Engineered Surfaces for Dew Harvesting

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THESIS

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1	INTRODUCTION1	
	1.1 Water crises around the world1	
	1.2 Existing technologies and research working towards water stress problems5	
	1.2.1 Desalination	
	1.2.2 Water Harvesting	
	1.3 Idea of trapping water from the atmosphere7	
2	FABRICATION OF ENGINEERED SURFACES11	
	2.1 Liquids used in the current study11	
	2.2 Preparation of the surfaces	
	2.2.1 Preparation of microposts surfaces	
	2.2.2 Preparation of black silicon surfaces	
	2.3 Scanning Electron Microscopy15	
	2.4 Sample Cutting	
	2.5 Salinization of the prepared samples	
	2.6 Preparation of liquid impregnated surfaces (LIS)	
3	EXPERIMENTAL SETUP	
	3.1 Experimental setup for nucleation experiments	
	3.2 Experimental setup for water formation	

TABLE OF CONTENTS

4	RESULTS AND	DISCUSSION	20
	4.1 Dew Form	nation	20
	4.1.1	Nucleation states and energetic barriers	20
	4.1.2	Comparing barrier energy	33
	4.1.3	Nucleation inside the oil	
	4.2 Dew coll	ection	40
	4.3 Results		43
	4.3.1	Results for microposts samples	44
	4.3.2	Results for nanograss samples	48
	4.3.3	Comparison between microposts and nanograss samples	49
	REFERENCE	ES	53
	VITA		64

LIST OF TABLES

TABLE		PAGE
1.	Scale of people facing water scarcity during a given number of months per year,	
	1996–2005	1
2.	Dimensions of the fabricated microposts silicon samples	14
3.	Sample texture dimensions, comparison between Φ parameter	49
4.	Properties of oil	51

LIST OF FIGURES

FIGURES			
1.	Quarterly averaged monthly water scarcity	. 4	
2.	(a) Image of a droplet in Wenzel state, the so-called wetting state. The image on the	e	
	right is after a certain interval of time when the droplet has impregnated into the	e	
	texture (b) Image of a droplet in Cassie state, the so-called non wetting state. The	e	
	image on the right is after a certain interval of time. The droplet compared to the	e	
	Wenzel state does not impregnate into the texture as much due to the air pocket	S	
	present in the texture (c) Schematic of the Wenzel state of the droplet (d) Schematic	С	
	of the Cassie state of the droplet	. 7	
3.	(i) Schematic showing lubricant covering the posts of a textured surface (ii) Drople	t	
	condensation on an LIS	. 9	
4.	. Schematic of fabrication of microposts sample, a): 1. Priming, 2. Photoresis	t	
	coating, 3. Soft bake, 4. Pattern develop, 5. Hard bake, 6. Pattern develop, 7. Etch	l,	
	8. Photo-strip. b) SEM of prepared sample	. 12	
5.	SEM images a. Nanograss sample b. Micropost sample, h=10.4 µm, a=b=10µm	. 15	
6.	SEM images a. Nanograss sample impregnated with BMIm b. Micropost sample	·,	
	h=10.4 μm, a=b=10μm impregnated with BMIm	. 16	
7.	Water formation setup. Test sample is mounted on a computer controlled peltie	r	
	cooler (placed horizontally). The sample is in an environment chamber that can	n	
	maintain surrounding temperature and humidity at a set value. A humidity sensor i	S	
	placed in the chamber, near the test sample to have an accurate humidity and	d	

	temperature settings. A thermocouple is attached to the copper plate to give surface	18
	temperature.	
8.	Water collection setup. Test sample is mounted on a computer controlled peltier	
	cooler (placed vertically). The sample is in an environment chamber that can	
	maintain surrounding temperature and humidity at a set value. Droplet coalescence	
	and shedding is visualized through a glass window.	19
9.	Various possible states of droplet upon nucleation in LIS. State I. Nucleation at the	
	air-substrate interface State II: Nucleation within the oil. State III: Nucleation at the	
	oil-substrate interface. State IV: Nucleation at the oil-air interface	26
10.	. a. Schematic of floating droplet on the oil with negative spreading coefficient, b.	
	Schematic of droplet submergence inside the oil with positive spreading	
	coefficient	28
11.	. a. Floating drop on Dodecane, b. Droplet submergence inside the kerosene	29
12.	. Water completely condensed on the micro textured surface	31
13.	. a. Case(I) Water droplet on the micropost (Cassie state), b. Case(II) Gaps between	
	posts are filled by oil (oil doesn't cover the top of the post, c. Case (III) the	
	condensed droplet floats on the LIS	33
14.	. b. The regime map showing conditions for nucleation within the oil is preferred over	
	nucleation in vapor for different ratios of $\gamma_{wo}/\gamma_{wa},$ c. The regime map showing	
	conditions where nucleation at oil-air interface is preferred over nucleation at the	
	solid-air interface for different solid surface wettabilities $\gamma_{ws(a)}$, d. The regime map	
	showing conditions where nucleation is preferred at oil-air interface over nucleation	
	within oil for different surface wettabiities in oil $\gamma_{ws(o)}$	38

viii

15. Schematic of water	droplet rolling on a lubricant-imp	pregnated surfaces	41
16. Plot between critica	l supersaturation ratio (SR*) for	nucleation for variable contact	
angles of water on th	ne solid surface in presence of air	r and oil as a function of surface	
wettability in air Θ w	vs(a), in oil Owo(o). Plot also sho	ows SR* for nucleation of water	
on a OTS surface in	air and OTS surface immersed	in different oils. SR* is highest	
for OTS			43
17. Plot between ΔT su	bcooling (K) and surfaces (OTS	S coated textured surface, OTS	
coated surface wit	h different oils impregnated).	Plot shows when nucleation	
occurred after reach	ing the dew point. $\Delta T = Tnucleat$	ion-Tdp	44
18. Plot shows droplet c	count with respect to time. Here,	different oils are considered to	
compare the increas	e in droplet count within a fram	ne, 1CN is 1-Chloronapthalene,	
EC is Ethyl cinnama	ate		45
19. Plot shows water fo	rmation and collection on 10µm	n posts. Unimpregnated surface	
is OTS coated 10 µ	n textured surface and others ar	e OTS coated textured surfaces	
immersed in differen	nt oils		46
20. Plot shows area bein	g covered by droplet on differen	t surfaces (OTS coated textured	
surfaces and OTS co	pated surfaces immersed in differ	ent oils)	47
21. Plot water formation	and collection on nanograss sar	mple. Unimpregnated surface is	
OTS coated nanogra	iss textured surface and others an	re OTS coated textured surfaces	
immersed in differen	nt oils		48
22. Plot shows compari	son between water formation or	$10\mu m$ posts and on nanograss	
textured samples. T	here are some oils with no data	because they have high vapor	
pressure and thus ev	aporates before the condensatior	process could start	50

