

SELF-ASSEMBLY OF NANOPARTICLES IN
PHOTONIC CRYSTAL CAVITIES FOR
OPTOELECTRONIC DEVICES

by

GEETHA THIRUVENGADAM

Presented to the Faculty of the Graduate School of
The University of Texas at Arlington in Partial Fulfillment
of the Requirements
for the Degree of

MASTER OF SCIENCE IN MATERIALS SCIENCE AND ENGINEERING

THE UNIVERSITY OF TEXAS AT ARLINGTON

August 2006

ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervising professor, Dr. Weidong Zhou for his constant encouragement, support and guidance throughout my research. His enthusiasm and hard work for research was a real inspiration for me. I would also like to thank Dr. Michael Jin and Dr. Yaowu Hao for their acceptance to be in my thesis defense committee and valuable editorial contributions in the documentation part.

My heartfelt thanks to Dr. Vance Ley and Dr. Nasir Basit for their help in carrying out SEM study for the test samples. I appreciate Dr. R. B. Timmons and Mr. D. Bhattacharya for preparing Teflon coated samples and their help in surface modification part of the research.

My heartfelt thanks to my friend Selva for his valuable time and guidance throughout my graduate studies. I owe credits to all members in NanoFAB for their help. I am also grateful to my friends Santosh, Puneet, Kajal, Amith and Pallavi who supported me throughout the research and Priti for her valuable suggestions during documentation. I would also like to thank my batch mates Dr. Zexuan, Hongjun and Li for their suggestions in various parts of fabrication.

Last but not the least, I would like to express my sincerest gratitude to my parents for their love, valuable suggestions and support throughout the study which has helped me to excel in all my endeavors. I would also like to thank my sister-in-law for her support. I am grateful to Vijay, my brother, without whom I would not have pursued my graduate degree.

July 10, 2006

ABSTRACT

SELF-ASSEMBLY OF NANOPARTICLES IN PHOTONIC CRYSTAL CAVITIES FOR OPTOELECTRONIC DEVICES

Publication No. _____

Geetha Thiruvengadam, M.S

The University of Texas at Arlington, 2006

Supervising Professor: Dr. Weidong Zhou

Photonic crystals (PhC) offer many advantages in optoelectronics field. The focus of this thesis is to investigate a self assembly process for the formation of thin film based one-dimensional PhC and the integration of nanoparticles with two-dimensional PhC. Nanoparticles like SiO₂, TiO₂, PolyStyrene, and PbSe (with different surface properties) were subjected to different experiments.

Various techniques, such as spin coating, immersion technique, evaporation induced assembly technique, have been carried out by varying parameters like time, temperature, position of the substrate, etc.,.

An optimized method for the fabrication of 1D PhC was found to be evaporation induced Self-Assembly method by varying temperature. For 2D PhC, a process was developed based on immersion technique and subsequent surface cleaning, where SiO₂ and PbSe nanoparticles are back filled into the air holes of 2D PhC. A theoretical study of radius of nanoparticles in 1D and forces acting on nanoparticles in 2D has been discussed.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	v
ABSTRACT	vi
LIST OF ILLUSTRATIONS.....	xiii
LIST OF TABLES.....	xviii
Chapter	
1. GENERAL INTRODUCTION.....	1
1.1 Nanotechnology	1
1.2 Photonic Crystals (PhC).....	2
1.3 Working Principle of Photonic Crystals.....	2
1.4 Types of Photonic Crystal	3
1.4.1 1D Photonic Crystals	3
1.4.2 2D Photonic Crystals	4
1.4.3 3-D Photonic Crystals.....	6
1.5 Photonic Band-Gap (PBG).....	6
1.6 Fabrication of Photonic Crystals	7
1.7 Self-Assembly	8
1.7.1 Types of Self-Assembly	10
1.7.2 Advantages of Self-Assembly	10

1.7.3 Disadvantages of Self-Assembly	11
1.7.3.1 Issues in synthesis and assembly of nanoparticles.....	11
1.8 Applications of Photonic Crystals.....	12
1.9 Objective and description of thesis.....	13
2. OUR FOCUS – SELF-ASSEMBLY OF NANOPARTICLES.....	16
2.1 Introduction.....	16
2.2 Nanoparticles.....	16
2.3 Properties of nanoparticles.....	17
2.4 Nanoparticles used for the study.....	17
2.4.1 Silica (SiO ₂) Nanoparticles	18
2.4.2 Lead-Selenide (PbSe) Nanoparticles	19
2.4.3 Titania (TiO ₂) Nanoparticles.....	20
2.4.4 PolyStyrene (PS) Nanoparticles.....	21
2.5 Construction of photonic crystal cavities using Self-Assembly.....	22
2.5.1 Spin-coating	23
2.5.2 Evaporation Induced Self-Assembly	24
2.5.3 Immersion Method.....	26
2.5.4 Langmuir-Blodgett Method (LB).....	28
3. FABRICATION OF 1D PHOTONIC CRYSTALS.....	29
3.1 Introduction.....	29
3.2 Basic experimental Setup	29

3.2.1 Spin-coating	29
3.2.2 Immersion Method.....	39
3.2.3 Convective assembly – IARI methodology.....	44
3.2.4 Evaporation Induced Self-Assembly Method.....	46
3.3 Comparison of methods for the fabrication.....	51
3.4 Factors involved in Self-Assembly of 1D crystals.....	53
3.4 Applications of 1D Photonic Crystals.....	54
4. ENCAPSULATION OF 2D PHOTONIC CRYSTAL CAVITIES.....	55
4.1 Introduction.....	55
4.2 Methods used for encapsulation.....	57
4.2.1 Spin Coating.....	57
4.2.2 Immersion Technique.....	62
4.2.3 Nanoparticle solution on the surface of substrate.....	65
4.3 Factors involved in Self-Assembly of 2D cavities.....	67
4.3.1 Capillary Forces.....	68
4.3.2 Diameter of holes and spacing between holes	68
4.3.3 Diameter of nanoparticles.....	69
4.3.4 Selectivity of nanoparticles	69
4.4 Applications of 2D Crystals.....	70
5. CHARACTERIZATION FOR 1D AND 2D PHOTONIC CRYSTALS.....	71
5.1 Introduction.....	71
5.2 Characterization Techniques.....	71

5.2.1 Scanning Electron Microscope (SEM).....	72
5.2.1.1 Substrate with silica nanoparticles.....	73
5.2.1.2 Substrate with lead-selenide nanoparticles.....	76
5.2.2 Ellipsometer	77
5.2.3 Profilometer.....	78
5.2.3 Optical Microscope.....	79
6. THEORETICAL CALCULATION OF THICKNESS OF LAYER IN 1D CRYSTAL AND FORCES IN 2D CAVITIES.....	81
6.1 Introduction.....	81
6.2 Equation and factors involved in Self-Assembly of nanoparticles in 1D crystal.....	81
6.3 Factors involved calculation of force in 2D cavities.....	83
6.3.1 Contact-line radius between particle and solution.....	84
6.3.2 Contact angle between the particle and solution.....	84
6.4 Conclusions based on theoretically derived equations.....	87
7. RESULTS AND CONCLUSIONS FOR PHOTONIC CRYSTALS.....	89
7.1 Introduction.....	89
7.2 Comparison of various methods in 1D PhC.....	89
7.2.1 Effects of weight% of nanoparticles on thickness of self-assembled layer.....	89
7.2.2 Effects of temperature on thickness of self-assembled layer.....	91
7.2.3 Effects of time on thickness of self-assembled layer.....	92

7.2.4 Effects of techniques on thickness of self-assembled layer.....	92
7.3 Conclusions on Self-Assembly of nanoparticles In 1D and 2D crystals.....	94
7.4 Future study.....	99
Appendix	
A. MICROSOFT EXCEL SHEET - PARAMETERS FOR CONVECTIVE ASSEMBLY – IARI EXPERIMENT.....	101
B. MICROSOFT EXCEL SHEET - PARAMETERS FOR IMMERSION TECHNIQUE	103
C. MICROSOFT EXCEL SHEET - PARAMETERS FOR EVAPORATION TECHNIQUE.....	105
REFERENCES	107
BIOGRAPHICAL INFORMATION.....	118

LIST OF ILLUSTRATIONS

Figure		Page
1	1D Photonic Crystal.....	3
2	2D Photonic Crystal.....	5
3	3D Photonic Crystal.....	6
4	Silica nanoparticles	19
5	Lead-Selenide nanoparticles	20
6	Titania nanoparticles	20
7	PolyStyrene nanoparticles	21
8	Solution dispensed at the center of the substrate.....	24
9	Spinning action.....	24
10	Evaporation of solution.....	24
11	Evaporation Induced Self-Assembly.....	25
12	Evaporation of nanoparticles involving forces.....	26
13	Self-Assembled nanoparticles	26
14	Immersion Method – before assembly of nanoparticles.....	27
15	Immersion Method – during Self-Assembly.....	27
16	Silica nanoparticle layers	31

17	SEM image of spin coated silica nanoparticles	32
18	SEM image of spin coated lead-selenide nanoparticles	33
19	SEM image of spin coated lead-selenide nanoparticles.....	34
20	SEM image of spin coated titania nanoparticles.....	36
21	SEM image of spin coated titania nanoparticles.....	37
22	SEM image of spin coated titania nanoparticles.....	37
23	SEM image of spin coated titania nanoparticles.....	38
24	SEM image of silica nanoparticles layers – Immersion Technique.....	40
25	Layer of silica nanoparticles	41
26	Layer of silica nanoparticles	41
27	Thick layer of silica nanoparticles.....	42
28	Lead-selenide nanoparticles - Immersion technique.....	43
29	Convective Assembly - IARI method for silica nanoparticles.....	44
30	CA – IARI method for 0.1ml SiO ₂ : 70ml EA	45
31	Evaporation method for 0.2ml SiO ₂ : 50ml EA	47
32	Evaporation method for 0.2ml SiO ₂ : 70ml EA	47
33	Evaporation method for 0.1ml SiO ₂ : 70ml EA [time=1sec, thickness=250nm and temperature = 50° C].....	48
34	Evaporation method for 0.1ml SiO ₂ : 70ml EA [time= 5 mins, thickness=250 nm and temperature = 75° C].....	48
35	Evaporation method for 0.1ml SiO ₂ : 70ml EA [time=1sec, thickness=20nm and temperature = 75° C].....	49

36	Evaporation method for monolayer of nanoparticles.....	50
37	Evaporation method for the monolayer of nanoparticles (repeated experiment with parameters from fig. 36).....	50
38	Evaporation method for Pb-Se nanoparticles.....	51
39	Evaporation method for a uniform layer of silica particles.....	52
40	Evaporation method for monolayer of silica nanoparticles.....	53
41	2D PhC structure in silicon substrate.....	56
42	Structure of the patterned silicon substrate.....	56
43	2D PhC – Patterns filled with silica nanoparticles.....	58
44	Silica particles on substrate and patterns.....	58
45	Patterns and surface of silicon filled with diluted silica particles.....	59
46	Patterns filled with diluted Pb-Se particles.....	60
47	PolyStyrene particles on patterned silicon substrate.....	61
48	Silica nanoparticles in a patterned substrate - Immersion Technique.....	63
49	Silica nanoparticles in patterned holes - Immersion Technique.....	64
50	Patterns filled uniformly with diluted silica nanoparticles.....	66
51	Uniform distribution of silica nanoparticles (repeated experiment).....	67
52	Scanning Electron Microscope in NanoFAB.....	72
53	Thick uniform layer of silica nanoparticles of thickness 250 nm.....	73
54	Monolayer of silica nanoparticles layer of thickness 20 nm.....	74

55	SEM image of 2D PhC of silica nanoparticles	75
56	Layer of Pb-Se nanoparticles of thickness 140 nm.....	76
57	Gaertner Ellipsometer for thickness measurement.....	77
58	KLA Tencor Profilometer.....	79
59	Nomarski Microscope in cleanroom, UTA NanoFAB center.....	80
60	Optical Microscope image of a ring pattern in the substrate.....	80
61	Capillary Force (F_c) illustrated at the vapor – solution – substrate interface.....	85
62	Graph between contact-line radius and perpendicular force.....	86
63	Graph between $\cos(\alpha)$ and perpendicular force	87
64	Effects of Weight% of nanoparticles on thickness of assembled layer.....	90
65	Effects of temperature on thickness of assembled nanoparticle layer.....	91
66	Effects of time on thickness of assembled nanoparticle layer.....	92
67	Effects of technique for Self-Assembly on thickness of assembled layer.....	93

LIST OF TABLES

Table	Page
1 Refractive Index for materials used in experiments.....	22
A.1 Parameters used for the Convective Assembly – IARI experiment	102
B.1 Parameters used for the Immersion Technique	104
C.1 Parameters used for the Evaporation Technique	106

CHAPTER 1
GENERAL INTRODUCTION

1.1 Nanotechnology

Nanotechnology is an art of manipulating materials at the atomic scale. This deals with the design and manufacture of very small electronic circuit components and mechanical devices [1]. Nanotechnology involves research at 1nm – 100nm range [2]. Nanotechnology creates structures that have novel properties because of their small sizes [2] [3]. Two approaches to fabricate devices at nanoscale are:

- Top-down approach [4]

This approach begins with a large scale and the nanoscale products are obtained by carving out components from the large scale. Example: Lithography

- Bottom-up approach [4]

This approach starts with atoms and molecules and required component is obtained by combining smaller atoms and molecules. This involves understanding of lots of forces of attraction because non-covalent forces work together to bind these atoms or molecules together [5]. These non-covalent interactions can be strengthened or weakened depending on environment. Example: Self-Assembly [6].

Self-Assembly has an ability to control the interaction of atoms/molecules in small scale materials using spontaneous interaction [5]. Self-Assembly is controlled by covalent interactions between the nanoparticle solution and the substrate. As the

nanoparticles are moved into the holes of crystal, they are held in the position by van der waals forces, gravitational forces existing between the nanoparticles.

1.2 Photonic Crystals (PhC)

Photonic crystals (PhC) are materials having periodic variation in refractive index. These crystals are man-made materials. PhC are considered to be an optical analogue of semiconductors [7]. Photonic Crystals are nanocrystals to guide photons and insulate light [2]. This is explained by the variation in refractive index.

PhC is an important topic in optoelectronic research because of their ability to control microscopic process of light – matter interactions through macroscopic modifications in the geometric characteristics of the structure [8]. Fabrication of PhC promises applications in fields like optoelectronic, nanophotonics, nanoelectronics, magnetoelectronics and biochemical sensing [9].

1.3 Working Principle of Photonic Crystals

Photonic crystals are photoemissive materials which emits photons when excited electrically or physically. The excited photons are emitted in different directions and have certain range of wavelengths.

Emitted photons move through an arrangement of transparent dielectric material. This dielectric material consists of a number of tiny air holes arranged in a regular pattern. Photons passing through the dielectric material will pass through regions of high refractive index and low refractive index (high refractive index being the dielectric material and low refractive index being air holes).

In PhC, at each interface the waves are partly reflected and transmitted. Phase of the waves is important as they determine the optical property or response of the system. When the phase of waves adds up constructively, system is shown to have complete reflection in that direction [10].

1.4 Types of Photonic Crystal

1.4.1 1D Photonic Crystals

1D crystals are periodic in one direction made of different layers of different refractive indices. When light is incident on the crystal due to different properties like frequency, refractive index, dielectric constant of these layers, they behave differently with the incident light. Due to the same, propagation of photons of certain wavelengths is forbidden. Thus, these crystals behave like mirrors.

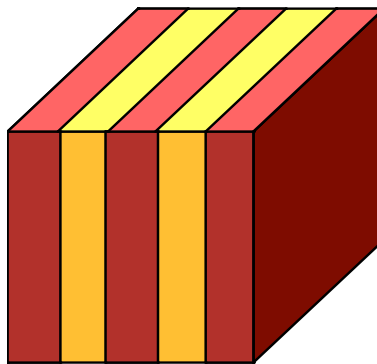


Fig. 1 1D Photonic Crystal [11]

1D crystals are fabricated by the deposition of multilayers of nanoparticles on top of the substrate. By stacking alternating layers of different materials, we change the optical property of the material when light is incident on it.

But selecting materials for the construction of alternating layers and achieving uniformity in layer formation are highly difficult as the properties of nanomaterials are yet to be studied completely and the compatibility of these layers are expected to be extremely good.

In this thesis, we have discussed various methods of Self-Assembly to achieve these monolayers on the substrate. Also, parameters like time, temperature, spin speed and spin time (in case of spin coating), weight percentage of nanoparticles in the solution, position of the substrate (being either horizontal or vertical) were varied to attain monolayer of nanoparticles. Then, these values were plotted in a graph, to study their influence on thickness of nanoparticle layer. Also, theoretical calculation for the total number of nanoparticles and thickness of nanoparticle layer on the surface of substrate was carried out.

1.4.2 2D Photonic Crystals

2D crystals are periodic in two directions and are fabricated either by drilling holes onto the dielectric materials or by constructing regular lattice of pillars to create wall like structures with certain periodicity. Refractive index contrast is created in these materials by filling the holes/etched parts of a substrate with different materials or by constructing wall like structures with certain periodic arrangement.

A rough calculation of spacing between the air holes in a substrate is given by the wavelength of light divided by the refractive index of a dielectric material [12]. The main advantage of 2D PhC is that they are compatible with the existing IC technology.

Due to the properties of 2D crystal cavities like controlling and manipulating flow of light (which is performed when photon passes through the substrate made of alternate high and low refractive index material), they are being fabricated for various applications in integrated optics in an optical chip which uses IC concepts for both electronic and optical functions.

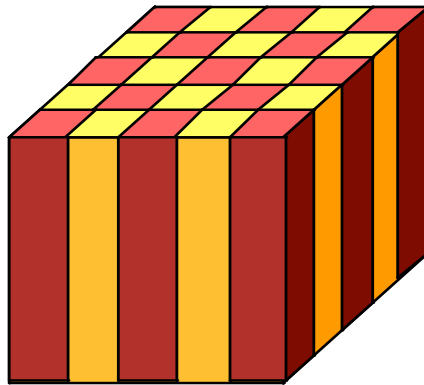


Fig. 2 2D Photonic Crystal [11]

Certain type of defect modes (like creating holes in the mid of regularly arranged nanoparticle layers) are introduced into the crystal which results in various properties of light within it. These defect modes are nothing but the disturbance in the lattice arrangement of the crystal which results in the localization of light with a certain frequency at the position of the defect.

In this thesis, we have shown various fabrication methods based on Self-Assembly to encapsulate these air holes in 2D cavities. Different methods like spin coating, immersion technique and nanoparticles solution filling the surface of substrate are also discussed. An optimum method to fill these air holes is shown along with the scanning electron microscope images. Various factors varied to achieve this

encapsulation are spinning speed, time, position of the substrate, weight% of nanoparticles in the solution.

1.4.3 3D Photonic Crystals

Though 2D crystals are used in the localization of light, 3D crystals are used for the complete localization of light [13]. They inhibit spontaneous emission in all directions. They are constructed by alternating layer deposition and etching process [14]. These structures are produced by stacking up two patterned layers on top of each other [10] [15] [16]. This shows that the crystals on substrates are of large structure. Few disadvantages in the fabrication of 3D PhC are that they are expensive, time-consuming and aligning layers on top of each other is very difficult.

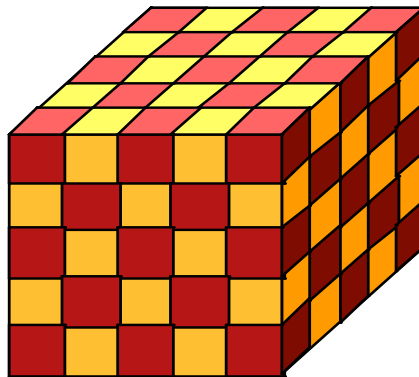


Fig. 3 3D Photonic Crystals [11]

1.5 Photonic Bandgap (PBG)

PBG is a range of energy and corresponding range in wavelength, for which neither absorption nor propagation of light is allowed. When there is a high contrast in refractive index of the crystal, the incoming light is unable to penetrate in any direction

in the crystal. This is the condition for photonic bandgap to exist which localizes the light inside a crystal or inhibits the light emission from atoms inside the crystal.

Photonic bandgap is the range of forbidden frequencies through which light cannot propagate within the bulk of a crystal [17]. Photons with energies lying in the bandgap region cannot propagate through the medium [16]. PBG in crystals suppresses the spontaneous light emission because of that the atoms are a part of crystals that forbids the propagation of light [18].

1.6 Fabrication of Photonic crystals

Silicon is used for our fabrication of photonic crystals because Si is transparent at near-infrared wavelength ($>1.1 \mu\text{m}$) and has a very high refractive index ($n = 3.45$ at $\lambda = 1.5 \mu\text{m}$). Also the fabrication of silicon materials is well known from semiconductor industries.

Methods used for the fabrication of 1-, 2- and 3-D photonic crystals are [19]:

- Self-Assembly of nanomaterials
- Spin coating
- Dip-coating
- Evaporation induced assembly
- Chemical vapor deposition
- Sedimentation in colloidal solutions
- Electron beam and X-Ray Lithography

- Wet and dry etching (like electrochemical and reactive-ion etching via plasma and focused-ion beams).

This thesis gives a detailed overview of spin coating, immersion method, evaporation induced Self-Assembly method, and convective assembly. It also discusses various parameters involved in each process like effects of size of nanoparticles, weight% of nanoparticles in the solution, time for which substrate is immersed in nanoparticles solution, speed at which the spinner was operated for spin coating process, temperature at which the evaporation was carried out for evaporation induced Self-Assembly method, and the position at which substrate was immersed in solution being either horizontal or vertical.

1.7 Self-Assembly

Self-Assembly is a spontaneous formation of structures due to the chemical interactions between nanoparticles [20]. As the size of system reduces, capillary forces dominate over few other forces like gravitational, hydrodynamic, magnetic, electrostatic and surface adhesion. It is the selective control of non-covalent interactions which creates structured components at molecular level [21]. Self-Assembly is governed by the interaction between nanoparticles which includes capillarity and wetting ability of the substrate [22].

Due to repeatability and simplicity, Self-Assembly method was made as the basic principle in this thesis. All techniques carried out for the Self-Assembly of nanoparticles in this thesis follows this methodology.

Self-Assembly is achieved by the involvement of different forces at each step of the fabrication process. For some applications, these forces are converted into velocities using a simulation software known as “Surface Evolver”. This software is used to convert the capillary forces into velocities [23]. Surface evolver is used to calculate the capillary forces from energies (like gravity and surface tension) applied by the liquid meniscus to the assembly of nanoparticles [24] [25].

In our thesis, as mentioned earlier, Self-Assembly is the main basic method based on which we carried out many other experiments. For Self-Assembly process to initiate, the nanomaterials (in some liquid environment) are made to fill the substrate. As the surface interactions dominate at nano scale, nanomaterials can be transported easily on the substrate when they are in a liquid environment. These nanomaterials will spontaneously align themselves to minimize the energy. Even if the nanomaterials do not stick to the substrate they will be moved to some other spot on the substrate by the fluid movement.

To attain minimum-energy some kind of lubrication/vibration method is used for the process. Fluidic agitation or ultrasonic vibration is applied to the system to reduce energy barriers or to assemble any disassembled parts [26]. Also, thermal treatment of self-assembled nanoparticles found to reduce the interparticle distances which results in change in type and strength of interparticle interactions [27]. This post heating of substrate with nanoparticles is sometimes known as “annealing”.

Once these materials are assembled onto the holes or their respective sites they are held in place by gravitational, van der Waals forces and capillary forces upon drying

[26]. These assembled nanoparticles have remarkable effect on the properties of the structures. Also these processes depend on nature for assembling instead of human factors.

1.7.1 Types of Self-Assembly

Self-Assembly is carried out by different forces on surface of the substrates depending on the surface properties of the substrate.

There are different types of Self-Assembly depending on the methodology used for the processes. They are as follows:

Types of Self-Assembly based on methodology are as follows:

- Physical Self-Assembly
- Chemical Self-Assembly
- Layer-by-Layer (LbL) assembly
- Molecular Self-Assembly
- Evaporation-Induced Self-Assembly

1.7.2 Advantages of Self-Assembly

Though there are many methods available for fabrication of crystals and cavities, we selected Self-Assembly method for the fabrication part in our experiments because of the following advantages:

- Self-Assembly carries out most of the difficult steps in nanofabrication-those involving *atomic-level modifications* of structures. This uses the very highly developed techniques of synthetic chemistry

- Bonds holding together a single molecule are far stronger than the weak interactions that hold more than one molecules together [28]
- Repeatability is easy
- Self-Assembly is one of the most important strategies used in biology for the development of complex, functional structures
- Self-Assembly results in *defect-free and self-healing structures* because it requires the target structures to be *thermodynamically most stable* ones
- Simplicity of the fabrication methodology and low cost of fabrication.

1.7.3 Disadvantages of Self-Assembly

Though Self-Assembly have lots of advantages as a bottom-up technique, it has few disadvantages like:

- *Exact set of components and interactions that will construct a given product can be difficult to determine*
- At times , statistical exploration of different possibilities make Self-Assembly difficult to settle on a single final structure
- Also, Self-Assembly finds it *difficult to resist continual environment aberrations/factors once assembled.*

1.7.3.1 Issues in synthesis and assembly of nanoparticles [29]

Few issues we had during the fabrication of crystals and cavities using Self-Assembly of nanoparticles are in controlling parameters like:

- Size of nanoparticles

- Composition of nanoparticles inside the solution
- Interfaces and distribution of these nanoparticles on the processed surface of the substrate.

1.8 Applications of Photonic Crystals

Photonic crystals are expected to replace electrons (as in semiconductors) with photons and this replacement demands new materials. This resulted in tailoring the propagation of light through the creation of photonic crystals [30]. Applications of these photonic crystals are:

- Construction of complex components like splitters, couples, filters, emitters, lossless mirrors [31]
- Devices in data communications
- Microlasers – Defects in PBG helps in designing microlasers
- Perfect dielectric mirrors
- Non-linear effects – by using materials with non-linear properties for the construction of PhC (Non-linear effects are the processes due to the interactions between light waves and materials transmitting them which affects the optical signals) [32] [33]
- Waveguides [34]
- Integrated optical devices [35]
- Optical switches
- Chemical and biochemical sensors

1.9 Objective and description of Thesis

The main objective of this thesis is to fabricate 1D photonic crystals cavities with a monolayer layer of nanoparticles on the substrate, encapsulate 2D crystal cavities to seal off the air holes in the silicon substrate, characterization of these crystal cavities using scanning electron microscope and theoretical calculation of total number of nanoparticle layers on surface of the substrate and thickness of nanoparticles for 1D crystals and calculation of force and its relation with radius of nanoparticle is carried out for 2D crystal cavities.

