

**1,2-dichloroethane based deposition of Graphene oxide Langmuir-
Blodgett thin films**

A dissertation

submitted in the partial fulfillment of the requirement for the award of degree of

MASTER OF SCIENCE

in

PHYSICS

Submitted By

Shivani Goyal

(Roll no: 301704031)



THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

Under the guidance of

Dr. Loveleen Kaur Brar

Assistant Professor

School of Physics and Materials Science

Thapar Institute of Engineering & Technology, Patiala- 147004,

July-2019

Certification

I hereby certify that this thesis entitled “1,2-dichloroethane based deposition of Graphene oxide Langmuir-Blodgett thin films” in partial fulfillment for the requirements for the award of Degree of Master of Science in Physics submitted to School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala is an authentic record of my own work and is carried under the supervision of **Dr. Loveleen Kaur Brar**. The matter submitted via this thesis report has not been submitted for the award of any degree to the best of our knowledge.

Date: 15 July, 2019
Place: Patiala

Shivani
Shivani Goyal
(301704031)

This is to certify that the above statement made by the candidate is correct and true to the best of my knowledge.

Loveleen Kaur Brar
Dr. Loveleen Kaur Brar

Assitant Professor
School of Physics and Materials Science
Thapar University, Patiala

Dedicated
To my
Mom for her
Love and support.

Acknowledgement

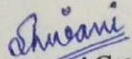
With immense pleasure, I am really thankful to my supervisor **Dr. Loveleen Kaur Brar**, School of Physics and Material Science (SPMS), Thapar Institute of Engineering & Technology (T.I.E.T), Patiala. Without her dedicated supervision, it would not have been possible for me to complete my thesis work. She always encouraged me whenever I felt down and motivated me to work harder. She was the one who motivated me to go for the work of my interest and every time I went to her with any kind of query she was always there for me.

I wish to express my sincere thanks to **Dr. O.P.Pandey**, Head of SPMS department for his support and encouragement. A special gratitude to **Dr.B.N.Chudasama** for availing me the facilities of his lab.

A special thanks to **Ms. Raveena** and **Ms. Amanpreet** for their valuable guidance in learning technique as well as in performing experiments.

I am glad to thank my friend **Shubham Rajput** for always motivating me to work harder and to move on with a positive spirit.

Last but not the least; I place a deep sense of gratitude to my Mother **Mrs. Anju Goyal** and my **family** for their sincere encouragement, being a source of inspiration throughout my thesis. Their blessings and love means a lot to me and inspires me pursue my work with full enthusiasm and great confidence.


Shivani Goyal

Date: 15 July, 2019

Abstract

Graphene oxide-a flexible, low cost material has attracted considerable interest in regards of its optical, mechanical and thermal properties. A Graphene oxide (GO) thin film finds wide range of applications: energy storage devices, conductive films, electronics and biomedical applications. So, their formation in a controlled manner for tailoring of their properties is an important research topic. Langmuir-Blodgett technique is well suited for producing tailor made GO thin films. In this work, uniform, transparent thin films of GO of variable thickness have been prepared using LB deposition process. The role of change in spreading solution composition, barrier compression rate as well as the sub-phase temperature on the film properties has been reflected upon. Surface pressure-area isotherms have been used to characterize the GO Langmuir layers on the water sub-phase prior to transfer onto solid substrate. The stability of the monolayers have been confirmed using hysteresis measurements of the GO Langmuir layers. The oscillating barrier measurements have been performed at different barrier compression rates for gaining an insight into the dissipation processes within the films by calculating visco-elastic parameters. Finally, the deposition of graphene oxide monolayers was done using Y-type deposition on glass substrates. Stable uniform graphene oxide thin films by 1, 2, 4 and 5 layer transfer for different barrier compression rates were deposited. AFM analysis of the deposited films shows that the films are continuous and smooth (low r.m.s. roughness). The roughness of the films increases with increasing number of transferred layers and smoother films are obtained for higher barrier compression rates.

Contents

CHAPTER 1: INTRODUCTION OF GRAPHENE OXIDE THIN FILMS	1-4
1.1 Introduction to Thin Films.....	1-1
1.2 Graphene Oxide.....	1-2
1.3 General Properties of Graphene Oxide	2-2
1.4 Properties of thin film of Graphene Oxide	2-3
1.5 Applications of Graphene Oxide thin films	4-4
1.6 References	4-4
CHAPTER 2: LITERATURE REVIEW.	5-8
2.1 Deposition of GO thin films using different techniques	5-5
2.2 Langmuir Blodgett technique for thin film Synthesis.....	6-6
2.3 Oscillating Barrier Measurements for Langmuir films	6-6
2.4 GO thin films using Langmuir Blodgett technique.....	7-7
2.5 References.....	7-8
CHAPTER 3: INTRODUCTION TO LANGMUIR- BLODGETT TECHNIQUE	9-16
3.1 Introduction.	9-9
3.2 Formation of Langmuir Monolayer.....	9-10

3.3 Pressure-Area Isotherm	11-12
3.4 Deposition Methods	12-12
3.5 Types of Langmuir-Blodgett Deposition.....	12-13
3.6 Oscillating Barrier Measurement	14-14
3.7 Langmuir-Blodgett Technique's Experimental Setup.....	14-16
3.8 Advantages	16-16
3.9 Disadvantages	16-16
3.10 References	16-16

CHAPTER 4: MATERIALS AND METHODS17-21

4.1 Materials used	17-18
4.2 Methods	18-19
4.2.1 Preparation of GO spreading suspension... ..	18-19
4.2.2 Preparation of Langmuir films and Langmuir Blodgett films.....	19-19
4.3 Characterization Techniques	19-21
4.3.1 Surface Pressure (Π) - Area (A) Isotherm	19-20
4.3.2 Hysteresis Method.....	20-20
4.3.3 Oscillating Barrier Method.....	20-20
4.3.4 Atomic Force Microscopy (AFM)....	20-21
4.4 References	21-21

CHAPTER 5: RESULTS AND DISCUSSION. 22-33

5.1 Surface Pressure (Π) –Area (A) Isotherms 22-28

 5.1.1 Effect of different ratios of solvent in spreading solution 22-23

5.1.2 Effect of barrier Compression Rate 23-24

 5.1.3 Effect of spreading solution volume 25-25

 5.1.4 Hysteresis curve analysis..... 25-26

 5.1.5 Effect of spreading solution with temperature 26-28

5.2 Oscillating Barrier Measurements 28-30

5.3 Deposition of Graphene Oxide Langmuir Blodgett films 30-31

5.4 Atomic Force Microscopy..... 31-33

CHAPTER 6: CONCLUSIONS AND FUTURE SCOPE... 34-34

6.1 Conclusion... 34-34

6.2 Future scope 34-34

List of Figures

Figure No.	Description	Page No.
1.1	Structure of Graphene Oxide	2
3.1	Spreading suspension on water subphase	10
3.2	Schematic diagram of formation of Langmuir-Blodgett Films.....	10
3.3	Schematic diagram of Surface pressure-area isotherm	11
3.4	Schematic diagram of deposition process	13
3.5	Langmuir Blodgett Setup	15
3.6	Whilmy plate and glass slide clipped on dipper.....	15
4.1	Structural formula of 1,2-dichloroethane	17
4.2	Schematic of Atomic Force Microscopy	21
5.1	(a) Π -A Isotherms at different Ratios	23
	(b) Graph between different Ratios having different Elasticity values corresponding to its solid phase.	
5.2	(a) Π -A isotherms of GO spread on deionized water at different	24
	compression rates	
	(b) Variation of Area with elasticity as well as surface pressure with compression rate.	
5.3	(a) Π -area isotherm for spreading solution volume having Rate-12mm/min....	25
	(b) shows effect of elasticity having solid phase area with different sub phase concentrations.	
5.4	(a) Π -A hysteresis curves for different rates	26
	(b) Variation of elasticity with different cycle numbers for rate of 30 mm/min and 50 mm/min.	
5.5	(a) Π -A isotherm of graphene oxide for different subphase temperature	27
	at rate=30mm/min.	
	(b) Π -A isotherms for different temperatures having rate-50mm/min	
	(c) Effect of Temperature with elasticity as well as solid phase area with rate=30mm/min	
	(d) shows the variation of temperature with its elasticity as well as the area	

	at which solid phase is formed having rate-50mm/min.	
5.6	(a)Surface pressure variations for barrier oscillations having different29 frequencies at a target of 8mN/m; (b) Oscillating barrier measurements for Rate-50 having target-8mN/m; (c)shows the variation of G, G', G'' with different frequencies at rate of 30mm/min; (d)Variation of frequency Vs. G, G', G'' for rate-50mm/min.	
5.7	(a)Graph between Transfer Ratio and Layer number at compression30 Rate-30mm/min and at Rate-50 mm/min.	
5.8	AFM images of multilayer GO films 32 a) Glass Substrate, b) 30 mm/min 1 Layer, c) 50 mm/min 1 Layer. d) 50 mm/min 2 Layers e) 50 mm/min 4 Layers, f) 50 mm/min 5 Layers.	

Chapter-1

Introduction of Graphene Oxide Thin Films

1.1 Introduction to Thin Films

Thin film can be described as coating of a suitable material (having nanometers to micrometers thickness) on a solid substrate. The deposition can be only possible using self-organizing arrangement of discrete particles on a substrate depending on physical conditions. Several properties of thin films: Optical, electrical, mechanical, thermal, chemical have been studied and can attribute in making devices such as photo voltaic cells, conducting devices etc[1].

The type of substrate used for depositing process widely affects the quality of the film. The substrates used should be chemically stable, electrically not interfering and feasible as well. The growth of the film depends on the nature of the substrate. It should be perfectly cleaned before depositing any film. Substrates like glass, silver, mica have been found to possess smoothness, so they are widely preferred for film.

1.2 Graphene Oxide

Chemically modified graphene has been a favourable route in view of several applications such as sensors, field effect transistor, energy storage device, biomedical fields. Graphene sheets having 2D carbon atoms are arranged in a honeycomb lattice. Graphene oxide consists of reactive oxygen with functional group namely hydroxyl, epoxy and carboxyl groups. The former are attached to the GO basal plane while the latter are present at the edges of GO. Due to the presence of these functional groups, GO is hydrophilic which readily disperses in water.