ABSTRACT

Structured surfaces have drawn considerable attention from both theoretical and experimental points of view due to their potential in enhancing the heat transfer coefficient by achieving desirable wetting properties, in many industrial applications such as thermal storage, water harvesting and power generations. Considering the water scarcity as one of the most challenging issue nowadays, here we apply a new technique for water harvesting through condensation phenomenon. This technique has the advantage of a) typically the source of the water for harvesting is external and comes from the nature such as sea or rain, but here a vapor stimulation process is applied to capture the vapors which have the potential to provide water by phase change process-condensation. b) Using remarkable less input energy compared to the typical techniques of water harvesting.

In the above mentioned application (water-harvesting), fast formation and subsequent removal of water droplets is critical for enhancing the efficiencies of their associated systems. Significant focus has been placed on the aspect of droplet removal from the surfaces that has led to development of superhydrophobic surfaces with special textures on which droplets are self-removed after coalescence. Due to their inherent low surface energy, nucleation energy barrier is also high. In contrast to conventional superhydrophobic surfaces, here we show the surfaces can be engineered such that the simultaneous benefits of high nucleation rates and fast droplet removal can be obtained during the condensation process. The main objective of this work is to develop a fundamental understanding of impregnated oils in textured surfaces from theoretical and from experimental point of view, for enhanced condensation further leading to the application of dew harvesting.

CHAPTER 1. INTRODUCTION

1.1 Water crises around the world

In the last three decades, it is noticed that due to steadily increasing demand, the unavailability of freshwater has become a threat of sustainable development of human society [3] [4]. According to World Economic Forum annual report 2015, water crisis has been listed as the largest global risk in terms of its potential impact [5]. Access to clean water resource continues to be the most difficult and effecting global issue that is resulting in hiking economic and ecological needs for water harvest efficient technologies. To meet the humanity's sleepily increasing demands for freshwater and protecting ecosystems consequently, therefore, trying to keep water around the world within maximum sustainable levels, happens to be the most hard and crucial challenges for today [6].

Number of	Billions of people facing low, moderate, significant, and severe water scarcity during <i>n</i> months per year			gnificant, and s per year	Billions of people facing moderate or	Billions of people facing severe
months per year (<i>n</i>)	Low water scarcity	Moderate water scarcity	Significant water scarcity	Severe water scarcity	worse water scarcity during at least <i>n</i> months per year	water scarcity during at least <i>n</i> months per year
0	0.54	4.98	5.22	2.07	6.04	6.04
1	0.12	0.81	0.66	0.31	4.26	3.97
2	0.12	0.19	0.13	0.37	3.95	3.66
3	0.35	0.05	0.03	0.37	3.55	3.28
4	0.33	0.01	0.001	0.59	3.15	2.91
5	0.30	0	0	0.55	2.56	2.32
6	0.33	0	0	0.27	2.09	1.78
7	0.47	0	0	0.21	1.76	1.50
8	0.59	0	0	0.29	1.46	1.30
9	0.40	0	0	0.30	1.13	1.01
10	0.40	0	0	0.12	0.78	0.71
11	0.30	0	0	0.09	0.66	0.59
12	1.78	0	0	0.50	0.54	0.50
Total	6.04	6.04	6.04	6.04		

Table 1 Scale of people facing water scarcity during a given number of months per year, 1996–2005. [1]

To assess global water scarcity in terms of grid cells, here used 30 x 30 arc min. Term 'blue water' refers to the volume of fresh surface water and groundwater available, 'Bluewater consumption'

refers to the volume of Bluewater that has been withdrawal and not returned because the water evaporated or was undertaken as a product. Total blue water availability (WF_{tot}) is the addition of the run off generated in the area plus in all upstream gird cells minus environmental flow requirement minus the water footprint grid cells [3]. The water scarcity can be examined taking the ratio of water in a measured area to the total water available in that area i.e. $WS = \frac{WF_{loc}}{WA_{tot}}$,

where WS is the water scarcity, WF_{loc} is the blue water in the grid cell and WA_{tot} is the total amount of blue water available in the cell. The scarcity is moderate if the WS is in the range of 1.0<WS<1.5, high in the range of 1.5<WS<2.0 and said severe if WS>2.0.

People facing different levels of water scarcity: In table 1, it is shown that the statistics of population having different level of water scarcity in the number of months every year at global level. It is noticed that around 71% of the population is living under moderate conditions to sever water scarcity for a minimum of 1 month every year. Around 66% people are facing severe water scarcity for a month of the year and of 66%, around 16.5% live in India and another 14.84% live in China. A significant number of people are going through water shortage issue in some part of the year in Bangladesh, United States of America.

Data shows that the number of people going through water problems for minimum 4-6 months is around 1.8-2.9 billion. Approximately half a billion people have water scarcity for almost the year round, millions of people live in India, Pakistan, Egypt, and Saudi. The countries in middle eastern part of the world are facing extreme vulnerable conditions currently. Some nations such as Libya and Somalia, Pakistan, Morocco, Niger and Jordan are having sever water crises where majority part of the population is suffering. Over 700 million people in 43 countries are suffering from water scarcity i.e. > 1000 m³/person. It is estimated that by 2025, there will be about 1.8 billion of population living in absolute water scarcity i.e. > 500 m³/person. The existing climate change scenario shows that half of the population in the world will be living in water stress situation by 2030 out of which around 250 million people will be from Africa.

Drinking water availability continues to hike up as the population increases. Access to clean water resources are depleting therefore the urgency of developing sustainable novel methods to meet the water requirement, is currently emphasized up more than ever. The effects of weather change, which is also another factor that is further complicating the balance between water supply and demand. This global issue has been exacerbated when it comes to developing methods that should be energy efficient along with affordability. Surprisingly, the world is made of 3% fresh water resources and out of which only 1% is accessible to humans. Rest of the world is (97%) consisting of saline water and due to ever-growing population rate around the world, the stress for freshwater requirement is higher than ever.