Experiments in this thesis are carried out to find a suitable method for assembling nanoparticles in photonic crystal cavities. Though there are very few standardized procedures for assembling nanoparticles into these man-made crystals and those available requires equipment and setup investment, we thought of assembling these nanomaterials in these cavities using a simple but effective method. It is at this point we decided to proceed with Self-Assembly of nanoparticles for our experiments, as the method does not require much investment for equipments and repeatability is achieved without much difficulty.

So we carried out the fabrication of 1D crystals with an idea of building a monolayer of nanoparticles on the surface of the substrate. We carried out different set of experiments with various techniques (like spin coating, immersion technique, convective assembly – immersion at regular intervals) and evaporation induced Self-Assembly method. When we carried out Self-Assembly as our first approach towards the end result of fabricating 1D crystals which is nothing but constructing layers of

nanoparticles on the surface of substrate, we got broken films of nanoparticle layers on the surface of substrate. Thickness of the nanoparticles was also too high in the range of 1 μm . We changed parameters like spin speed, spin time, weight% of nanoparticles in the solution by adding more of IsoPropanol solution (in which silica was immersed) or ethanol solution. Though the thickness range of less than 1 μm was achieved, layer on the surface of substrate was seen as broken films. Reasoning for this type of broken films is discussed in chapter-2.

We then proceeded with immersion method. In this method, the substrate was immersed vertically or horizontally into a solution. Solution was let to evaporate in atmospheric air. Depending on the evaporation rate of solution and position of the substrate (horizontal or vertical), thickness of the nanoparticle layer varies. Though the thickness of nanoparticle layer was thin compared to that of spin coating method, this method gave broken layers.

Then the same method was slightly modified because of the broken film formation, where the new technique involved movement of the substrate at regular intervals into and out of the solution. When this method gave us a thin layer of uniform layers, we proceeded with the method which involved heating of the solution with the substrate lying inside the solution undisturbed. This method concluded our fabrication method of 1D crystals by forming a monolayer and 2 – layers of nanoparticles on the surface of substrate.

Same approaches of spin coating and immersion technique were used for the encapsulation of 2D crystal cavities. In 2D crystal cavities, our main objective was to

fill the holes of the silicon substrate with nanoparticles. But these two methods, though gave us substrate with nanoparticle filled holes, nanoparticles were seen to fill the surface of the substrate also. So we modified the immersion technique to achieve the results for 2D crystal cavities. Method we used was to keep the substrate on a flat plate. Then a few drops of nanoparticle solution were poured on the surface of substrate. They are let to air dry. Few more drops of nanoparticles solution were again poured. Then the substrate was washed with IPA solution which helps in maintaining the surface of substrate without nanoparticles.

Also, the fabrication and encapsulation of photonic crystals are characterized by SEM. This is carried out to check the thickness of nanoparticle film on the surface of substrate for 1D photonic crystal and distribution of nanoparticles in 2D crystals and to check whether the air holes are properly sealed off in 2D photonic crystals.

Then a theoretical study is carried out for the better understanding of mathematical relations between the total numbers of colloidal layers on the surface of the substrate, weight fraction of the component in the solution, thickness of nanoparticles layer on the substrate, radius of nanoparticles and contact-angle between nanoparticles and solution.

Also, graphical presentation of thickness with respect to other factors like weight-volume %, time, temperature, weight% of nanoparticles in the solution is shown. This thesis gives an idea about how different methods are being used in the fabrication and encapsulation of photonic crystals.

CHAPTER 2

OUR FOCUS – SELF-ASSEMBLY OF NANOPARTICLES

2.1 Introduction

The main objective of this research is to form monolayers on top of silicon substrate, to seal off the holes in 2D silicon crystal cavities. This can be achieved by filling these holes on the substrate using nanoparticles. Due to their unique properties, nanoparticles are being considered for optical, electronics, mechanical, chemical and magnetic field applications. Also, suitable method to fill the substrate with these nanoparticles is selected considering various factors like cost, repeatability and ability of these materials to perform at different conditions.

This chapter explains in detail why we used certain nanoparticles for the fabrication of PhC cavities and reasons for choosing Self-Assembly as a basic method for the assembling nanoparticles in PhC cavities.

2.2 Nanoparticles

Nanoparticles have been the subject of interest over the past decade as they are being used in many applications in industrial, biomedical, electronic and optical fields. These particles are less than 100nm in size. The dimensions of these particles are less than that of the wavelength of light. This property offers them their transparent characteristics. These are either man-made or natural material.

2.3 Properties of nanoparticles

Two important properties of nanoparticles are:

- Increase in the ratio of surface area to volume
- Size of these particles - where quantum effects predominate [36]

The surface-area-to-volume ratio increases as the particle size decreases. This results in the active atoms on the surface of the nanoparticle whose behavior dominates than those on the interior of the particle. This property affects the behavior of nanoparticles when they are used as particles alone or during the interaction of these particles with other materials. But this exposed surface area is a dependent factor on the interaction between elements and particles.

The aggregation of these nanoparticles forms “Nanocrystals”, also known as “Clusters”. These nanocrystals have improved hardness, increased ductility, toughness, and excellent magnetic, electronic and optical properties [37].

2.4 Nanoparticles used for the study

Nanoparticles used for this thesis are selected based on their properties when they are treated alone or when they interact with other nanoparticles. Nanoparticles used for the study are as follows:

- Silica (SiO_2) nanoparticles in IsoPropanol Solution
- Lead – Selenide (Pb-Se) nanoparticles in hexane solution
- Titania (TiO_2) nanoparticles in water
- PolyStyrene (PS) nanoparticles in water

Nanoparticles are immersed in solution for Self-Assembly process to occur. The molecules must be mobile for the easiness of Self-Assembly. It is normally carried out in a solution. In solution, thermal motion of the molecules binds them together [37]. The interaction of the components with environment is a very important factor in Self-Assembly process.

Inorganic nanomaterials are used because of their physical properties which depend on the chemical environment of the particle. These nanomaterials adsorb themselves to the surface of the particle which changes the physical properties like magnetism, color and conductivity [38].

2.4.1 Silica (SiO₂) Nanoparticles

These silica nanoparticles were dispersed in IsoPropanol (IPA) solution. The weight-volume ratio of these silica nanoparticles in the IPA solution 30%: 70%.

Three different diameters of the nanoparticles in IPA solution are 15-20 nm, 40-60 nm, and 70-90 nm. These solutions were purchased with these specifications from Duke Scientific and Nissan Chemical Houston Corporation. Different sizes were selected to check the distribution of nanoparticles with the variation in nanoparticle size. Since 100nm particles did not give us proper distribution on the surface of the substrate, most of the experiments in this thesis were carried out with 15-20nm and 40-60nm particles. Though sizes of particles inside the solution were not completely uniform, they were uniform to such an extent that they didn't create any difference in assembly during fabrication.

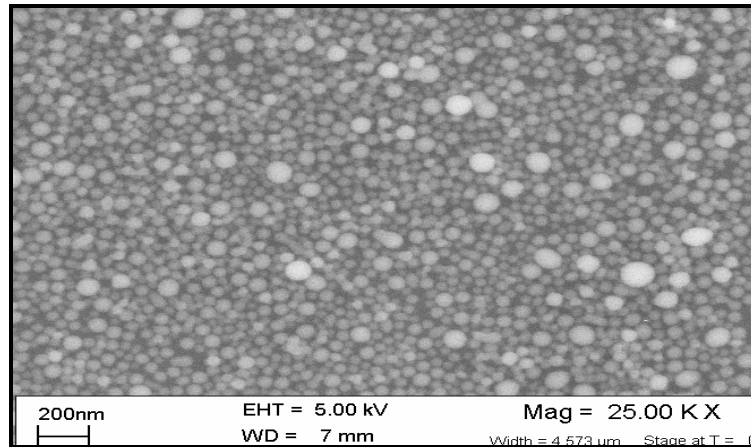


Fig. 4 Silica nanoparticles

Silica nanoparticles are compatible with Silicon microfabrication processes. Also they are optically transparent which helps in detection applications. Also self-assembled layers of silica material were proved to have greater chemical, mechanical, thermal stability [39].

2.4.2 Lead-Selenide (Pb-Se) Nanoparticles

Two types of Pb-Se nanoparticles were used for this study, both were of diameters less than 40 nm. Pb-Se solution was purchased with the size specification from Evident Technologies and Rice University. Evident Technology solution was dispersed in hexane and the one got from Rice University was dispersed in tetrachloroethylene.

Pb-Se nanoparticles has high dielectric constant with a bandgap of 0.42nm which can fit into nanometer sized holes / patterns. Also, these nanoparticles can be tuned to be sensitive to particular infra-red wavelengths. Pb-Se Nanoparticles are being used in infrared detectors, thermal imaging [40]. Lead-Selenide particles are used

because of their photoconductivity at the infrared wavelength of 1550 nm. This wavelength is preferred for optical communication. [41]

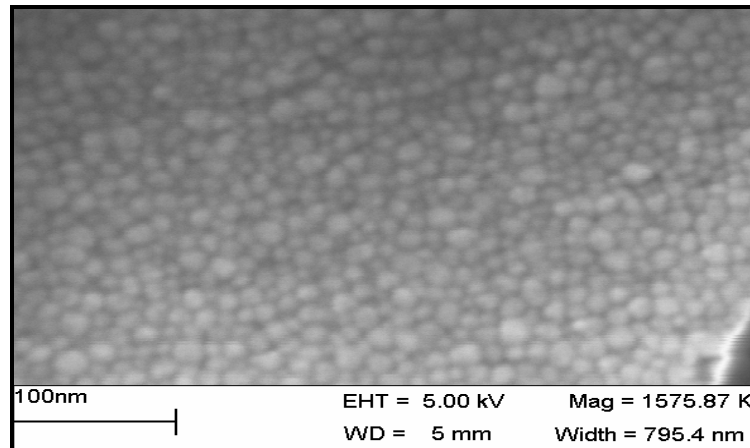


Fig. 5 Lead-Selenide nanoparticles

2.4.3 Titania (TiO_2) Nanoparticles

Titania nanoparticles used for the fabrication were dispersed in water. They weight percentage of dispersion of titania nanoparticles in water is 5%. Diameter of these nanoparticles was less than 40 nm.

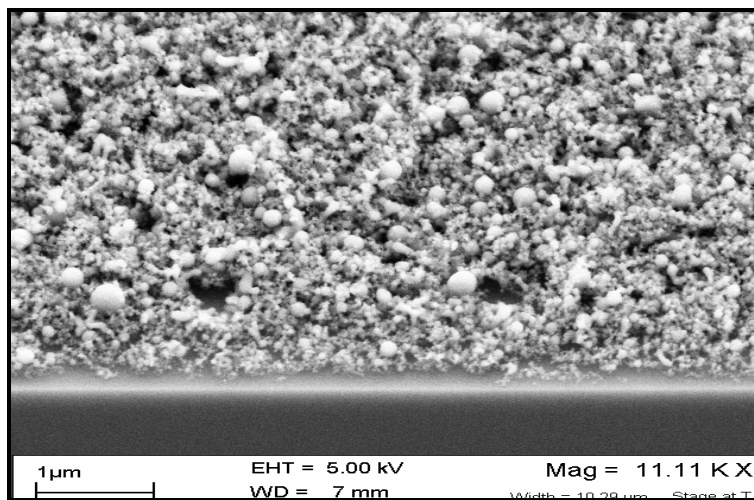


Fig. 6 Titania Nanoparticles

Titania nanoparticles have been widely processed for their applications in sensors, photocatalysis, solar energy conversion, optical coatings. Titania absorbs ultraviolet radiation due to its wide band-gap. It also exhibits photo-catalytic properties when irradiated with ultra-violet radiation [42]. Titania has a very high refractive index ($n = 2.4$).

2.4.4 PolyStyrene (PS) Nanoparticles

PolyStyrene nanoparticles were dispersed in water and the diameter of PolyStyrene nanoparticle was 220 nm. These particles are extremely hydrophobic. So they were used to study the surface properties along with surface modification. In general, the self-assembled monolayer of PS spheres is used as templates for the synthesis of nanomaterials [43].

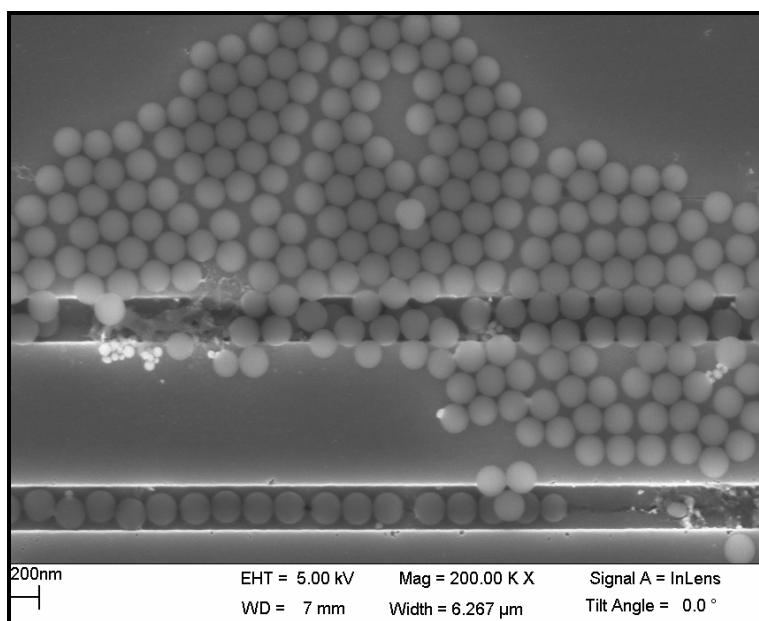


Fig. 7 PolyStyrene Nanoparticles

Table 1 Refractive Index of materials used in this thesis

Material	Refractive Index
Silica	1.45 – 1.5
Lead-Selenide	4.5
Titania	2.5 – 2.9
PolyStyrene	1.55

2.5 Construction of Photonic Crystal Cavities using Self-Assembly

Self-Assembly is a spontaneous and autonomous arrangement of molecules or nanomaterials into organized and well-defined aggregates [44]. considered to be an effective method as it has more advantages compared to top-down approach like defect free structures, atomic level fabrication, low cost of fabrication. In this thesis, PhC are fabricated using Self-Assembly method. They are as follows:

- Spin-coating
- Evaporation Induced Method
- Immersion Method
- Langmuir-Blodgett films (known as ‘Immersion At Regular Intervals (IARI)’ in this thesis)
- Convective assembly

Spin coating, Evaporation-Induced SA and Immersion method are techniques used for the Self-Assembly which does not require any equipments except for spin

coater or spinner for spin coating whereas Langmuir-Blodgett (LB) method uses Langmuir-Blodgett trough for monolayer formation and here monolayers are formed in a solution and then transferred to the substrate. This is not a direct method of monolayer formation on the substrates. But in our experiments we used the concept behind LB methodology. LB uses the principle of immersing the substrate into the solution and taking it out at regular intervals.

Also the thickness of the layer and molecular arrangement is controlled in LB method [35]. This method is known as ‘Immersion At Regular Intervals’ (IARI).

2.5.1 Spin Coating (SC)

Spin coating is a method to obtain a uniform layer of particles on the surface of the substrate. Spin coating is used even for films of thickness in the range of 10 nm. In this method substrate is placed at the center of the chuck in spinner.

Few advantages of spin coating are as follows [45]:

- Speed of the process
- Low-volume of solute required
- Availability of instrument for spin coating purpose
- Easiness in the usage of the spinner

Spin coating process takes place in three steps that includes dispensing the solution, spin coating operation with spin speed and time adjustments, volatilization of the solute. The process of spin coating along with figures is given below:

- Nanoparticles solution is dispensed at the center of the substrate.



Fig. 8 Solution dispensed at the center of the substrate [46]

- Spinner is then rotated at a desired speed for required time.



Fig. 9 Spinning action [46]

- The solution evaporates leaving a thin nanoparticle layer on the surface of the substrate.

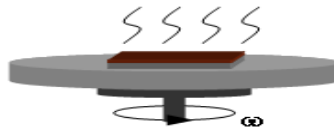


Fig. 10 Evaporation of solution [46]

Thickness depends on speed of the spinner, time of the process, pre-bake that is done to remove the moisture content on the substrate and viscosity of the solution. As the solution used for the process is volatile it evaporates along with the process.

2.5.2 Evaporation-Induced Self-Assembly [47]

In this method the substrate is drawn vertically into a container filled with nanoparticles solution as shown in Fig. 11.

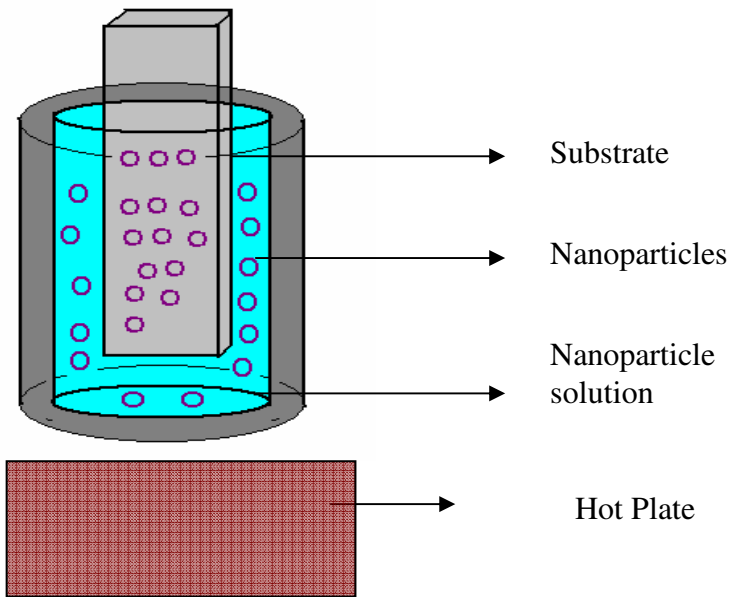


Fig. 11 Evaporation Induced Self-Assembly [48]

The procedure followed in this method is as follows:

- The solution is kept on a hot plate along with the substrate.
- As the solution evaporates, nanoparticles start to settle on the surface of the substrate.
- The substrate will not be disturbed when it is inside the solution.

Evaporation Induced Self-Assembly method is also known as “dip coating”.

Thus dip coating refers to the method governed by evaporation of solvent from the nanoparticles solution from a thin liquid film wetting the substrate that is kept inside the solution [49]. Evaporation induced Self-Assembly depends on various factors like capillary forces, nanoparticle flow and flow of solution carrying nanoparticles, surface

tension between the substrate and the solution, evaporation rate of the nanoparticle solution [50].

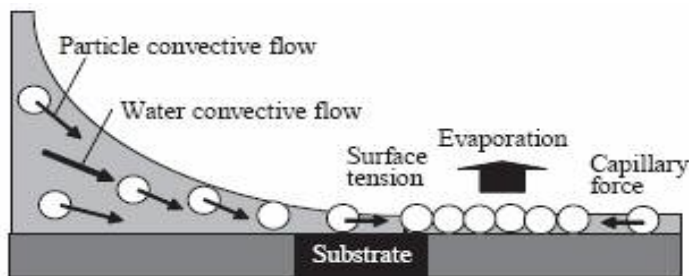


Fig. 12 Evaporation of nanoparticles involving forces [50]

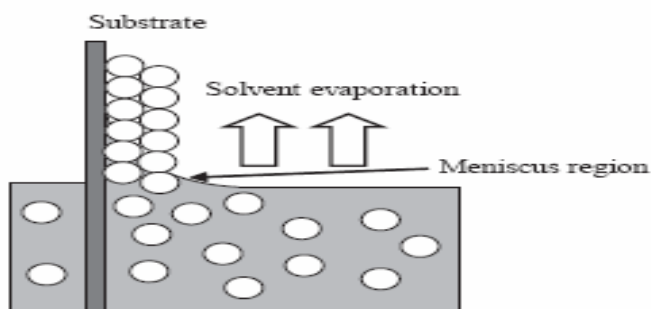


Fig. 13 Self-Assembled nanoparticles [50]

2.5.3 Immersion Method

In this method, the substrate is immersed into nanoparticle solution. The substrate can remain inside the solution during evaporation of the solution or can be disturbed. This method is similar to that of the evaporation induced Self-Assembly method except that here the experiment is carried out at room temperature without any external heating. Also, the substrate can be kept inside the solution or disturbed by some vibrations (or even removing and inserting the sample with the nanoparticles solution at regular time intervals).

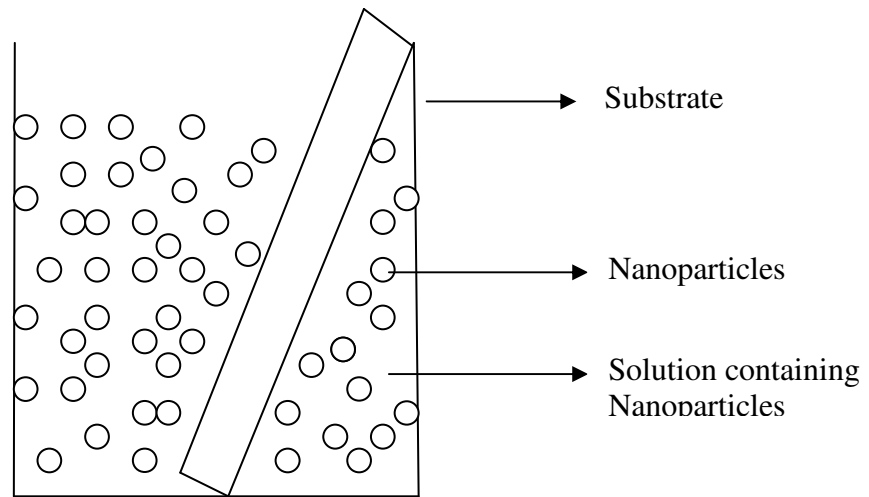


Fig. 14 Immersion Method – before assembly of nanoparticles [51][52][53][54]

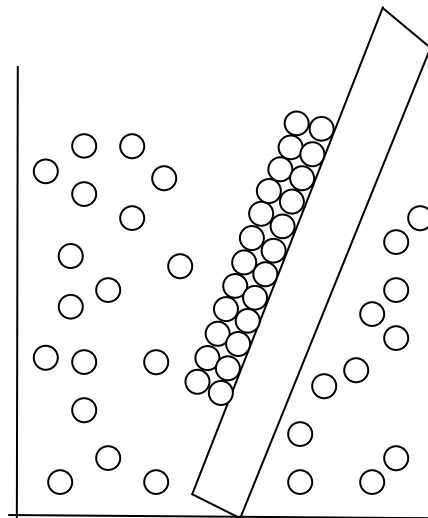


Fig. 15 Immersion Method – during Self-Assembly [51] [52] [53] [54]

Disadvantages of this method are: [55]

- Slow process
- Large volume of nanoparticles solution is required
- Uniform filling of patterns is difficult

2.5.4 Langmuir-Blodgett Method (LB)

In this method, as described above, the concept of moving the substrate into and out of the solution alone is considered for the experiment. The substrate is kept inside the solution. This solution can be placed in a hot plate for heating or in hood for the reaction to take place at room temperature. The substrate is then immersed into the solution and can be moved out and into the solution using a tweezer. This helps in alignment of nanoparticles even if they are not placed in proper position. This method is known as “Immersion At Regular Intervals” in this thesis.

The LB trough method for LB film formation uses amphiphiles (compound which possess both hydrophobic and hydrophilic nature), semiconducting quantum dots, polymers and nanoclusters.

CHAPTER 3

FABRICATION OF 1D PHOTONIC CRYSTALS

3.1 Introduction

1D PhC are structures that are periodic in one direction. Nanoparticles used for the fabrication of 1D PhC, self-assemble themselves on the surface of Silicon substrate. The total number of layers that can be on the surface of the substrate varies between 2 to 8 [56]. The process that is carried out for a type of nanomaterial should be compatible with other materials. This is very important criteria in 1D PhC. Otherwise, if a layer is self-assembled at 90 ° C, and we assemble second material onto the surface (which has a flash point at 50 ° C), then it is difficult to assemble first material (for the construction of 1D PhC) as a third layer, because of a very low flash point of the second material.

3.2 Basic Experimental Setup

3.2.1 Spin Coating

Spin coating is carried out to get a uniform layer of nanoparticles on the surface of substrate. Spin coating is carried out for silica, lead-selenide and titania nanoparticles. Though the thickness of layer of nanoparticles was different for all these materials, the variation of thickness with respect to speed and time remained constant throughout.

○ **Silica Nanoparticles:**

Silicon wafers are always treated with Buffered HydroFluoric acid (HF) before starting the fabrication of PhC. It is then washed in De-Ionized (DI) water. This cleaning of substrate is done to make sure that the surface of silicon substrate becomes rich in hydroxyl (OH) molecules.

Deposition of silica nanoparticles on the surface of substrate does not produce good result if the silicon substrate used does not have any OH group molecules. Thus cleaning the substrate with HF acid and DI water results in good deposition of silica nanoparticles on the surface of the silicon substrate [57].

Silica nanoparticles were spun on silicon surface at different speeds and time. The minimum speed carried out was 1500 rpm for 30 secs and maximum was 4500 rpm for 60 secs with different combinations in time and speed. Though the results vary in thickness, uniformity of nanoparticles was not attained as a repeatable factor. This lead to non-uniform results from this experiment.

Silica nanoparticles solution was always taken in a diluted form. The dilution rate for the experiments is: 0.2 ml of Silica with 50 ml of Isopropanol solution (IPA) and 0.2 ml of Silica with 70 ml of Ethyl Alcohol solution (EA)

After spin coating, the substrate was studied using Scanning Electron Microscope (SEM) to check the uniformity of nanoparticle layer on the surface of substrate. Silica nanoparticle forms broken layer because of their thickness which is in the range of few microns shown in Fig. 16.