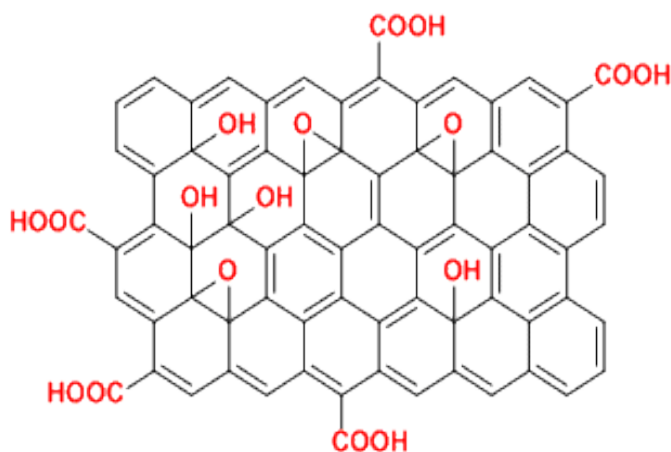


Fig.1.1 Structure of graphene oxide [3].

1.3 General Properties of Graphene Oxide

Properties of GO are as follows:

NAMES	
Chemical name	Graphene oxide
Chemical formula	GO
Properties	
Molecular formula	$C_{140}H_{42}O_{20}$
Band gap	2.7 eV
Molecular weight	2043.856 g/mol
Appearance	Raw black Powder
Optical transmittance	97.7%
Dispersability	Easily

1.4 Properties of thin film of Graphene Oxide:

- Morphology and physical properties:** The graphene oxide thin films consist of carbon that readily forms a colloidal solution in water due to electrostatic repulsions b/w phenol hydroxyl and ionized carboxylic groups. As the no. of layers increases the electrostatic forces also increase. As the thickness of thin film increases, wrinkling also increases.

This is attributed to the fact that substrate is no longer flat because of the presence of GO sheets.

- **Dispersability:** Due to its hydrophilicity, graphene oxide is easily exfoliated in water to provide stable dispersion. The GO dispersion can also occur in different organic solvents as well such as THF (tetrahydrofuran), EG (Ethylene glycol), ethanol etc. Thus, GO is believed to be amphiphilic having edges more hydrophilic and the core more hydrophobic, so it acts like a surfactant.
- **Optical properties:** Band gap of graphene oxide thin film is nearly equal to 2.5 eV to 3.0 eV. Films with larger no. of layers result in higher degree of light absorption. It was found that GO thin films have higher transparency of about ~90%.
- **Toxicity:** The GO as well as RGO are more toxic to human epithelial cells and may inhibit the bacterial growth. It was revealed that its toxicity would be completely dependent on its dose. If the dose would be $>50\mu\text{g/ml}$ then damage was observed towards human fibroblast cells. So, the blood compatibility and its toxicity are completely dependent on its exfoliation level, dose and its sheet size as well [5].
- **Intercalation with water (hygroscopicity):** Graphene oxide being hydrophilic because of oxygen-containing functional groups like hydroxyl, carboxyl, epoxy and can absorb water molecules in between the interlayer sheets. So, GO is hygroscopic which is completely dependent on humidity [6].
- **Mechanical properties:** GO monolayer consists of Young's modulus and fracture strength. The self-assembled graphene sheets showed lower modulus and after annealing, defect-free graphene thin films have Young's modulus of 1.0 TPa and its fracture strength is of the order of 130 GPa [7].
- **Thermal properties:** The formation of graphene oxide thin films on a Si substrate has been affected by temperature. It was found that the graphene oxide nanosheets having a minimum thickness of 1.35 nm were reduced to graphene nanosheets with thickness of 0.37 nm using one-step reducing process at higher temperature. Similarly, low-concentration graphene films were also produced using two-step process which resulted in efficient reduction of GO thin films at $< 500^\circ\text{C}$ [8].

1.5 Applications of GO thin films

- **Field effect transistors:** have been used as chemical sensors which were functionalized with glucose oxidase and can be deposited as an electrode.
- **Transport conductive films:** as hole transport layers in solar cells and LEDs.
- **Biosensors:** widely used to detect hormonal catecholamine molecules and DNA.
- **Energy storage devices:** used for high capacity storage devices in lithium ion batteries.
- **Biomedical field:** as a drug delivery system [9].

References

1. D.L.Smith, Thin film deposition: principles and practice, New York: McGraw-Hill, (1995).
2. E.V.Seliverstova, N.K.Ibrayev, R.K.Dzhanabekova, Study of Graphene oxide solid films prepared by Langmuir Blodgett technology, 7(2016), 65-70.
3. L.Dong, Z.Chen, X.Zhao, S.Li, K.Leng, H.Lu, K.P.Loh, Molecular Engineering of Polymers,3(2018), 1-8.
4. H.Kinoshita, Y.Nishina, A.A.Alias, M.Fujji, Carbon 66(2014), 720-723.
5. .M.S.Eluyemi, M.A. Eleruja, A.V.Adedeji, O.Fasakin, A.T.Famajuro, S.A Ayinde, E.O.B.Ajayi, Dept. of Physics and Engineering Physics, 5(2016), 143-154.
6. Z.U. khan, A. Kausar, H.Ullah, A.Badshah, W.U.Khan, National center for Physics, 0(2015),1-45.
7. Q.Zheng, X.Lin, N.Yousefi, K.K.Yeung, Z.Li, J.K.Lim, Dept.of Mechanical Engineering, 5(2011), 6039-6051.
8. J.W.Suk, R.D.Piner, R.S.Ruoff, Dept of Mechanical Engineering, 4(2010), 6557-6564.
9. O.Akhavan, Dept. of Physics, 48(2010), 509-519.
10. Y.Zhu, S.Murali, W.Cai, X.Li, J.W.Suk, J.R.Potts, R.S.Ruoff, Dept. of Mechanical Engineering, 22(2010), 3906-3924.

Chapter-2

Literature Review

This chapter deals with the literature review that was carried out for the preparation of Langmuir Blodgett GO thin films. The first section deals with some basic papers for preparing GO thin films by various other techniques. The second part describes the general use of Langmuir-Blodgett technique as a thin film synthesis. The third section discusses about the oscillating barrier measurements. The last section includes the deposition of GO thin films by Langmuir Blodgett technique.

2.1 Deposition of GO thin films using different techniques

G. Eda et al 2009 [1]: GO films were synthesized using spin coating method which was doped on Si substrates. It was concluded that as the flake size increases (24 μm), its mobility increases. The highest electron and hole mobilities were found to be 0.2 & 0.7 $\text{cm}^2/\text{V sec}$.

M.A. Worsley et al 2010 [2]: Aerogels with high electrical conductivity were used to prepare graphene films with densities approaching to $10\text{mg}/\text{cm}^3$. The graphene aerogels exhibit an electrical conductivity of ($1 \times 10^2 \text{ S/m}$) with large surface areas ($584 \text{ m}^2/\text{g}$) and pore volume ($2.96 \text{ cm}^3/\text{g}$) which are widely used in energy storage, catalysis and sensing applications.

N.W.Pu et al 2011 [3]: The graphene films were deposited by drop casting technique at different surfactants namely cationic, anionic and polymer type. It was concluded that dispersion of graphene with 200 ppm C0890 surfactant yields lower sheet resistance (50 $\text{K}\Omega$) and higher electrical conductivity at a transparency (at 550nm) of 80%.

E. Kymakis et al 2011 [4]: Graphene oxide thin films were coated on glass substrate used as an electrode in obtaining photo voltaic devices. It was concluded that photo voltaic characteristics were obtained with efficiency of about 0.2% having 75% transparency & sheet resistance of (2 $\text{K}\Omega$).

2.2 Langmuir-Blodgett technique for thin film Synthesis

S.Huang et al 2003 [5]: Effect of Surface Pressure of alkanethiol gold nanoparticles on the monolayer using LB has been studied. It was found that at low area, it yields to expansion with greater area. While higher surface results in compression of monolayer. Moreover, it was shown that monolayers of alkanethiol capped gold particles have been capable of forming stable ordered structure.

S.A.Hussain et al 2005 [6]: The LB technique was a unique tool for controlling structure of films. Moreover it can be useful in finding out crystal parameter that contains envisioned applications in technology as in optical and molecular devices, in signal processing and transformation.

H.L.Nie et al 2015 [7]: LB assembly has been widely used for the spreading of water immisible solvents that can be transferred on solid substrates. It was found that electrospray spreading yields high suspension of colloidal materials on water subphase.

M.Mercedes et al 2016[8]: LB assembly is used for the deposition of films using vertical deposition of the substrate being immersed on water subphase. It was shown that this technique allows continuous variation of density of material and packing by compressing the barriers. The 2D nanoparticles have attractive applications in production of solar cells as well as in LEDs because of its band gap tunability.

A.Holm et al 2018[9]: LB deposition technique has been widely used for spreading of graphene sheets onto water-air interface . It was found that solvent(methanol) gives rise to marangoni flow which leads to inherent disruption of depositions.

2.3 Oscillating barrier measurements for Langmuir Films

K.R.Zavadil et al 2015 [10]: GO monolayers will assembled on LB trough. Oscillatory Barrier calculations have been used for characterizing compression & shear modulli as a function of surface pressure. It was proposed that angle dipping is best suited for monolayers that exhibits shear modulus.

G.J.silverberg et al 2017[11]: The roughness of (silica, spheres,GO, lipids) can be controlled. It was concluded that by measuring stress to strain rate, the visco-elastic properties can be determined.

2.4 GO thin films using Langmuir Blodgett Technique

Q. Zheng et al 2011 [12]: Transparent conductive films are produced by Langmuir Blodgett technique on a Si substrate. The oxide films consists of remarkable sheet resistance about 500 Ω having 90% transparency along with DC to optical conductivity ratio of 7.29.

Q.Zheng et al 2012[13]: Ultralarge GO were obtained layer by layer via Langmuir Blodgett assembly process. The optoelectronic properties was studied with greater ease. It was concluded that thin films had remarkable sheet resistance in range 180-560 Ω having optical transmittance 77-86% which depends on number of layers. Moreover the conductivity of thin films obtained was \sim 400 Ω .

X. Lin et al 2013 [14]: GO thin films were produced on PET substrate. The PET substrate determines surface morphology & chemistry of films; a strong covalent bonds as well as their π - π interactions was studied. The LB assembly is well suited for fabrication of transparent conductive films on a large scale.

E.V. Seliverstova et al 2015[15]: GO thin films were deposited onto solid substrates. The absorption spectra of films were studied & it was found that it exhibits a broad band in UV as well as in visible region. The transparency in visible region is higher than 90%.

E.A. Danilov et al 2018[16]: LB thin films was directly exfoliated on Si substrate which enables the formation of conductive coatings having high transparency (90%), sheet resistance of about (143 Ω).

