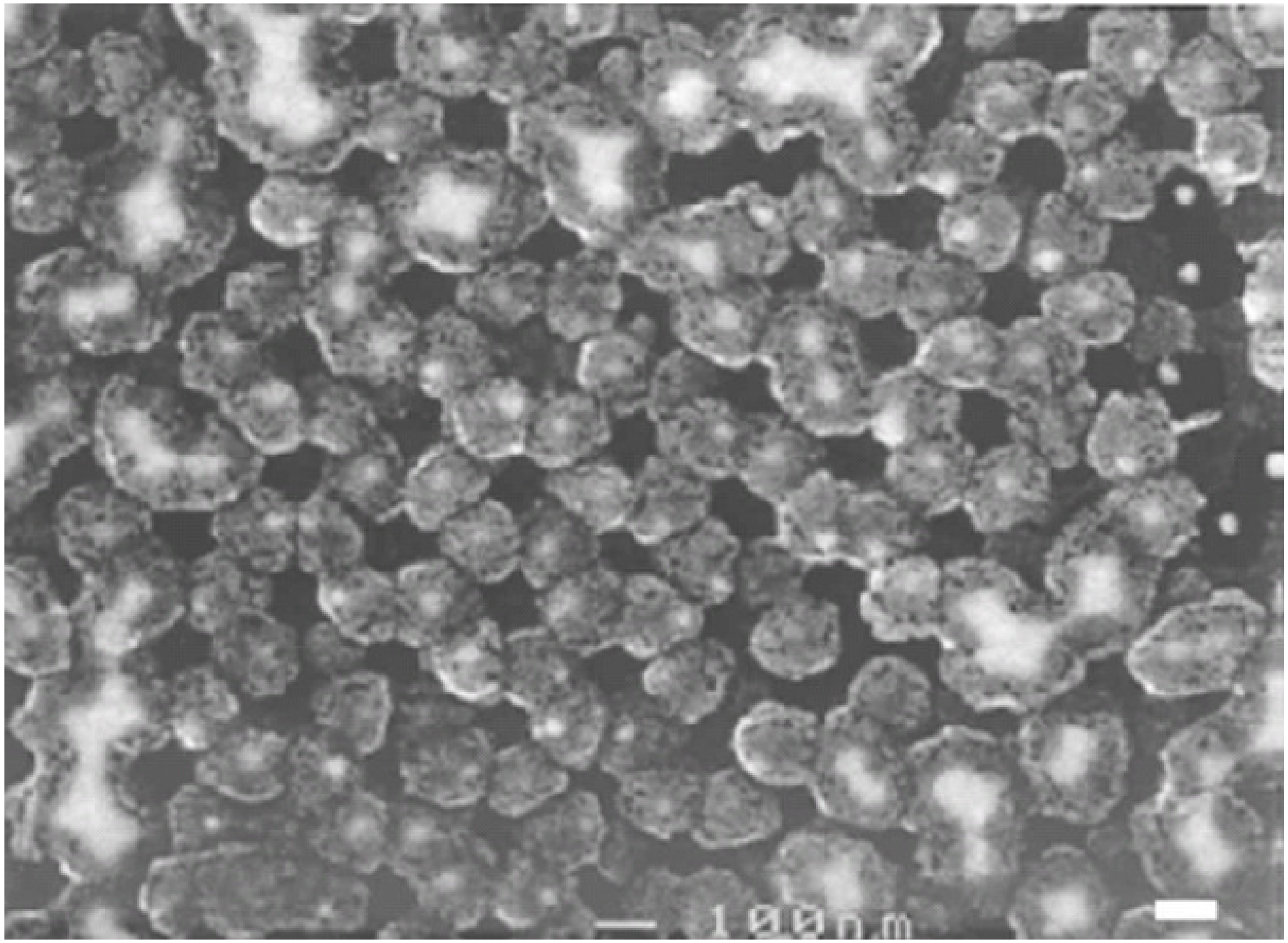
[1] A. Hatzor et al, J. Exp. Nanoscience, Vol. 2, Nos. 1-2, 3-11 (2007)

