AN INVESTIGATION OF PHYSICAL PROCESSES IN NANOSPHERE LITHOGRAPHY

by

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ABSTRACT

Various physical processes have been investigated in order to improve the Nanosphere Lithography (NSL) technique by modifying the nanosphere structures. Polysytrene (PS) nanospheres used in NSL can be modified in three schemes: Electron beam, heat and chemical manipulation techniques. The most successful scheme to modify nanosphere structures is by the electron beam manipulation technique. Using electron beam irradiation, both the size and shape of the nanospheres can be modified in a controlled manner. An ordered array of spheres can be modified by electron beam irradiation to create a pattern otherwise not available through self-assembly alone. Mechanisms of polymer degradation induced by energetic electrons are discussed.

Heat and chemical manipulation techniques have created freestanding transportable nanospheres thin films (FTNFs) that can be further processed with reactive ion etching (RIE) to create a freestanding transportable lithography mask. A unique honeycomb structure has been created when PS nanospheres were treated with organic solvents. The formation of the honeycomb structure depends on the concentration of the organic solvents and the nanosphere dissolution rate when in contact with organic solvents.

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"If you changed one thing you change everything".

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LIST OF ABBREVIATIONS

1	α-MST	α-Methylstyrene
2	AFM	Atomic Force Microscope
3	AR NSL	Angle Resolved Nanosphere Lithography
4	B	Biological self-assembly
5	CNT	Carbon Nanotube
6	D	Dynamic self-assembly
7	DNA	Deoxyribonucleic acid
8	DPN	Dip-Pen Nanolithography
9	DWW	Direct Write to Wafer
10	EBL	Electron Beam lithography
11	ESL	Edge-Spreading Lithography
12	F_c	Capillary Force
13	F_e	Electrostatic Force
14	F_g	Gravitational Force
15	FTNF	Freestanding Transportable Nanosphere Film
16	ISCNT	Isolated Single Carbon Nanotube
17	ITO	Indium tin oxide
18	LPSR	Localised Surface Plasmon Resonance
19	MEK	Methyl ethyl ketone
20	MFM	Magnetic Force Microscopy
21	MHA	Mercatohexadecanoic acid
22	MIBK	Methil isobutyl ketone
23	MMA	Glycidyl methecrylate
24	NSL	Nanosphere Lithography
25	ODT	Octadecanethiol
26	PDADMAC/PSS/PDADMAC	Poly(diallydimethylammonium chloride/Poly(sodium 4-styrene sulfonate)/ Poly(diallydimethylammonium chloride
27	PDMS	Poly(dimethyl siloxane)

28	PMMA	Polymethyl metacrylate
29	PPA	Periodic Particle Arrays
30	PS	Polystyrene
31	PSD	Position Sensitive Detector
32	PSGMA	Poly(styrene-co-clycidyl methacrylate)
33	RIE	Reactive Ion Etching
34	RNA	Ribonucliec acid
35	S	Static self-assembly
36	SEM	Scanning Electron Microscope
37	SPR	Surface Plasmon Resonance
38	STM	Scanning Tunnelling Microscope
39	T	Templated self-assembly
40	T_g	Transitional Glass temperature
41	TASA	Template-Assisted Self-Assembly
42	TEM	Transmission Electron Microscopy
43	UV	Ultraviolet
44	XRL	X-ray Lithography

Chapter 1

INTRODUCTION

This chapter begins by discussing the background of self-assembly in nature. Mimicking nature's ability in fabricating nanomaterials has been one of scientists' ambitions. Discussions on nanofabricating techniques started with photolithography, continued with other nanolithography techniques, and finally followed by Nanosphere Lithography.

One of the greatest researches of this century is the research of the origin of life, which was estimated to start some 4.8 billion years ago. Life was said to begin from a simple cell, which later evolved into complex, multi-organ organisms. The complexity of nature was said to arise from self-organisation or self-assembly. [1,2]

Autonomous organization of components into patterns or structures without human intervention is defined as self-assembly. [3] The components could be a group of molecules or segments of a macromolecule that interact with each other. These molecules or molecular segments may be the same or different. Their interaction leads to some less ordered state (a solution, disordered aggregate, or random coil) to a final state (a crystal or folded macro molecule) that is more ordered.