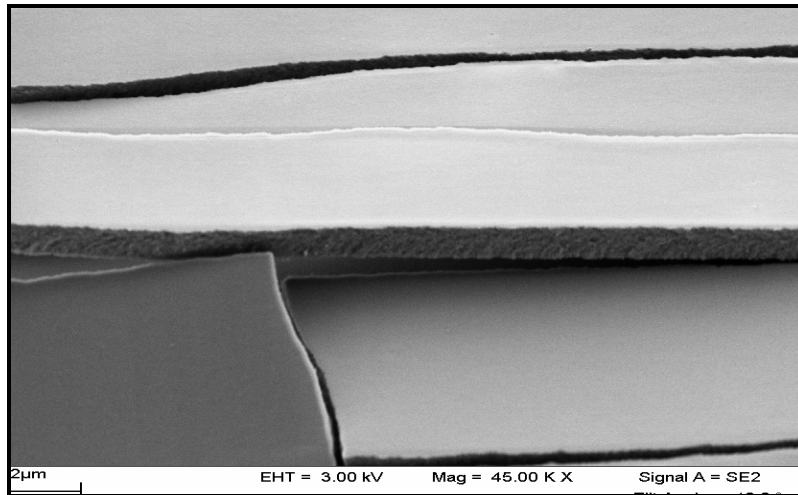


Fig. 16 Silica nanoparticle layers

This thickness has to be reduced for 1D PhC (to start with the construction of monolayers on silicon substrate) for the uniformity of the layer on the substrate.

Parameters on this sample are as follows:

- ❖ Spin coating speed: 1500 rpm
- ❖ Spin coating time : 40 secs
- ❖ The layer of nanoparticles on the substrate was very thick and this was the sole reason for the non-uniformity on the surface of the substrate. This can be rectified by using method wherein spin speed is very high and time may either be the same or different.

SEM image shown in fig. 17 shows the substrate which was spin coated with silica nanoparticles. Parameters for spin coating on this sample:

- ❖ Spin coating speed : 4500 rpm
- ❖ Spin coating time : 40 secs

- ❖ Composition of nanoparticles - 0.2 ml SiO₂ and 50 ml EA

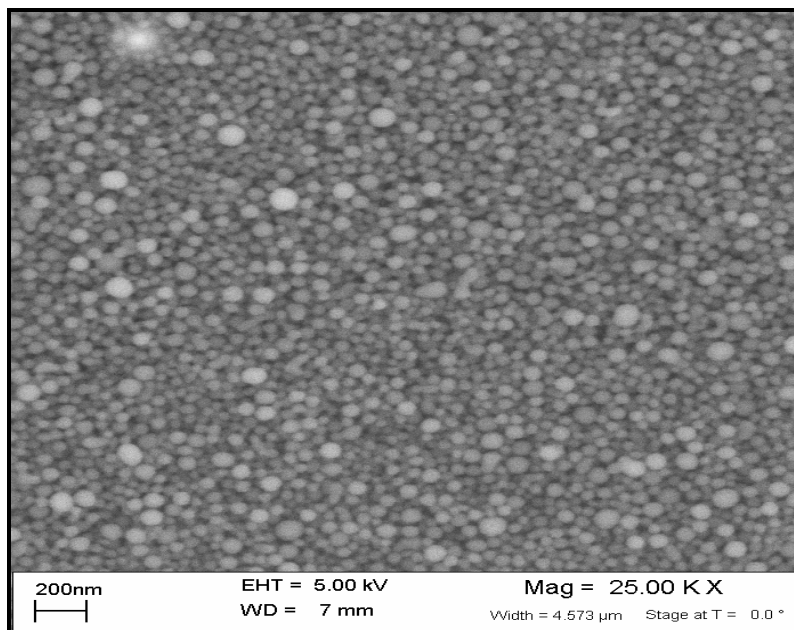


Fig. 17 SEM image of spin coated silica nanoparticles

Though the thickness was reduced to some extent, uniformity was not achieved for the 1D PhC. After a few set of experiments, with different spin speed and time parameters, since we were not able to achieve uniform layer of nanoparticles, we carried out our remaining experiments with the Immersion Technique for silica nanoparticles. Same set of experiments was carried out for lead-selenide particles to check the uniformity of nanoparticles.

- **Lead-Selenide Nanoparticles:**

Lead-Selenide particles were also subjected to spin coating at the same speed and time. Spin coating yielded uniform layer of nanoparticles in the case of Lead-Selenide. SEM image of Pb-Se nanoparticles is shown in fig. 18.

Parameters on this sample are as follows:

- Spin coating speed: 1500 rpm
- Spin coating time : 40 secs

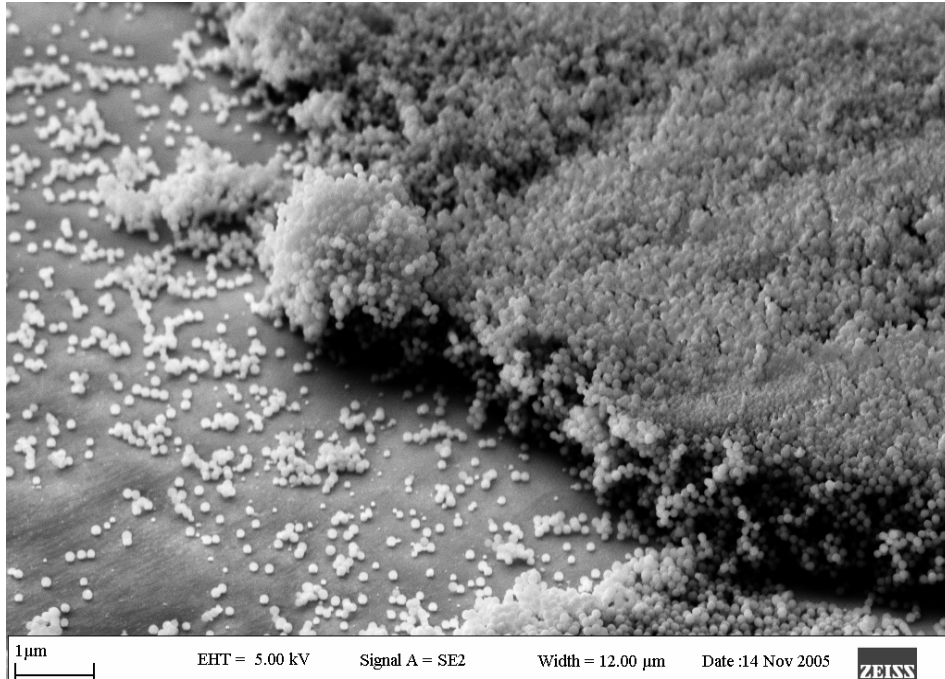


Fig. 18 SEM image of spin coated lead-selenide nanoparticles

SEM image of Pb-Se nanoparticles at a spin speed of 4500 rpm and 30 secs is shown in fig. 19. Small holes in this substrate are due to the evaporation of solvent (tetrachloroethylene). High speed and time were selected to achieve thin layer of nanoparticles on the surface of substrate.

Thickness of this layer was found to be 140 nm which is a cluster of 3 lead-selenide nanoparticles. Though thickness was in the expected range, evaporation of solution containing nanoparticles leaves irregular structure on the substrate with non-uniform distribution of nanoparticles.

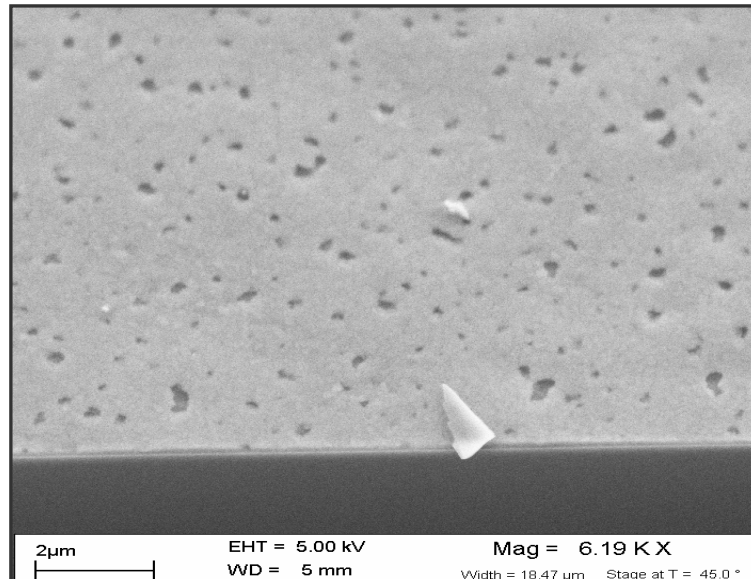


Fig. 19 SEM image of spin coated lead-selenide nanoparticles

○ **Titania Nanoparticles:**

Titania films were found to exhibit high thermal and chemical stability, high dielectric constant and has a very high transmittance in the visible spectral range [58].

Titania nanoparticles were immersed in water at a weight-volume ratio of 5%. Titania nanoparticles form clusters when they are spin coated on silicon substrate instead of single or multilayers. Due to the nature of titania nanoparticles, water present as the solution containing titania particles falls on such surfaces and rolls along the surface without actually wetting it [59]. This is due to the hydrophobic nature of the titania particles. Many experiments were carried out for titania particles.

➤ Single run Spin coat (Spin coat the nanoparticles onto the silicon substrate for a specific time and speed)

- Spin coat the nanoparticles – Leave the sample for air dry – spin coat it again. The total number of runs for this particular experiment may vary from 2 spin coatings to 6 spin coatings. (In this experiment for titania nanoparticles, we followed 3 set of spin coating methods. Spin coatings were carried out by the same procedure of dispensing the solution, letting it air dry and then carrying out the spin coating process again).
- Nanoparticles solution was dispensed onto the substrate. This solution was let to air dry for few seconds. Spin coating is then carried out for this sample.
- Single run spin coating was carried out by dispensing HexaMethylDiSilazane (HMDS) onto the substrate before actually dispensing the titania nanoparticles. This is done to improve the adhesion property of nanoparticles to the substrate. Then the nanoparticles are dispensed on the substrate and spinner is set to a spin speed of 4500 rpm and spin time of 30 seconds.
- The alternate method of spin coating and dispensing nanoparticles is carried out in different style. Even in this method, HMDS is dispensed onto the substrate to improve the adhesion property of titania nanoparticles. After dispensing HMDS onto the substrate, titania nanoparticles were dispensed. Spinner was set to a spin speed of 3500 rpm and spin time of 30 secs. Then the substrate was let to air dry.

Nanoparticles was again dispensed onto the substrate, spinner was set to same speed for one set of experiments and different speed to the other set of experiments. This procedure was repeated 3 times.

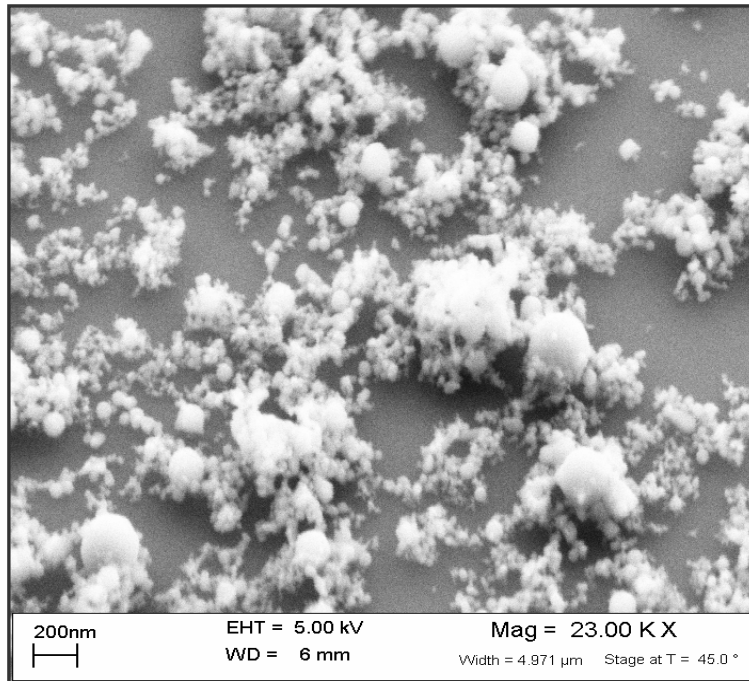


Fig. 20 SEM image of spin coated titania nanoparticles

This procedure was carried out assuming that the nanoparticles will self-assemble themselves on the surface of the silicon substrate by repetitive spinning action. But even after this, nanoparticles were found to form clusters instead of layers.

➤ Last method for titania nanoparticles was to dispense some solution on the surface of the substrate and let it dry in the air for few seconds and spin coat it at a rate of 4000 rpm for 30 secs. When this method was carried out initially, thick clusters were formed. We thought that by diluting the solution, thin layers can be obtained.

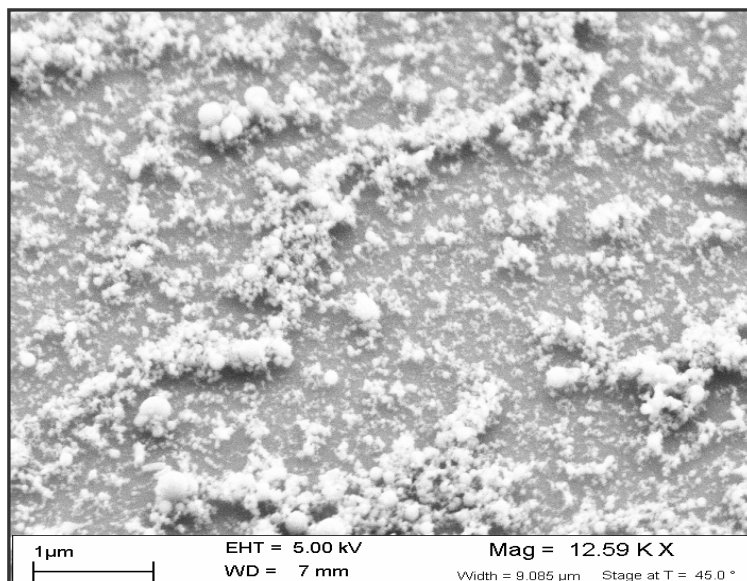


Fig. 21 SEM image of spin coated titania clusters

Solution was then diluted to 0.5 ml Titania – 50 ml of Water. When this method was carried out at the same spin speed of 4000 rpm and spin time of 30 secs, they showed cluster formation.

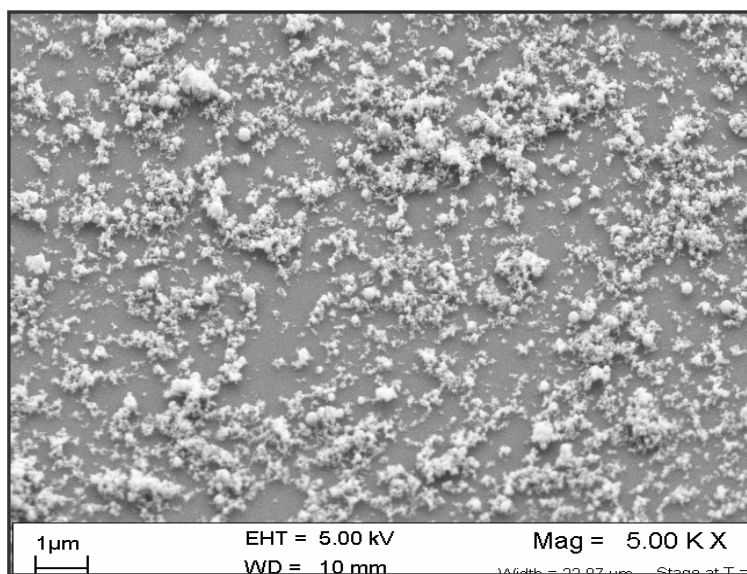


Fig. 22 SEM image of spin coated titania nanoparticles

Then, we changed the solution for dilution by considering ethyl alcohol instead of water. Titania nanoparticles solution was diluted at the rate of 0.5 ml of Titania to 50 ml of Ethyl alcohol. But even with this method, SEM image showed that the titania nanoparticles formed on the surface of the silicon substrate was not layer but cluster.

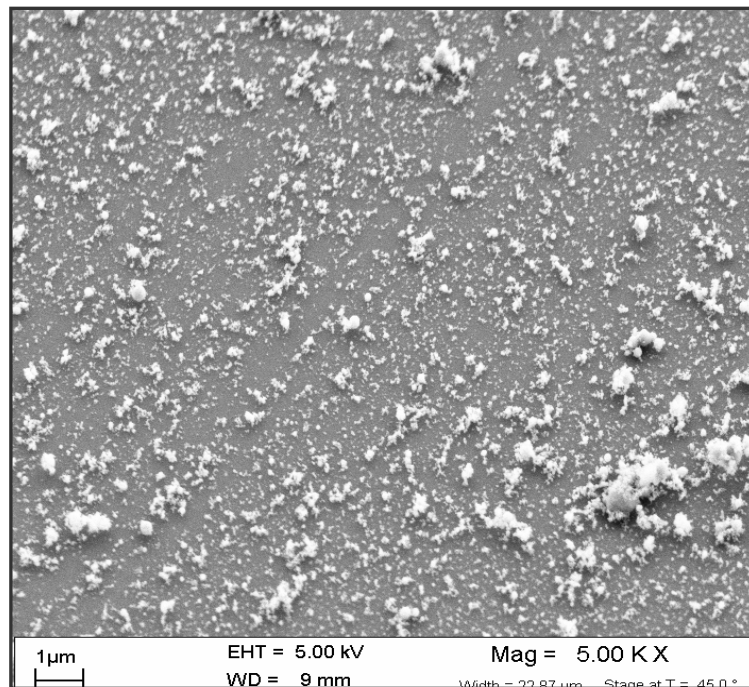


Fig. 23 SEM image of spin coated titania nanoparticles

It was then concluded that spin coating does not yield layer formation results for titania nanoparticles when it comes to layer of nanoparticles on the substrate. Spin coating process resulted in thick films of nanoparticle layer. Those films on the surface of substrate were broken because of the thickness of layer. Few reasons for the non-uniform layer of nanoparticles and broken layers are:

- Spin speed and spin time variation
- Weight% of nanoparticles in solution

➤ Insufficient adhesion of nanoparticles to the substrate which causes peeling of layers from the surface

These problems with spin coating can be corrected by:

- Accurate spin speed and time
- Weight% of nanoparticles yielding required number of layers on the surface
- Surface modification of the substrate or nanoparticles such that either of them is adhesive to a greater extent or both of them are adhesive to a great extent.

Due to repeated thick broken films of nanoparticles from spin coating process, we changed the fabrication methodology with another technique known as “Immersion Method”

3.2.2 Immersion Method:

Immersion method was carried out to deposit nanoparticles uniformly on the substrate. When it was initially carried out, the thickness of the nanoparticle layer on the silicon was noted down. This gave us an idea about changing parameters like weight% of nanoparticles in the solution, time for the substrate to be inside the solution, solution being either covered or uncovered. By changing parameters and plugging in the right values for them, a thin layer of nanoparticles can be obtained. This is achieved at room temperature. This process was carried out for silica and Pb-Se nanoparticles.

○ Silica Nanoparticles :

Silicon substrate was immersed in silica nanoparticles solution. Then they are either covered or uncovered with aluminium foil depending on the desired evaporation rate of the solution. The solution is let to evaporate with the nanoparticles settling

slowly on the substrate. Substrate was immersed in nanoparticles solution which was uncovered. The evaporation rate is faster in this case compared to covered substrate. The time for this experiment was 30 mins.

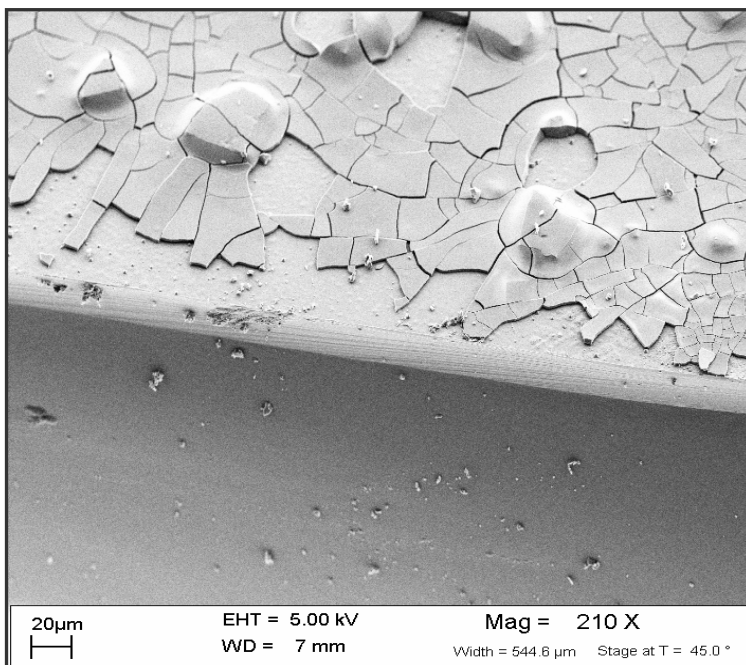


Fig. 24 SEM image of silica nanoparticles layers – Immersion Technique

Though complete evaporation of solution didn't take place, the film on surface of substrate was found to be thick. Thickness of the nanoparticle film on the surface was found to be 693 nm. This is shown in fig. 25. This shows that even when the evaporation rate is slow, thickness of the layer on substrate is high because of the weight% of nanoparticles in the solution. By combining these parameters, we can attain a thin layer of nanoparticles on the surface of substrate.

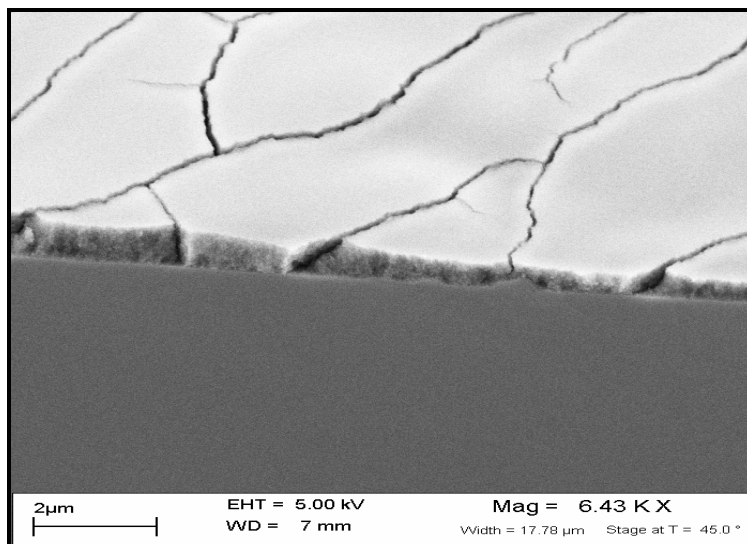


Fig. 25 Layer of silica nanoparticles

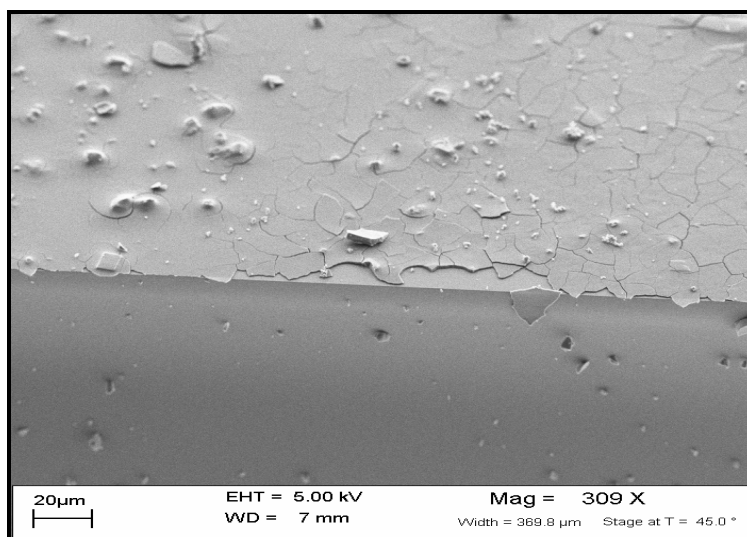


Fig. 26 Layer of silica nanoparticles

When the solution was covered with aluminium foil, the evaporation rate of the solution was decreased and more particles settled on the surface of the substrate for the same time of 30 mins (time for the experiment with uncovered solution). Even in this

case complete evaporation doesn't take place. Thickness of film on the surface of the substrate was found to be 1.480 μm .

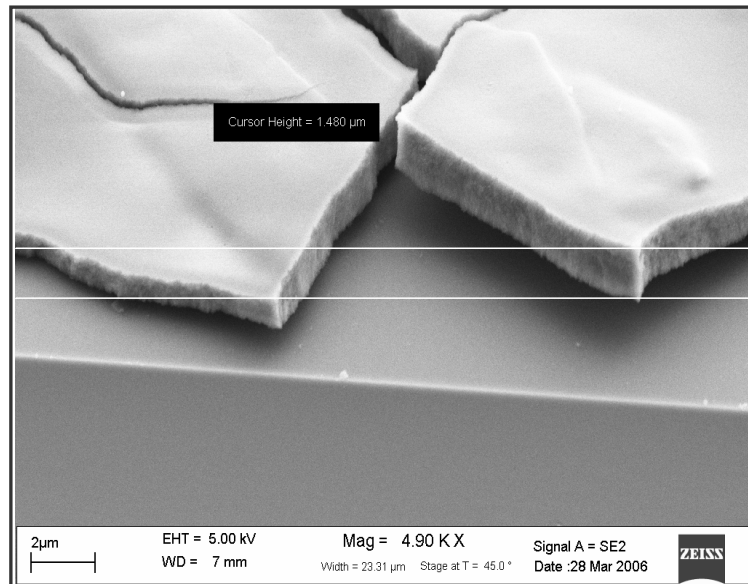


Fig. 27 Thick layer of Silica nanoparticles

- Lead-Selenide nanoparticles

When substrate was immersed in Pb-Se particle solution, layer formation was not seen for any time setup from immersion technique. Though a thin layer forms on the surface of substrate, due to the evaporation of nanoparticles solution (if Evident Technologies product, then the solution was hexane and if Rice university product then the solution was tetrachloroethylene) small holes were seen in many places on the substrate.