Nanosphere/molecular ruler - 4



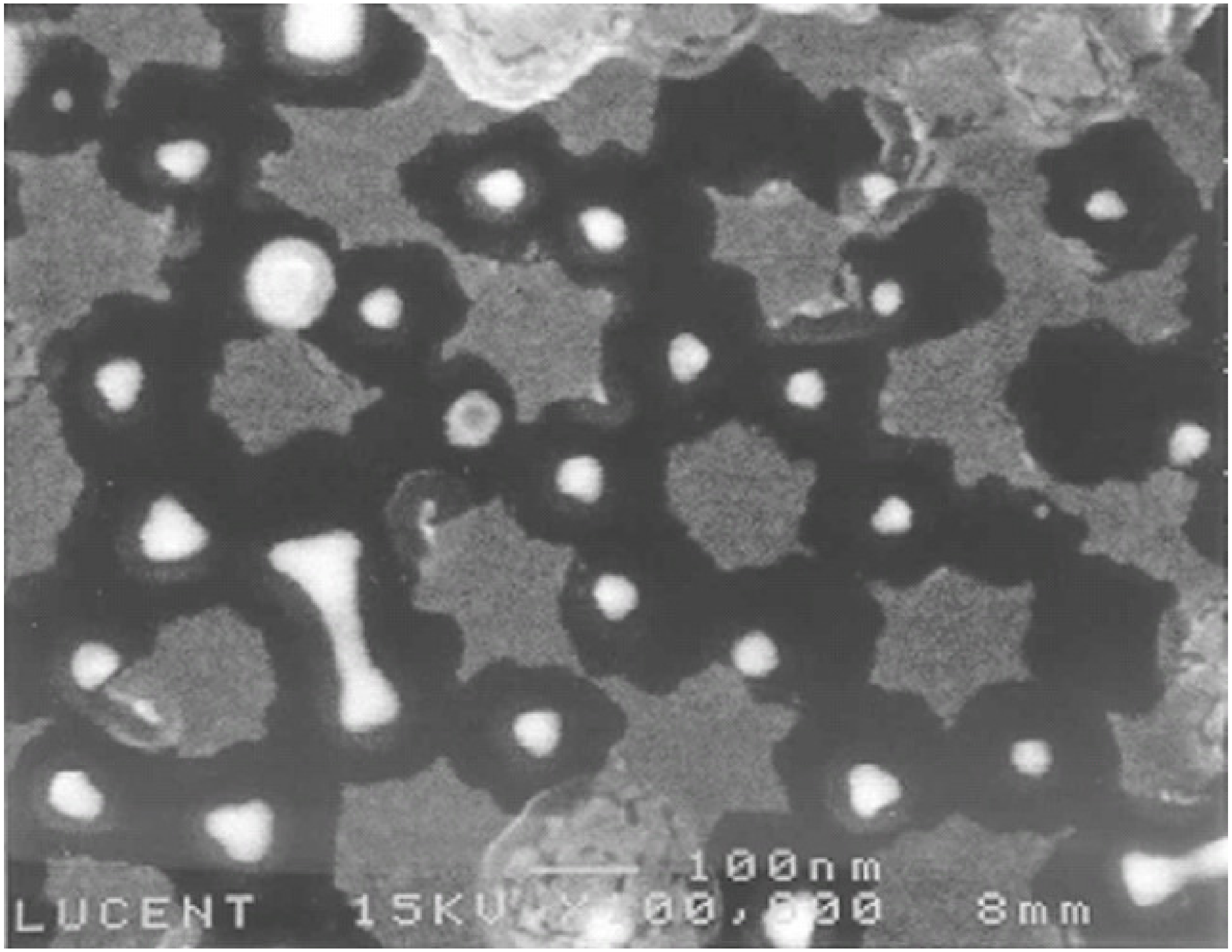
[1] 10 layers of Cu2+ complexed 16-mercaptohexadecanoic molecular layers grown on a gold dot array. The sample was coated with 2nm evaporated gold to enhance SEM contrast and to stabilize the organic structures that are otherwise sensitive to the electron beam. Nanospheres with diameters of 240nm were used as a mask for this gold dot arrays. Scale bar = 100nm

Nanosphere/molecular ruler - 5



[1] 20 layers of Cu2+ complexed mercapto-alkanoic molecular layers grown on a gold dot array: The sample was coated with 2nm evaporated gold to enhance SEM contrast and to stabilize the organic structures that are otherwise sensitive to the electron beam. Nanospheres with diameters of 240nm were used as a mask for this gold dot arrays. Scale bar = 100nm.