Self-assembly occurs when molecules interact with one another through a balance of attractive and repulsive interactions. Examples of the interactions are hydrogen bonds, ionic bonds (electrostatic interaction), hydrophobic interaction, van der Waals interactions, and water-mediated hydrogen bonds. [4] The simplest form of hydrogen bond is in the water molecule, where a proton (H^+ ion) gets between two atoms, oxygen and another hydrogen atom, polarizing and attracting them by means of the induced dipoles. Hydrogen bond plays an important role in protein assembly, such as in the double helix of chromosome. [5] Thymine was linked to adenine molecule in the chromosome by hydrogen bonds that were created by different polarized charges in the adenine and thymine molecules. Hydrogen bond, as the name implies, uses the hydrogen atom to interact with electronegative elements, such as oxygen, nitrogen or fluorine. [6] The hydrogen bond energy is usually less than 0.5 eV. An Ionic bond is an interaction between oppositely charged atoms while Van der Waals bond is an

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interaction between the electric dipole moments of atoms or molecules and has binding energy of 0.1 eV or less compared to a stronger ionic bond which can reach to 5 eV in energy.

Although the bonds mentioned above are relatively insignificant in isolation, when combined together as a whole, they govern the structural confirmation of all biological macromolecules and influence their interactions with other molecules. [7] Therefore, the autonomous organization of components will depend on information coded in molecular structures, such as, in the form of shapes, surface properties, charges, magnetic dipoles or masses. [3]

Self-assembly in nature's living organisms, is a process of automated assembly of materials at nanoscale precision, in which small particles, like atoms, molecules and atomic clusters are regularly added or removed to construct functional systems or structures. [8] One example is haemoglobin protein, which absorbs and releases oxygen and carbon dioxide in our blood circulation system. These precise absorptions and releases of oxygen and carbon dioxide in our blood circulation system are examples of nature's nano-assembling and nanofabrication abilities.

The living organisms' method of nano-assembling and nanofabrication of materials is called the "bottom up" manufacturing method. Living organisms depend much on self-organization in various stages of their lives. They are built "bottom up" by cells, which are also built by the "bottom up" method by smaller units, such as DNA (Deoxyribonucleic acid) and RNA (Ribonucleic acid). DNA and RNA are other examples of nanofabrication machine units, where RNA reads the DNA and translates the code into protein, which is the basic compound of life.

Living organisms prefer small building blocks (atoms, proteins, RNA, DNA, organic materials, etc) and mostly soft, low-Young's modulus materials (muscles, skin, etc), at atmospheric condition and room temperature. Nature (living organisms), through eons of time has developed manufacturing methods, materials, structures and intelligence, which is far more complex, better and advanced from human technological capabilities. [8]

Human, on the other hand, have been mostly using the "top-down" manufacturing method, where bigger materials are reduced to smaller pieces to create functional materials and devices. Human manufacturing methods operate at various temperatures and conditions, using inorganic or stiff materials (silicon, stainless steel) and at various scale dimensions. The constant drive for smaller devices has led human into micro and nano technologies. Much of the efforts are concentrated on the semiconductor industry, particularly in finding ways to create more and dense integrated circuit within smaller area of semiconductor materials.

Producing materials at micro and nanoscale dimensions, especially in the semiconductor fabrication technology, has forced human to make use of the idea of lithography. Lithography is a process of imitating the original pattern and transferring it to another medium. One technique that has been successfully used to fabricate micro and nanoscale dimension devices is photolithography.

Photolithography is a process of using a light source to illuminate a photo mask, where the desired pattern from the mask is then projected onto a substrate coated with photosensitive polymer called photoresist. [9,10] The polymer photoresist radiated with a light source changes its chemical properties, either to become more

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resistant or more soluble to solvents or developers. If the polymer resist becomes more resistant after being exposed to a light source, it is called a negative photoresist. However, if it becomes more soluble, it is called a positive photoresist.