Figure 1 Quarterly averaged monthly water scarcity

1.2 Existing technologies and research working towards water stress problem

There are several ongoing research studies trying to overcome the problem of water stress around the world.

1.2.1 Desalination

It is perhaps a surprising fact that only 3% of Earth's water resources are fresh and only 1% of that is easily accessible resources and therefore coming to the other 97% of water which is saline. Until sometime most of techniques primarily concentrated on making sea water into portable water using desalination, filtration of waste-water or water treatment. For over five decades, desalination has been recognized as one of the major contributor to reduce water stress in coastal areas by producing freshwater from saline water. Methods such as Reverse Osmosis, Distillation, Electrolysis etc. are mainly focusing on desalting of sea water [7-15].

Undoubtedly, distillation has been practiced widely since 90's and has provided valuable opportunity to avoid complete depletion and diminishment of freshwater. The basic principle behind distillation is to boil the sea water and heat it up to 100C (B.P. of water). The fresh water then evaporates and passes through the condenser where heat is removed from the vapor and converted into liquid form. This principle is based on differential boiling points of the consisting components in the solvent (here, sea water). Distillation is a process which requires high energy consumption and therefore turns to be an expensive source of producing freshwater. It is though widely used by the countries in Middle East, which uses about 70% of worldwide capacity; and in North Africa, which uses about 6% of worldwide capacity. Another technique of desalination, Reverse osmosis, is being an increasingly common method due to its lower energy consumption as compared to distillation. The method involves passage of seawater through a membrane by

applying enough pressure to overcome osmotic pressure, that is driven by chemical potential differences of the solvent. The result of this method is such that the solute (salt) is retained on the side of the membrane where pressure is applied and the solvent (fresh water) is passed through it. Since this method requires pressure to use the concept of osmosis in opposite direction, therefore the energy utilized here for the pressure is considerably high. Also, one very distinct problem with these technique is such that it can be beneficial only if the desalination plant is setup near the water reservoir or where the transportation of sea water is possible. Whereas, some areas around the world that are facing severe water crises are away from any kind of natural water resource and thus the application of desalination in such places boils down to zero. Per say, there is enough of drinking water available from the natural resources but it is unevenly distributed and too much of it is unapproachable. Also, these methods are thermodynamically driven, the amount of money required for setting up these plants is infeasible for many water stressed countries.

The burgeoning population growth, urbanization and industrialization have increased the demand of reliable water resources, and to meet the on-going global challenge to provide water and alleviate the alarming problems- has become a necessity

1.2.2 Water Harvesting

The water harvesting methods are being widely applied to overcome the problem of water crises such as bunding, pitting, micro- catchments water harvesting, flood water and ground water harvesting [16]. Rainwater harvesting has been effective for facing water scarcity in some areas with little rainfall too. The idea behind it is collecting, filtering, storing and using rainwater for irrigation and for various other purposes. At many places, this method is used at many household places primarily for drinking water. With the erratic climate changes, the predictability of rainfall is has reduced quite drastically. Apart from predictability, the quality of rainwater has said to deteriorate in the last couple of decades, additionally, the storage of water for a longer time in tanks with rust results in making this water unfit for drinking. It is no more advisable to be dependent on rainfall harvesting for the places where it is very little rainfall and thus, practiced only at places that face heavy rainfall [17-25].

1.3 Idea of trapping water from the atmosphere

Recent investigations [1, 26] have however brought to light the fact that while many natural and synthetic superhydrophobic surfaces enhance droplet condensation they reduce drop mobility considerably due to the nucleation of droplets within texture features resulting in sticky Wenzel droplets. To come with a solution to this problem, surfaces hybrid hydrophobic and hydrophilic that enhance the Cassie condensation [27-29], have been developed by a few researchers. Intricate designs hinder their universal applicability thus emphasizing the need to develop a cost effective, easy to implement and efficient method. There are numerous examples in nature which employ



Fig 2: (a) Image of a droplet in Wenzel state, the so-called wetting state. The image on the right is after a certain interval of time when the droplet has impregnated into the texture (b) Image of a droplet in Cassie state, the so-called non wetting state. The image on the right is after a certain interval of time. The droplet compared to the Wenzel state does not impregnate into the texture as much due to the air pockets present in the texture (c) Schematic of the Wenzel state of the droplet (d) Schematic of the Cassie state of the droplet. Adapted from [2].

the concept of condensation to harvest water from the air, such as Namib desert beetle (*Stenocara gracilipes*). This beetle has troughs on its back body that are supposedly with hydrophobic and hydrophilic patterns that facilitate dropwise condensation, further leading to water harvesting for its own survival in such arid area [30]. There are several research groups currently trying to solve the mystery behind Namib Beetle. Another very significant nature inspiration in the advancement of condensation is of Lotus leaf, giving rise to the idea of creating textures on a surface for promoting dropwise condensation[22, 30-39]

The main objective of this work is to develop a fundamental understanding of impregnated oils in textured surfaces from theoretical and from experimental point of view, for enhanced condensation further leading to the application of dew harvesting, Fig. 3. Using oil instead of the air requires addressing some issues arise from the hydrodynamic characteristics of oils such as viscosity, Interfacial and surface tensions (condensate configure on the oil interface), evaporation rate and so on. In this thesis, we investigate these effects by employing different oils.

There are three stages of condensation on Lubricant Impregnated Surfaces that are highly impacted by the properties of the oil impregnated in the surface. The nucleation energy barrier for condensation is observed to lower and as a result it gives enhanced water formation, when compared to superhydrophobic surfaces that poses identical surface chemistry. [40-42].

Mode of condensation is dependent on many properties of the surface, in particular the surface energy and related phenomena. Hydrophobic surfaces are expected to promote dropwise condensation whereas hydrophilic surfaces tend to promote film-wise condensation. To better extent, superhydrophobic surfaces, combination of hydrophobic surface chemistry and nano-micro texturing, have been proposed to enhance the hydrophobicity to gain drop wise condensation and more importantly roll-off of droplets formed on the surface that would result in hundred times improvement in the heat transfer associated condensation processes[2, 27, 43-46].