References

1. G.Eda, M.Chhowalla, Materials Science and Engineering, 9(2009),814-818.
2. M.A.Worsley, P.J.Pauzauskie, T.Y.Olson, J.Biener, J.H.Satcher, T.F.Baumann, Materials Science & Engineering, 132(2010), 14067-14069.
3. N.W.Pu, C.A.Wang, Y.M.Liu, Y.Sung, D.S.Wang, M.D.Ger, Chemicals & Materials Engineering, 43(2012), 140-146.
4. E.Kymakis, E.Stratakis, M.M.Stylianakis, E.Koudoumas, C.Fotakis, Thin solid Films, 520(2011), 1238-1241.
5. S.Huang, K.Minami, H.Sakaue, S.Shingubara, T.Takahagi, Adv. Sciences of Matter, 20(2004), 2274-2276.
6. S.A.Hussain, S.DeB, D.Bhattacharjee, Dept. of Physics, 4(2005), 1-8.
7. H.L.Nie, X.Duo, Z.Tang, H.D.Jang, J.Huang, Materials Science & Engineering, (2015), 305-350.
8. M.Mercedes, V.T.Alejo, D.L.Diaz, M.D.Merchan, dept. of Engineering Science, (2016), 1-42.

-
9. A. Holm, C.Wrasman, K.C.Kao,A.R.Riscoe,C.W.Frank, ACS,5(2018),1-13.
 10. K.R.Zavadil ,K.L.Harrison,,L.B.Biedermann,, Materials Science & Engineering, 31(2015), 9825-9832.
 11. G.J.Silverberg, A.McClelland, S.G.Nascimento, C.Girabawe, J.P.Kadow, L.Mahadevan, C.D.Vecitis, ACS, 121(2017) ,5078-5085.
 12. Q.Zheng, X.Lin, N.Yousefi, K.K.Yeung, Z.Li, J.K.Lim, Dept.of Mechanical Engineering, 5(2011), 6039-6051.
 13. Q.Zheng, X.Shen, N.Yousefi, Z.D.Huang, J.K.Kim, Dept. of Mechanical Engineering, 22(2012), 25072-25082.
 14. X.Lin, N.Yousefi, X.Shen, J.K.Kim, Dept. of Mechanical Engineering, 1(2013), 6869-6877.
 15. E.V.Silverstova, N.K.Ibrayev, R.K.Dzhanabekova, Institute of Molecular Nanophotonics, 7(2016), 65-70.
 16. E.A.Danilov, V.M.Samoilov, A.V. Nikolaeva, D.V.Ponomareva, E.I.Timoshchuk, Inorganic Materials, 9(2018), 794-802.

Chapter-3

Introduction to Langmuir-Blodgett Technique

3.1 Introduction

- **Monolayer:** Formation of layer on air-water interface is known as **Langmuir monolayers**.
- **Langmuir-Blodgett films:** When the above monolayers have been deposited on a solid substrates then these films are known as **Langmuir-blodgett films**.
- **Types of substrates:** It is of two types-a hydrophobic and hydrophilic. As the name indicates Hydrophobic is usually water repelling having non-polar nature whereas hydrophilic is water loving which is having polar nature. Some well-known substrates are silicon, glass, mica, gold.

In LB technique, a monomolecular and multimolecular films having amphiphilic which means hydrophobic head and hydrophilic tail substance was made on water surface. After that it get transferred on solid substrate.

Why Langmuir-Blodgett films are required?

LB technique are usually good for the preparing thin films because

- Allows continuous variation of particle density.
- Deposition can be done on any kind of substrate.
- There is a homogeneous deposition of monolayers over the larger area.
- There is a sharp control in thickness of monolayer.

3.2 Formation of Langmuir monolayer

Monolayer consists of a layer of narrowly single packed atoms, molecules and cells. Langmuir monolayer is formed by spreading unsolvable any kind of organic material on liquid interface. Monolayer consists of an amphiphilic compounds.

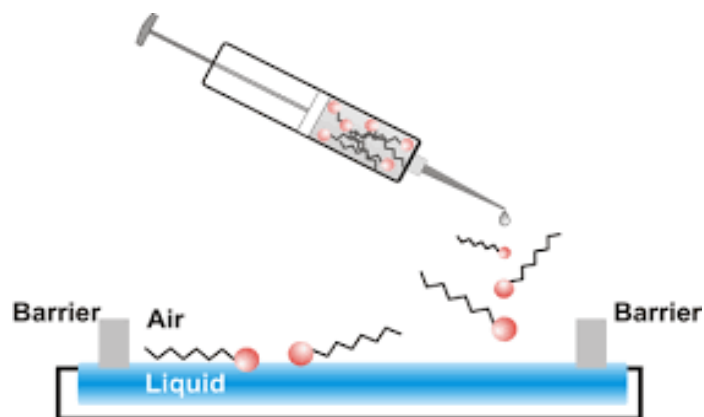


Fig. 3.1 Spreading suspension on water subphase [1].

To form a monolayer, a solution of surfactant (Graphene oxide in 1,2 di-chloro ethane) has to be mixed in a suitable solvent (ethanol) is deposited dropwise on surface of air-water subphase using the help of micro-pipette. The solvent selected must be insoluble in water which is to be evaporated easily after a certain amount of time i.e. about 25-30 mins. As the solvent evaporates, there is a complete spreading of surfactant as a monolayer on water subphase until an “equilibrium spreading pressure” has been reached beyond which no more spreading takes place. Using the aid of moving barriers, the monolayer gets compressed which results in Langmuir films. When we transfer these Langmuir films on any solid substrate. the films formed are called as Langmuir-Blodgett films [1].

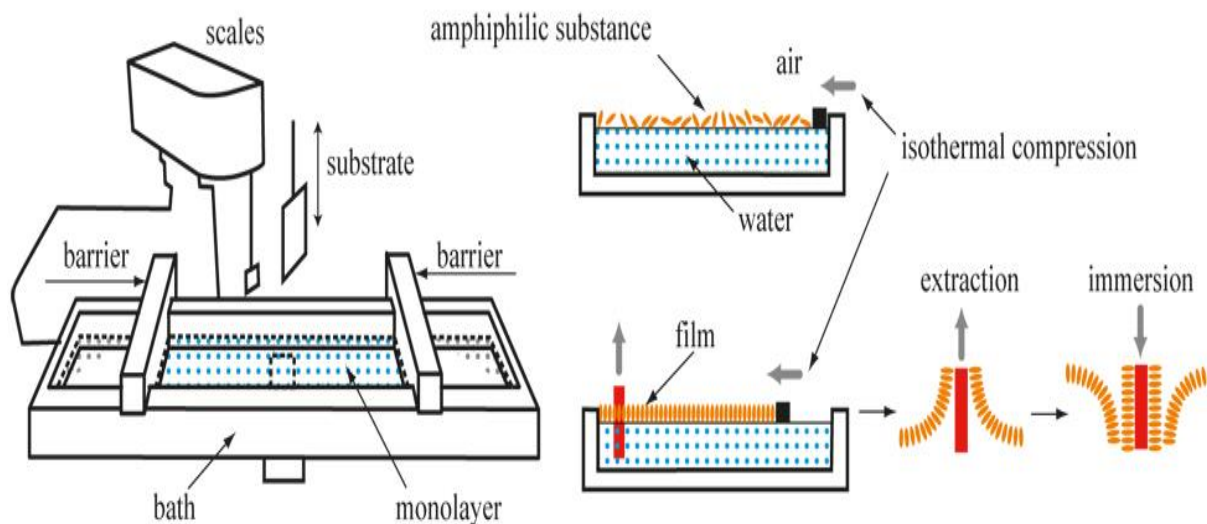


Fig. 3.2 Schematic diagram of formation of Langmuir-Blodgett films [2].

3.3 Surface pressure-area Isotherm

The isotherm is important to know the surface behaviour of the molecules on the air-water interface and to investigate a suitable pressure for the stability of monolayer. The plot obtained (Surface pressure vs Area at a constant temperature) is known as pressure-area isotherm or simply isotherm.

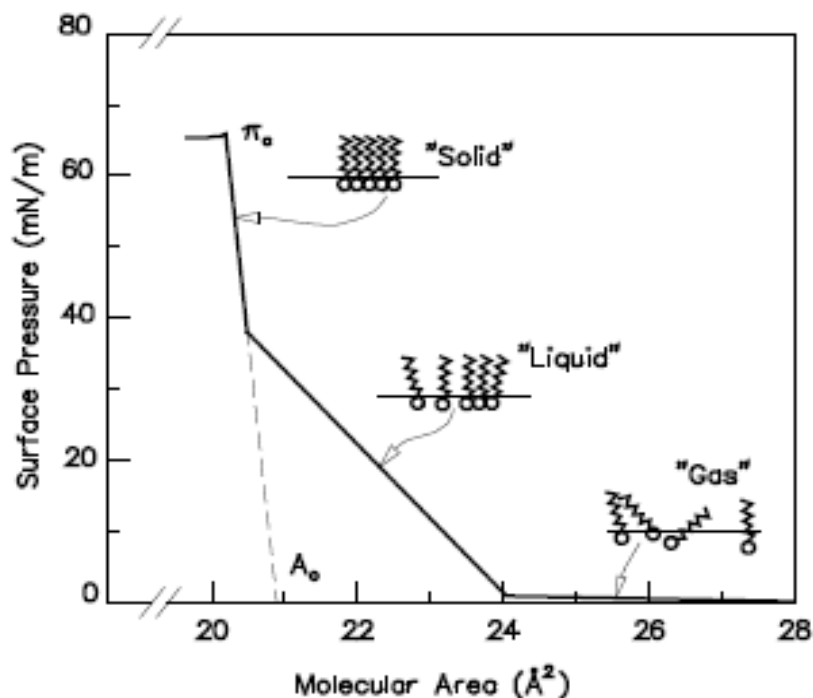


Fig. 3.3 Schematic diagram of Surface pressure-Area isotherm [3].

There are different phases involved in the formation of isotherm.

- **Gas phase:** when the concentration of molecule were spread on water. They are very loosely packed as shown in fig.3.3 when barriers are at rest that indicates low surface pressure and high molecular area.
- **Liquid phase:** When we decreases the area by closing the barriers then it results in formation of liquid phase. It means compressibility changes due to change in surface pressure with decrease in molecular area occur.
- **Solid Phase:** As the barriers are closed further low molecular area and high surface pressure is obtained .It means the solid phase typically comprises of 2D lattice structure on water interface.

Compressing the barriers further, there occurs a collapse in monolayer which results in breaking of films. Hence generally, it is avoided.

The Surface pressure measurements have been done by Wilmy plate. It is given by:

$$\Pi = \gamma_0 - \gamma$$

Where γ is surface tension (which results from the fascination between liquid molecule) of monolayer and γ_0 is surface tension of uncontaminated liquid [2].