When a negative photoresist is developed with an organic solvent, desired patterns are formed by the remains of the radiated photoresist. Once the patterns are transformed, the process can be repeated or combined with other processes, such as annealing, etching and chemical treatment to produce functional devices.

Photolithography has gradually evolved from using the visible emission of mercury discharged lamps (g line, $\lambda = 436$ nm), to the near Ultraviolet (UV) emission of mercury lamps (i-line, $\lambda = 365$ nm), to the so-called deep-UV emission of KrF eximer laser ($\lambda = 248$ nm) and even deeper UV emission of the ArF eximer laser ($\lambda = 193$nm). [11] Printed dimensions will be in the range of 50-70 nm or less in a few years time, when another possible wavelength, the Ar_2 emission at $\lambda = 126$ nm is introduced.

The success story of photolithography is under challenge, since the optical resolution achievable through conventional optical means in photolithography techniques is restricted by the diffraction limit of light, $\lambda/2$. Spatial resolution below 100 nm will be difficult since diffraction of light and the lost of light intensity while passing through the optical lenses, will be the limiting factors for the optical resolution of the photolithography technique. Another limiting factor is that it works only on photoresist materials. [12] Future nanofabrication will have to deal with diverse types of materials and conditions. A few techniques have been developed to tackle the diffraction limit of photolithography, including using much shorter wavelengths of the radiation source.

Scientists have considered shorter wavelength radiation sources, such as X-Ray and electron beam, to be used to modify the chemical properties of the polymer resist, hence they are called the X-ray lithography (XRL) and electron beam lithography (EBL) techniques. EBL can create smaller features on the polymer resist since it can be focused to less than 10 nm in diameter. [13,14] Serial processing method, where an electron beam is rastered line by line on the polymer resist, is one of the disadvantages of EBL. Other disadvantages of EBL include high sample and initial capital costs. Meanwhile, X-ray lithography technique is characterised by its high initial capital costs but high sample throughput. Structures with resolution down to 30 nm can be produced simultaneously using XRL [15] but with its high initial capital cost, researchers are currently focusing on other fabrication techniques.

Other newly developed techniques for the fabrication of nanostructures on materials are the Scanning Tunnelling Microscope (STM) and the Atomic Force Microscope (AFM). [16,17] Both techniques have low throughput, since they also adopt the serial processing method. In STM or AFM, molecular and atomic manipulation of materials can be achieved, but its serial processing method is not yet suitable for mass production of devices.

The aforementioned disadvantages of 'top-down" fabrication methods, UV Photolithography, EBL, XRL, etc., have directed scientists to focus on other fabrication methods. The ideal nanofabrication technique would be materials and substrates general; inexpensive; flexible in nanoparticle sizes, shapes and spacing parameters; and massively parallel. [18] Thus, parallel nanolithography and self-

assembly nanofabrication methods, could fulfil the ideals of the nanofabrication technique.

Staying focused on parallel nanolithography techniques have led scientists to explore diffusion-controlled aggregation at surface, [19] laser focus atom deposition, [20-22] and nanosphere lithography (NSL). [23-25] As self-assembly techniques are championed by nature, scientists have also considered mimicking nature's self-organization process as an essential part of future technological capabilities in producing smaller and functional devices.