Following the above objectives, at the first step, we made hydrophobic samples by fabrication technique, photolithography and etching. We made nanograss and microposts structured surface to compare the effect of the geometry of the surfaces on formation and nucleation rate[26, 30, 47-50]. The impregnated oils were coated on the micropost/nanograss by dip coating process. The formation/collection of water droplets on structured surface were studied by experiments and the results were explained based on the Gibbs Free energy difference. For ensuring that the samples are fully covered by the oil the dimensionless parameter (capillary number) was set to the value much less than one so that the required velocity is achieved such that the gap between micropillars and nanograss is filled by capillary forces rather than viscose force. The results revealed that impregnated oil (LIS) has significant role in reducing the barrier energy which should be dominated to proceed the nucleation and this was in agreement to the Gibbs free energy difference which was derived for different assembly of structures and droplet position on them. By comparing energy, it was shown that the nucleation on the oil interface is more likely to happen than condensation on the pillars (inside the oil or at air presence) while the condensation inside the oil



Fig 3: (i) Schematic showing lubricant covering the posts of a textured surface (ii) Droplet condensation on an LIS

is impossible to occur. The results also show that formation rate of drops on nanograss is more than micro post for both impregnated and un-impregnated cases.

The theory shows that shedding velocity of drop on the oils having higher viscosity is less than ones with low viscosity. The results depict that while the viscosity can prevent the motion of drop downward and this can consequently decrease the collection rate however on the other side the nucleation rate also should be taken into account means that the oil which undergoes higher nucleation rate is likely to give higher collection rate. Interesting to note that the viscosity effect is not limited to the rolling velocity such that higher viscosity results in hindering the coalescence between droplets and the size of the droplets would be smaller compared to the lower viscosity. And smaller drop size is expected to be affected by resistant forces (pinning force+ shear viscosity) more leading to less collection rate.

Chapter 2. Fabrication of Engineered Surfaces

Superhydrophobic surfaces [43-45, 49, 51] are made with two fundamental properties: roughness and water repellency. The relation between roughness and water repellency were worked out by Cassie and Baxter [52] as well as Wenzel [53]. To create roughness, various etching methods have been investigated over the years[54-89]. To induce surface chemistry as per the requirement of water repellency, method of salinization is practiced.

The surfaces play different roles depending on the interplay of surface roughness and surface chemistry [90]. The phenomena can be classified into three categories: 1. Water drop suspended on top of the hydrophobic roughness features, called as Cassie state because liquid is rested on surface made of solid and air. 2. Water drop impaled in the hydrophobic features, called as Baxter state because the liquid is rested in between the surface textures. 3. Superwettability, where the droplet gets sucked on the surface, making a contact angle of almost zero [47, 52, 62, 91-98].

2.1 Liquids used in the current study

The liquids used in this study for impregnating samples (1-Chloronapthalene, Ethyl Cinnamate, Dodecane, Pentadecane, Tetradecane, Perflurobutylamine, Phenyldodecane) were purchased from Sigma Aldrich and silicone oil (BMIm) from Iolitec Ionic Liquids Technologies. Solvents for salinization (OTS and Toulene) were purchased from Sigma Aldrich The chemicals were analytical grade and was used with no further purification.

2.2 Preparation of the surfaces

Silicon wafer (100mm, P type, Boron, <100> ON, TTV<5um, Prime Stock) purchased from Silicon Materials, Inc. In a typical process, the silicon wafer was cleaned using in acetone,

methanol, IPA and distilled water for 4 mins each, dried using spin coater and later dehydrated on a hot plate at 95C for a minute.



Fig 4. Schematic of fabrication of microposts sample, a): 1. Priming, 2. Photoresist coating, 3. Soft bake, 4. Pattern develop, 5. Hard bake, 6. Pattern develop, 7. Etch, 8. Photo-strip. b) SEM of prepared sample

2.2.1 Preparation of microposts surface (Fig 4)

Step 1. <u>**Primer</u>**: To prepare the silicon surface for good adhesion of the photoresist, a process named as priming is used with a chemical called - hexamethyldisilizane (HMDS) is performed. This step consists of spin-coating at the speed of 3200rpm with 60ml of HDMS dispensed over the cleaned sample.</u>

Step 2. <u>*Photoresist coat*</u>: Once the sample is ready with uniform monolayer of HMDS, the sample is coated with a photoresist (MRS 703) using spin coater at the speed of 3200rpm for a minute to produce 0.96µm thick mask layer.

Step3. *Soft bake*: The photoresist is generally made of 50-60% of solvent, that is required for smooth coating on the surface. Once the coating is done, the presence of solvent is not required and therefore, it's removal is important to solidify the resist film. After baking, the solvent content reduces to approximately 10-12%. Soft bake was performed on hot plate with typical temperature ranging from 90-115C. This step is optimized to result in absolute removal of the solvents at the photoresist-sample interface.

Step 4. *Exposure*: The masked substrate is exposed to lithographer, here used- Heidelberg MLA 150 Direct Write Lithographer. In lithographer, the photoresist is exposed to a pattern of intense light using g-line and i-line (depending on the resolution) wavelength. The exposure to light causes a chemical change in the photoresist that removes some of the desired areas using a developer. For this study, arrays of posts were printed with different configuration of spacing (edge to edge), refer table 2

Step 5. <u>*Hard bake*</u>: After exposure, the substrate is baked on a hot plate at temperatures between 100-120C for a minute. This step is crucial to remove the liquids that are absorbed in the substrate and further crosslinking with the left photoresist.

13

Step 6. <u>*Pattern develop*</u>: Now, the substrate is dipped in the developer solution, AZ 726 MIF. Developer solution is used for dissolving away the areas of the photoresist that were exposed to light. After immersion, the surface is patterned with the patterned image as desired.

Step 7. <u>*Etch*</u>: The developed substrate is dry etched using a Deep Reactive Ion Etcher using Bosch process to fabricate micropillars of required dimensions.