SEM image in fig. 28 shows that Pb-Se nanoparticles were not seen throughout the surface of substrate. This might be because of the weight% of nanoparticles in the

solution which was very low. These holes on the surface of substrate are due to the evaporation of solution and due to very less distribution of nanoparticles.

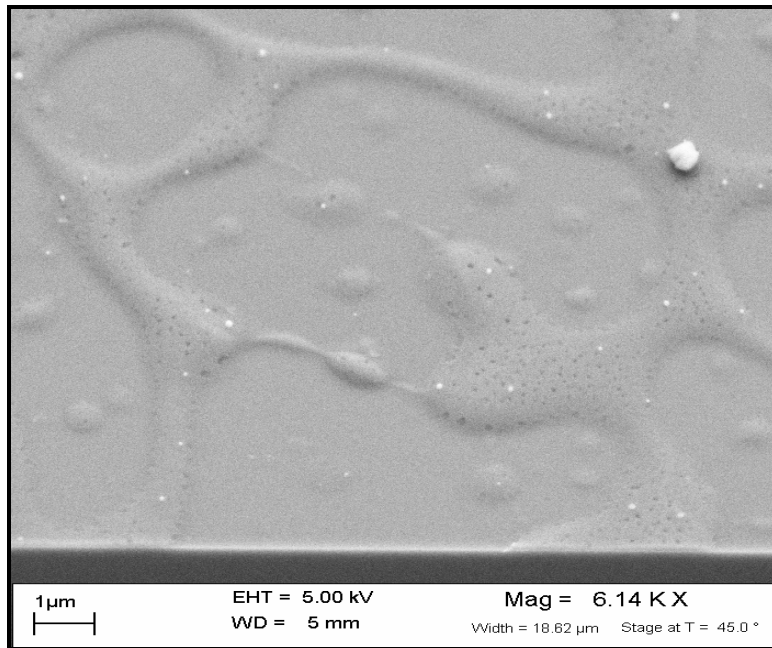


Fig. 28 Lead-Selenide nanoparticles - Immersion technique

Though immersion technique gave a thin layer of nanoparticle layer on surface of substrate, those films were found to be broken because of their weight%. Also, reducing the weight% of nanoparticles along with decreasing the evaporation time and uncovering the solution (which increases the evaporation rate by decreasing evaporation time and in turn decreases the number of nanoparticles settling on the surface of substrate) was found to yield thin layers of particles. With these adjustments as preliminary parameters, we moved on to convective assembly – IARI methodology which involved moving the substrate in and out of the evaporating solution. Effects of

temperature in the nanoparticle layer formation and its variation with time were studied from this experiment.

3.2.3 Convective assembly – IARI Methodology

In this method, sample was immersed into the solution. They are moved in and out of the solution at certain time intervals. This was done to improve the distribution and thereby the assembly of nanoparticles. The substrate movement into the solution is a technique that is being used in Langmuir-Blodgett technology and Convective assembly is the technique wherein the substrate is immersed into the solution. Here the solution was also heated to 70 ° C. Dilution rate for Silica nanoparticles was: 0.1 ml Silica + 50 ml (IPA).

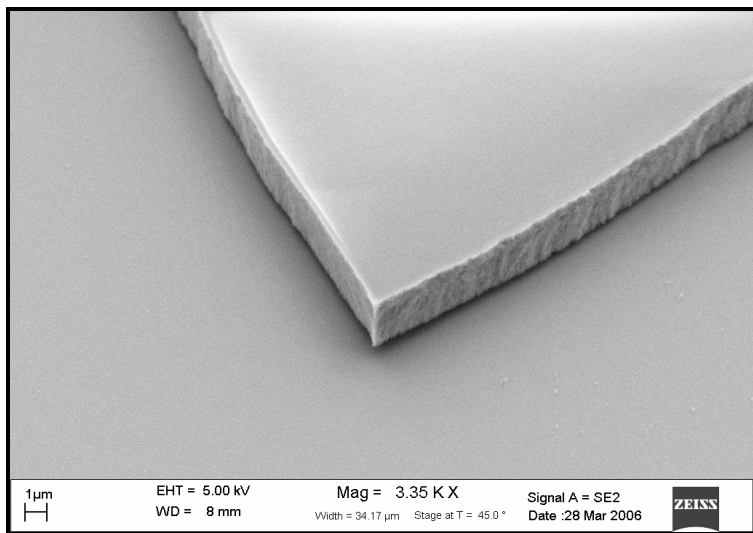


Fig. 29 Convective Assembly – IARI method for silica nanoparticles

Different dilution rate tried for this method was 0.1 ml of Silica nanoparticles + 70 ml of EA. Though the thickness of nanoparticle layer compared to previous methods was reduced to some extent, repeatability was not achieved to a greater extent. Thin

layer of nanoparticles was achieved on the substrate (though not a monolayer). But when the experiment was carried out with same parameters, repeatability was not achieved. For the same temperature, weight% of nanoparticles in solution, pre-processing (cleaning of substrate), and post-processing (letting the substrate to dry in air), we got different results from that of the previous ones.

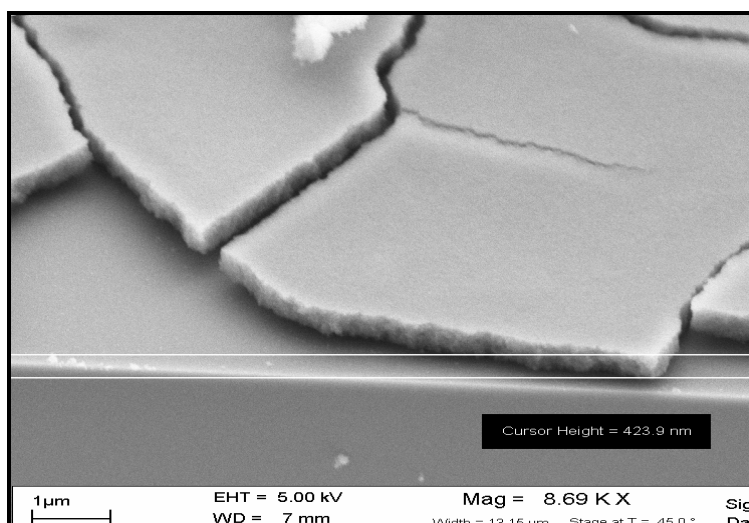


Fig. 30 CA– IARI method for 0.1ml SiO₂ : 70ml EA

Variation between the results for the set of same parameters was very large. Hence, this experiment was not carried out any further. The same methodology was taken for our next technique, except the movement of substrate into and out of the solution. We used temperature factor as a main parameter for the next set of experiments known as “Evaporation Induced Self-Assembly method”. Instead of moving the substrate, which we thought might disturb the layer formation, we kept the substrate inside the solution without disturbing it.

3.2.4 Evaporation Induced Self-Assembly Method

This method uses the evaporation technique of nanomaterials by external heating. The substrate is placed inside the solution and the solution containing beaker is kept on a hot plate. Temperature of the solution is checked with a thermometer and when the desired temperature is reached the beaker can either be removed from the hot plate or kept in the hot plate for the required time.

Various factors are taken into consideration for this process. They are

- Boiling point of the solution
- Flash point of the solution
- Polymerization of nanoparticles in the solution
- Characteristics of the solution (whether it is hazardous to heat the solution at a temperature greater than a particular temperature)

This method was carried out for silica nanoparticles. This method worked out successfully yielding a monolayer of silica nanoparticles on the surface of the substrate. Different combinations were tried for this method. Since factors like dilution of silica nanoparticles, time and temperature were taken into consideration, thickness varied with any of these factors.

Silica nanoparticles solution was diluted to a rate of 0.2 ml of silica with 50 ml of Ethyl alcohol solution. Temperature was varied from 50 ° C to 75 ° C (maximum temperature considers the boiling point of the ethyl alcohol solution). Time factor was varied from 1 sec to 5 mins. SEM images of this experiment with the given parameter variation shows that thickness is very high which drove us to dilute the solution further

with more of EA solution. As dilution rate was found to be very important for this method, silica nanoparticles solution was then diluted to a rate of 0.2 ml of silica with 70 ml of EA solution. Temperature was varied from 50 °C to 75 °C (maximum temperature considers the boiling point of the EA solution).

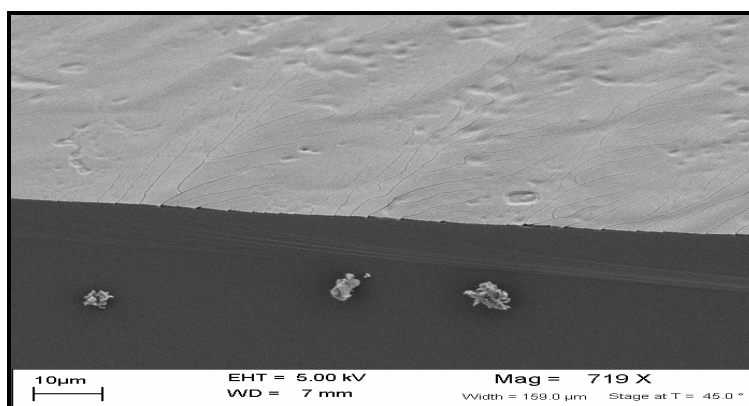


Fig. 31 Evaporation method for 0.2ml SiO₂: 50ml EA

Time factor was very critical for this method. It was varied from 1 sec to 5 mins. In case of 1 second, instead of placing the substrate inside the solution and boiling the solution, the solution was boiled to the desired temperature and then the substrate was immersed into the solution for a second and removed immediately.

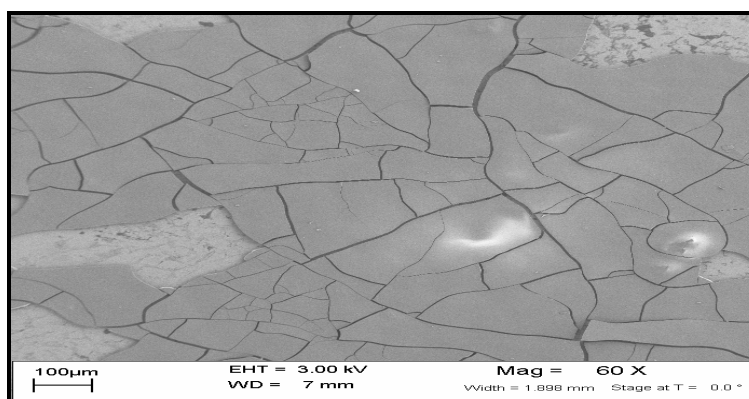


Fig. 32 Evaporation method for 0.2ml SiO₂ : 70ml EA

Surprisingly, two experiments carried out at time of 1 second and 5mins gave the same uniform thickness of 250nm on the substrate. But temperature parameter was not the same in both these methods.

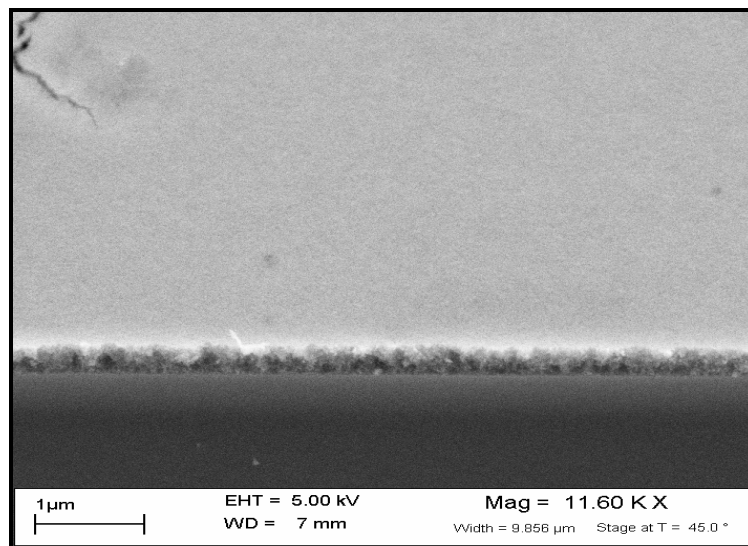


Fig. 33 Evaporation method for 0.2ml SiO₂ : 70ml EA [time = 1 sec, thickness = 250nm and temperature = 50 ° C]

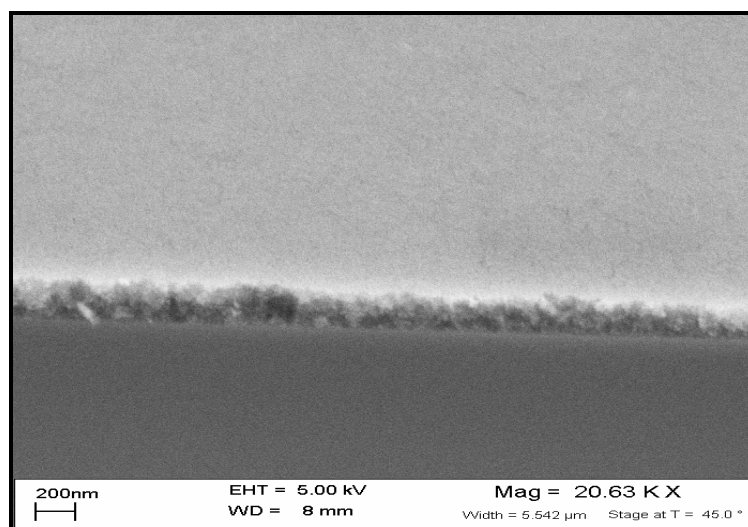


Fig. 34 Evaporation Method for 0.2ml SiO₂ : 70ml EA [time = 5 mins, thickness = 250nm and temperature = 75 ° C]

But in general, uniform thickness was got for substrate which was subjected to a temperature of 75 ° C, with time factor varying between 3 secs - 1 min and dilution rate of 1 SiO₂ : 350 Ethyl Alcohol.

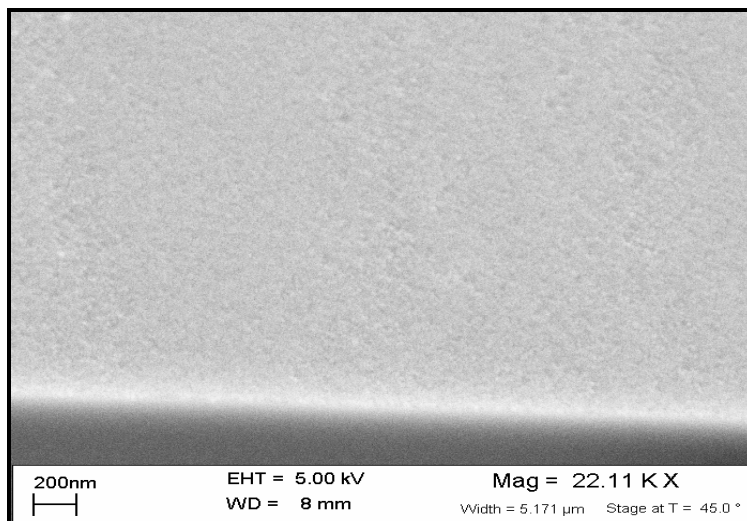


Fig. 35 Evaporation Method for 0.2ml SiO₂ : 70ml EA [time = 1 sec, thickness = 20nm and temperature = 75 ° C]

The experiment was found to produce the same result when tried again. The thickness of the layer on the substrate was 28 nm which is roughly a single nanoparticle on the surface. When the experiment was carried out at the same temperature, weight% of nanoparticles in the solution, and time setup, thickness of the nanoparticle layer was found to be the same as that of the first experiment. This shows that this experiment is capable of maintaining the results and thus repeatability was achieved from this experiment.

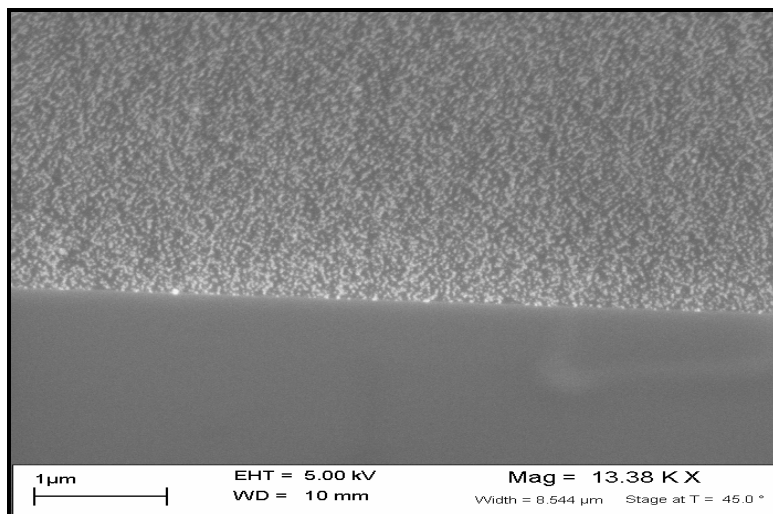


Fig. 36 Evaporation method for monolayer of nanoparticles

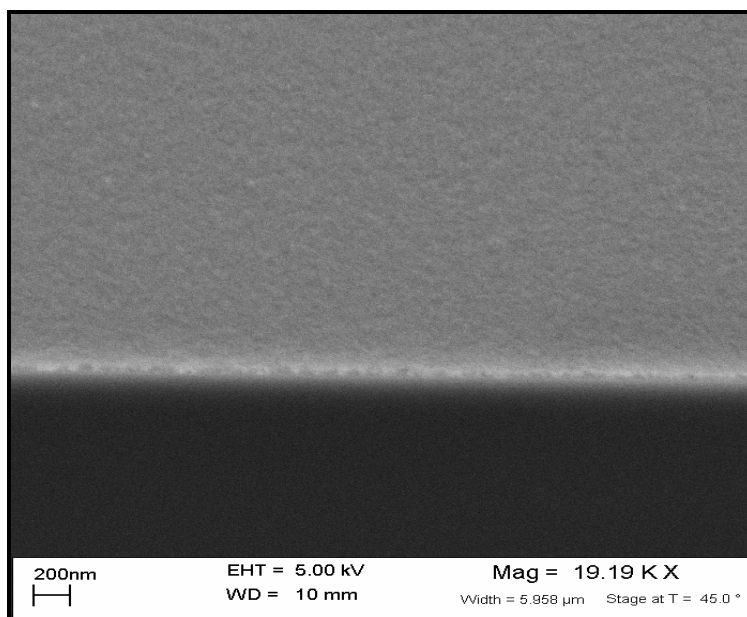


Fig. 37 Evaporation Method for monolayer of nanoparticles (repeated experiment with parameters from Fig. 36)

But when working with the same procedure for Pb-Se, it was not advisable to heat the solution as it had Pb-Se nanoparticles with either hexane or tetrachloroethylene

which has a low boiling point. Few nanoparticles were seen on the substrate for solution heated at 50 ° C.

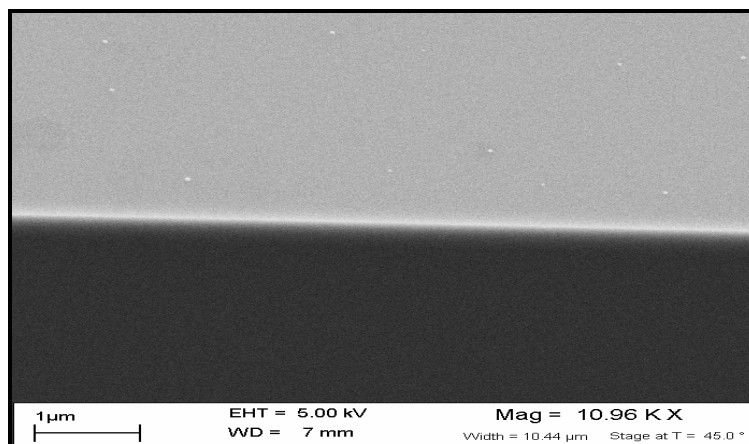


Fig. 38 Evaporation method for Pb-Se nanoparticles

This method was not that productive for Pb-Se nanoparticles due to the temperature limitations of Pb-Se nanoparticles. Also, the thickness of the layer on the substrate was not found to be uniform due to the evaporating nature of solution in which Pb-Se particles were immersed and low weight% of nanoparticles in the solution. The above mentioned experiments for evaporation induced Self-Assembly method shows that they are very effective for the fabrication of 1D crystals and thus repeatability was also achieved from these experiments.

3.3 Comparison of methods for the fabrication

Though different methods and different nanomaterials were used for the fabrication of nanoparticles, some methods were found to be effective for some nanomaterials and some were not. To obtain a monolayer on the surface of a substrate, evaporation assisted Self-Assembly method was found to be very effective. Though

other methods gave thin layers on the surface of the substrate, they were either broken layers (due to the thickness of the film) or clustered (due to the hydrophobic nature of the particles), they were not taken down to a nanolayer of single particle like the one got from evaporation-induced assembly method. This might be because of the spin speed variations, weight% of nanoparticles (we got thin layer of nanoparticles with 0.2 ml of silica and 70ml of EA solution which shows that the weight% of silica is very low)

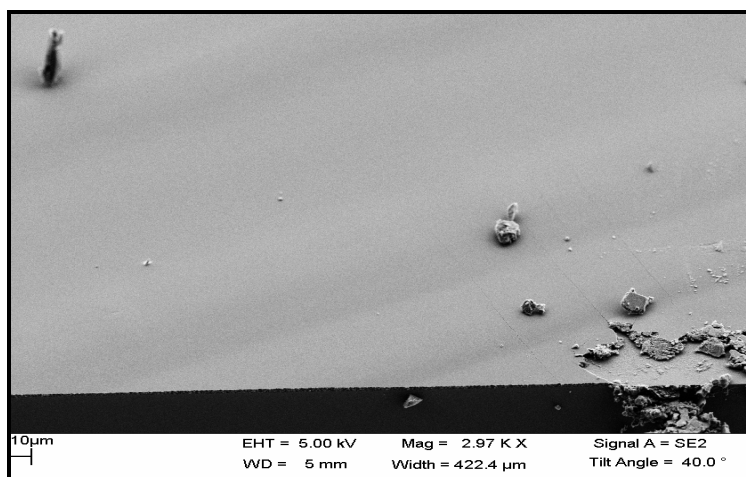


Fig. 39 Evaporation method for a uniform layer of silica particles

Though evaporation induced method gave repeatable monolayer, the factors considered for the deposition of nanoparticles were very critical as even an extra factor of these parameters lead to unexpected results. Thus temperature was optimized to 75 ° C with time between 3 secs – 1 min and dilution rate of 0.2 ml of silica nanoparticles with 70 ml of ethyl alcohol. Graphs for this result with temperature varying with respect to thickness of nanoparticle layer are discussed in chapter-7.

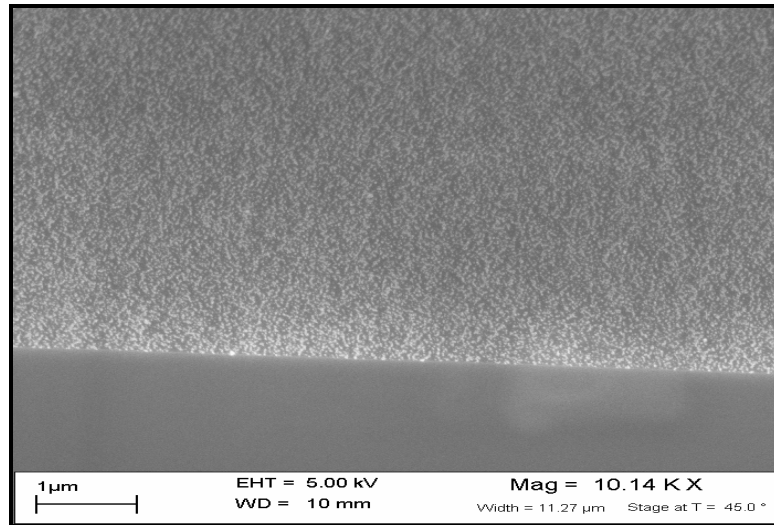


Fig. 40 Evaporation method for monolayer of silica nanoparticles

When the same set of parameters was followed for 0.2 ml of silica nanoparticles with 50 ml of EA solution, the thickness was in the range of 250nm – few microns. Reasons for this can be the improper distribution of nanoparticles in the solution. This in turn results in particles settling as clusters on the surface of substrate.

3.4 Factors involved in Self-Assembly of 1D crystals

Self-Assembly involves number of forces which are main reason for the nanoparticles to move freely on the substrate and as the solution gets evaporated, these forces hold these nanoparticles together in their place. Various factors involved in the successful Self-Assembly of encapsulation of 1D crystals are:

- Capillary forces
- Diameter of holes and spacing between holes on the surface of substrate
- Diameter of nanoparticles
- Selectivity of nanoparticles

- Sedimentation factors of nanoparticles which is being affected by the slow moving neighboring particles
- Hydrodynamic interactions between the nanoparticles inside the solution
- van der waals forces (which is the force of attraction between neutral molecules)

3.5 Applications of 1D Photonic Crystals

1D PhC can be used in ThermoPhotoVoltaic (TPV) systems. TPV systems can be used in generators and in places where there is a need for the supply of heat and electricity. TPV system consists of photovoltaic cells, ceramic tube and reflecting funnels. By continuous burning of fuel in ceramic tube, they glow at red hot. Photovoltaic cells surrounding this ceramic tube convert this heat from the ceramic tube into power. Though 1D crystals exhibit a complete reflectance because of the arrangement of nanoparticles on the surface, they are being used in mirrors [60]. Other application of these 1D crystals is waveguides [61] which can be fabricated by creating a path for the flow of the light on the deposited nanoparticle layer the surface of substrate. This is done by leaving some empty space (continuously in a shape of a line or any shape we want our waveguide to be) on the surface of the substrate which lines up in between the nanoparticle layer.

CHAPTER 4

ENCAPSULATION OF 2D PHOTONIC CRYSTAL CAVITIES

4.1 Introduction

2D PhC are being used widely in optoelectronic field nowadays as the fabrication of these crystals is comparatively easier than the other two types of crystals. 2D PhC has periodic holes in its structure, which is then filled with nanoparticles.