The interest of mimicking nature's self-assembly process, is clearly visible, if we look into the citation counts for the self-assembly process related researches (Figure 1.1). There is an exponentially increase in the number of published papers in the world scientific journals. [26] Self-assembly, self-repairing and self-replicating are scientists' popular words, which have translated scientists' ambitions to fabricate future materials and devices using the understanding and mimicking nature's ways of creating and fabricating materials.
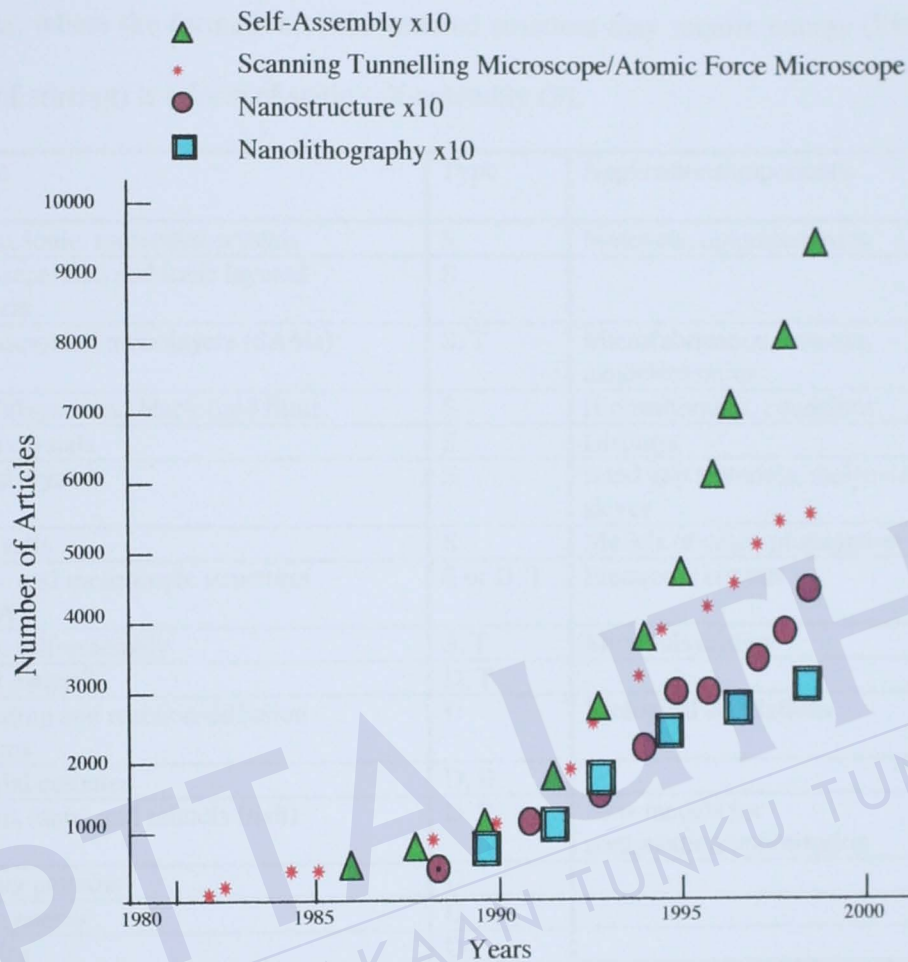
Figure 1.1: Nanoscience Literature Citation Counts (courtesy of AMPTIAC: American Department of Defence 2002, vol. 6)

Table 1.1 shows the classification of self-assembly materials and its applications and importance. [3] There are two main kinds of self-assembly; static and dynamic. Dynamic self-assembly (D) is nature's (living organisms) way of producing vast and spontaneous organisation of materials, such as the organization of the DNA bases in cells. Study on D is more challenging since life itself is a dynamic process. The formation of colloidal crystal into two-dimensional lithographic mask on silicon

surface, where the formation of the ordered structure may require energy (like in the form of stirring) is a form of static self-assembly (S).

System	Type	Applications/importance
Atomic, ionic, molecular crystals	S	Materials, optoelectronics
Phase-separated and ionic layered polymers	S	
Self-assembled monolayers (SAMs)	S, T	Microfabrication, sensors, nanoelectronics
Lipid bilayers and black lipid films	S	Biomembranes, emulsions
Liquid crystals	S	Displays
Colloid crystals	S	Band gap materials, molecular sieves
Buble rafts	S	Models of crack propagation
Macro- and mesoscopic structures (MESA)	S or D, T	Electronic circuits
Fluidic self-assembly	S, T	Microfabrication
"Light matter"	D, T	
Oscillating and reaction-diffusion reactions	D	Biological oscillations
Bacterial colonies	D, B	
Swarms (ants) and schools (fish)	D, B	New models for computation/optimization
Weather patterns	D	
Solar systems	D	
Galaxies	D	