Nanosphere/molecular ruler - 6

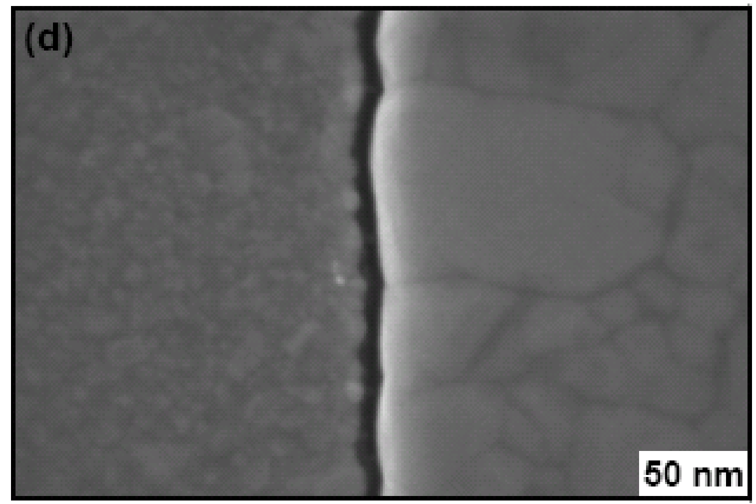


[1] Subsequent gold deposition on the sample, followed by organic layers removal to form an array of star-shaped nanostructures within the original gold-dot array.

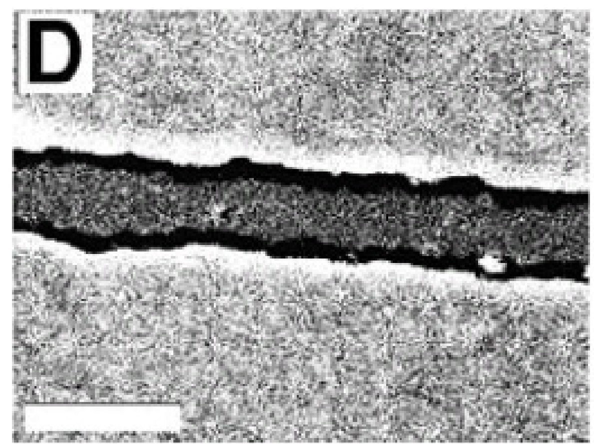
[1] A. Hatzor et al, J. Exp. Nanoscience, Vol. 2, Nos. 1-2, 3-11 (2007)

Limitations

- Surface quality of the parent structures. Molecular ruler will follow the edge roughness.
- Precision limited only by length of molecule → fractions of a nm possible
- Non-uniformity
- Number of max layers achievable. Up to 50 layers (100nm) has been reported
- Organic resist sensitive to electron beam



[7] C. Srinivasan et al, Proc. SPIE 6517, 65171I (2007)



[2] A. Hatzor et al , Science, 291, 1019 (2001)

Summary and conclusions

- Lithography techniques using molecular based ruler has been described
- Experiments has shown that gaps of 10nm can be achieved
- Molecular ruler growth highly dependent on parent structures → degradations over generations of structures
- Uniformity over multilayers not known
- Organic molecular resist can be manipulated by irradiation
  - Position-selected molecular ruler [5]

[5] H. Tanaka et al, Jpn. J. Appl. Phys., 43, L950 (2004)

References

[1] A. Hatzor, A. D. Wissner-Gross, G. Lavallee and P. S. Weiss, "Arrays of Cu21-complexed organic clusters grown on gold nano dots," Journal of Experimental Nanoscience, Vol. 2, Nos. 1-2, March-June 2007, 3-11

[2] A. Hatzor, P. S. Weiss. Molecular rulers for scaling down nanostructures. Science, 291, 1019 (2001).

[3] M. E. Anderson, R. K. Smith, Z. J. Donhauser, A. Hatzor, P. A. Lewis, L. P. Tan, H. Tanaka, M. W. Horn, P. S. Weiss. Exploiting intermolecular interactions and self-assembly for ultrahigh resolution nanolithography. J. Vac. Sci. Technol. B, 20, 2739 (2002).

[4] M. E. Anderson, L. P. Tan, H. Tanaka, M. Mihok, H. Lee, M. W. Horn, P. S. Weiss. Advances in nanolithography using molecular rulers. J. Vac. Sci. Technol. B, 21, 3116 (2003).