Encapsulation of holes is done in 2D PhC to seal off the air holes completely. This is done to create an alternate material of different refractive index and dielectric constant thereby creating a difference in surface property. Here the propagation of light is forbidden at some frequencies and allowed at certain frequencies. In 2D structures, controlling surface functionalization is difficult because of selectivity of deposition of nanoparticles [62] [63] [64]. Crystal cavities controlled by this means are being used in microelectronics and optoelectronics industry [65]. With these periodically arranged holes, we can actually create photonic bandgaps by changing the periodicity. These light properties motivate many research groups to work on 2D crystals [66].

Silicon substrate with holes is used for this method. These holes were drilled using Electron Beam Machining from University of Texas at Austin. These holes are then filled with the required nanoparticles such that they are sealed off completely creating a difference in properties of materials like refractive index, dielectric constant, thereby fabricating a material whose response to light varies in each part (that is the

hole-filled part and substrate). In fig. 41, patterned silicon substrate is shown. The holes in substrate are to be filled with nanoparticles. By doing this we create a material possessing two different properties, one being the holes filled by nanoparticles and other being the surface of substrate. As a result, silicon substrate consists of silicon and holes filled by nanoparticle material which has different refractive index compared to silicon. This results in the variation of properties within a same substrate which yields optical applications.

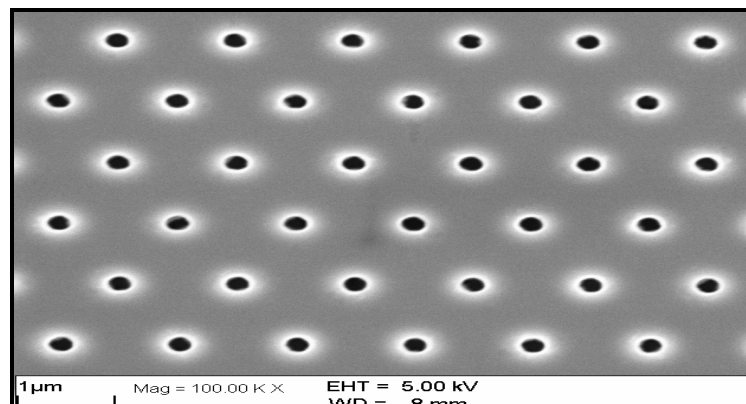


Fig. 41 2D PhC structure in silicon substrate

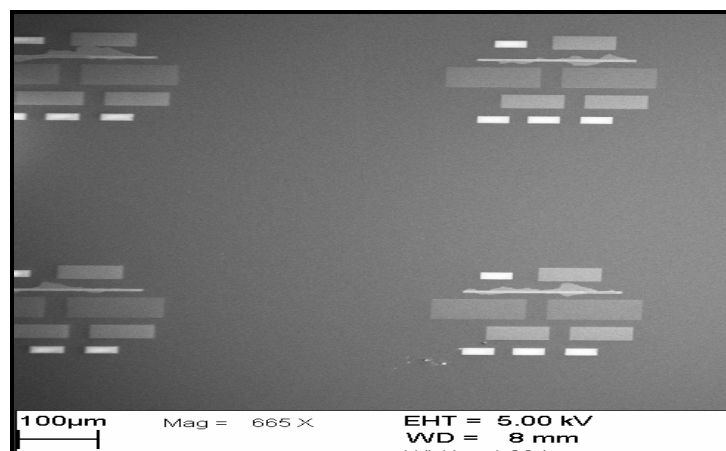


Fig. 42 Structure of patterned silicon substrate

In fig. 42, each square in the represents many holes in the substrate like in fig. 41. Dimensions of these patterns are decided based on the wavelength of the visible light as these crystal cavities are being used for optical applications. Dimensions are as follows:

- Hole diameter : 450 nm
- Distance between two holes : 955 nm
- Depth of these holes : 450 nm

Nanomaterials used for sealing off these air holes are Silica nanoparticles immersed in IPA solution, Pb-Se particles in hexane solution and PS nanoparticles immersed in water.

4.2 Methods used for encapsulation

4.2.1 Spin Coating

Spin coating (procedure of spin coating is the same as that of 1D PhC) was carried out for the construction of 2D PhC. With the speed and time of spinner, nanoparticles were expected to fill the holes and thus the surface of substrate would be free from nanoparticles. But after spin coating, particles were seen on the surface of the silicon substrate and in some cases the holes of the substrate were not filled properly. This might be because of inappropriate spin speed, time, weight% of nanoparticles, improper positioning of substrate on the chuck and improper cleaning of substrate.

Spin coating of silica nanoparticles (of size 10 – 50nm) filled the holes of silicon substrate. But along with that deposition, these nanoparticles filled the surface of the substrate which is to be avoided. Spin speed of the process was 4000 rpm and spin

time was 40 secs. High speed and time yields low thickness of nanoparticle layer. From fig. 43 and 44 it is clear that the nanoparticles filled the surface along with the holes. This is because of the properties of holes and surface of the substrate. As surface was not modified for the substrate, nanoparticles show same behavior towards surface and the patterned holes. This can be changed by either modifying the surface or reducing the weight% of nanoparticles in the solution.

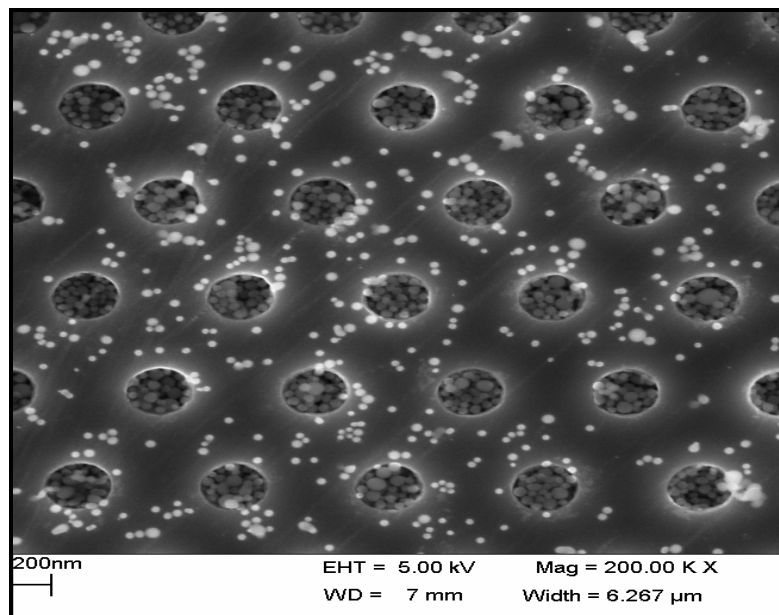


Fig. 43 2D PhC - Patterns filled with silica nanoparticles

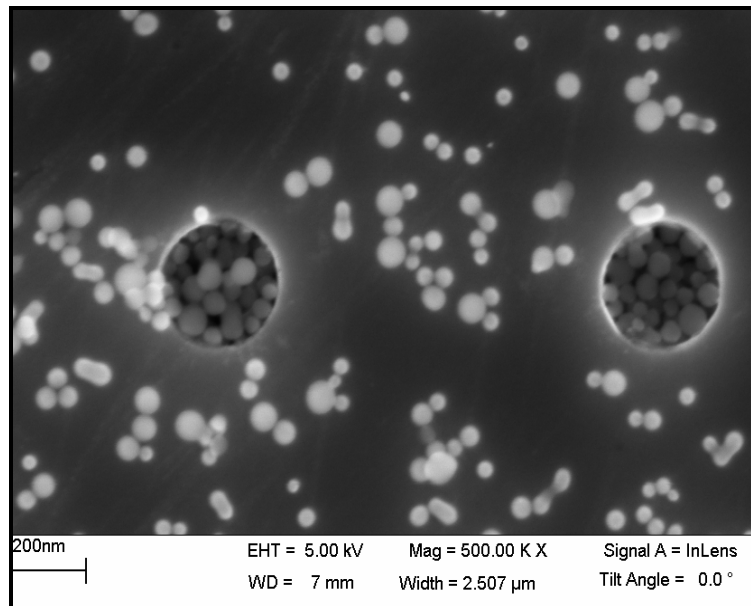


Fig. 44 Silica particles on substrate and patterns

These nanoparticles are diluted with IsoPropanol solution. 10% of silica nanoparticles in IPA solution (33ml of silica solution and 67ml of IPA solution) were chosen for this experiment. Even with this rate of dilution nanoparticle solution, surface of the substrate had some nanoparticles. Though it was not densely occupied by nanoparticles like in fig. 45, it was occupied by nanoparticles to some extent. Repeated experiments of spin coating also gave the same result of nanoparticles occupying the surface of substrate. Spin speed and time was varied from one extreme to the other, as the deposition of nanoparticles on the surface of substrate depends on spin speed and time. Even by this variation, surface of substrate had nanoparticles to some extent.

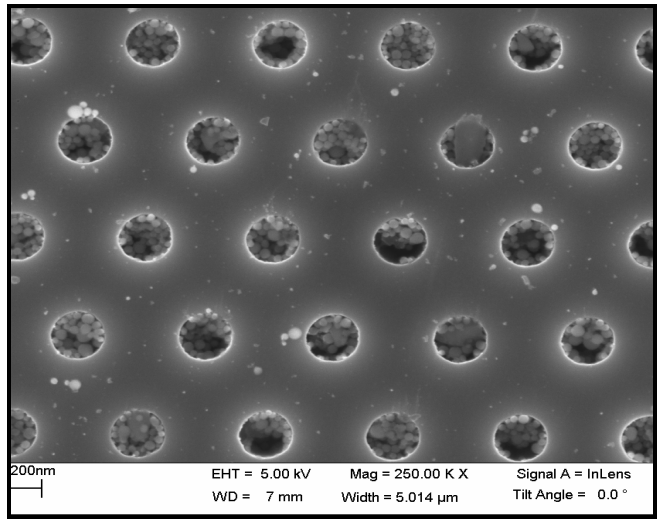


Fig. 45 Patterns and surface of silicon filled with diluted silica particles

Lead-Selenide particles (of size less than 40nm) were also spun on the substrate.

Lead-Selenide particles were diluted with IPA solution (50ml of IPA to 10 ml of Pb-Se solution). The spin coating process parameters were:

- ✚ Spin speed – 1000 rpm
- ✚ Spin time – 50 seconds.

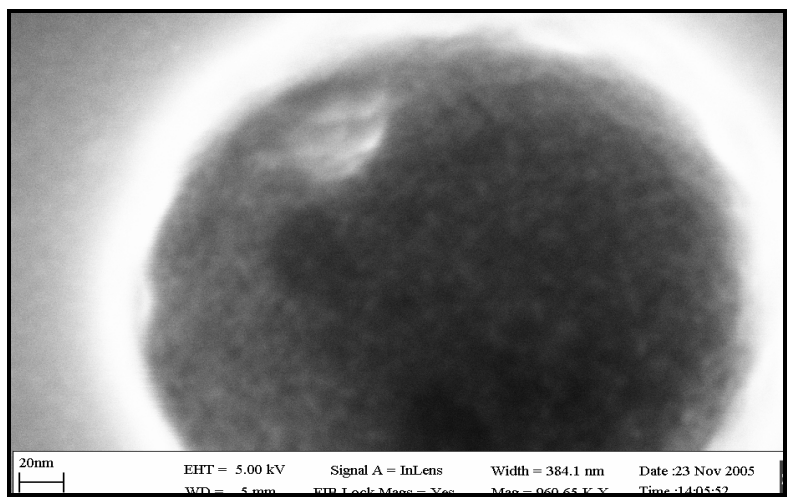


Fig. 46 Patterns filled with diluted Pb-Se particles [77] [78] [79]

Though nanoparticles are seen inside the patterns, the repeatability of this experiment was not achieved.

Spin coating of PolyStyrene nanoparticles (of size 220nm) was studied for experiment setup. This material was used to check the surface modification of the substrate. As PolyStyrene particles are extremely hydrophobic, they were spin coated to check whether they settle uniformly on the patterns of the substrate avoiding surface but they were not deposited uniformly on both the parts of the substrates.

Parameters on spin coating were:

- ✚ Spin speed: 4000 rpm
- ✚ Spin time : 30 secs

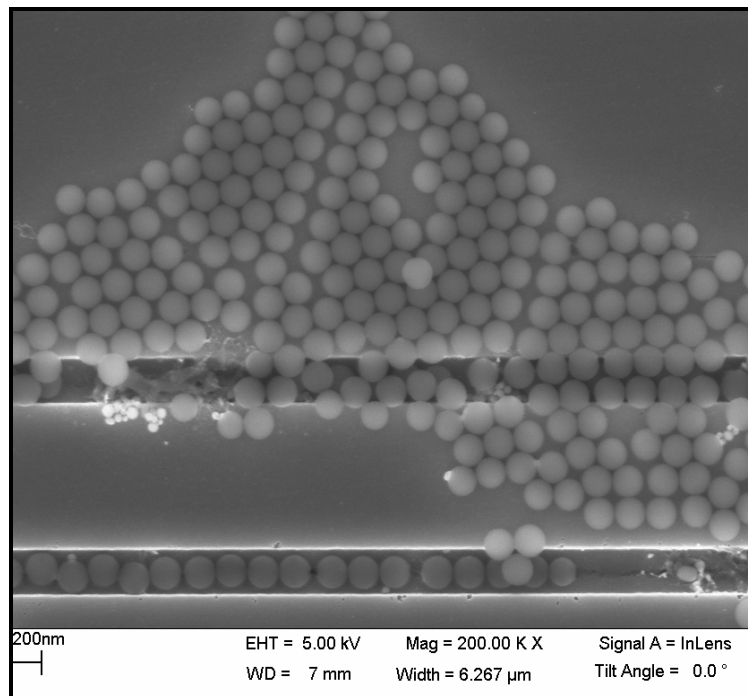


Fig. 47 PolyStyrene particles on patterned silicon substrate

Possible reasons for the deposition of nanoparticles on the substrate were:

- ❖ Spin speed and time
- ❖ Weight% of nanoparticles
- ❖ Position of the substrate
- ❖ Due to the absence of post-processing procedures

By adjusting these parameters, we would be able to get uniform deposition of nanoparticles onto those holes. As spin coating method resulted in nanoparticles occupying the substrate, after a different set of combinations of parameters we followed with immersion technique.

4.2.2 Immersion Technique:

Substrate was immersed in nanoparticles solution in this technique. Due to the immersion of the substrate in vertical position, the nanoparticles were expected to slide down the substrate till they settle onto the patterns. Even the variation in time didn't give uniform settlement of nanoparticles. Three factors were varied for this set of experiments. They were as follows:

- Time of the experiment (time for the substrate to be inside the solution)
- Position of the substrate (vertical or horizontal)
- Either the solution is taken in beaker and substrate was immersed into the beaker or substrate was positioned vertically inside the beaker and nanoparticles were filled using fillers. In fig. 48, time for the evaporation of the solution was taken to be the time for the experiment (7hours).

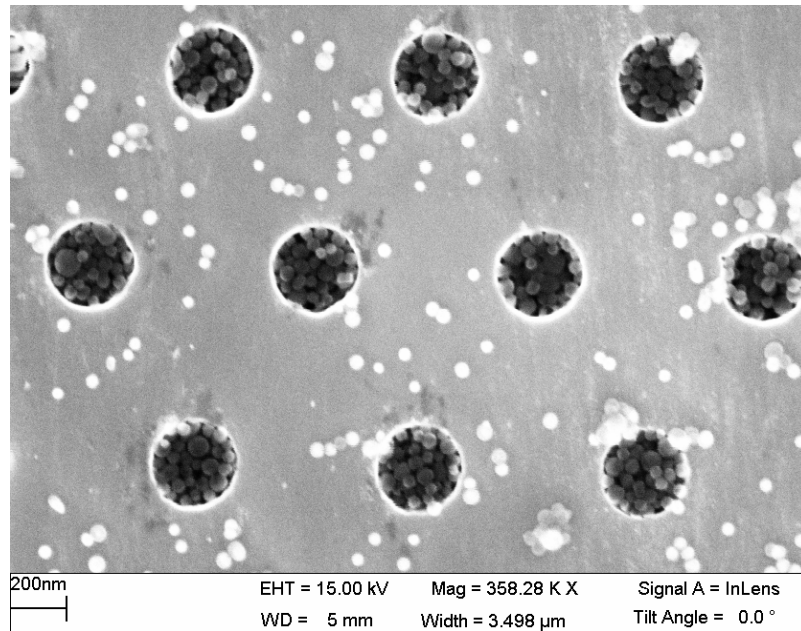


Fig. 48 Silica nanoparticles in a patterned substrate - Immersion Technique

Position of the sample was vertical. Substrate was immersed in nanoparticle solution. Though the deposition of nanoparticles on the surface is not that dense as it was in spin coating, few nanoparticles were seen on the surface. To avoid this, we can decrease the weight% of nanoparticles in the solution.

In fig. 49, time for the experiment was reduced to 5 secs (substrate was immersed in nanoparticle solution for 5 secs. Position of the sample was vertical. From the figure it is seen that the nanoparticles didn't fill the holes completely. Though the surface of substrate is clean, patterned holes were also seen without nanoparticles.

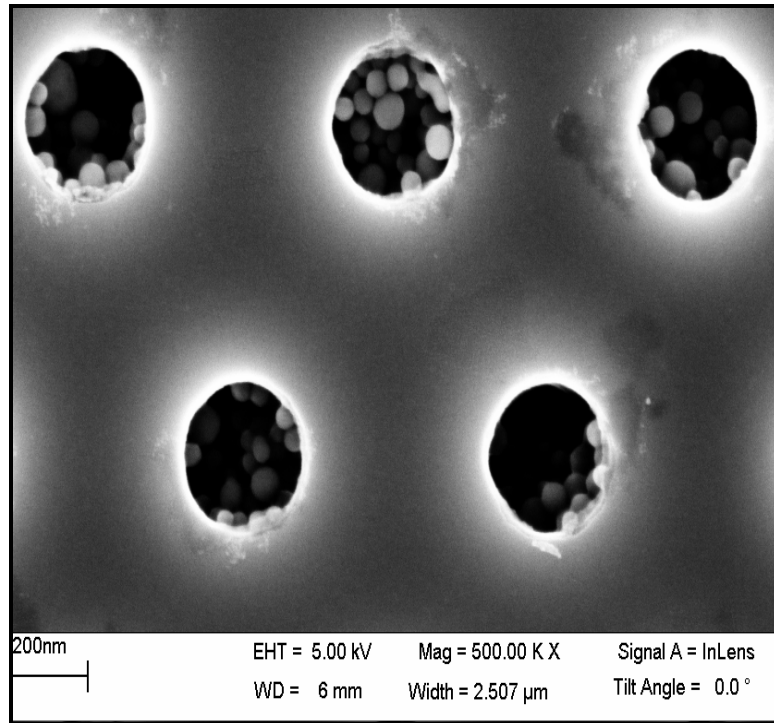


Fig. 49 Silica nanoparticles in patterned holes - Immersion Technique

This method didn't give uniform particles in the holes. Even changing the parameters at a very minor rate didn't yield uniform particles onto the holes. Since changing parameters like time for which the substrate was immersed into the nanoparticle solution and weight% of nanoparticles did not yield any significant changes, we carried out our next method. In the next method, nanoparticles solution on the surface of substrate, instead of immersing the substrate into nanoparticles solution, few drops of nanoparticles solution was poured on the substrate and post-processing was carried out to encapsulate these crystal cavities.

4.2.3 Nanoparticle solution on the surface of substrate:

Method of wetting the surface of substrate using nanoparticles yields uniform distribution of nanoparticles onto the patterns without any nanoparticles on the surface.

Description of this method is as follows:

- Silicon substrate taken is kept on a flat plate.
- Nanoparticles solution is poured on the surface of substrate.
- After few seconds, when the solution starts evaporating, few ml of nanoparticles solution is poured on the surface again.
- Substrate is then let to dry in atmosphere air for few seconds (though not completely).
- IPA solution is then used to wash the surface of the substrate. (Substrate is held at a slanting position and IPA solution is poured onto the substrate for few seconds continuously). This IPA solution wets the nanoparticles (which are dried particles on the surface) and washes them out moving onto the holes.

Thus nanoparticles ultimately settle onto the holes after IPA washing of the substrate. These nanoparticles can either be diluted or undiluted. For our experiments, diluted silica nanoparticles solution was used. The dilution rate of these nanoparticles was 10 % (33 ml of silica nanoparticles solution + 67 ml of IPA). When the weight% of silica nanoparticles were reduced to such an extent and when post-processing was carried out (cleaning of the substrate with IPA solution), it was clearly seen that the nanoparticles filled the holes without much on the substrate.

Fig. 50 shows the SEM image of the uniform distribution of nanoparticles onto the patterns without any on the surface.

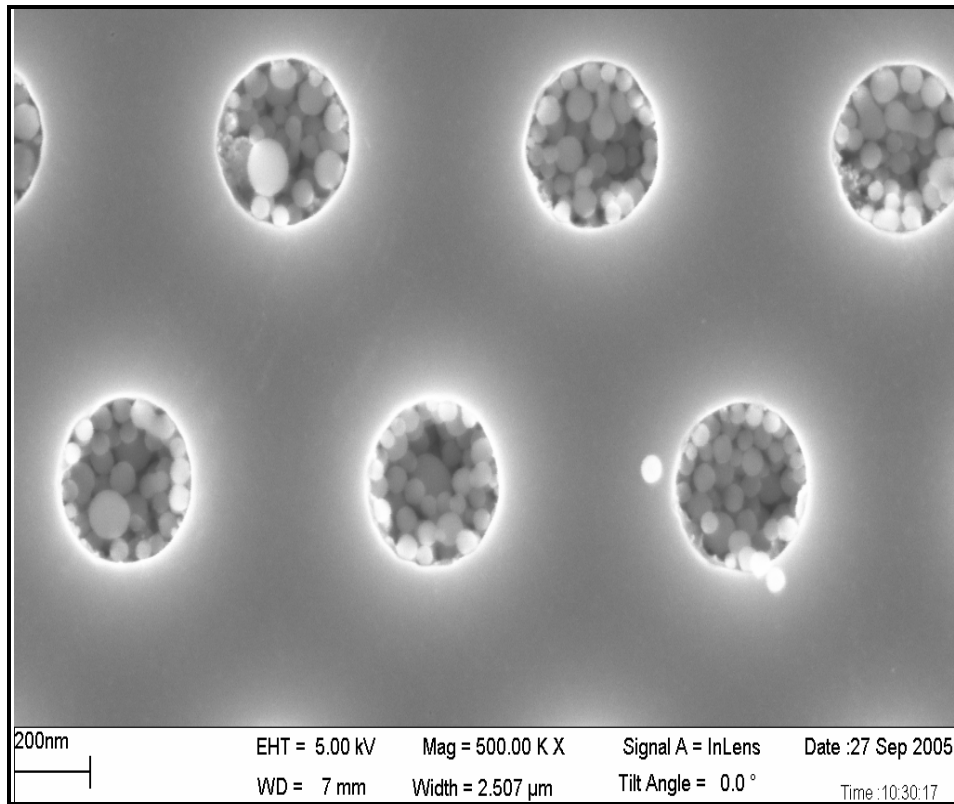


Fig. 50 Patterns filled uniformly with diluted silica nanoparticles [77] [78] [79]

Thus, nanoparticles filling the holes through this method are achieved by pushing the nanoparticles away from the surface using IPA solution. As encapsulation was achieved, repeatability of this method with the same parameters has to be verified. Hence, we carried out the same experiment with same parameters used for the above experiment.

When the experiment was repeated with the same parameters like weight% of nanoparticles in the solution, time for which the substrate was kept in air with

nanoparticle solution on its surface, and volume of IPA solution used for the cleaning purpose, the results got from the experiment was the same like that of the previous experiment as shown in fig. 50. This is shown in fig. 51.

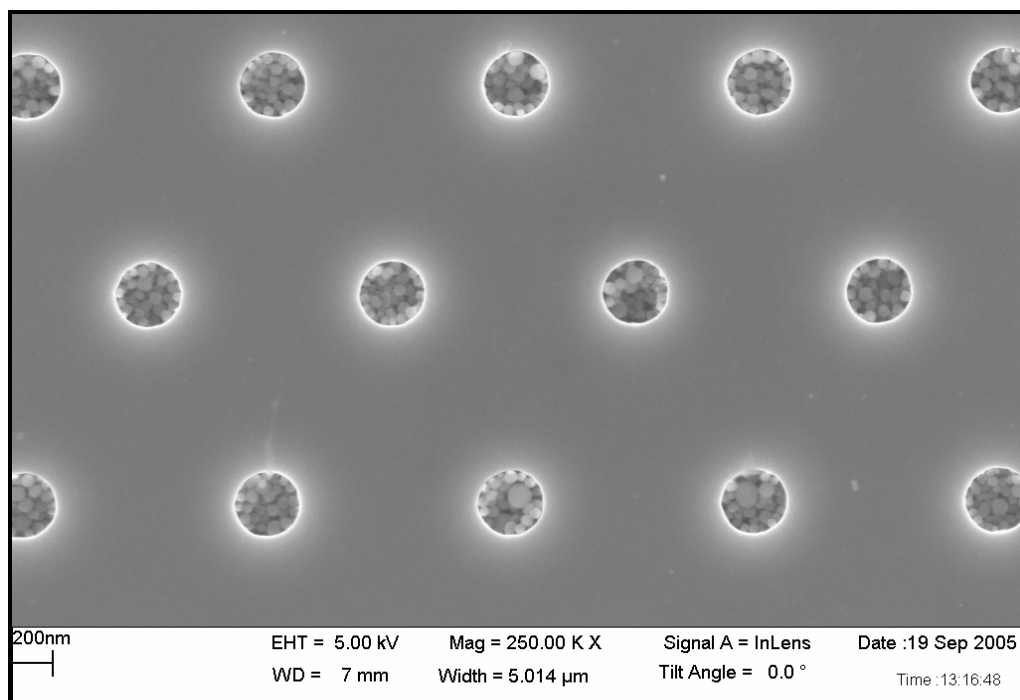


Fig. 51 Uniform distribution of Silica nanoparticles (repeated experiment)

Thus, just like evaporation method for 1D PhC, pouring nanoparticles solution on the surface of the substrate was found to be very effective for the encapsulation of 2D PhC.