Table 1.1: Examples of self-assembly (S, static, D, dynamic, T, templated, B, biology). Courtesy from G. M Whitesides et al. [3]

There are also two further variants of self-assembly which are templated self-assembly (T) and biological self-assembly (B). Templated self-assembly is a way to code the formation of surfaces or environment, as a component that will interact with the desired components, such as colloids to form into three-dimensional photonic crystals. Biological self-assembly is characterised by its variety and complexity of the functions that it produces. One technique that applies both self-assembly and parallel nanolithography process is NSL. It is originally known as "natural lithography" [23],

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which used a monodispersed nanosphere template as a deposition mask to fabricate

arrays of metal particles, the size of which depends on the sizes of the nanospheres

used.
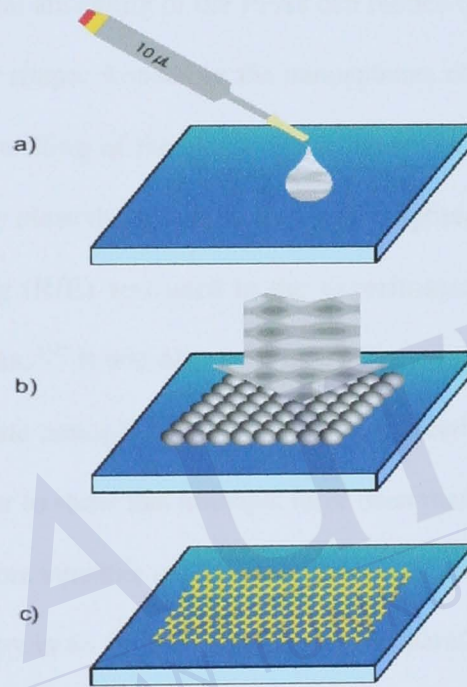
Figure 1.2: Principle of basic NSL: a) application of suspension, b) deposition of metal onto ordered monolayer, c) regularly arranged metal structures on the surface after removal of the particles. Courtesy from F. Burmeister et al. [27]

Basic NSL is a process that includes the self-assembly of nanospheres on a

substrate to create a single monolayer lithographic mask. This process was used in the

experiments throughout the course of this study. In the experiments, metal particles

were evaporated to fill the voids defined by the interstitial of the nanospheres. After

removing the mask using an appropriate organic solvent, periodic particle arrays

(PPAs) of metal nanoparticles were left on the substrate surface. The shapes of the

metal particles created from NSL are usually triangular, truncated, with their size depending on the size of the nanospheres used.

Smaller PPAs can be formed if double-layer nanospheres were used as a lithographic mask [28]. Thermal annealing of the PPAs can reduce the size of the voids, [29] as well as changing their shape. Annealing the nanospheres at T_g (glass transition temperature) [30] will cause swelling of the nanospheres, which will reduce the size of the voids, or even completely close the gap between the nanospheres.

Reactive Ion Etching (RIE) was used in the experiments to create different patterns of lithographic masks. [31] It was also used to try to modify the shapes and the sizes of the PPAs or to create nanopillars. [32-37] Other modifications to NSL will be mentioned in the next chapter to show that attempts have been made to further develop NSL in order to make it a more versatile parallel nanolithographic fabrication method.

Nanosphere lithograpy is an inexpensive, inherently parallel, high-throughput and materials general nanofabrication technique that is potentially useful in studies of size dependent optical, magnetic, catalytic, thermodynamic, electrochemical, and electrical transport properties of materials. [38,39] Limited patterning capability of NSL is one of the limiting factors that should first be addressed before it could be used as a versatile lithography technique. Previous investigators have tried to use pre-patterned surface to guide the self-assembly of nanospheres on the substrate surfaces. [40,41] This assembly of nanospheres to the pre-patterned substrate surface was later defined as template-assisted self-assembly (TASA). [42-46]

Scanning Electron Microscope (SEM) has long been used as an imaging machine. It can be used not only to scan the image of the nanospheres, but also to

modify them. [47] Previous researches have shown that nanospheres can be modified by heat and RIE techniques. In this thesis, other methods to modify nanosphere structures were explored, including the use of electron beam radiation, heat and chemical treatments.