[5] H. Tanaka, M. E. Anderson, M. W. Horn, P. S. Weiss. Position-selected molecular ruler. Jpn. J. Appl. Phys., 43, L950 (2004).

[6] M. E. Anderson, M. Mihok, H. Tanaka, L.-P. Tan, M. W. Horn, G. S. McCarty, P. S. Weiss. Hybrid approaches to nanolithography: photolithographic structures with precise, controllable nanometer-scale spacings created by molecular rulers. Adv. Mat., 18, 1020 (2006).

[7] C. Srinivasan, J. N. Hohman, M. E. Anderson, P. Zhang, P. S. Weiss, and M. W. Horn, “Molecular-ruler nanolithography,” Proc. SPIE 6517, 65171I (2007)

Short references

[1] A. Hatzor et al, J. Exp. Nanoscience, Vol. 2, Nos. 1-2, 3-11 (2007)

[2] A. Hatzor et al , Science, 291, 1019 (2001)

[3] M. E. Anderson et al, J. Vac. Sci. Tech. B, 20, 2739 (2002)

[4] M. E. Anderson et al, J. Vac. Sci. Tech. B, 21, 3116 (2003)

[5] H. Tanaka et al, Jpn. J. Appl. Phys., 43, L950 (2004)

[6] M. E. Anderson er al, Adv. Mat., 18, 1020 (2006)

[7] C. Srinivasan et al, Proc. SPIE 6517, 65171I (2007)