3.4 Deposition methods

For the formation of LB films we will transfer the monolayers on different solid substrate. There are two ways of transporting the monolayers:

- Horizontal deposition (Langmuir-Schaefer Technique)
- Vertical deposition (Langmuir-Blodgett technique)

Horizontal deposition: Langmuir-Schaefer technique was introduced by scientists Langmuir and Schaefer. In this type of deposition, monolayer is horizontally transferred from water sub phase onto solid substrate.

Vertical deposition: was introduced by Langmuir and Blodgett. Here, Langmuir layer has been vertically transferred on solid substrate at water-air subphase [3].

3.5 Types of Langmuir-Blodgett deposition

There are 3 main types of depositions which are categorized as:

- X-Type deposition
- Y-Type deposition
- Z-Type deposition

X-Type deposition: When the deposition was carried out by down stroke only then it is known as X-Type deposition. Mostly this type of deposition is carried out for high pH values.

Y-Type deposition: when the coatings gets transferred using up as well as down stroke both then these kind of deposition is called as Y-Type deposition. It is widely preferred for fatty acids.

Z-Type deposition: When the deposition is done by up stroke only then it is known as Z-Type deposition. This type is usually seen in aromatic molecules which contains carbon chains.

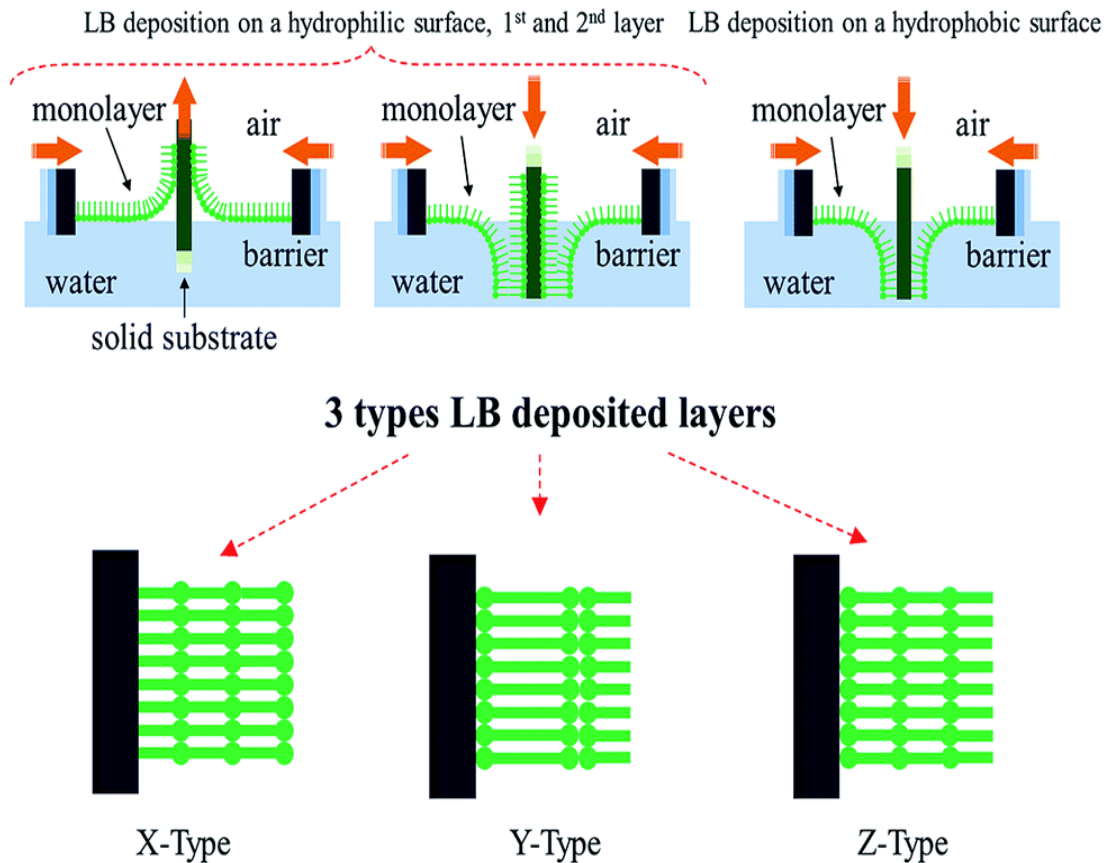


Fig. 3.4 Schematic diagram of deposition process [7].

To obtain uniform film, surface pressure ($15\text{-}20 \text{ mNm}^{-1}$) as well as temperature ($17\text{-}23^{\circ}\text{C}$) have been maintained. The parameters which affect LB film are nature of spreading film, sub phase composition, type of solid substrate, deposition speed.

The quality as well as the quantity of a monolayer have been measured by its Transfer Ratio (TR). It is basically a good measurement of how well a film has been transferred on a solid substrate.

$$TR = \frac{\text{decrease in area of monolayer } (A_L)}{\text{area of substrate } (A_s)}$$

For an ideal transfer the value of TR is nearly equal to 1 [4].

3.6 Oscillating barrier measurement

These measurements are used to characterize mechanical properties such as elasticity, stress, strain. This method is suitable for viscoelastic properties of the monolayer. We can calculate dynamic viscoelastic properties such as elastic modulus (G), storage elastic modulus (G'), as well as loss modulus (G''). As the target frequency is reached then the barriers will start to oscillate.

The relation between above the three moduli is given as:

$$G = G' + iG''$$

Where G is overall complex quantity.

3.7 Experimental setup of LB technique

- **Lab environment:** Proper cleanliness is required to avoid any kind of contamination. Airborne particles tend to accumulate at the surface of water, so to remove that a room where setup is placed should be ventilated to ensure that the fumes of solvent do not accumulate. However there should not be any kind of disturbance as it can lead to collapse of monolayer films.
- **Trough:** The NIMA trough are made from polytetrafluoroethylene (PTFE) at which monolayer is formed. Furthermore compression or expansion on surface will result in modifying its area per molecule. There is a well in between center of the trough at which there is deposition of larger number of layers.
- **Barriers:** It is Teflon material which are placed parallel to the walls of the trough. These are hydrophilic material that ensures that the film will remain in between these barriers and will not escape from it.

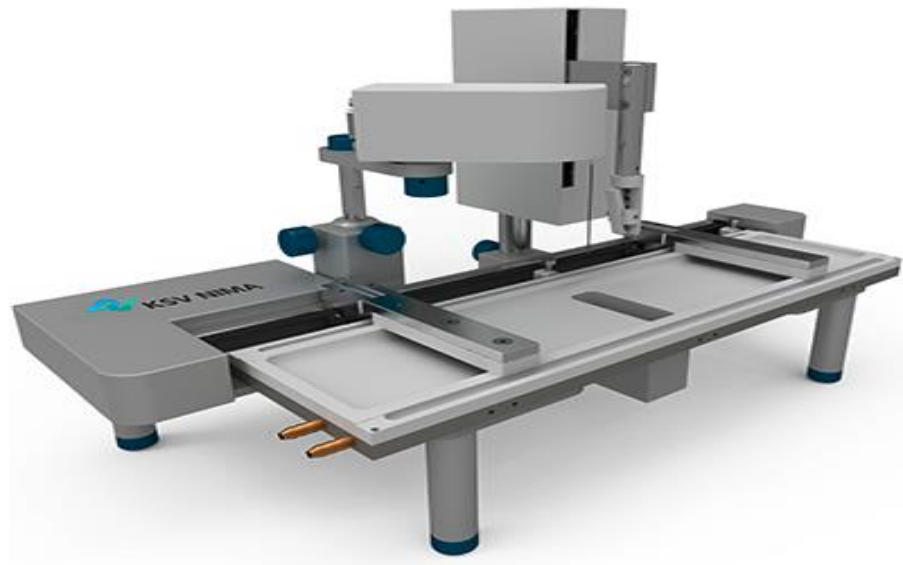


Fig.3.5 Langmuir Blodgett Setup [4].

- **Balance:** A Platinum plate having dimensions of $38\text{mm} \times 19.62\text{mm} \times 10\text{mm}$ is used to measure the pressure which is known as Wilmy plate. The force act on it will be calculated by an electro-balance which is known as surface balance.



Fig. 3.6 Representing Wilmy plate and glass slide clipped on dipper [4].

-
- **Dipper:** A substrate is clipped in it for depositing multiple layers. Further speed of dipper as well as other essential parameters should be controlled for an ideal deposition.
 - **Layer Builder:** It is a connecting unit in between a computer as well as other parts of LB setup. It is an interface unit which displays surface pressure and barrier position [5].

3.8 Advantages

- can deposit multiple layers on any substrate.
- Can easily controls the thickness of monolayer.
- Also there is a homogeneous deposition which can apply to micro levels.
- Furthermore, we are able to characterize its elasticity, area, viscoelastic properties.

3.9 Disadvantages

- Time taking process especially if thick films are needed.
- Temperature plays crucial role in forming thin films, a slight variation of temperature results in change in monolayer property.
- If there is any kind of contamination then it can destroy the film. These films results in poor chemical uniformity at the surface of water.

References

1. M.C.Petty, Handbook of Langmuir-Blodgett Films, Cambridge University(1996).
2. Mikkelson, Alexander, Experimental Studies of flow and electric properties of oil Droplets including suspended clay particles,(2012).
3. I R Peterson, J. Physics. D: Applied Physics, 23(1990), 379.
4. S.Huang, K.Minami, H.Sakaue, S.Shingubara, T.Takahagi, Adv. Sciences of Matter, 20(2004), 2274-2276.
5. KSV Instruments Software Manual LB device.
6. S.A.Hussain, S.DeB, D.Bhattacharjee, Dept. of Physics, 4(2005), 1-8.
7. G.Roberts, Ed. Langmuir Blodgett Films, plenum press, New York (1990).

Chapter-4

Materials and Methods

This chapter deals with the materials used for performing the work in this thesis. Also, this chapter sheds light upon methods used for preparing and characterization of Graphene oxide LB thin films.

4.1 MATERIALS USED

The utmost essential chemicals used for preparing Langmuir Blodgett thin films are:

1. **Graphene oxide:** GO, black crystalline powder, is readily dispersed in organic solvents as well as water. The large size graphene oxide sheets can be dispersed in various organic solvents such as DMF (dimethyl formamide), THF (tetrahydrofuran), DCE (1,2-dichloroethane), acetone, ethanol so as to get uniformly stable Langmuir and LB films. The multilayer GO used in this work consisted of ~ 6 layers with an interplanar spacing 0.80 nm .
2. **1,2 dichloro-ethane:** $C_2H_2Cl_2$ also named as ethylene dichloride having a M.Wt. of 98.96g/mol has been acquired from Loba Chemie Pvt. Ltd. with 99% purity. It is a colourless liquid having chloroform like odour and is a powerful non-polar solvent.