The aim of this research reported within this thesis was to explore the use of electron beam radiation as a means of modifying the nanosphere structures thus creating a new lithographic mask that is very different from the ordinary NSL. It was found that the irradiated nanospheres gradually shrink, creating a hexagonal structure under electron beam exposure. The extent of the modification was found to be dependent on the number of electrons that bombarded the nanospheres and the applied acceleration voltages.

Polystyrene (PS) molecules in the nanospheres are believed to have been degraded and polymer degradation under electron beam radiation are usually in the form of macromolecular chain splitting, creation of low mass fragments, production of free radicals, oxidation, and crosslinking. Irradiated nanospheres are believed to cross-link with each other to create dense, hexagonal structures. The irradiated nanospheres or the hexagonal structures should also show some changes to their chemical properties, which was later found to become more resistant to oxygen plasma etching.

The interactions of the accelerated electrons with PS nanospheres molecules have also created low mass fragments that are deposited in the voids of the irradiated nanospheres site, covering the substrate surface. Therefore, if metal particles were to be evaporated and deposited, PPAs will only exist at the voids of the non-exposed, non-irradiated nanospheres. Somehow, we can regard this technique as negative

lithography, where the irradiated regions will act as shields for depositing metal particles. In this way, patterning the PPAs is achieved, without the need to pre patterned the substrate surface, such as in the TASA's technique.

Longer electron beam exposure to the nanospheres will also separate them from one another and sometimes displace the PS nanospheres laterally. Further investigations also show that these affected, irradiated nanospheres were becoming more attached to the substrate and were difficult to be removed by organic solvents in the lift-off process.

Heating the nanospheres to their T_g could also produce new lithography masks. When heated, they swell and close the voids between them. Subsequently these voids can be reopened by RIE, to create controllable PPAs on the substrate surface.

Creating chemically modified nanospheres by means of evaporating the vapour of organic solvents is also reported in this study. Despite the difficulty to control the amount of the organic solvent vapour, honeycomb structures have been formed successfully. Nanospheres partially dissolved into a semi-liquid material when in contact with an organic solvent. The surface tension and the associated capillary forces drive the liquid material into the gaps of the particle arrays.

Surface tension and the associated capillary forces are among factors that influence the fabrication of the honeycomb structure. The honeycomb structure was assumed to have formed when each partially dissolved nanosphere acts as an island, while the semi-liquid material, partly from the dissolved nanospheres, flows to it's surrounding or at the circumference of the nanospheres. When the semi-liquid materials hardened, they act as walls. These walls and the semi-liquid materials are

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constantly produced depending on the amount of solvents involved. They will create equal surface tension and capillary forces that will displace the dissolved nanospheres, the semi-liquid materials to be deposited to these walls and form honeycomb structures.

Freestanding transportable thin films of nanospheres are created by either chemical or heat treatment. If a monolayer nanosphere film is carefully evaporated with an organic solvent for a few minutes, they will create a semi-liquid material that will later harden when the organic solvent evaporates, enhancing the bonding between the nanospheres in the thin monolayer film. This thin layer film can be floated on the water surface and later placed on a copper grid to act as a lithography mask. Although the result is not completely satisfactory, the procedure can be explored further, as it could provide a way to create cheaper freestanding lithography masks.

Heating the monolayer nanosphere film above its T_g will melt the nanospheres and upon cooling, will create much stronger bond between the nanospheres. When heated, part of the nanospheres will melt and flow beneath the nanospheres, creating a large contact area between them. This monolayer, melted nanosphere film can be floated on water surface to create a freestanding film which could be used to create an inexpensive nanolithography mask.

The main achievements of my PhD project are thus:-

a) controllable modification of PS nanosphere structures by electron beam irradiation. Fabrication of dense hexagonal structures.

b) new lithography mask that can be used to pattern the formation of the PPAs.

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APPENDIX

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