4.3 Factors involved in Self-Assembly of 2D cavities

There are various factors involved in the successful Self-Assembly of encapsulation of 2D crystals cavities. They are similar to that of 1D crystals. Some are:

- ❖ Capillary forces
- ❖ Diameter of holes and spacing between holes on the surface of substrate

- ❖ Diameter of nanoparticles
- ❖ Selectivity of nanoparticles
- ❖ Sedimentation factors of nanoparticles which is being affected by the slow moving neighboring particles
- ❖ Hydrodynamic interactions between the nanoparticles inside the solution
- ❖ van der waals forces (which is the force of attraction between neutral molecules)

4.3.1 Capillary Forces

Capillary forces at the interface between nanoparticles and the solution play a very important role in encapsulation of 2 crystal cavities. As the size of particle decreases the capillary interaction energy decreases. This leads to the dominance of the thermal fluctuation energy.

When the patterned structures are immersed in a solution containing nanoparticles, due to the capillary interaction energy, nanoparticles are selectively forced into the holes of the substrate. The calculation of this force is discussed in detail in chapter – 6.

4.3.2 Diameter of holes and spacing between holes

Diameter of holes on the substrate also plays a very important role in the encapsulation of 2D crystals. If the holes are too small to accommodate many nanoparticles, then they can have only a very few particles. Though this is desired in many applications, it should be made sure that the accommodated particles are stacked properly without any space in between them. Also, the distance between these holes is

important as they lead to the movement of nanoparticles on the surface which increases the velocity of particles in the solution.

If the distance between these holes is very small, the nanoparticle will not have much space to move on the surface before getting into the hole. This at times may lead to accumulation of nanoparticles on the same hole. So, depending on the visible light wavelength, these holes are to be drilled on the substrate and the distance between holes are also calculated roughly depending on that. This diameter is controlled by lithography process.

4.3.3 Diameter of nanoparticles

Diameter of nanoparticles depends on the application of the crystals. As the size of the particle decreases, capillary interaction energy diminishes. Thermal fluctuation energy dominates at this part. So, to overcome thermal fluctuation energy nanoparticles are expected to have large diameter. Total number of particles deposited onto the holes of the substrate depends on the ratio between diameter of holes and diameter of nanoparticles.

4.3.4 Selectivity of nanoparticles

Deposition of nanoparticles to encapsulate the air holes also depends on the selectivity of nanoparticles which deals with the chemistry side of nanoparticles. Though this selectivity is predominant in nanoparticle layer in 1D crystal, it is discussed here to show that this factor also affects the total amount of particles deposited on the surface or onto the holes. It depends on whether the nanoparticle has affinity to the substrate and whether they can stay in the hole after the process. For example, in 1D

crystals, if there is no affinity between these nanoparticles and substrate material, then the layer just peels off from the substrate. In this case there will be a gap between the layer and the surface of the substrate.

4.4 Applications of 2D crystals

Applications of 2D Crystals are in Photonic Integrated Circuits. This is due to the easiness in fabrication of these crystals. Also, the multifunctionality concepts (ability to perform multiple operations with the same technology) of 2D crystals are being used in circuit technology. [67].

These crystals are also used in thermophotovoltaic (TPV) systems as discussed in chapter-3.

CHAPTER 5

CHARACTERIZATION FOR 1D AND 2D PHOTONIC CRYSTALS

5.1 Introduction

Self-Assembly of nanoparticles being the fundamental technique to construct PhCs, is achieved by various methodologies. This chapter gives an overview of characterization of PhC using various equipments, parameters used in those experiments, effective method for the fabrication of PhC and comparison of few methods with respect to the thickness of the layer.

5.2 Characterization Techniques

Fabrication of 1D and encapsulation of 2D PhCs carried out using various methods in cleanroom using Self-Assembly of nanoparticles concepts has to be characterized. Characterization of crystals is done to check for the changes that can be made with the consecutive testing methods and parameters.

Though fabrication of 1D PhC was discussed in chapter – 3 and encapsulation of 2D PhC was discussed in chapter- 4, this chapter gives details about various characterization techniques used for the PhC, images of characterization equipments, images of PhC with nanoparticle layers, parameters used for those PhC are to be discussed in this chapter.

For this thesis work, we worked on characterization techniques like Scanning Electron Microscope (SEM), Ellipsometer, Profilometer and Optical Microscope.

5.2.1 Scanning Electron Microscope (SEM)

SEM was used almost for the entire thesis. SEM in NanoFAB is capable of detecting particles of nanometer size. So distribution of nanoparticles on the surface of substrate or onto the patterns of holes on the substrate is checked. This gave us few ideas about changing parameters for the next set of experiments.

SEM used for the characterization in this thesis is ‘Zeiss Supra 55 VP Scanning Electron Microscope’. The resolution of this SEM is 1 nm. This SEM is shown in fig. 52. Whole characterization in this thesis was carried out by SEM which gave us excellent clarity in images helping us to proceed with further steps for improvement.

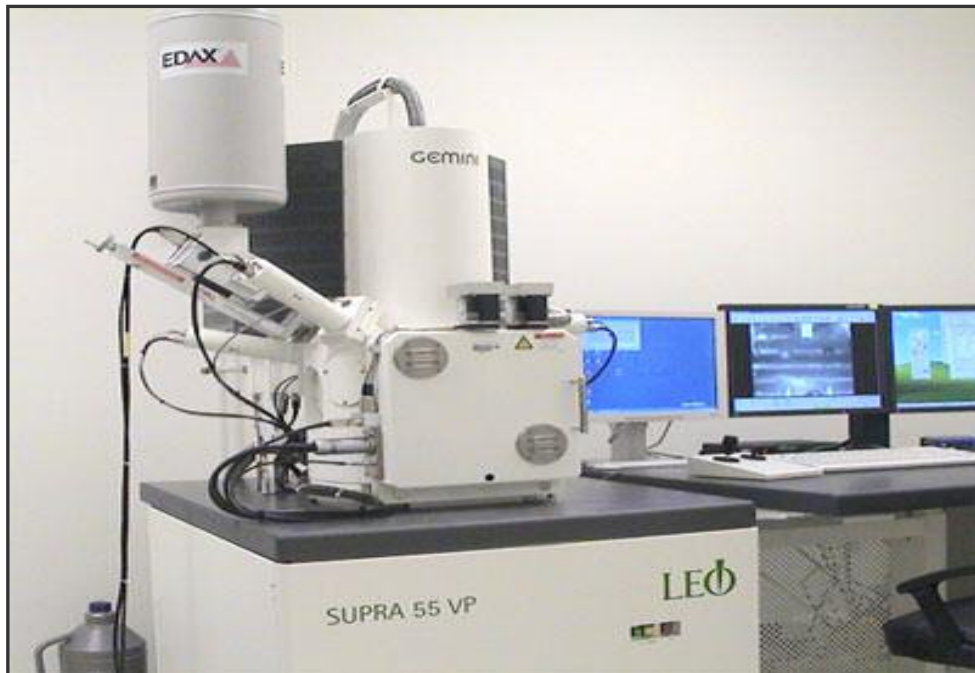


Fig. 52 Scanning Electron Microscope in NanoFAB [68]

5.2.1.1 Substrate with silica nanoparticles

SEM images for 1D PhC is as shown in fig. 53. Here the nanoparticles of silica self-assembled themselves to give a thin layer on the surface of the substrate. Size of these nanoparticles varied from 10 – 40 nm.

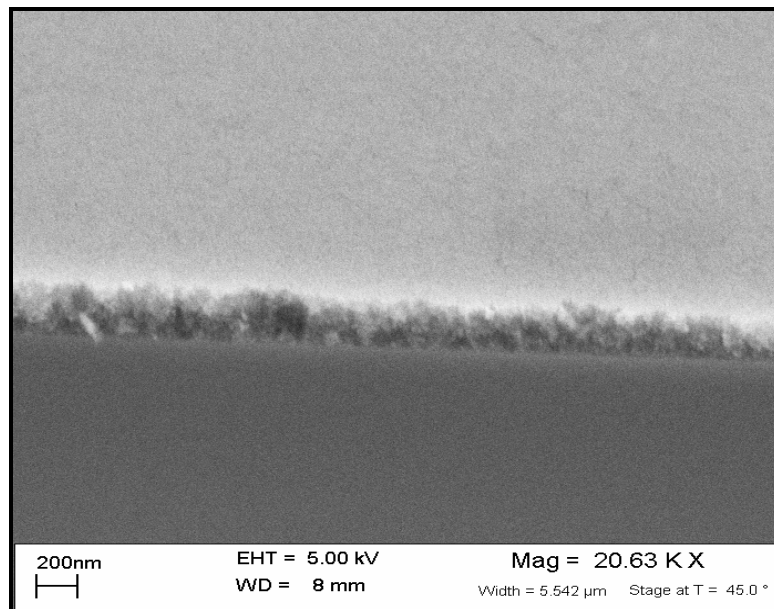


Fig. 53 Thick uniform layer of Silica nanoparticles of thickness 250 nm

Parameters used to obtain 1D PhC like the one shown in above figure are:

- ❖ Technique : Evaporation Method for Self-Assembly of nanomaterials
- ❖ Dilution rate : 0.2ml SiO₂ : 70ml EA
- ❖ Temperature: 75 ° C
- ❖ Time : 5 min

Monolayer of nanoparticles was also seen on the surface of the substrate. This is carried out by adjusting various parameters like temperature, time, and weight% of nanoparticles in the solution. This is shown in fig. 54.

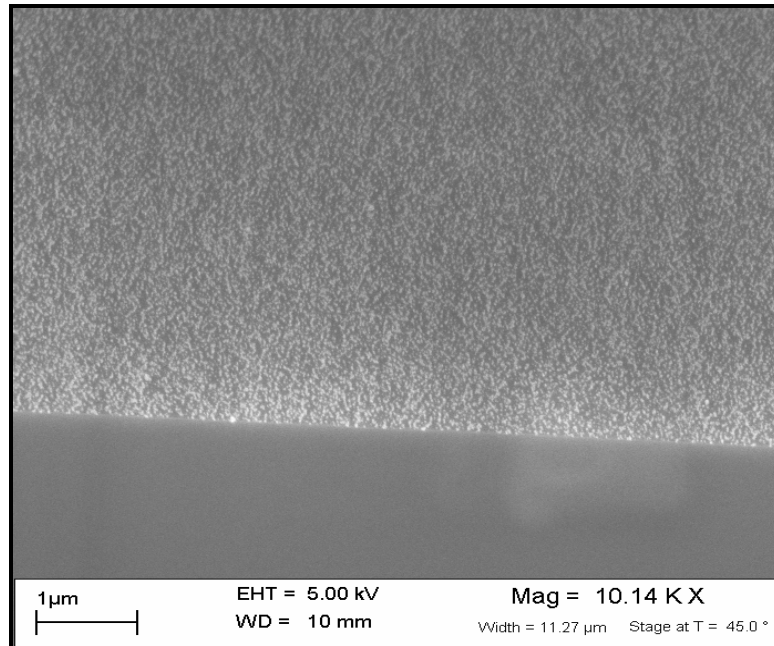


Fig. 54 Monolayer of Silica nanoparticles layer of thickness 20 nm

Parameters to obtain monolayer of nanoparticles as shown in the above figure

are:

- ❖ Technique : Evaporation Method for Self-Assembly of nanomaterials
- ❖ Position of the substrate : Vertical
- ❖ Dilution rate : 0.2ml SiO₂ : 70ml EA
- ❖ Temperature: 75 °C
- ❖ Time : 15 secs

2D PhC was also studied using SEM. In this, distribution of nanoparticles inside the holes were studied thoroughly which helped in modifying the parameters used for the experiment.

For example, if the image showed stacked layers of nanoparticles on the substrate and if the substrate is expected to have a monolayer on the surface, then these nanoparticles can be diluted to a required amount which in turn reduces the thickness of the layer by reducing the cluster thickness of nanoparticles ultimately yielding the expected thickness of layer on the surface of the substrate.

Nanoparticles used for the encapsulation of PhC shown in fig. 55 below are silica nanoparticles. This shows that silica nanoparticles have uniformly filled the patterns on the substrate.

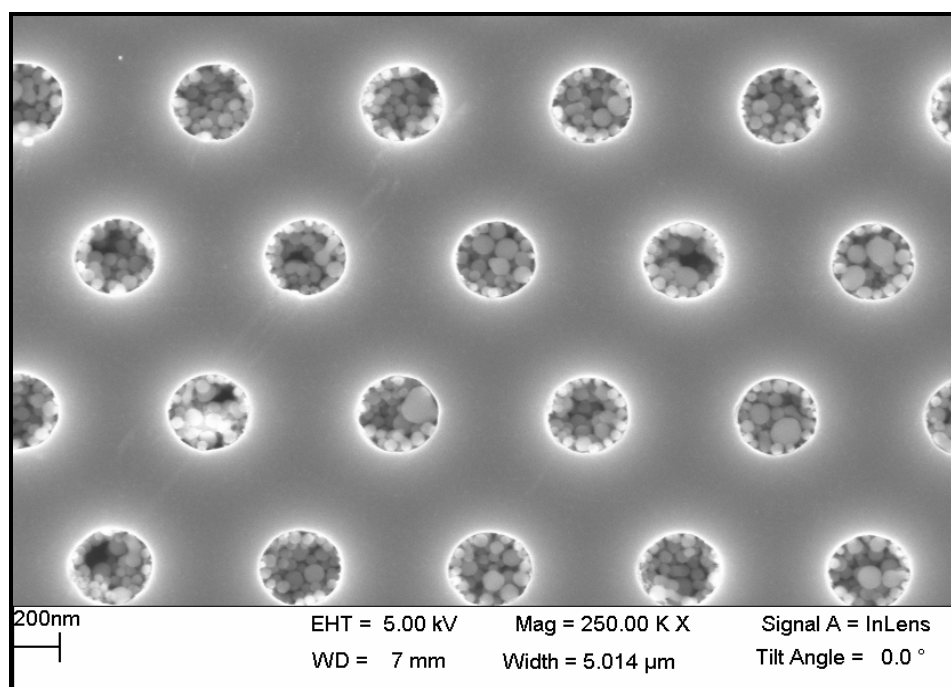


Fig. 55 SEM image of 2D PhC of silica nanoparticles

Parameters used for this crystal are :

❖ Technique : Filling the surface of substrate with nanoparticles solution and using IPA to wash the surface after the complete drying of nanoparticle solution.

- ❖ Dilution : 10 %
- ❖ (33 ml of silica nanoparticles solution + 67 ml of IPA).
- ❖ Temperature : Room temperature
- ❖ Time : Evaporating time of the nanoparticles solution.

5.2.1.2 Substrate with lead-selenide nanoparticles

Pb-Se nanoparticles also formed monolayers on the surface of the substrate. But due to tetrachloroethylene (TCE) solution (solution in which Pb-Se particles are immersed), monolayer of Pb-Se is disturbed to some extent by small holes in many places which is due to the evaporation of TCE solution. Fig. 49 shows monolayer of Pb-Se particles along with few small holes.

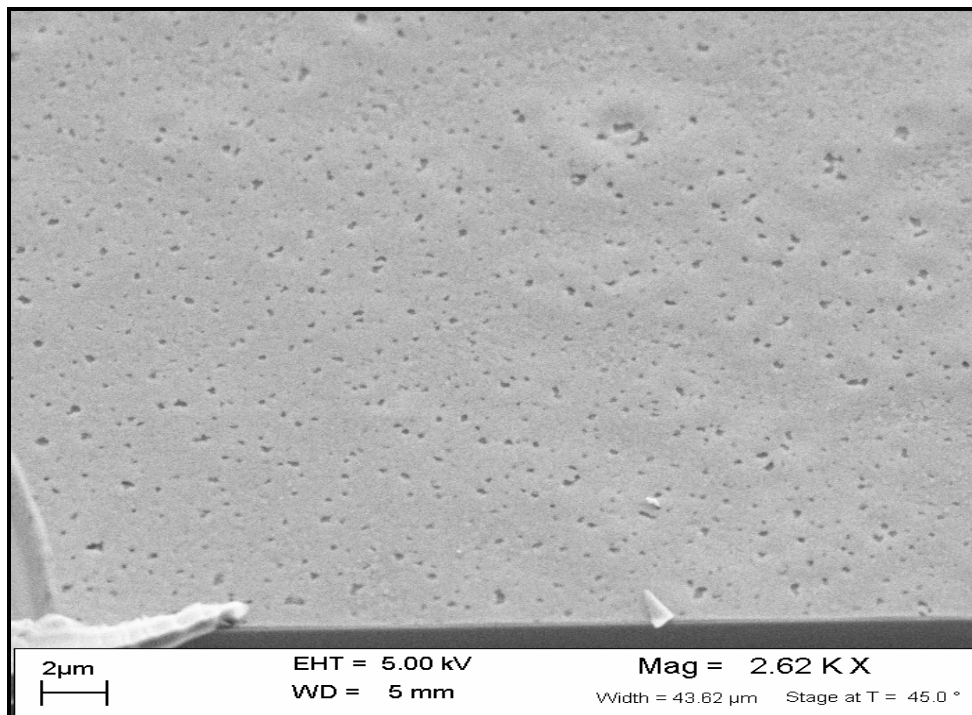


Fig. 56 Layer of Pb-Se nanoparticles of thickness 140 nm

Thickness of this layer was found to be 140 nm (size of a Pb-Se nanoparticle is less than 40 nm). Thus a minimum of 3 nanoparticles were stacked together.

Parameters used for this 1D PhC are:

- ❖ Technique : Spin coating
- ❖ Temperature : Room temperature
- ❖ Spin speed : 4500 rpm
- ❖ Time : 30 secs

5.2.2 Ellipsometer

Ellipsometer was used to find the thickness of the material layer on the surface of the silicon substrate. In this method, the refractive index and rough estimate of the thickness of the layer should be given as input.

Ellipsometer used for this thesis is 'Gaertner Ellipsometer' in NanoFAB. It is interfaced to the computer such that the results are displayed in the monitor. Fig. 57 shows the ellipsometer equipment used for the thickness measurement.



Fig. 57 Gaertner Ellipsometer for thickness measurement [69]

The output (thickness of the layer and refractive index) varies according to the input thickness. If thickness to be given as input is unknown then finding thickness of layer from this method is very difficult. Thus this method is not that accurate for measurements for unknown thickness. This technique was not used for the thin layer measurement in this thesis. Instead they were used for HMDS or photoresist layer thickness measurement when spin coating or etching has to be done for silicon substrate. Since it gives the thickness depending on input thickness, we did not use this experiment for thickness verification.

5.2.3 Profilometer

Profilometer was used to measure the depth profile. While using patterned substrate, profilometer was used for depth profile to check for the presence of nanoparticles on the holes. This is then compared with the diameter of patterned hole for distribution of particles. 'KLA Tencor Profilometer' is used for this measurement. It is shown in fig. 58.

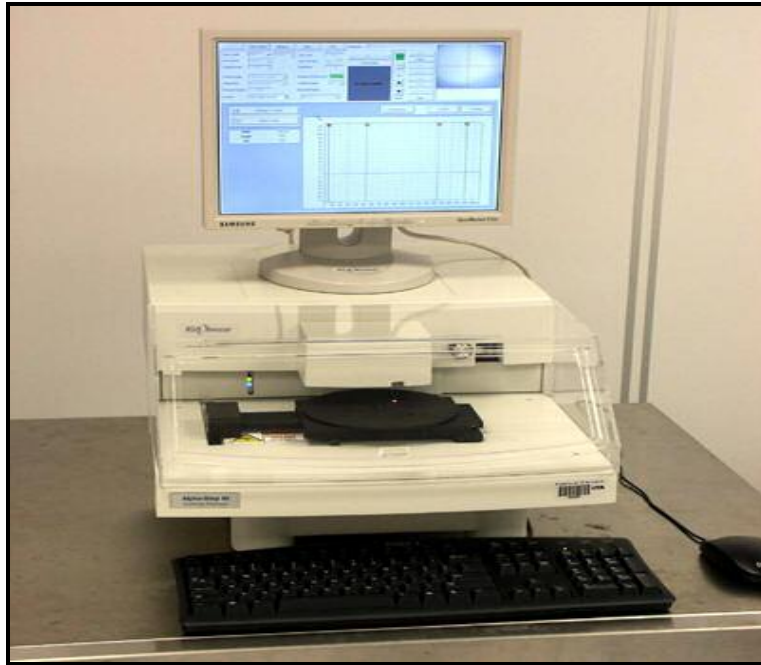


Fig. 58 KLA Tencor Profilometer [70]

A stylus tip in this equipment does the step height profile giving out images which detects and displays height variation or surface roughness in the substrate. Profilometer was used in this thesis to check for the thickness of patterns after wet etching. This equipment can also be used to measure the surface roughness of the substrate.

5.2.4 Optical Microscope

Optical microscope was used for taking images of substrates with nanoparticles. Though the image will not reveal nanoparticles like SEM, surface layer roughness was seen using this equipment. The optical microscope used for the characterization was 'Nomarski Microscope'.



Fig. 59 Nomarski Microscope in cleanroom, UTA NanoFAB center [71]

Fig. 60 shows an optical microscope image of a ring pattern on silicon substrate after the removal of photoresist. Though the visibility of images were not that clear, images from optical microscope gave us some idea about whether to proceed with SEM technique to study the substrate in detail or to redo the experiments. This image also shows various scratches on the surface of the substrate which helped us in finding the surface property of the substrate.



Fig. 60 Optical Microscope image of a ring pattern in the substrate

Thus the various characterization techniques used for different nanoparticles in this thesis was discussed.

CHAPTER 6

THEORETICAL CALCULATION OF THICKNESS OF LAYERS IN 1D CRYSTAL AND FORCES IN 2D CAVITIES

6.1 Introduction

1D crystal involves layer-by-layer deposition of nanoparticles on a silicon substrate. These multilayers may consist of same material or different materials. If different material, this fabrication results in the superposition of properties exhibited by each nanoparticle layer [72]. This layer formation was discussed in detail in chapter-3.

A theoretical calculation of number of nanoparticle layer on the surface of the substrate is calculated using an equation. Also, thickness of the layer on the surface of the substrate is calculated using the equation.

2D cavity formation is made possible by the interaction of capillary forces at the solution interface [73]. Encapsulation of 2D crystals is discussed in detail in chapter-4. Highly ordered structures are formed with nanoparticles by the action of these Capillary forces on the substrate and solution interface. A theoretical calculation of force is calculated which shows the efficiency of capillary forces.

6.2 Equation and factors involved in Self-Assembly of nanoparticles in 1D Crystals

Convective assembly which is used for fabrication of these multilayers [74] helps in controlling thickness of these nanoparticles on the surface of the silicon

substrate. Convective assembly uses capillary forces at the meniscus of the nanoparticle solution and the substrate which draws the nanoparticles together to form a crystal of closely packed nanoparticles [75]

Total number of nanoparticle layer deposited on the surface of the substrate was taken to be “k”. The relationship between volume fractions of these nanoparticles in the solution and size of the nanoparticles is then derived as an equation to calculate the value of “k”. Value of k was found to be as shown in equation 1: [72] [75] [76].

$$k = \frac{\beta * L * \varphi}{0.605 * d * (1 - \varphi)} \longrightarrow (1)$$

Where,

- ✓ L is the meniscus height,
- ✓ β is the ratio between the velocity of a nanoparticle in the solution and the velocity of fluid. This value is considered to be a constant and is equal to 1,
- ✓ φ is the volume fraction of nanoparticles in the solution and
- ✓ d is the diameter of a nanoparticle.

From the above equation, it is understood that the number of colloidal layers on the substrate depends on various factors like:

- ✓ Meniscus height - this can be either convex or concave depending on the response of molecules of solution to the molecules of container
- ✓ Volume-fraction of the nanoparticles in the container – which depends on the quantity of nanoparticles and their distribution in the solution

✓ Diameter of the nanoparticle – which is a main factor depending on which the number of layers are decided.

This value of “k” controls the photonic bandgap behavior in multilayer nanoparticles [72]. Since the number of nanoparticle layers deposited on the substrate depends on height of meniscus, diameter of nanoparticle and volume-fraction of nanoparticles in the solution, it can be varied by varying any of these parameters. Depending on the total number of nanoparticle layers, other factors can be varied or vice-versa.

Also, thickness of the layer on the surface of the substrate can be got from this value of “k” and diameter of the nanoparticle,

$$\text{Thickness of the nanoparticle layer} = k * d \longrightarrow (2)$$

Where,

- ✓ k is the number of nanoparticle layers on silicon substrate
- ✓ d is the diameter of nanoparticle.

Multilayers of nanoparticles when used with different nanoparticles of different sizes yields different optical behavior. When multilayers are fabricated, packing of nanoparticles is also considered to be a very important factor. Stacking can be either different particles of same size or different particles of different size or same particle of different size or same particles of same size.

6.3 Factors involved in calculation of force in 2D cavities

Factors involved in the calculation of force in 2D cavities are:

- ❖ Contact-line radius between particle and solution

❖ Contact angle between the particle and solution

6.3.1 Contact-line radius between particle and solution

Capillary energy, as is directly proportional to the size of the nanoparticle, the interaction energy is derived for 2 nm particles [73] which indicated that the energy is less than the thermal fluctuation. This energy is directly proportional to the contact-line radius between the particle and water.

6.3.2 Contact angle between the particle and solution

Force is directly proportional to the contact-angle between particle and water. Though it is very difficult when the size of the particle is very small, capillary force was roughly estimated such that it overcomes thermal fluctuations. Considering all the factors affecting the capillary interaction energy, the equation for capillary force was roughly estimated to be [73]:

$$F_c = 2 \Pi r \sigma \sin\phi \longrightarrow (3)$$

Where,

- ✓ F_c is the magnitude of capillary force
- ✓ r is the particle-water contact-line radius
- ✓ σ is the surface-tension between water and air
- ✓ ϕ is the contact-angle between particle and water.

Since water is considered to be the solution in this equation, force calculation can be done only for titania particles in this thesis. Titania particles were suspended in water. Due to their hydrophobic nature, they are not miscible with water.

From fig. 61 shown in reference [73], it can be seen perpendicular force required to push the particle into the hole takes an angle α with respect to the contact-line radius and total force.