Step 8. <u>*Photo strip*</u>: After the wafer is etched, remaining photoresist needs to be removed using either chemical stripping or plasma stripping. Here using chemical stripping, NMP is boiled at 90°C for 15 mins on a hot plate. The substrate is immersed in the heated NMP beaker for another 15mins (still on the hot plate) and later sonicated for 30 mins.

a (post width) µm	h (pillar height) μm	b (spacing, edge-to-edge) μm
		2.5
	10.4	5
		10
10		25
		50
		75
		100

Table 2 Dimensions of the fabricated microposts silicon samples

2.2.2 Preparation of Black silicon surfaces. The cleaned wafer is fed in DRIE for 8 mins applying mixed mode of fabrication recipe involving gases like SF_6 and O_2 with respective flow rates to achieve nanograss. The etching gas, SF_6 reacts with Si creating Si_xF_y which is desorbed away due to the high vapor pressure of F ions. The passivation gas, O_2 reacts with Si creating Si_xO_y which

develops a polymer layer. Continuous flow of etching and passivation gas develops grass type structures, Fig. 4 [42]

2.3 Scanning Electron Microscopy

All specimens were fixed to aluminum stubs and examined in a FEI Quanta 650 FEG SEM (Pritzker Nanofabrication Facility, Chicago, Department of Molecular engineering, Chicago) to confirm the micro/ nano texture geometry, Fig. 5



Fig 5 SEM images a. Nanograss sample b. Micropost sample, h=10.4 µm, a=b=10µm

2.4 Sample Cutting

The 4inch processed sample is cut into pieces, here required 1inch square size, using TYKMA Electrox Laser Marking System (Nanofabrication core facility, UIC)

2.5 Salinization of the prepared samples

To induce superhydrophobicity in the etched sample, method of salinization is used. Before salinization, etched sample is plasma cleaned in Herrick Barrel Plasma Etcher (Nanofabrication Core Facility, UIC) to remove any organic contaminants present on the surface for further processing. The contact angle of water droplet on the sample after plasma cleaning was $\sim 0^{\circ}$. For

salinization, OTS and toluene was mixed in a certain proportion in a glass beaker in which the sample was sonicated for around 2mins. Post salinization, the samples had contact angles ranging from 120° -162° with respect to their texture geometry, thus surface chemistry was altered as per the requirement.

2.6 Preparation of Liquid Impregnated Surfaces (LIS):

The superhydrophobic sample is dipped in an oil bath by a using dip coating setup. To make sure there is no excess oil present on the sample it must be withdrawn at a controlled velocity.



Fig 6 SEM images a. Nanograss sample impregnated with BMIm b. Micropost sample, $h=10.4 \ \mu m$, $a=b=10 \ \mu m$ impregnated with BMIm

This velocity, is calculated taking into consideration the surface tension of the oil/air interface, viscosity of oil and also the geometry of the surface. Quéré [48] shows how the thickness of oil could be calculated using Landau–Levich–Derjaguin (LLD) equation given below taking into account the geometry of the surface: $h_{film} \sim 0.94 \ a \ Ca^{2/3}$

Here, $a = \gamma / \rho g$ is the capillary length and $Ca = \eta V / \gamma$ the capillary number, η is the viscosity of the oil and V is the velocity with which the sample is withdrawn and γ is the interfacial tension between the oil/air interface.

Chapter 3. Experimental Setup

This chapter gives a detail information of the experiments that were carried out to study nucleation rates on fabricated samples, further dew formation and collection to observe dew harvesting.

3.1 Experimental setup for nucleation experiments. To observe the nucleation on surfaces, the experiments were performed under an optical microscope (Zeiss, Axio Zoom v16). The subcooling temperature on the cooling plate of the peltier was set around 5° C lower than the dew point. The experiment was to observe the nucleation of water droplets and coalescence. Copper chamber was manufactured with precise dimensions to fit with the bottom of the optical microscope lens. A wet water absorbing foam was set in the inner wall of the chamber to create humidity during the experiment.

3.2 Experimental setup for water formation. The sample was mounted on the extruded part of the copper plate that is set on the cold plate of the peltier using thermally conductive tape (McMaster Carr 6838A11). The copper plate temperature was monitored by thermocouples (Omega, model KK). The environmental temperature is set at 15°C, relative humidity at 80%, peltier temperature at 2°C. The measurement of water formation on the sample was done by measuring the weight of sample before starting the experiment and measuring after 1 hour. To avoid any loss of water during after measurement, a water absorbent is used to soak big drops initially, as the big drops can fall off the surface while moving the sample from the peltier to the weighing scale.



Fig 7 Water formation setup. Test sample is mounted on a computer controlled peltier cooler (placed horizontally). The sample is in an environment chamber that can maintain surrounding temperature and humidity at a set value. A humidity sensor is placed in the chamber, near the test sample to have an accurate humidity and temperature settings. A thermocouple is attached to the copper plate to give surface temperature.

3.3 Experimental setup for water collection

The sample is mounted vertically on the extruded portion of the copper plate set on the cooling side of the peltier using thermally conductive tape. The experimental conditions are same as described in 3.2. The collection of water from the sample during the experiment was collected in a glass vial that is placed under the sample. The rest of the copper surface was covered by a water absorbing foam to avoid the collection of undesired area.



Fig 8 Water collection setup. Test sample is mounted on a computer controlled peltier cooler (placed vertically). The sample is in an environment chamber that can maintain surrounding temperature and humidity at a set value. Droplet coalescence and shedding is visualized through a glass window.

Chapter 4

Results and Discussion

Our aim in this chapter is to explore formation and collection of dew on surfaces possess different surface characteristics (wettability). A comparison was made between unimpregnated surfaces (microposts and/or nanograss) and the ones which are covered by oil (Lubricant impregnated surfaces, LIS). The effect of oil properties on the nucleation rate and collection amount were addressed with respect to the classical nucleation theory and by performing a hydrodynamic force balance exerted on a water condensed droplet.

4.1 Dew Formation

4.1.1 Nucleation states and energetic barriers

The process of nucleation is observed during the first order transition (the phase transition which involves Latent Heat). This transition is driven by lowering of the free energy in the formation of new phase. The original state remains metastable when it is close to the equilibrium transition, thus, a fluctuation is needed to show the appearance of the first region of the new phase, called as the nucleation point [1, 98-101].