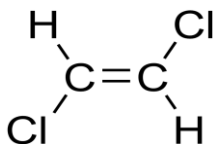


Fig.4.1 Structural formula of 1,2-dichloroethane [3].

3. **Ethanol:** C_2H_5OH with M.Wt. 46.07g/mol had been acquired from fine chemical Pvt. Ltd. with 99.9% purity.
4. **Methanol :** CH_3OH with M.Wt. 32.04g/mol , SDFC(HPLC Grade) with purity of 98.3% has been used for cleaning.
5. **Propan-2-ol :** C_3H_8O having M.Wt. of 60.10g/mol acquired from Fischer Scientific with 99.7% purity have been used for cleaning of trough and barriers.

-
6. **Sulphuric acid:** H_2SO_4 with M.Wt. of 98.07g/mol, SDFCL with 98% purity had been used for cleaning substrate.
 7. **Hydrogen peroxide:** H_2O_2 having M.Wt.34.01g/mol has been bought from Loba Chemie Pvt. Ltd. Was also used for cleaning of substrate.
 8. **Acetone:** CH_3COCH_3 with a M.Wt.of 58.08g/mol was acquired from SDFCL with purity more than 99%.
 9. **De-ionized water:** The subphase used for experiment was DI which was obtained from Millipore Q3 system with a resistivity of 18.2 M Ω . Furthermore it was also used for final cleaning of barriers and trough.
 10. **Substrate:** Borosil microscope glass slides with dimensions of 76 mm \times 26 mm \times 1 mm have been cut in size:1.5 cm \times 2 cm. It was cleaned by piranha method with a volume ratio H_2SO_4 and H_2O_2 as of 7:3 followed by rinsing with deionized water. Just before the deposition the substrates was ultrasonicated in acetone, then with methanol and finally in deionized water.

4.2 Methods

The trough and barriers was thoroughly cleaned before putting solution onto it. Nitrile gloves are used so to avoid any contamination. The Teflon trough and barriers were firstly cleaned by Methanol using soft brush and after that by propan-2-ol. Then final rising was done firstly with distilled water and then with deionized water [1].

4.2.1 Preparation of GO spreading solution:

Nature of the solvent used for preparing the spreading solution for the LB film synthesis plays significant role for determining the properties of Langmuir monolayers including its elasticity compaction and stability. And these properties contribute to the transfer characteristics as well as morphology of the LB film after transfer on to the solid substrate.

DCE is a good non-polar organic solvent and also it can readily evaporate from air-water interface so it is a good candidate as solvent for preparing the spreading solution for GO LB films.

After the addition of dry GO powder in DCE solvent through the ultrasonication process the particles gets dispersed. However after resting it for about 15 mins the aggregates settled down at the bottom of the vial. So, DCE alone is not helpful for dispersion of graphene particles. The GO

forms extremely stable dispersions with/in ethanol. So we added different amounts of ethanol to DCE for preparing the stable spreading solutions and tested the GO Langmuir layers using the Π -A isotherms. All the spreading solutions had 0.00625mg/ml of GO.

4.2.2 Preparation of Langmuir films and Langmuir-Blodgett films:

KSV NIMA apparatus with trough area of 24300mm² have been used for the formation of Langmuir monolayer and LB films. Deionized water is added to the trough as subphase and its surface was checked for contamination. Appropriate amount of the as prepared GO spreading solution was added drop-wise onto the surface of the aqueous sub-phase at a constant rate of 450 μ l/min. After allowing 30 minutes for solvent evaporation the barriers were compressed for the formation and characterization of the Langmuir films.

Films were allowed to stabilize for 10 mins before the dipping/transfer. For the deposition process target was set at 6mN/m with 2 min wait for drying before the down stroke. During the dipping the transfer ratio (TR) is monitored and the dipping speed for upstroke and downstroke was set based on achieving TR of \sim 1 [4].

4.3 Characterization Techniques:

4.3.1 Pressure-area Isotherms

Fundamental characterization of Langmuir monolayer is via its surface pressure-Area isotherm analysis [5]. A brief description of the method is already provided in division 3.3.

In the current work the Langmuir monolayers of the GO on the water sub-phase were characterized using Π -A isotherms for the following parameters:

- a) Spreading solution:** The ethanol: DCE ratio in the spreading solution was varied as 1:5, 1:8, 1:13, 1:20. The barrier rate was 30 mm/min.
- b) Barrier compression rate:** The barrier compression rate (in mm/min) was varied as: 4, 12, 15, 30, 40, 50.
- c) Temperature:** The role of sub-phase temperature in determining the properties of the GO Langmuir layers were studied at: 17 °C, 19 °C, 21 °C, 23 °C.

d) Amount of spreading solution: The effect of amount of spreading solution on the GO Langmuir layers were studied by varying the amount of spreading solution: 1000 μl , 1250 μl and 1500 μl .

4.3.2 Hysteresis method:

Hysteresis isotherms refer to repetitive compression as well as expansion. The GO sheets Langmuir layers on the sub-phase should be extremely stable for transfer.

The hysteresis isotherms were recorded at different rates-12,30,50 mm/min. at sub phase temperature of 21⁰C [6].

4.3.3 Oscillating barrier method:

The oscillating barrier measurement gain control was 2.0, area change was set to 1.2 A_0 and the barrier rate was 30 mm/min and 50 mm/min. The target was set to 8 mN/m. The barrier oscillation frequency was varied from 30 mHz to 50 mHz having step size of 5 mHz in each trial. The oscillating barrier measurements was performed at different:

- Oscillation frequencies (30,35,40,45,50 mHz)
- Different barrier speeds (30 mm/min and 50 mm/min) [7].

4.3.4 Atomic Force Microscope (AFM)

Atomic force microscopy (AFM) is type of scanning probe microscopy (SPM) in which we are able to measure interaction forces between probes and a sample at a separation of few nm. It consists of cantilever (probe) with a sharp tip that is used for scanning of specimen. When the tip is brought near (\sim nm) to the sample the forces between them leads to deflection in cantilever. The cantilever movement is detected by a laser beam reflected from the back of the cantilever and sensed by a photo detector. There are two modes with which microscope work that can be categorized as constant force (widely used for most applications as scanner can move up or down so to keep cantilever deflections constant) and constant height mode (height of scanner is fixed, it is mostly used when speed is essential or when the deflections of the cantilever are small).

Quantitative measurement and view of surface texture of surface roughness makes this a perfect method for the examination of topography of the film. The topography of the surface is categorized by knowing average roughness as well as root mean square roughness (r.m.s.) [8].

The AFM imaging has been done for different thin films of graphene oxide in non-contact mode at NT-MDT Solver Next. The scan rate was 0.8 Hz and a Si cantilever was used for imaging. The topographical view of GO thin films is attained and the roughness value has been calculated.

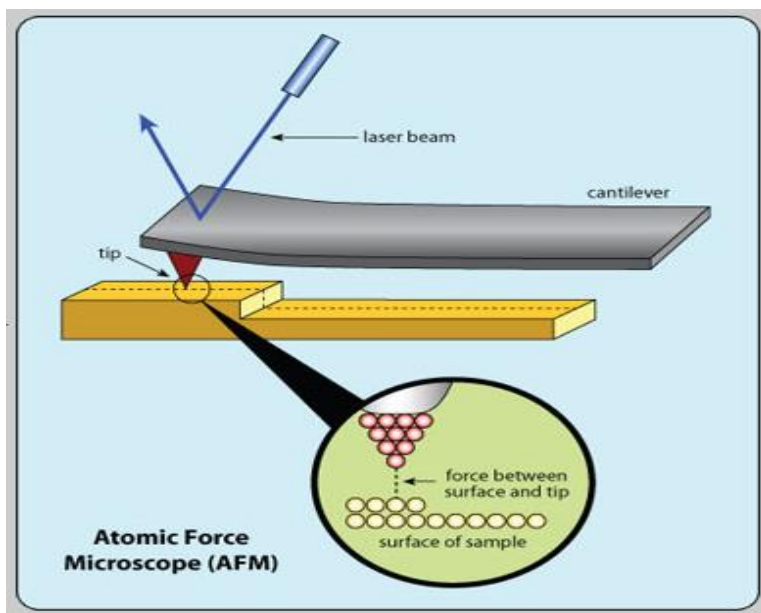


Fig. 4.2 Schematic of Atomic Force Microscopy [8].

References:

1. M.C.Petty, Handbook of Langmuir-Blodgett Films, Cambridge University(1996).
2. KSV Instruments Software Manual LB device.
3. .L.Xu, A Thesis on Langmuir films of graphene based materials towards large area monolayer deposition, University of waterloo,2017.
4. G.Roberts, Ed. Langmuir Blodgett Films, plenum press, New York (1990).
5. S.Huang, K.Minami, H.Sakaue, S.Shingubara, T.Takahagi, Adv. Sciences of Matter, 20(2004), 2274-2276.
6. Q.Zheng, X.Lin, N.Yousefi, K.K.Yeung, Z.Li, J.K.Lim, Dept.of Mechanical Engineering, 5(2011), 6039-6051.
7. K.L.Harrison, L.B.Biedermann, K.R.Zavadil, Materials Science & Engineering, 31(2015), 9825-9832.
8. M.Raposo, Q.Ferreira, P.A.Ribeiro, A guide for Atomic force Microscopy analysis of soft condensed matter,Modern Research and Educational Topics in Microscopy,1(2007).

Chapter-5

Results and Discussions

Overview

This chapter discusses the experimental results that are obtained from different characterization techniques. The techniques used are Surface pressure-area isotherm, Hysteresis analysis, Oscillating barriers analysis, Atomic force microscopy.

5.1 Surface pressure-area isotherms

In order to get knowledge of static elasticity as well as phase formation of Langmuir monolayer at water subphase, an isotherm plays a major role. Thus it is furthermost important and widely used technique in characterizing Langmuir monolayers. Static elasticity value can be determined using surface pressure-area isotherm of monolayer.

$$E = -A \frac{d\Pi}{dA} \text{ (mN/m)}$$

Where, E represents static elasticity, Π stands for Surface pressure and A represents Area.

As the Graphene oxide consists of large number of cluster of particles, so due to the presence of sheets, number of molecules are absent in this case. Moreover the graphene oxide which was used in this work consists of 6 number of layers with an interplanar spacing of 0.80 nm. Hence, we are not able to take Mean molecular area so the area is in cm^2 .