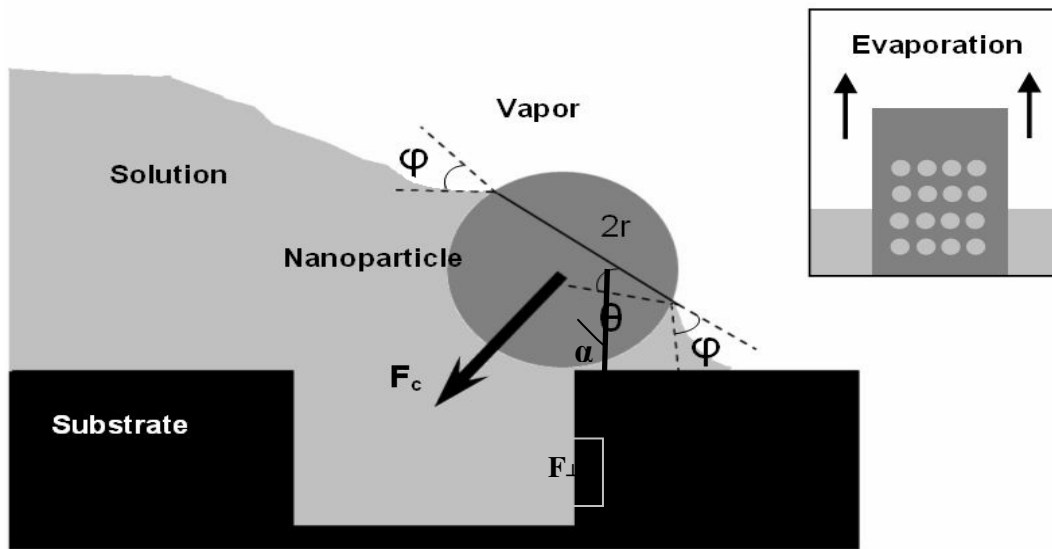


Fig. 61 Capillary Force (F_c) illustrated at the vapor-solution-substrate interface [73]

This angle is used to calculate the force perpendicular to the total force and indirectly helps in specifying the angle between the side wall of the substrate and force.

Perpendicular force is then found to be :

$$F_{\perp} = F_c * \cos(\alpha) \longrightarrow (4)$$

$$F_{\perp} = 2 * \Pi * r * \sigma * \sin(\phi) * \cos(\alpha) \longrightarrow (5)$$

Where,

- ✓ r is the contact-line radius between the particle and water,
- ✓ ϕ is the particle-water contact angle (which is assumed to be 45° with respect to the contact-line radius,

- ✓ α is the angle made by force perpendicular to the capillary force which is 120° when contact-angle is 45°
- ✓ σ is the water-air surface tension which was found to be 3.82 from the calculations in reference [62].

$$F_{\perp} = 2 * 3.14 * r * 3.82 * \sin 45^\circ * \cos 120^\circ$$

$$F_{\perp} = 8.48 r$$

With this relation between contact-line radius and capillary force, a graph is plotted for values of radius from 2nm to 100nm. To calculate values for angle, α , we redo the calculations with a known value of diameter of the nanoparticle as 20 nm.

$$F_{\perp} = 2 * 3.14 * 20 * 10^{-9} * 3.82 * \sin 45^\circ * \cos(\alpha)$$

$$F_{\perp} = 678.5 \cos(\alpha)$$

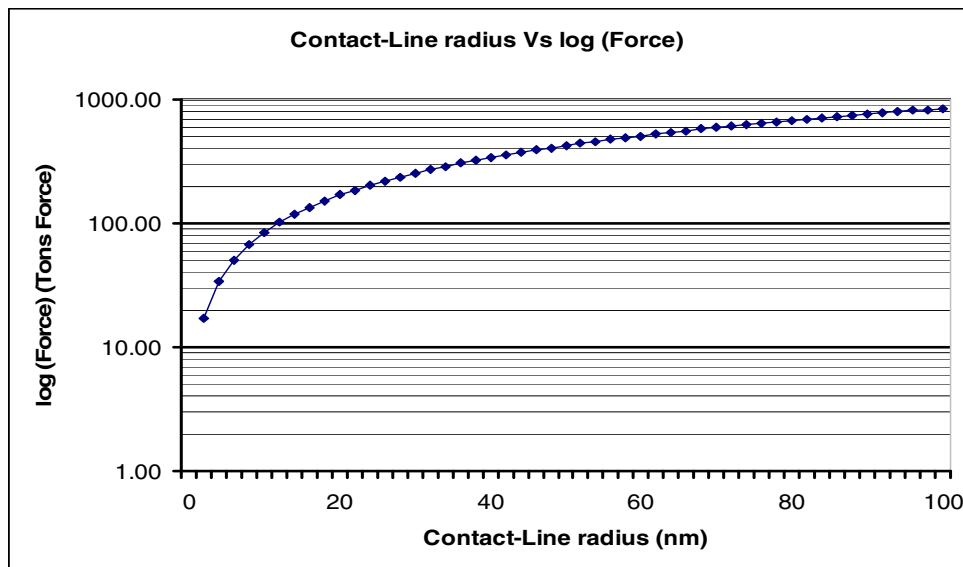


Fig. 62 Graph between contact-line radius and perpendicular force

Same values of capillary force when plotted with the angle between the capillary force and contact-line radius were found to be as shown in the fig[63]:

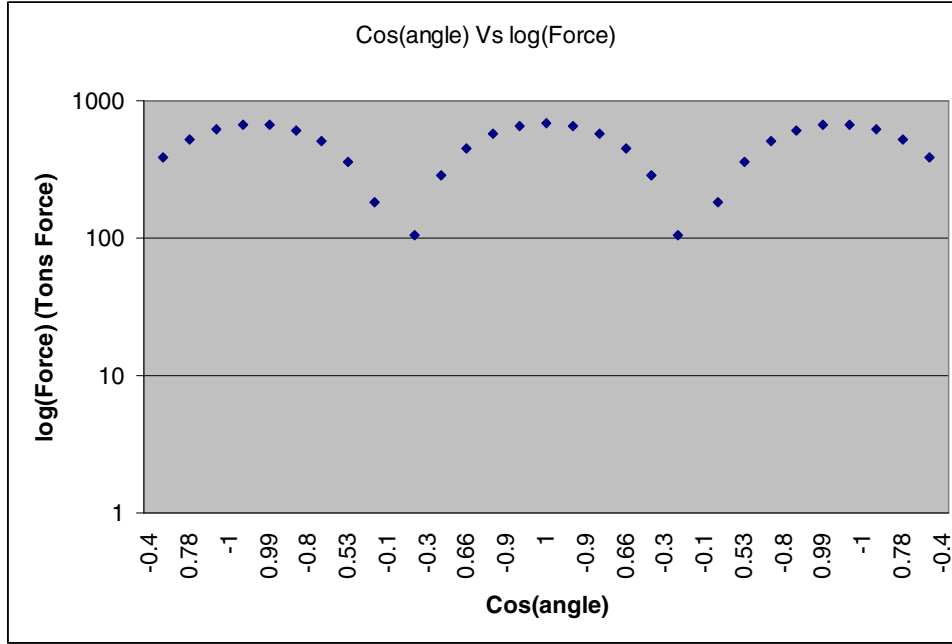


Fig. 63 Graph between $\cos(\alpha)$ and perpendicular force

6.4 Conclusions based on theoretically derived equations

In 1D crystals, total number of nanoparticle layers is calculated using equation (1). The product of equation (1) with diameter of a nanoparticle yields thickness of the layer of nanoparticles on surface of the substrate. This calculation is carried out theoretically for Self-Assembly method.

Due to the diffractive optical properties, colloidal crystals are considered to be a type of PhC. This shows that the calculations performed theoretically, can be tested for PhC. We found it to be the same with the experimental values. Since we did this

comparison only for 2 values and we did not repeat the comparison, results for the comparison is not included in this documentation.

In 2D encapsulation, theoretical calculation procedure satisfies equation (2). The optimum angles calculated theoretically from the above equations and assumptions was based on factors from experiments (like the size of nanoparticles used for the encapsulation). Results from theoretical calculation of force shown in fig. 62 and fig. 63, gives an idea that the calculated force is directly proportional to contact-line radius and doesn't show any significant change when angle of perpendicular force is changed.

Thus the force with which a nanoparticle falls into a patterned hole is less for a particle of smaller diameter than for a particle of diameter $>80\text{nm}$. Comparison of theoretical values with experimental values is difficult in this 2D cavities because of the unknown angle between the nanoparticle, contact-line radius and hole of the substrate. As the size of these holes is in nanometer, it is very difficult to measure the angle between these parameters.

CHAPTER 7

RESULTS AND CONCLUSIONS FOR PHOTONIC CRYSTALS

7.1 Introduction

This chapter compares various methods used to fabricate monolayer of nanoparticles on the silicon substrate finding out effective method for the fabrication of PhC considering factors like temperature, time, and concentration of nanoparticles. Reason for the selective mobility of nanoparticles into the holes assembly of is also discussed.

7.2 Comparison of various methods in 1D PhC

Methods used for the fabrication of 1D PhC were compared using graphical methods. Here, thickness of nanoparticle layer is taken along X-axis and other parameters (like time, temperature, dilution rate and technique) along Y-axis. This method gives the effects of temperature, time, dilution rate and technique on thickness of layer for the fabrication of 1D PhC.

7.2.1 Effects of weight % of nanoparticles on thickness of self-assembled layer

Experiments for the fabrication of 1D PhC shows that Evaporation Induced method is very effective compared to other techniques used. Also, weight-volume % of silica nanoparticles in the solution is taken into consideration when thin layers are to be formed on the surface of the substrate.

As the rate of dilution increases, the thickness of nanoparticle layer on the surface of substrate is reduced. This is shown in fig. 64 wherein the graph shows the thickness of layer with various dilution rates of silica nanoparticles. Processes involved are evaporation induced method, immersion method and Convective Assembly (CA) method.

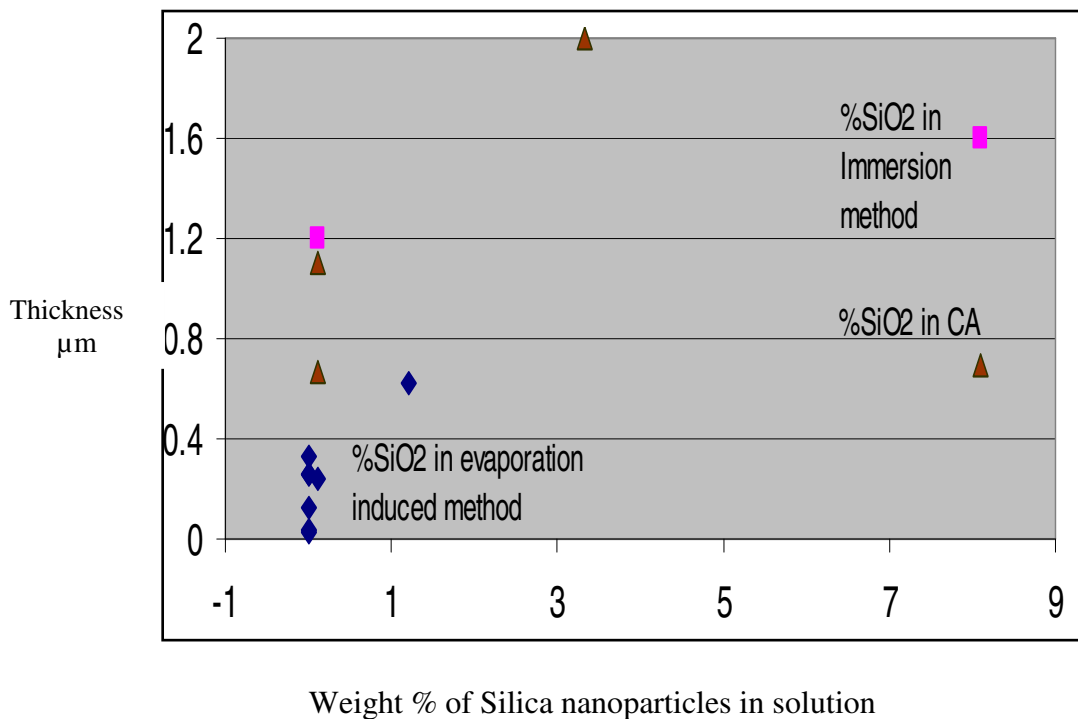


Fig. 64 Effects of Weight% of nanoparticles on thickness of assembled layer

Thus the graph above shows that the thickness of nanoparticle layer increases with increase in nanoparticles inside the solution. Also, it is seen that when same weight-volume % is used for evaporation induced technique, convective assembly and immersion methods, thickness of layer in evaporation technique is lesser compared to the other two methods.

7.2.2 Effects of temperature on thickness of self-assembled layer

Temperature was found to play a major role in the layer formation of nanoparticles. When the temperature was maintained closer to boiling point of the solution, the particles self-assembled themselves uniformly on the surface of substrate.

Fig. 65 shows the comparison of temperature with thickness of self-assembled nanoparticle layer. From the above graph, it is clear that at same temperature, the variation in thickness of nanoparticle layer is from 20nm to few microns.

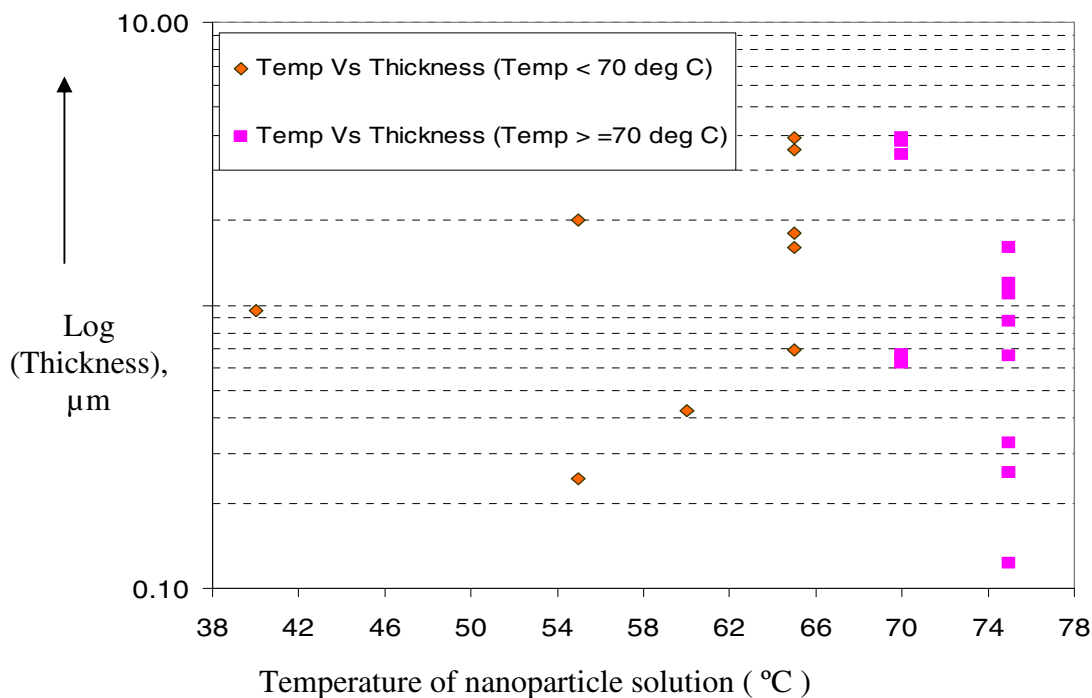


Fig. 65 Effects of temperature on thickness of assembled nanoparticle layer

But the optimized temperature is 75 ° C as it is close to the boiling point of ethanol (solution used for these experiments along with silica nanoparticles solution and its boiling point is 79 ° C) and that it yields monolayer at that particular temperature.

7.2.3 Effects of time on thickness of self-assembled layer

The variation in thickness when time is varied from few seconds to few minutes does not show any significant effect on the thickness of assembled layer. Fig. 66 shows the graph representing thickness along time factor.

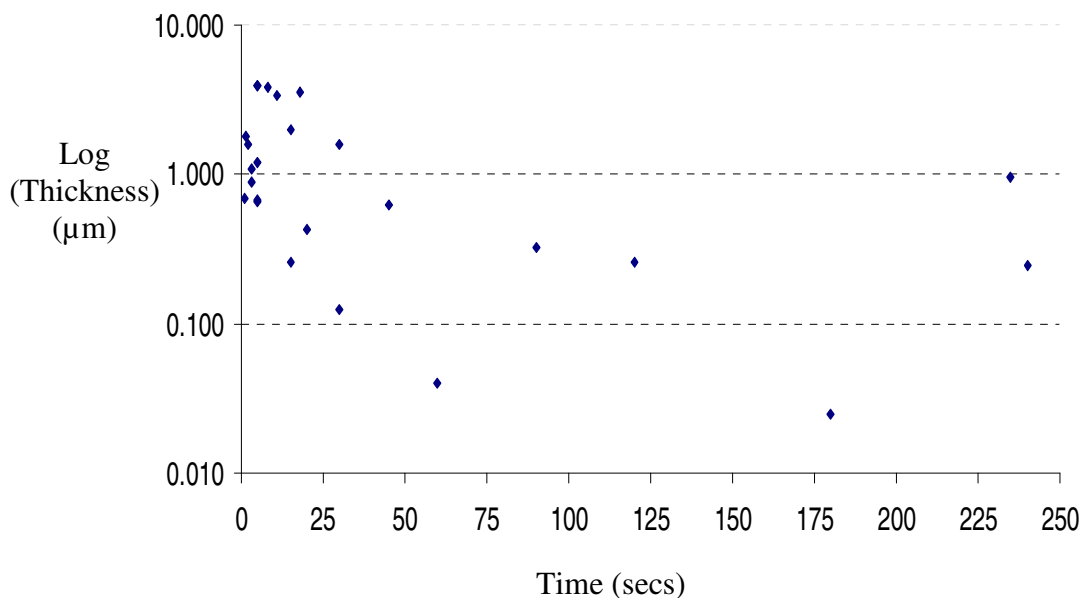


Fig. 66 Effects of time on thickness of assembled nanoparticle layer

From the above graph, it is seen that at time lesser than 25 Secs, nanoparticles assemble to produce thick films, whereas when time \sim 180 secs, we get thin layer of nanoparticle film compared to other time values. This shows that time doesn't play a significant role in the process of thin layers though they yield thick films when time is less and thin film when time factor is high.

7.2.4 Effects of techniques on thickness of self-assembled layer

As discussed in chapter- 3, evaporation method was found to be very effective compared to other methods used for the fabrication of PhC. Fig. 67 shows that thin layer of films can be achieved using evaporation induced Self-Assembly method.

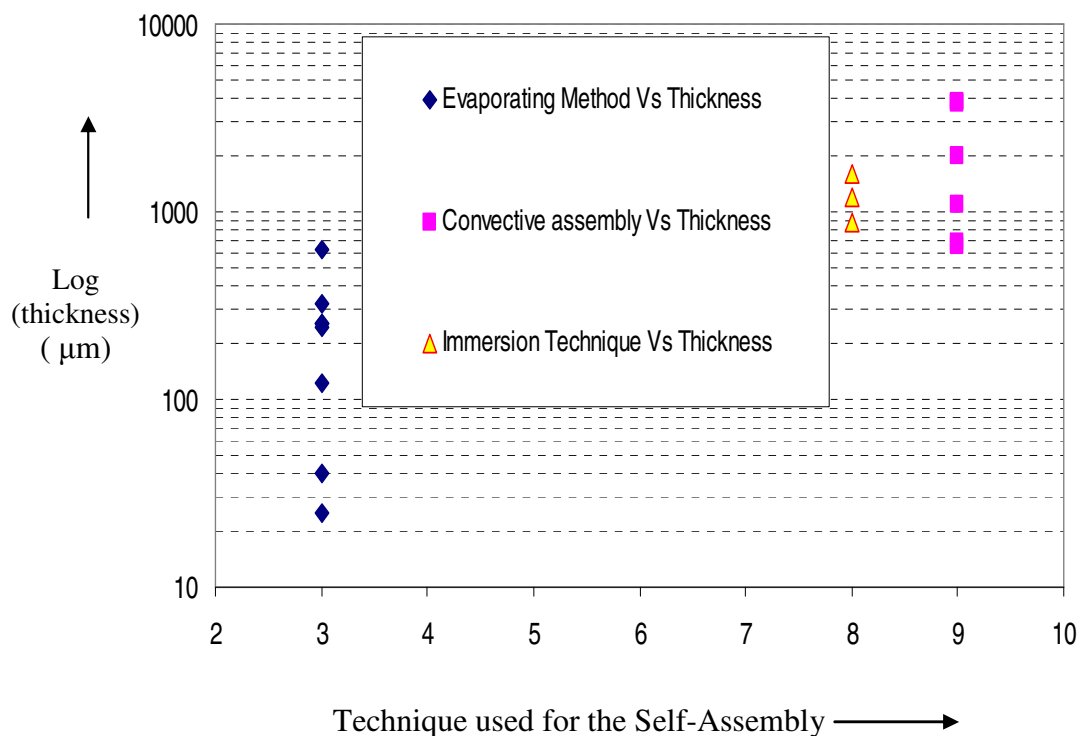


Fig. 67 Effects of technique for Self-Assembly on thickness of assembled layer

In fig. 67, number 3 in X-axis represents evaporation method, 8 represents immersion technique and number 9 represents convective assembly. Methods were represented as numbers for the easiness of plotting the thickness values in the form of a graph. Numbers were given for the methods to plot them as a graph. This graph shows that even if thick film of nanoparticle layer is to be achieved, evaporation induced method can be used as the graph shows both thick and thin film formation for

evaporation induced technique whereas in convective assembly or immersion technique only thick layer of nanoparticles are achieved. Thus the comparison of various techniques helps in achieving the desired nanoparticle layer on the surface of the substrate.

7.3 Conclusions on Self-Assembly of nanoparticles in 1D and 2D crystals

Self-assembly of nanoparticles is used for the fabrication of 1D crystals in this thesis as this method yields repeatability and does not require costly equipments.

Different methods were tried in self-assembly for the fabrication of 1D crystals.

Initially, we tried spin coating experiment for the fabrication. Different combinations of spin speed and spin time were tried to achieve thin layer of nanoparticles on the surface of substrate. Different spin speeds tried for the experiments varied from 1500rpm to 4500rpm. Low speed was tried as they yield thick layers and high speed was tried to achieve thin layers of nanoparticles. Range of speeds were tried to achieve uniform layer of nanoparticles. Silica nanoparticles were selected for our experiment as few researchers carried out experiments with these silica nanoparticles and they were successful. When experiments were tried at a low speed of 1500rpm for 40 seconds, thick layer of nanoparticles was achieved. But these layers were broken because of their thickness which was in the range of few micrometers. Due to the formation of multiple layers on surface of substrate, these layers broke and peeled off from the surface. Then we tried experiments with 4500rpm for 40 seconds. At this speed, though uniformity was not achieved thickness was reduced to some extent. Thus, spin coating at low speed gave us thick layers due to the time for settlement of

nanoparticles on the surface of substrate. As the speed was very low, nanoparticles settled themselves on the surface and arranged themselves to layers and because of low speed, multiple layers were formed on the surface. Reducing the time of spin coating did not result in thin layer of nanoparticles. This might be because of the insufficient time for the formation of monolayers.

Nanoparticles like Pb-Se and titania were also tried for the fabrication. These nanoparticles, which were selected for their surface property, when spun on the surface yielded clusters instead of layers. Hence, many clusters were seen on the surface and they were non-uniform. Most of the surface did not have nanoparticles while few other places had clusters of nanoparticles. As spin coating did not yield thin layer of nanoparticles, we decided to proceed with experiments where instead of filling the surface of substrate with nanoparticle solution, we immersed the substrate into nanoparticles solution and left it in the solution. Substrate was then removed after the evaporation of solution. As the substrate was not disturbed in this process, thin layer of nanoparticles were expected on the surface. But due to the time for which substrate was immersed in the solution, thick layers were seen on the surface. Though we reduced time for which the substrate was immersed in solution, which was accompanied by reducing the composition of nanoparticles in the solution (by adding more IPA or EA solution), minimum thickness obtained from this method was 693nm. Then, we tried to modify this experiment. Instead of immersing the substrate in the solution, we immersed the substrate into the solution for few seconds and removed it from the solution. This process was carried out several times before removing the substrate from

the solution for drying purpose. One more factor included in this experiment was heating the solution. Solution was heated and substrate was immersed and taken out of the solution. As heating of solution and immersion of substrate was carried out simultaneously, nanoparticles arranged themselves uniformly on the surface. Thickness obtained from this method was 423.9nm. Though different compositions of nanoparticles were tried for achieving thin layers, broken surfaces were seen on the surface. Due to the manual movement of the substrate, broken layers were formed on the surface. So we thought of proceeding with a method, which follows the same procedure except for the disturbance of the substrate. In the method we followed to replace the previous method of manual immersion of substrate, we involved parameters like temperature, weight% of nanoparticles in the solution and time for which the substrate was immersed in nanoparticles solution. Nanoparticles solution was heated to a temperature required to carry out the process and when solution reaches the desired temperature, sample was immersed in the solution and the solution was then kept in the hot plate. This method can also be carried out by immersing the substrate in the nanoparticles solution and keeping the beaker (containing solution) on a hot plate. By this method, disturbance to the substrate was reduced and thus peeling of layers from the surface was reduced. This method gave us monolayer of nanoparticles on the surface of substrate and in other experiment, it gave us two layers of nanoparticles on the surface of substrate. As the desired thickness can be obtained from this method, we came to a conclusion of impact of temperature on the fabrication. As the solution is being heated, layer formed on the surface of substrate was very found to be uniform.

This is because of the rapid heating of the solution and because of this, the solution in between the nanoparticles and substrate evaporated which leads to a strong bond between them. Evaporation method was found to be a very effective method for the fabrication of 1D crystals.

Encapsulation of 2D crystal cavities was carried out on a silicon substrate with periodic holes of diameter 450nm. This diameter was selected based on the wavelength of visible light which lies in between 400nm – 700nm. Different self-assembly methods carried out for the encapsulation of crystal cavities were spin coating, immersion technique and filling the surface of substrate with nanoparticles solution followed by cleaning of the solution. When few experiments were tried at a high speed of 4000 rpm for 40 seconds, nanoparticles were seen to fill the holes. But they occupied the surface of substrate along with the filling of holes. Since we need nanoparticles only on the holes (if nanoparticles are throughout the substrate then there will not be any property change within them. They will be just like silicon substrate filled with nanoparticles.), we reduced the composition of nanoparticles in the solution as we thought reduction in composition of nanoparticles will limit the nanoparticles settlement only onto the holes. Spin speed was then varied to 1500 rpm for spin time 30seconds. Even with this slow speed, nanoparticles were seen on the surface of substrate. When same procedure was followed for Pb-Se nanoparticles, we got the same result of nanoparticles occupying the holes completely and filling the surface of substrate. Then, we proceeded with immersion technique, as spin coating did not yield us uniform distribution of nanoparticles into the holes. Reasons for this have been discussed in chapter – 4.