Nucleation is achieved thermally and depends on the intensity of free energy barrier; the rate of nucleation can be slow or fast. In the case of slow rate of nucleation, there could be large deviation from the equilibrium before the stable first phase appears, therefore, significant hysteresis come into picture during the transition. According to the classical nucleation theory, the rate of nucleation slows exponentially with the height of the free energy barrier. In other words, nucleation is defined as a process which determines how much time would be required for the formation of a new thermodynamic phase; in this study, formation of water drop from the

atmosphere. Nucleation rate determines the number of condensed droplets at each second, per unit area of the surface or per unit volume of the droplet in the heterogeneous and homogeneous condensation respectively. This quantity is obtained through the kinetic approach of nucleation whereas the distance between the vapor molecules and the droplet surface is compared with the free path distance of vapor molecules. When the vapors are become close to the cold surface (droplet) the probability of collision between molecules and surface is more than the collision between each other. Here a new layer with the characteristic distance (same order of magnitude as the mean free path of vapor molecules) is introduced called Knudsen layer. The molecules placed out of this region collide each other and move (mass and energy are transferred to the droplet surface through the diffusion mechanism) to the Knudsen Layer where non-equilibrium and subsequently are adsorbed by the droplet surface. The rate at which vapor molecules are transformed and attached (J) to the droplet can be described by the flux of vapor molecules incorporating to the cluster forming, number of vapor molecules around the surface area of the cluster, the activation energy required for vapor molecules to pass the interface of drop-gas and a prefactor-Zeldowich factor) [102] which gets the value other than one, when the kinetic process is non-equilibrium. Since this work is based on the thermodynamic approach, so here we just briefly point out the nucleation rate formula as:

$$J[m^{-3}s^{-1}] = \rho Z J \exp\left(\frac{-\Delta G_{barrier energy}}{K_B T}\right)$$
$$\exp\left(\frac{-\Delta G_{barrier energy}}{K_B T}\right): The probability of occuring condensation$$
$$K_B T: Thermal energy \quad , \ \rho: The number of nucleation sites per unit volume$$

without reviewing in detail. However, according to the nucleation rate, regardless of homogeneities or heterogeneous conditions, Lowering the energy barrier leads to the higher nucleation rate and this is considered as a major cause affecting the formation process, which is

the focus of the first part of this work. The first section endeavors to interpret the formation mechanism by defining the barrier energy for different cases.

As mentioned earlier, the well-designed structured surface combined by nanoscale roughness features combined with chlorine based chemistry can boost the water-repellency (hydrophobicity) which in turn enhances the water harvesting performance. The water harvesting process consists of three steps: transportation of vapor clusters (moist) onto the surface, capturing the moisture by surface and then collecting the water from the surface. By adjusting the relative humidity as 80% then sufficient moisture is supplied on the surface. The moist near the cold surface undergoes a phase change process in which the vapor state changes to the liquid phase called condensation. According to the relative humidity and temperature condition inside the humidity controlled chamber the dew point is determined $(T_{dew} = T_{amb} - \frac{100 - RH}{5})$. Since the relative humidity is not one hundred percent it means that the medium is not filled by its maximum capacity to hold water vapors then the homogeneous condition is less likely to happen and dew point is not equal to the surrounding temperature. Interesting to note that at saturation condition the dew point is equal to the surrounding temperature while here the dew point is less than the surrounding temperature and near the cold surface since the temperature is less than the dew point then vapor clusters adjacent to the surface no longer can be hold separately and tend to merge to each other and heterogeneous condition takes place whereas water vapor molecules release their Latent heat energy (the energy which was adsorbed during evaporation process) and water droplets are captured by the surface. According to the wettability of the surfaces, dropwise condensation is a dominated mode of condensation rather than filmwise condensation means that instead of having the film layer of water here, individual water droplets are formed on the surface. For water harvesting purpose, dropwise mode is desirable since in filmwise condition as the layer which is formed on the surface

after time passes acts like a thermal barrier and prevents heat transfer to take place between the cold surface and the surrounding area which results in lower efficiency, therefore superhydrophobic surfaces are ideal to repel water droplets approaching the surface and prevent it from getting wet. Despite fog harvesting where tiny droplets are convected towards the surface in dew harvesting, the only mechanism plays role is condensation which in turn is sensitive to the surface wettability. Dew harvesting requires an optimal wettability to satisfy two purposes 1) increase the nucleation rate and water capturing 2) removal rate of condensed mass. Therefore, higher hydrophobicity for water removal versus lower hydrophobicity for dew capture are to be satisfied. Since wettability is the prominent factor, here its role is discussed from the thermodynamic view point. To show how the wettability can affect the nucleation rate and water removal, the concept of free energy as an indicator of spontaneity of the process is considered. To start with, the Gibbs Free energy is defined as below:

$$G = H - TS \rightarrow H = U + PV \rightarrow G = U - TS + PV$$
1

Based on the Gibbs free energy hypothesis, a process can occur spontaneously when the energy difference between the two states is negative means that the system tends to run in a way that release its total energy. Therefore, to predict whether the vapor clusters changes to the droplets, one requires to measure the free energy difference by taking a differentiate:

$$\Delta G = \Delta U - T\Delta S - \Delta TS + P\Delta V + V\Delta P$$
²

From the second law of thermodynamic:

$$Q = T\Delta S$$
 3

From the first law of thermodynamic we know that:

$$Q - W = \Delta U \rightarrow \begin{cases} W = P\Delta V ; The work done by the system \\ Q = T\Delta S ; The heat adsorbed by the system \\ \Delta U = T\Delta S - P\Delta V \end{cases}$$

Substituting the above expression in Eq(2) one get :

$$\Delta G = -\Delta T S + V \Delta P \tag{5}$$

4

Since any phase change takes place at constant temperature and considering that droplet and vapor are not in equilibrium due to the different partial pressure by a small perturbation on pressure we will have:

$$\Delta G_{v}(V_{v}\Delta P) - \Delta G_{d}(V_{d}\Delta P) \rightarrow \Delta (G_{v} - G_{d}) = \Delta P(V_{v} - V_{d})$$

$$V_{v} \gg V_{d} \rightarrow \Delta (G_{v} - G_{d}) = \Delta P(V_{v}) \rightarrow \int \Delta (G_{v} - G_{d}) = \int \Delta P(V_{v})$$

$$Ideal \ gas: \ PV = RT \ (V = \frac{volume}{mass} : specific \ volume):$$

$$G: Free \ energy \ per \ unit \ mass$$

$$V_{v} = \frac{RT}{P} \rightarrow G_{v} - G_{d} = \int \Delta P(\frac{RT}{P}) \rightarrow G_{v} - G_{d} = RT \ \ln P + const$$