Position-selected molecular ruler

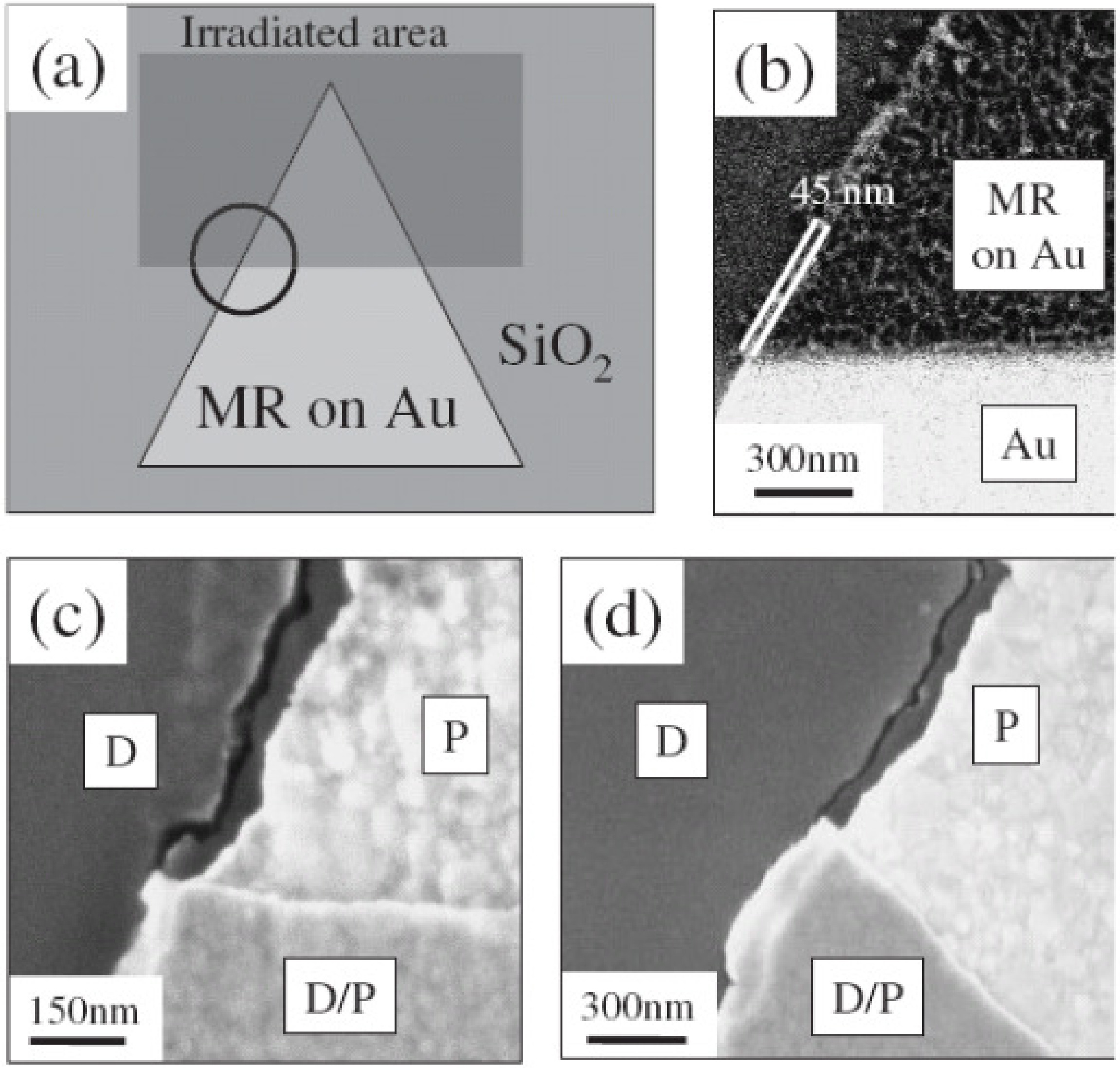
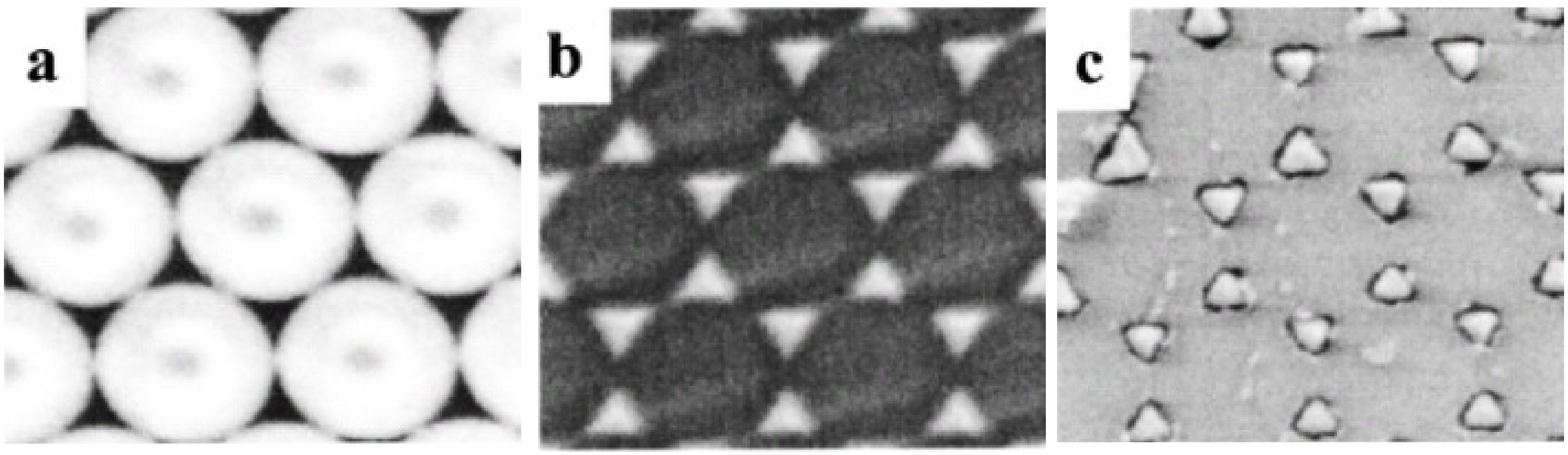


Fig. 3. (a) Schematic of the sample during electron irradiation. PS-MR sample was observed by FE-SEM around the circled area. FE-SEM images of (b) Position-selected molecular ruler and (c) Position-selected gap between parent and daughter structures. Gaps are obtained between the parent and daughter structures only where the molecular ruler was present. (d) Gap created by PS-MR of another sample. Electron beam irradiated the sample 30 min to obtain the PS-MR.

Nanosphere



[4] molecular ruler process combined with nanosphere lithography. (a) Close-packed monolayer of polystyrene spheres is formed. (b) Triangular nanostructures created by gold deposition through the interstitial spaces of the PS mask (c) After five layers of the MHDA/CU2+ molecular rulers process, uniform gaps of ~11nm were defined around each nanostructure in the array

[4] M. E. Anderson et al, J. Vac. Sci. Tech. B, 21, 3116 (2003)