5.1.1 Effect of different ratios of solvents in spreading solution:

Fig 5.1(a) shows Π -A isotherms obtained for GO Langmuir monolayers formed on air-water interface for the different ethanol : DCE ratios within the spreading solution. Fig 5.1(b) graphs show the variations in elasticity and area of the solid phase of the film for the isotherms. Table 5.1 and fig5.1 clearly shows that film compaction gets enhanced with increase of DCE in the spreading solution but the elasticity of the films decreases. Based on these results the 1:13

(ethanol:DCE) ratio of solvent is used for further experiments as further increase in the DCE results in a drastic loss in elasticity of the film.

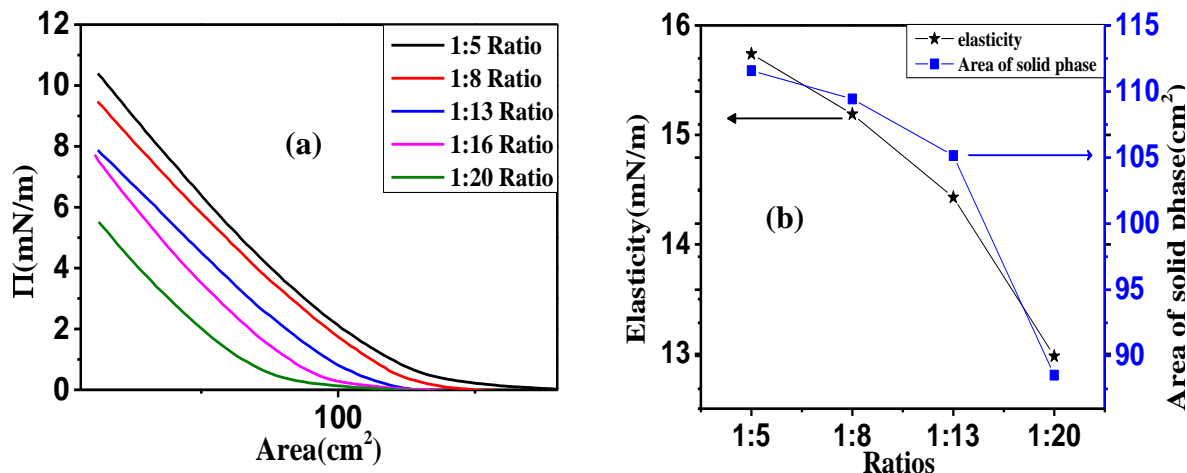


Fig. 5.1(a) Π -A Isotherms at different Ratios; **(b)** Graph between different Ratios having different Elasticity values corresponding to its solid phase.

Table 5.1 Variation of elasticity and area of the solid phase with the spreading solution composition.

Ratios	Elasticity(mN/m)	Area of solid phase(cm ²)
1:5	15.74	111.57
1:8	15.19	109.43
1:13	14.43	105.15
1:20	12.98	88.54

5.1.2 Effect of barrier compression rate:

The Surface pressure–area isotherms (Π -A) at the air-water interface have been recorded for different barrier compression rates are shown in fig.5.2 (a). Table 5.2 shows the static elasticity values for the solid phase as well as its area. Fig 5.2 (b) shows that as the compaction rate increase area of the film also gets enhanced indicating that slower compaction rates may be allowing for the GO flakes to overlap. This conjecture is supported by the lower elasticity for

slower compaction. The elasticity values are highest for rate-30 mm/min and rate-50 mm/min. So further experiments were carried out for these compression rates.

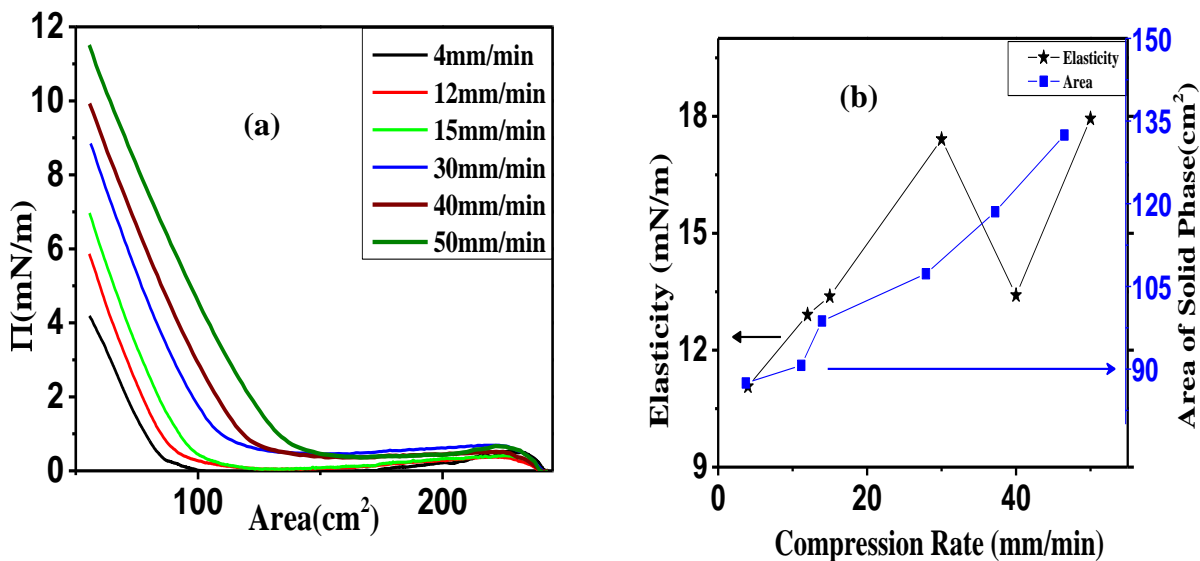


Fig.5.2 (a) Π -A isotherms of GO being spread on deionized water for different compression rates; (b) Variation of Area with elasticity as well as surface pressure with compression rate.

Table 5.2 Area of the solid phase and there static elasticity values have been calculated accordingly for different compression rates.

Compression Rates (mm/min)	Elasticity(mN/m)	Area of solid phase(cm ²)
4	11.07	87.47
12	12.91	90.68
15	13.38	98.73
30	17.41	107.29
40	13.41	118.55
50	17.94	132.46

5.1.3 Effect of spreading solution volume :

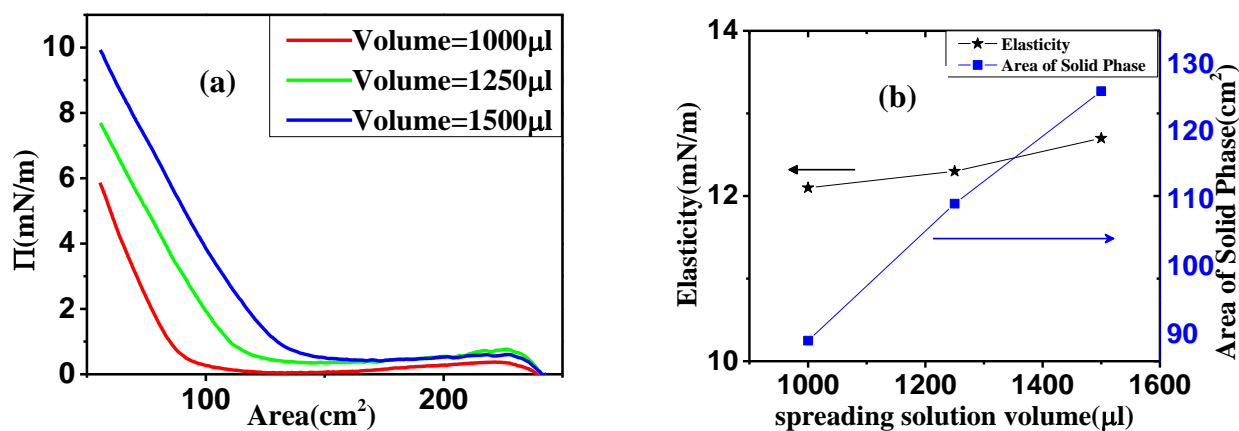


Fig. 5.3 (a) Π -area isotherm for spreading solution volume having Rate-12mm/min; (b) shows effect of elasticity having solid phase area with different spreading solution volume.

Table 5.3 shows elasticity value with respect to their corresponding solid phase area at different spreading solution volume.

Volume(μ l)	Elasticity(mN/m)	Area of Solid Phase(cm ²)
1000	12.1	89.04
1250	12.3	109.37
1500	12.7	126.04

Figure 5.3(a,b) and Table 5.3 clearly shows that increase in the spreading solution volume from 1000 μ l to 1500 μ l enhances the area of the solid phase of the film but has no major effect on the elasticity value.

5.1.4 Hysteresis curves analysis

The complete reversibility Π -A isotherm during the compaction and expansion cycles indicates stability of the Langmuir films. The hysteresis curves for different compression rates i.e. 12mm/min, 30mm/min and 50mm/min have been recorded. Hysteresis Π -A curves for different compaction rates are given in figure 5.4(a). These graphs clearly indicate that 2D GO Langmuir films are highly stabilized at barrier compression rate-30 mm/min and 50 mm/min because of the

complete reversibility. Table 5.4 and fig 5.4(b) gives the variation of the values of elasticity corresponding to solid phase for each cycle.

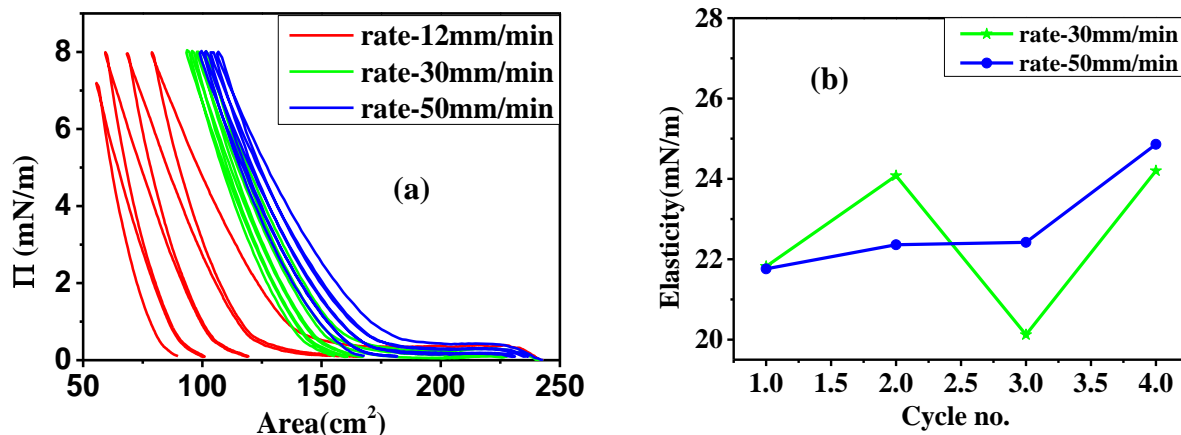


Fig.5.4 (a) Π -A hysteresis curves for different rates;(b) Variation of elasticity with different cycle numbers for rate- 30 mm/min and 50 mm/min.