Considering that when the system reaches the saturation condition the free energy of vapor and droplet is equal then:

$$0 = RT \ln P + const \rightarrow const = -RT \ln P_s$$

$$G_v - G_d = RT \ln p - RT \ln P_s = RT(\ln P - \ln P_s) = RT(\ln \frac{P}{P_s})$$

$$7$$

Now if we consider the system at the initial state which is completely filled by vapors and the state at which the droplets are formed along with the presence of vapor phase, the free energy difference can be defined as below (Note: Above the free energy difference per mass was obtained not total energy).

initial mass:
$$m_0$$

After phase change: m_d (droplet mass) + m_v (vapor mass)
mass balance: $m_0 = m_d + m_v$

It should be mentioned that after droplet formation, the energy of the system not only is related to the bulk energy but also the new surface is formed which in turn implies the surface energy. Therefore, total energy at the second stage is composed of bulk and surface energy. Surface energy stems from minimizing the energy and forming spherical droplets and depends on the shape (area) of the droplets as well as surface tension per area of the water droplet.

$$G_{0} = m_{0}G_{v}, G = m_{d}G_{d} + m_{v}G_{v} + \sigma A$$

$$G - G_{0} = m_{d}G_{d} + m_{v}G_{v} - (m_{d} + m_{v})G_{v} = m_{d}(G_{d} - G_{v}) + \sigma A$$

$$G - G_{0} = -m_{d}RT(\ln\frac{P}{P_{s}}) + \sigma A$$

$$A_{d} = 4\pi R^{2}, V_{d} = \frac{4}{3}\pi R^{3}, m_{d} = \rho_{w}V_{d} = \rho_{w}(\frac{4}{3}\pi R^{3})$$

Therefore, the final expression for free energy difference of the system for generation water droplets through the vapor phase is as following:

$$G_{0} = m_{0}G_{v}, G = m_{d}G_{d} + m_{v}G_{v} + \sigma A$$

$$G - G_{0} = m_{d}G_{d} + m_{v}G_{v} - (m_{d} + m_{v})G_{v} = m_{d}(G_{d} - G_{v}) + \sigma A$$

$$G - G_{0} = -\rho_{w}(\frac{4}{3}\pi R^{3})RT(\ln\frac{P}{P_{s}}) + \sigma 4\pi R^{2}$$
10

The above expression corresponds to the homogeneous nucleation (Case II). Investigation of the condensation entails a systematic analysis of the possible mechanisms through which droplets may form on LIS. Three plausible scenarios for droplet generation in LIS are investigated and juxtaposed against a situation where droplet condensation occurs directly on the substrate in the absence of a lubricant (State I). The three other scenarios are (labelled as II, III and IV) in Fig. 5.1: State I represents the scenario when nucleation occurs on substrate in the absence of a lubricant.



Π

Fig 9 Various possible states of droplet upon nucleation in LIS. State I. Nucleation at the air-substrate interface State II: Nucleation within the oil. State III: Nucleation at the oil-substrate interface. State IV: Nucleation at the oil-air interface. [1]

In homogeneous condensation, the supersaturation is the criteria and the pressure should be more than saturation pressure (Relative humidity greater than 100 percent) to allow the free energy to decrease while in heterogenous condensation the relative humidity is less than saturation ratio however close to the cold surface the saturation pressure is decreased and the ratio of P/Ps is increased such that allows the free energy difference to get the value less than zero. In both mechanisms, the surface energy acts like a barrier which prevents free energy reduction. As can be seen, the free energy is decreased when the size of the drop reaches the critical value, which below this value the droplets tends to shrink(evaporate) and above this value the size of the droplet grows spontaneously. For obtaining this critical size, one needs to differentiate the free energy relation versus radios as below:

$$G = G_0 - \rho_w (\frac{4}{3}\pi R^3) RT(\ln\frac{P}{P_s}) + \sigma 4\pi R^2 , \quad \frac{dG}{dR} = -\rho_w 4\pi R^2 RT(\ln\frac{P}{P_s}) + \sigma 8\pi R = 0.0$$
¹¹
$$R_{critical} = \frac{2\sigma}{\rho_w RT(\ln\frac{P}{P_s})}$$

For addressing the heterogeneous condensation since the formed droplets are not spherical and their shape strongly depends on the wetting conditions or surface properties, then surface energy
parts should be modified. In this work lubricant-impregnated surfaces were used to enhance the dew harvesting therefore water droplets are supposed to get formed on the oil surface. Depending on the interfacial tension between the oil and water and surface tension of water droplet and oil, drops having various shapes and contact angles are formed on the interface of oil and air. Since surface energy depends on the surface area, the surface energy needs to be modified based on each configure. It should be mentioned that in this study textured surface were used with and without lubricant oils. It has already been demonstrated by many studies that surfaces impregnated by lubricants enhance the mobility of condensed drops due to the capillary force induced by microscopic texture and in turn boost dew harvesting performance. Therefore, shape of condensed droplet on oil is completely different compared to the unimpregnated superydrophobic surface where drops stay on the solid surface in the presence of air. Which in former, different oils exhibit different contact angles and wettability. The parameter which emphasizes these differences is barrier energy (surface energy) which needs to be diminished. Hence, efforts were made to optimize the surfaces by comparing their surface energy. Since, four phases (air-water-oil and solid) contribute in the lubricant impregnated case, Type of the oil reflects the contact line morphology which can promote/ demote the mobility of droplets. On the other side, the viscosity of oils has a significant effect on the coalescence phenomena as well as shedding velocity occurs on the interface of oil-air and subsequently droplet size. Another important factor is the evaporation rate which leads to the depletion of oils. Last but not least, the spreading coefficient determines whether a condensed droplet is cloaked by oil which in turn leads to the submergence of drops into the oil. Spreading coefficient $S_{ws(a)} = \sigma_{sa} - (\sigma_{sw} + \sigma_{wa})$ is a difference between adhesive and cohesive energies which required to bring out the adhesive between the unlike molecules and separate the molecules of water respectively. Positive spreading coefficient means

the energy required to break out the liquid molecules is low indicating that water molecules tend to separate from each other compared to the adhesive energy which is high implying that high energy is required to dominate the adhesion between unlike molecules (solid and water), therefore water tends to spread on hydrophilic surface (high surface energy) and bounce back on hydrophobic surface (low surface energy). Replacing water and solid by oil and water gives us the spreading coefficient of oil on water as a determination of whether oil cloak the water $S_{ow(a)} = \sigma_{wa} - (\sigma_{wo} + \sigma_{oa})$. To demonstrate the spreading coefficient effect on the water droplet, Dodecane and Kerosene were selected possessing negative and positive spreading value respectively. As can be seen water droplet can float on the Dodecane while in the case of Kerosene a thin film of oil cloaks the water droplet, disjoins it from the air and finally the droplet falls inside the oil.