Immersion technique involves manual immersion of substrate into nanoparticles solution. Due to this process of immersion of substrates, substrates were immersed in a vertical position inside the solution. As we expected the nanoparticles to slide into the holes from the surface, we immersed the substrate into the solution or we kept the substrate angle inside a container and poured the solution on its surface. Either of these methods was not successful to fill the holes without occupying the surface. When we tried the same experiment by reducing the weight% of nanoparticles, significant result was not achieved. Since these nanoparticles filled the surface, we thought of pouring the nanoparticles solution on the surface of substrate drop by drop (instead of immersing the substrate into the solution). Initially, when this method was tried, it gave few nanoparticles on the surface of substrate. But then subsequent cleaning of the substrate with IPA solution resulted in nanoparticles filling only the holes. Cleaning of substrate was carried out by pouring IPA solution (using filler) on the substrate. When IPA solution was poured on the surface with a little bit of force, they act with the nanoparticles on the surface (as the nanoparticles on the surface were just individual particles and not layers) and moved them either out of the substrate or into the holes.

Deposition of nanoparticles selectively into holes of the substrate concludes that the nanoparticles solution on the surface of substrate is an effective method compared to other methods. Also, these nanoparticles occupying the holes on the substrate are held in place by various forces like gravitational, van der waals and capillary forces. Presence of these capillary interactions has remarkable effect on various properties of the assembled structures [73].

7.4 Future study

This thesis explained characterization techniques using SEM to study the substrate after Self-Assembly of materials. Thus various factors in 1D cavity help in confirming a monolayer formation on the substrate.

Few experiments can be repeated by varying parameters like temperature, time, methodology to form multilayers with different materials or same material on the surface of substrate. Thickness of each layer is calculated before processing using the wavelength and refractive index of the materials to be deposited. In most of the methods used in this thesis, the problem of adhesion of nanoparticle layer to the surface of substrate was seen. This can be eliminated by the proper adhesion of nanoparticles and substrate by modifying the surface of substrate or nanoparticle or both. By this surface modification process, we change the property of surface and nanoparticles along with the interaction between them.

A suitable method without involving temperature factor is to be found because of the incompatibility of temperature with the boiling point or flash point for some materials. For 2D crystal cavity, surface modification can be done by making the surface hydrophobic or hydrophilic depending on the nanomaterials to be used. Then they can be etched at selective places so that when nanomaterials solution is allowed to flow on the surface they fill the holes selectively. Instead of cleaning the surface of substrate using IPA solution, some method which cleans the surface along with the deposition of nanoparticles can be followed.

Nanoparticle deposited substrate is to be subjected to a material and optical study for its response in both materials and optical fields. This is done to study the substrate completely so that it can be further used in various applications in optoelectronics, biomedical, mechanical and in many other fields. Thus this topic adds on to the scope for future study.

APPENDIX A

MICROSOFT EXCEL SHEET -
PARAMETERS FOR CONVECTIVE ASSEMBLY – IARI EXPERIMENT

Table A.1 Parameters used for the Convective Assembly – IARI Experiment

Concentration (Silica – EA) (ml)	Temp (°C)	Time (secs)	Thickness (nm)	% weight volume of Silica - IPA - EA
15 - 40	55	1.5	1800	8.1% SiO ₂ + 19% IPA + 73%EA
15 - 40	55	15	2000	3.3%SiO ₂ + 7.7%IPA + 88.9% EA
10 - 45	65	5	10900	5.5% SiO ₂ + 12.7% IPA + 82% EA
5 - 40	65	5	3900	3.3%SiO ₂ + 7.7%IPA + 88.9% EA
5 - 65	70	5	3900	2.1% SiO ₂ + 5% IPA + 93% EA
1 - 50	70	8	3800	0.6% SiO ₂ + 1.6% IPA + 98 % EA
0.2 - 50	75	5	663	0.12% SiO ₂ + 0.3% IPA + 99.6%EA
0.2 - 50	75	3	1100	0.12% SiO ₂ + 0.3% IPA + 99.6%EA
15 - 40	65	1	693	8.1% SiO ₂ + 19% IPA + 73%EA

APPENDIX B
MICROSOFT EXCEL SHEET -
PARAMETERS FOR IMMERSION TECHNIQUE

Table B.1 Parameters used for the Immersion Technique

Concentration (Silica – EA) (ml)	Temp (°C)	Time (secs)	Thickness (nm)	% weight volume of Silica - IPA - EA
10 - 50	60	20	423	5% SiO ₂ + 11.7% IPA + 83.3% EA
1 - 50	70	5	666	0.6% SiO ₂ + 1.6% IPA + 98 % EA
5 - 65	70	11	3400	2.1% SiO ₂ + 5% IPA + 93% EA
15 - 40	40	2	1600	8.1% SiO ₂ + 19% IPA + 73%EA
15 - 40	75	30	1600	8.1% SiO ₂ + 19% IPA + 73%EA
0.2 - 50	75	5	1200	0.12% SiO ₂ + 0.28% IPA + 99.6%EA
0.2 - 50	75	3	880	0.12% SiO ₂ + 0.28% IPA + 99.6%EA

APPENDIX C
MICROSOFT EXCEL SHEET -
PARAMETERS FOR EVAPORATION TECHNIQUE

Table C.1 Parameters used for the Evaporation Technique

Concentration (Silica – EA) (ml)	Temp (°C)	Time (secs)	Thickness (nm)	% weight volume of Silica - IPA - EA
0.2 - 50	65	235	960	0.12% SiO ₂ + 0.28% IPA + 99.6%EA
1 - 25	70	45	623	1.2% SiO ₂ + 2.7% IPA + 96.2% EA
0.2 - 50	65	240	243	0.12% SiO ₂ + 0.28% IPA + 99.6%EA
0.2 - 70	75	15	256	8E-6% SiO ₂ + 1.9E-5% IPA + 99.7 % EA
0.2 - 70	75	30	123	8E-6% SiO ₂ + 1.9E-5% IPA + 99.7 % EA
0.2 - 70	75	60	40	8E-6% SiO ₂ + 1.9E-5% IPA + 99.7 % EA
0.2 - 70	75	90	652	8E-6% SiO ₂ + 1.9E-5% IPA + 99.7 % EA
0.2 - 70	75	120	256	8E-6% SiO ₂ + 1.9E-5% IPA + 99.7 % EA
0.2 - 70	75	180	25	8E-6% SiO ₂ + 1.9E-5% IPA + 99.7 % EA

REFERENCES

- [1] E.L.Foster, *Nanotechnology: science, innovation and opportunity*, Upper Saddle River, New Jersey : Prentice Hall PTR, 2006.
- [2] R.Booker and E.Boysen, *Nanotechnology for dummies*, New Jersey: Wiley Publishing Inc., 2005.
- [3] D.Minoli, *Nanotechnology applications to telecommunications and networking*, Hoboken, New Jersey : Wiley-Interscience, 2006
- [4] J.A.DeFranco, B.S.Schmidt, M.Lipson, and G.G.Malliaras, "Photolithographic patterning of organic electronic materials", *Organic Electronics*, Vol. 7, pp.22-28, 2006.
- [5] B.L.Frankamp, "Directed Self-Assembly of nanoparticles", Ph.D dissertation, University of Massachusetts, 2005.
- [6] P.A.Kralchevsky and N.D.Denkov, "Capillary forces and structuring in layers of colloidal particles", *Current Opinion in Colloida and Interface Science*, Vol. 6, pp. 383 – 401, 2001.
- [7] J.Mondia and H.W.Tan, "Photonic Crystal Experiments", Physics Department, University of Toronto, Canada, March 2004.
- [8] M. V. Erementchouk, L. I. Deych, and A. A. Lisyansky, "Optical properties of 1D photonic crystals based on multiple-quantum-well structures", City University of New York, PACS numbers: 72.15.Rn, 05.40.-a, 42.25.Dd, 71.55.Jv, pp. 1 – 10.

- [9] K.Mertens and V.Putkaradze, D. Xia and S. R. J. Brueck, “Theory and experiment for one-dimensional directed Self-Assembly of nanoparticles”, *Journal Of Applied Physics*, Vol. 98, pp. 034309-1 – 034309-6, 2005.
- [10] K.Sakoda, *Optical properties of photonic crystals*, 2nd edition, Berlin: New York, Springer, 2005.
- [11] S.G. Johnson and J.D. Joannopoulos, *Photonic Crystals: The Road from Theory to Practice*, Boston, Kluwer, 2002.
- [12] M.J.A. De Dood, E.Snoeks, A.Moroz and A. Polman, “Design and optimization of 2D photonic crystal waveguides based on silicon”, *Optical and Quantum Electronics*, Vol. 34, pp. 145-159, 2002.
- [13] J. Schilling, F. Muller, S. Matthias, R. B. Wehrspohn, U. Gosele, and K. Busch, “Three-dimensional photonic crystals based on macroporous silicon with modulated pore diameter”, *Applied Physics Letters*, Vol. 78, no. 9, Feb 2001.
- [14] E.Ozbay, I.Bulu, K.Aydin, H.Caglayan, and K.Guven, “Physics and applications of photonic crystals”, *Photonics and Nanostructures – Fundamentals and Applications*, Vol. 2, pp. 87–95, Aug 2004.
- [15] J.D. Joannopoulos, R.D.Meade, and J.N.Winn, *Photonic Crystals: Molding the Flow of Light*, Princeton, Sep 1995.
- [16] J.D.Joannopoulos, P.R.Villeneuve, S.Fan, “Photonic crystals: putting a new twist on light”, *Nature*, Vol. 386, pp.143 – 149, Mar 1997.
- [17] John D. Joannopoulos, “Self-Assembly lights up”, *Nature*, Vol. 414, no. 15, pp. 257 – 258, Nov 2001.

- [18] Eli Yablonovitch, "Photonic crystals: Semiconductors of light", *Scientific American (International Edition)*, Vol.285, no.6, pp. 47-55, Dec 2001.
- [19] A. Volta, "Silicon-based photonic crystals for the control of light propagation and emission", *Semiconductor and Solid State Theory Group*, a project of MIUR (Italian Ministry of Education, Universities and Research), 2004.
- [20] C.J.Barrett and K.Yager, "Thin Films of Light-Responsive Polymers for Sensing and Surface Patterning", *Active Materials: Behavior and Mechanics, Proceedings of International Society for Optical Engineering*, pp. 51-60, Aug 2003.
- [21] B.Hemtanon, H.Warad, C.Thanachayanont and J.Dutta, "Nanoparticle diode with Layer-by-Layer deposition technique", Asian Institute of Technology, National metals and Materials Technology Center, 2nd ECTI Annual Conference (ECTI –CON 2005), Pattaya, Thailand, May 2005.
- [22] E.Rabani, "Self-Assembly of Nanoparticles: Theory and experiments meet", School of Chemistry, Tel Aviv University, Technical Report, pp.3-6.
- [23] S.Griffith, "Tools for Designing Programmatic Self-Assembling Systems," 6.978, 2002.
- [24] K.F.Bohringer, U.Srinivasan, and R.T.Howe, "Modeling of Capillary Forces and binding sites for Fluidic Self-Assembly", Proceedings in 14th International Conference Micro Electro Mechanical Systems, Switzerland, pp. 21-25, Jan 2001.
- [25] W.C. Carter, "The forces and behavior of fluids constrained by solids", *Acta Metallurgica*, Vol. 36, no. 8, pp. 2283 – 2292, 1988.

- [26] U.Srinivasan, M.A.Helmbrecht, R.S.Muller, R.T.Howe, “MEMS; Some Self-Assembly required”, *Optics and photonic news, optical society of America*, Vol. 13, no. 11, pp-20-24, Nov 2002.
- [27] H.Zeng, J.Li, L.Wang, J.P.Liu, and S.Sun, “Interparticle Interactions in Annealed FePt Nanoparticle Assemblies”, *Institute of Electrical and Electronics (IEEE) Transactions on Magnetics*, Vol. 38, no. 5, pp. 2598-2600, Sep 2001.
- [28] K.Yoshihara, “General theory of nano-technology”, *Materials Science and Technology (Japan)*, Vol. 39, no. 5, pp. 169 – 173, Oct 2002.
- [29] R.W.Siegel, E.Hu and M.C.Roco, *Nanostructure Science and Technology: R & D Status and Trends in Nanoparticles, Nanostructures Materials, and Nanodevices*. Kluwer Academic Publishers, 1999.
- (This book is available online at: <http://itri.loyola.edu/nano/final/>)
- [30] S.G.Johnson, J.D.Joannopoulos, “Designing synthetic optical media: photonic crystals”, *Acta Materialia*, Vol. 51, no. 19, pp 5823 – 5835, 2003.
- [31] B. Gralak, S. Enoch and G. Tayeb, “Anomalous refractive properties of photonic crystals”, *Journal of Optical Society of America. A*, Vol. 17, no. 6, June. 2000.
- [32] J.Hecht, *Understanding Fiber optics*, Prentice Hall, Apr 2005.
- [33] M.Soljačić and J.D. Joannopoulos, “Enhancement of nonlinear effects using photonic crystals”, *Nature materials*, Vol. 3, pp. 211 – 219, Apr 2004.
- [34] R.Bhave, *Inorganic Membranes: Synthesis, characteristics, and applications*, Springer: 1 edition, New York : Van Nostrand Reinhold, 1991.

- [35] M. Qi, E. Lidorikis, P.T. Rakich, S.G. Johnson, J.D. Joannopoulos, E.P. Ippen and H.I. Smith, “A three-dimensional optical photonic crystal with designed point defects”, *Nature*, vol. 429, pp. 538 – 542, June 2004.
- [36] Holister, J-W Weener, C.R.Vas, T.Harper, “Nanoparticles”, *Cientifica, Technology white papers*, P Nanoparticles nr.3, pp.1 – 11, Oct 2003.
- [37] G. Cao, *Nanostructures and nanomaterials: synthesis, properties and applications*, London: Imperial College Press, 2004.
- [38] F. Osterloh, “Silica-gold nanoparticle clusters as chemical sensors”, *The International Society for Optical Engineering, Nanotechnology 3*, Nanotechnology E-Bulletin, Sept 2004.
- [39] H.Fan, K.Yang, D.M.Boye, T.Sigmon, K.J.Malloy, H.Xu, G.P.Lopez and C.J.Brinker, ”Self-Assembly of Ordered, Robust, Three-Dimensional Gold Nanocrystal/Silica Arrays”, *Science*, Vol. 304, pp.567 – 571, April 2004.
- [40] C.Murray, S.O’Brien, F.Redl, K.S.Cho, “Magnetic and semiconducting Nanoparticles assembled”, *Global Publication of record for High Performance Computing*, Vol. 12, no. 25, June 27, 2003.
- [41] K.R.Choudhury, Y.Sahoo and P.N.Prasad, “Hybrid Quantum-Dot-Polymer Nanocomposites for infrared Photorefractivity at an Optical Communication Wavelength”, *Advanced Materials*, Vol. 17, no. 23, pp. 2877 – 2881, October 19, 2005.
- [42] A. Hernández-Ayala, T. López, P. Quintana , J. J. Alvarado-Gil and J. Pacheco, “Time Evolution of the Thermal Properties during Dehydration of Sol-Gel Titania Emulsions, *Azojomo - Journal of Materials Online*, Vol. 1, december 2005.

- [43] X.Wang, C.J.Summers and Z.L.Wang, “Large-Scale Hexagonal-Patterned Growth of Aligned ZnO Nanorods for Nano-optoelectronics and Nanosensor Arrays”, *Nanoletters*, Vol. 4, no. 3, pp. 423 – 426, 2004.
- [44] J.C Huie, “Guided molecular Self-Assembly: a review of recent efforts”, *Institute of Physics Publishing- Smart Materials and Structures*, Vol. 12 , pp. 264–271, March 27, 2003.
- [45] D.Xia, S.R.J.Brueck, “Lithographically directed deposition of silica Nanoparticles using spin coating”, *Journal of Vacuum Science and Technology. B*, Vol. 22, no. 6, pp. 3415 – 3420, December 2004.
- [46] R.Plass, “Device Preparation”, Institute of Chemical Sciences and Engineering, LPI - Solid state group, <http://sbg.epfl.ch/dev-prep.html>.
- [47] C.J. Brinker, Y.Lu, A.Sellinger and H.Fan, “Evaporation-Induced Self-Assembly: Nanostructures Made Easy”, *Advanced Materials*, Vol.11, no. 7, pp. 579 – 585, 1999.
- [48] S.M.Yang, H.Miguez and G.A.Ozin, “Opal Circuits of Light – Planarized Microphotonic Crystal Chips”, *Advanced Functional Materials*, Vol. 12, no. 6 + 7, pp.425 – 431, June 2002.
- [49] G. Prevo, Y. Hwang, and O.D. Velev, “Convective Assembly of Antireflective Silica Coatings with Controlled Thickness and Refractive Index”, *Chem. Mater*, Vol.17, pp. 3642-3651, 2005.

- [50] H.Nakamura, “Colloidal Crystals – Self-Assembly of Monodispersed Colloidal Particles”, *R & D Review of Toyota CRDL*, Vol. 39, no. 4, pp. 33 – 39.
- [51] Y.Xia, B.Gates, Y.Yin, and Y.Lu, “Monodispersed Colloidal Spheres: Old Materials with New Applications”, *Advanced Materials*, Vol. 12, no. 10, pp. 693 – 713, 2000.
- [52] Gi-Ra Yi, J.H Moon, V.N. Manoharan, D.J. Pine, and S.M. Yang, “Packings of Uniform Microspheres with Ordered Macropores Fabricated by Double Templating”, *Journal of American Chemical Society*, Vol.124, pp. 13354-13355, 2002.
- [53] D.J.Norris, E.g. Arlinghaus, L. Meng, R.Heiny, and L.E.Scriven, “Opaline Photonic Crystals: How Does Self-Assembly work?”, Report, University of Minnesota, Minneapolis, Chemical Engineering and Materials Science, March 25, 2004.
- [54] D.J.Norris, E.G. Arlinghaus, L.Meng, R.Heiny, L.E.Scriven, “Opaline photonic crystals: How does Self-Assembly work?”, *Advanced Materials*, Vol.16, no.16 , pp.1393- 1399, Aug 18, 2004.
- [55] D.Xia and S.R.J.Brueck, “A Facile Approach to Directed Assembly of Patterns of Nanoparticles Using Interference Lithography and Spin Coating”, *American Chemical Society*, NanoLetters, Vol.4, no.7, pp.1295 – 1299, 2004.
- [56] M.Patrini, M.Galli, M.Belotti and L.C.Andreani, “Optical response of one-dimensional Si/SiO₂ Photonic crystals”, *Journal of Applied Physics*, Vol. 92, no. 4, pp.1816 – 1820, 2002.

- [57] C.J.Huang, M.P.Huang, Y.H.Wang, N.F.Wang, and J-R.Chen, “Improved formation of silicon dioxide films in liquid phase deposition”, *Journal of Vacuum Science and Technology A, American Vacuum Society*, Vol. 16, no. 4, pp. 2646 – 2652, February 1998.
- [58] N.B.Chaure, A.K.Ray and R.Capan, “Sol-gel derived nanocrystalline titania thin films on silicon”, *Semiconductor Science and Technology*, Vol.20, no. 8, pp.788 – 792, August 2005.
- [59] A. Sugunan, J.Duttam, “Nanoparticles for nanotechnology”, *Journal of Physics Science and Idea*, Vol. 4, no. 1 & 2, pp. 50 – 57, 2004.
- [60] I.Celanovic, F.O’Sullivan, N.Jovanovic, M.Qi, and J.Kassakian, “1D and 2D Photonic Crystals for Thermophotovoltaic Applications”, Report, Massachusetts Institute of Technology, Cambridge, 2004.
- [61] F.Riboli, N.Daldosso, M.Melchiorri, P.Bettotti, G.Pucker, A.Lui, S.Cabrini, E.D.Fabrizio, and L.Pavesi, “1D photonic crystals on ridge waveguides: a tunable Fabry-Perot cavity and a mode matched high quality factor microcavity”, Iowa State University, Condensed Matter Physics Program and Trento University, Italy.
- [62] Z.Q.Hua, F. Denes, R.A.Young, “Surface functionalization of polymeric substrates from radio-frequency-plasma-generated silylium ions”, *Journal of Vacuum Science and Technology A*, Vol.14, no. 3, pp.1339 – 1347, 1996.
- [63] J.C.Meiners, H.Elbs, A.Ritzi, J.Mlynek, and G.Krausch, “Chemically functionalized surfaces from ultrathin block-copolymer films”, *Journal of Applied Physics*, Vol. 80, no. 4, pp.2224 – 2227, August 15, 1996.

- [64] M.K.Shi, L.martinu, E.Sacher, A.Selmani, M.R.Wertheimer, A.Yelon, "Angle-resolved XPS study of plasma-treated teflon PFA surfaces", *Surface and Interface Analysis*, Vol. 23, no. 2, pp.99 – 104, 1995.
- [65] T.S.Phely-Bobin, R.J.Muisener, J.T.Koberstein, and F.Papadimitrakopoulos, "Preferential Self-Assembly of Surface-Modified Si/SiO_x Nanoparticles on UV/Ozone Micropatterned Poly(dimethylsiloxane) Films", *Advanced Materials*, Vol. 12, no. 17, pp. 1257 – 1261, September 15, 2000.
- [66] W.Park, J.S.King, C.W.Neff, C.Liddell, and C.J.Summers, "ZnS-Based Photonic Crystals", *Physica Status Solidi (b)*, Vol. 229, no. 2, pp. 949-960, January 16, 2002.
- [67] I. Alvarado-Rodriguez, "Fabrication of Two-Dimensional Photonic Crystal Single-Defect Cavities and their Characterization by Elastic Scattering", PhD dissertation, University of California, EE Dept., Los Angeles, 2003.
- [68] Zeiss Supra VP 55 Scanning Electron Microscope, Nanofab Research and Teaching Facility, University of Texas at Arlington, College of Engineering.
<http://www.uta.edu/engineering/nano/facility.php?id=53&cat2=SEM>
- [69] Gaertner Ellipsometer, Nanofab Research and Teaching Facility, University of Texas at Arlington, College of Engineering.
<http://www.uta.edu/engineering/nano/facility.php?id=59&cat2=Teaching%20Facilities>
- [70] KLA Tencor Profilometer, Nanofab Research and Teaching Facility, University of Texas at Arlington, College of Engineering.
<http://www.uta.edu/engineering/nano/facility.php?id=51&cat2=Characterization>

[71] Nomarski Microscope, Nanofab Research and Teaching Facility, University of Texas at Arlington, College of Engineering.

<http://www.uta.edu/engineering/nano/facility.php?id=44&cat2=Characterization>

[72] P.Jiang, G.N.Ostojic, R.Narat, D.M.Mittleman and V.L.Colvin, “The fabrication and Bandgap engineering of photonic multilayers”, *Advanced Materials*, Vol.13, no.6, pp. 389 – 393, March 16, 2001.

[73] Y.Cui, M.T.Bjork, J.A.Liddle, C.Sonnichsen, B.Boussert, and A.P.Alivisatos, “Integration of Colloidal Nanocrystals into Lithographically Patterned Devices”, *Nanoletters*, Vol. 4, no. 6, pp. 1093 – 1098, 2004.

[74] V.L.Kovin, “From Opals to Optics: Colloidal Photonic Crystals”, *MRS bulletin*, pp. 637 – 641, August 2001.

[75] P.Jiang, J.F.Bertone, K.S.Hwang, and V.L.Colvin, “Single-Crystal Colloidal Multilayers of Controlled Thickness”, *American Chemical Society’s Chemistry of Materials*, Vol. 11, no.8, pp. 2132 – 2140, July 15, 1999.

[76] R.Bhave, *Inorganic Membranes: Synthesis, characteristics, and applications*, Springer: 1 edition, New York: Van Nostrand Reinhold, 1991.

[77] W. D. Zhou, V. Nair, G. Thiruvengadam, “The Impact of High Dielectric Constant on Photonic Bandgaps in PbSe Nanocrystal based Photonic Crystal Slabs”, *Proceedings of International Society for Optical Engineering*, Vol. 6128, pp. 50 – 57, 2006.

[78] W. D. Zhou, G. Thiruvengadam, V. Nair, “Encapsulated Photonic Crystals and Nanoparticle Self Assembly on Patterned Photonic Crystal Structures” (Poster), 3rd Annual SPRING Conference, Houston, Texas, Associated Nanotechnology Congress, October 2005.

[79] G. Thiruvengadam, H.J. Yang, W. D. Zhou, “Encapsulated photonic crystals and nanoparticle self assembly on patterned photonic crystal structures (Poster)”, *JSPS – UNT Joint Symposium on Nanoscale Materials for Optoelectronics and Biotechnology*, University of North Texas, Texas, February 2-3, 2006.

BIOGRAPHICAL INFORMATION

Geetha Thiruvengadam was born in Trichy, TamilNadu, India. Her parents Mr.Thiruvengadam Alagiri and Mrs.Indrani Ramanujam live together in India. Geetha's brother Mr. Vijay Thiruvengadam works in Austin, TX.

Geetha Thiruvengadam completed her Bachelor of Engineering from PSG College of Technology, Coimbatore, TamilNadu, India. During her Bachelor's degree, she worked in many companies like Integral Coach Factory (ICF), Visteon Automotives (Ford India Limited), India Forge and Drop Stampings Limited, PSG Neelambur Foundry as Trainee Engineer as a part of her curriculum. It was during this time, she developed an interest towards Materials Science and Engineering and their applications in semiconductor industry. She joined University of Texas at Arlington in Fall 2004 as a Graduate Student to pursue her Master of Science in Materials Science and Engineering.

After graduation, Geetha Thiruvengadam looks forward to work in a semiconductor industry as Materials Science Engineer where she can implement various techniques in semiconductor fabrication on which she had been working for the past two years.