Table 5.4 Area of solid phase and static elasticity of compression cycles at different rates.

No. of Cycle	Elasticity (mN/m)		Area of Solid Phase (cm ²)	
	Rate-30 mm/min	Rate-50 mm/min	Rate-30 mm/min	Rate-50 mm/min
1	21.82	21.76	157.1	170.27
2	24.08	22.36	153.9	170.08
3	20.12	22.42	146.11	163.72
4	24.20	24.86	143.1	157.73

5.1.5 Effect of subphase temperature:

The Π -A isotherms at various sub phase temperature for the two barrier compression rates (30mm/min and 50 mm/min) were recorded and are given in figure 5.5 (a,b). While table 5.5 represents the area at which solid phase is formed as well their static elasticity value for different temperature.

Data clearly shows that as temperature increases area of the solid phase decreases. This may be due to the increase in the kinetic energy of the GO flakes allowing for more stable configuration. This conjecture is supported by the enhancement in elasticity of the Langmuir films for higher temperature. Beyond 21 °C the compaction as well as the elasticity is lost. This may be due to the repulsions between the flakes coming into play at smaller distances.

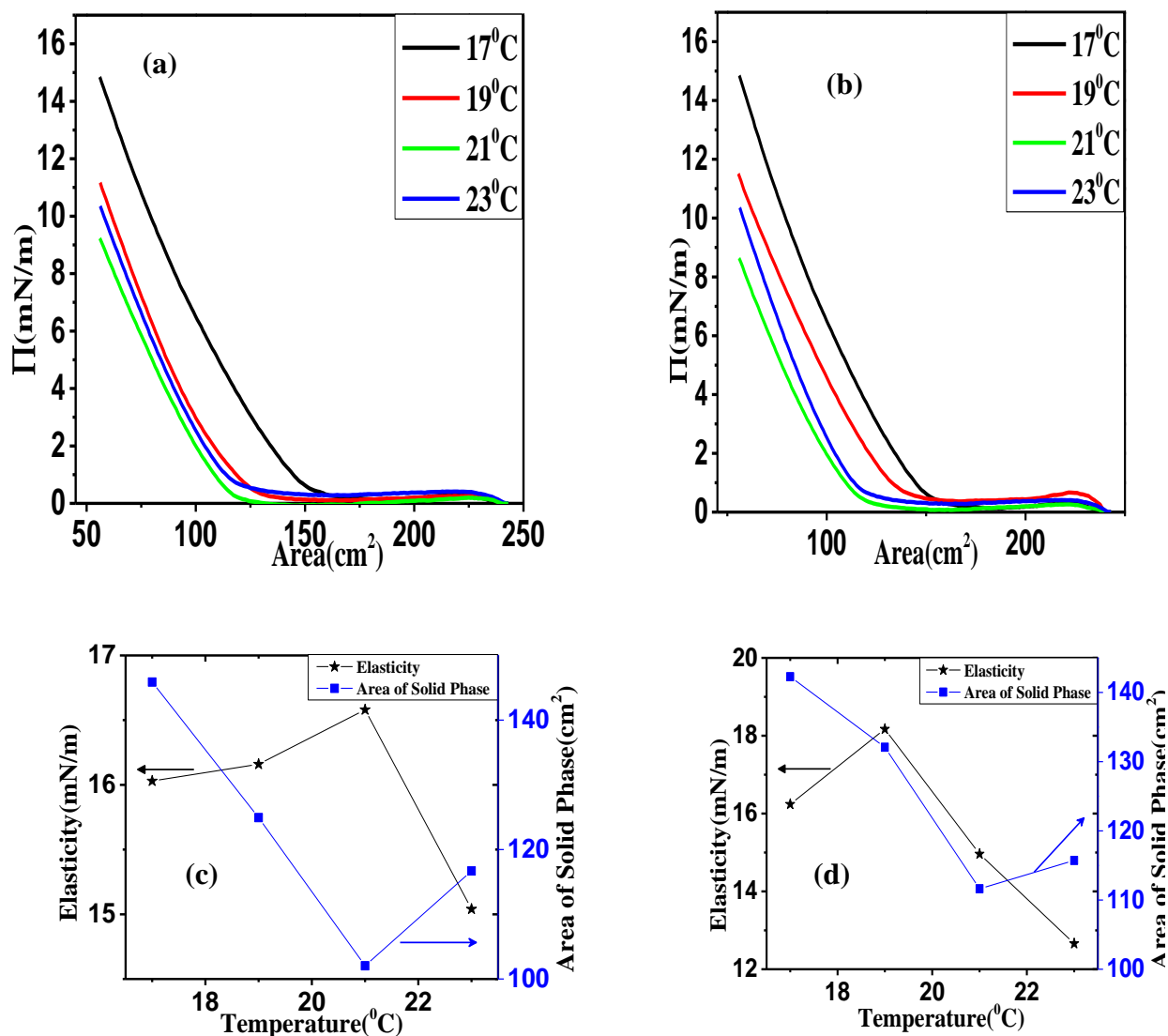


Fig. 5.5(a) Π -A isotherm of graphene oxide for different sub phase temperature at rate=30mm/min; **(b)** π -A isotherms for different temperatures having rate-50mm/min; **(c)** Effect of Temperature with elasticity as well as solid phase area with rate=30mm/min;**(d)** shows the variation of temperature with its elasticity as well as the area at which solid phase is formed having rate-50mm/min.

Table 5.5 Solid phase area with corresponding elasticity values at different subphase temperature is recorded.

Temperature (°C)	Elasticity (mN/m)		Area of Solid Phase(cm ²)	
	Rate-30 mm/min	Rate-50 mm/min	Rate-30 mm/min	Rate-50 mm/min
17	16.03	16.24	145.88	142.28
19	16.16	18.17	124.94	132.08
21	16.58	14.96	102.05	111.63
23	15.04	12.66	116.70	115.72

So 21⁰C is usually preferred for all further experiments.

5.2 Oscillating barrier measurements:

The oscillations are done at different frequencies which can be varied from 30 mHz to 50 mHz. Dynamic elasticity measurements tells us about interaction as well as relaxation process within the films. In order to study the viscoelastic properties, monolayer is compressed at the prescribed compression rate of 30 mm/min or 50 mm/min. The resultant values of Elastic modulus (G), Storage modulus (G') and loss modulus (G'') have been recorded using an inbuilt software for the LB trough system.

The dynamic elastic modulus of monolayer increases with increasing frequency with maximum at 45 mHz. Further increase in oscillations results in decrease in value of storage modulus which decreases the overall modulus. It may be found that at 45 mHz frequency there occurs relaxation process in formation of monolayers.

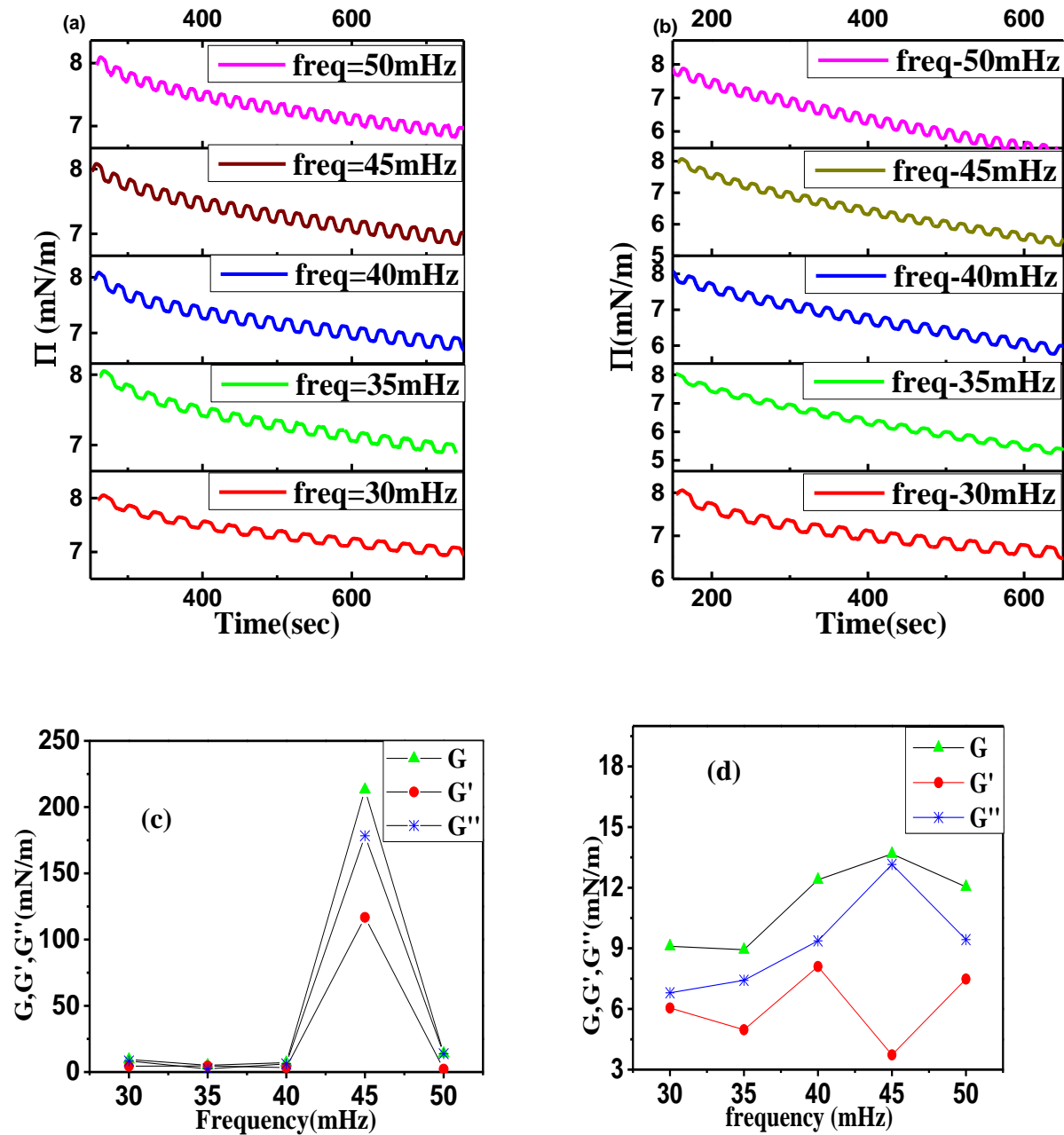


Fig. 5.6(a) Surface pressure variations for barrier oscillations having different frequencies at a target of 8 mN/m; (b) Oscillating barrier measurements for Rate-50 having target-8 mN/m; (c) shows the variation of G, G', G'' with different frequencies at rate of 30 mm/min; (d) Variation of frequency Vs. G, G', G'' for rate-50 mm/min.

Table 5.6 Dynamic viscoelastic properties have been determined at different frequencies at a target of 8mN/m.

Frequency (mHz)	G(Elastic) (mN/m)		G'(storage) (mN/m)		G''(Viscous) (mN/m)	
	Rate-30 mm/min	Rate-50 mm/min	Rate-30 mm/min	Rate-50 mm/min	Rate-30 mm/min	Rate-50 mm/min
30	9.45	9.1	4.44	6.05	8.34	6.8
35	5.17	8.93	4.59	4.97	2.37	7.42
40	7.1	12.39	3.44	8.1	6.21	9.37
45	213.16	13.67	116.77	3.73	178.32	13.15
50	14.02	12.04	2.25	7.48	13.84	9.43

5.3 Deposition of graphene oxide Langmuir-Blodgett films:

Fig. 5.7 shows the graph between layer number and transfer ratio for a set of transfer of film. For an ideal transfer of the film, it should lie in the range above 0.8 and below 1.2. The graph clearly indicates that it is Y-Type deposition of the film because the deposition can be done on both strokes i.e. up and down strokes, thus results in homogeneity of the film.

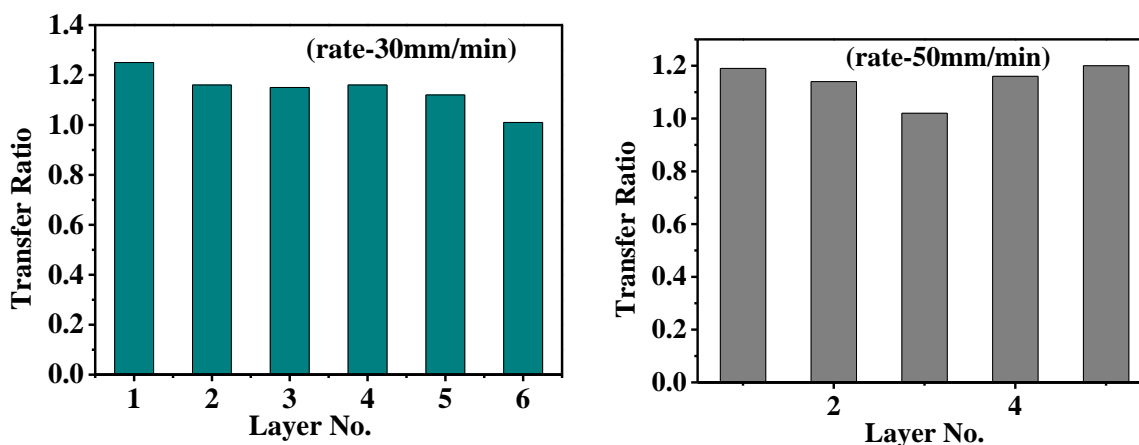


Fig.5.7 shows graph between Transfer Ratio and Layer number at compression Rate-30mm/min as well as at rate-50 mm/min.

The films were transferred at different compression rates and it was found that there is a complete transfer of films even if we change the rate also and deposited layers are completely homogeneous. Thus results in Y-type having up and down stroke.

The deposited films were allowed to dried for about half an hour on dipper clip and finally it was put in vacuum desiccator so to remove any air contamination on thin films.

5.4 Atomic force microscope characterization of multilayer GO films

Multilayer GO LB films deposited at different barrier rates (50 mm/min and 30 mm/min) were characterized topographically using AFM to know the effect of the rate on the deposition as well as the evolution of the films with successive layers.

Table 5.7 R.M.S. roughness values obtained from AFM data for different samples:

Substrate	Barrier Speed (mm/min)	Layers	r.m.s. roughness (nm)
Glass	-	0	0.39
Glass	30	1	1.15
Glass	50	1	0.86
Glass	50	2	1.13
Glass	50	4	1.60
Glass	50	5	2.42

Fig 5.8 show the representative $3\mu\text{m} \times 3\mu\text{m}$ AFM images obtained for the bare substrate as well as the GO films. Table 5.7 gives the average r.m.s. roughness values obtained from AFM data for different samples. AFM image for the bare substrate (Fig 5.8 (a)) shows that the glass substrate used is smooth with the r.m.s roughness of 0.39 nm. A comparison of the 1 layer GO films deposited for 30 mm/min and 50 mm/min barrier speeds (Fig 5.8 b) and c)) clearly show that the films deposited for rate 30mm/min are much more rough. We believe that this may be due to the slower barrier speed allowing for the relaxing and hence the wrinkling of the GO sheets whereas the barrier speed of 50 mm/min does not allow the GO sheets to relax.

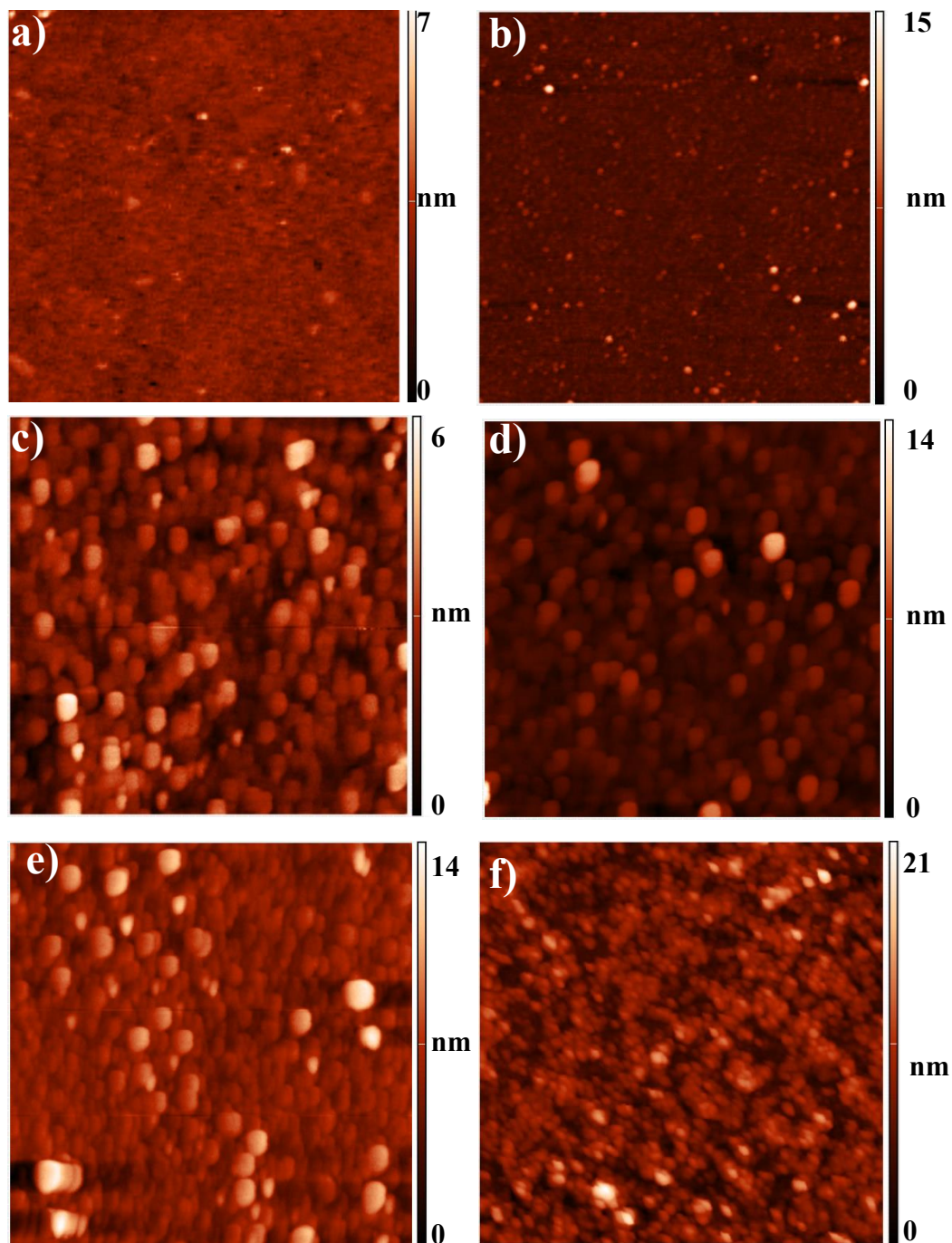


Fig 5.8: $3\mu\text{m} \times 3\mu\text{m}$ AFM images of multilayer GO films. **a)** Glass Substrate, **b)** 30 mm/min 1 Layer, **c)** 50 mm/min 1 Layer. **d)** 50 mm/min 2 Layers **e)** 50 mm/min 4 Layers, **f)** 50 mm/min 5 Layer.

The further roughness analysis for multilayer films was carried out only for films deposited at the barrier speed of 50 mm/min. Roughness analysis of the successively more number of layers shows that the roughness of the films increases as the number of layers deposited increases. r.m.s roughness value obtained for 5 layer transparent GO film deposited on the glass substrate is 2.42 nm.

Chapter-6

Conclusions and Future scope

6.1 Conclusions

In this work, the thin uniform films of graphene oxide were prepared using LB method. Stable and well compacted Langmuir monolayers are the very first step in LB film deposition. Their characteristics are helpful in deciding the quality of films and morphology of the final transferred film. To obtain good transfer characteristics, the graphene oxide monolayers on the water surface were characterized for different compression rates, different solvent concentrations and subphase temperature. The Π -A isotherm analysis, hysteresis analysis, barrier oscillation experiments have shown that the most stable GO films were obtained at 21⁰C for 30mm/min and 50 mm/min compression rates and 1:13 (ethanol:DCE) spreading solvent. The oscillating barrier measurements have been performed at different barrier compression rates for gaining an insight into the dissipation processes within the films by calculating visco-elastic parameters. Finally, the deposition of graphene oxide monolayers was done using Y-type deposition on glass substrates. Stable uniform graphene oxide thin films by 1, 2, 4 and 5 layer transfer for different barrier compression rates were deposited. AFM analysis of the deposited films shows that the films are continuous and smooth (low r.m.s. roughness). The roughness of the films increases with increasing number of transferred layers. And smoother films are obtained for higher barrier compression rates (50 mm/min).

6.2 Future scope

The Graphene oxide films using this method should be deposited on atomically smooth substrates to have complete understanding of the morphology properties and factors which control it. Further, GO films need to be deposited on conducting substrates and characterized for electrical properties to enable device synthesis.