Fig 10 a. Schematic of floating droplet on the oil with negative spreading coefficient, b. Schematic of droplet submergence inside the oil with positive spreading coefficient

The oil can completely or partially wet the surface whereas tops of the post can be submerged in the oil or remain dry respectively. Therefore, contact angle of oil and solid in air presence distinguishes these two cases. As mentioned above different configurations can be shaped and the corresponding surface energy per area is different.



Fig 11 a. Floating drop on Dodecane, b. Droplet submergence inside the kerosene

The stable thermodynamic state is obtained by comparing these surface energies. Suppose that a drop condensed on the oil-air interface., then surface area is no longer a spherical shape and three phase contact angles (three phase flow) is replaced by two phase flows. If (α, β, γ) are corresponding to air, water and oil phase, then surface energy of the system is measured by the following steps (case IV) [1]:

$$R_{\beta\gamma}\cos(\theta) = r = R_{\alpha\beta}\cos(\theta) , \theta + \varphi = 90, R_{\beta\gamma}\sin(\theta) = R_{\alpha\beta}\sin(\theta)$$

$$L_{\alpha\beta\gamma} = 2\pi r = 2\pi R_{\alpha\beta}\cos(\varphi) = 2\pi R_{\alpha\beta}\sin(\theta)$$

$$A_{\alpha\beta} = 2\pi R_{\alpha\beta}h_{1}, h_{1} = R_{\alpha\beta} - R_{\alpha\beta}\sin(\theta - \theta) = R_{\alpha\beta}(1 - \cos(\theta))$$

$$A_{\alpha\beta} = 2\pi R^{2}_{\alpha\beta}(1 - \cos(\theta))$$

$$A_{\beta\gamma} = 2\pi R_{\beta\gamma}h_{2}, h_{2} = R_{\beta\gamma} - R_{\beta\gamma}\sin(\theta - \varphi) = R_{\beta\gamma}(1 - \cos(\varphi))$$

$$A_{\beta\gamma} = 2\pi R^{2}_{\beta\gamma}(1 - \cos(\varphi)) = 2\pi R^{2}_{\alpha\beta}\frac{\sin^{2}(\theta)}{\sin^{2}(\varphi)}(1 - \cos(\varphi))$$

$$A_{\rho} = \pi r^{2} = \pi (R_{\alpha\beta}\cos(\varphi))^{2} = \pi R^{2}_{\alpha\beta}\sin^{2}(\theta)$$
volume drop $:\frac{4}{3}\pi R^{3}_{\alpha\beta}.f(\theta,\varphi) , f(\theta,\varphi):shape factor$

$$f(\theta,\varphi) = \frac{1}{4} \left\{ (2 - 3\cos(\theta) + \cos^{3}(\theta)) + \frac{\sin^{3}(\theta)}{\sin^{2}(\varphi)}(2 - 3\cos(\varphi) + \cos^{3}(\varphi)) \right\}$$

$$G - G_{0}(surface part) = \sigma_{\alpha\beta}A_{\alpha\beta} + \sigma_{\beta\gamma}A_{\beta\gamma} + \sigma_{\alpha\gamma}(A - A_{\rho}) - \sigma_{\alpha\gamma}(A)$$

$$G - G_{0} = \sigma_{\alpha\beta}A_{\alpha\beta} + \sigma_{\beta\gamma}A_{\beta\gamma} - \sigma_{\alpha\gamma}A_{\rho} - f(\theta,\varphi).\rho_{w}(\frac{4}{3}\pi R^{3})RT(\ln \frac{P}{P_{s}})$$

$$Surface free energy change Value tric free energy change Valu$$

(without considering line tension at tripleline)

For droplet on the flat surface (case I, III) by considering the $\varphi = 0$. Then shape factor can be obtained as: $f(\theta, \varphi) = \frac{1}{4} \{2 - 3\cos(\theta) + \cos^3(\theta)\}$ and the free energy difference can be modified.

As can be clearly seen the energy difference was changed due to the heterogeneous condensation. However, other mechanisms are possible such that a drop can settle on the super hydrophobic surfaces. For instance, in the case of circular posts the surface energy can be obtained by knowing the fraction of areas occupied by the interface of air-water, air-solid and oil-solid. If a,b,h are width, edge-to edge and height of the posts respectively then the fraction area occupied by a post

is
$$\Phi = 0.25\pi \frac{a^2}{(a+b)^2}$$
 and the fraction of surface area is as $r = 1 + \frac{\pi ah}{(a+b)^2}$, therefore $(1-\Phi)$ is the

fraction area between the top of the posts . Now if we consider the case which the gap between the

circular posts filled by the oil and then water drop settles on the oil then by knowing the fraction areas, surface energy per area can easily be obtained. In the figure (4), area by fraction Φ is occupied by water and solid, $(1-\Phi)$ occupied by water and oil, and $r-\Phi$ is the contact area between solid and oil. Therefore:

$$G - G_0(surface part) / area = \sigma_{ws} \Phi + \sigma_{wo}(1 - \Phi) + \sigma_{os}(r - \Phi) + \sigma_{wa}$$
¹⁴

In the case of oil-impregnated textured surface many other mechanisms are likely to occur. By comparing the surface area corresponding to the different cases, one can obtain the preferable



Fig 12 Water completely condensed on the micro textured surface

cases. Obviously, the geometry properties play a remarkable role in determining the surface energy and that's why lots of research are devoted on finding the optimal geometry. For instance, one question which can be posed is that whether water droplet can be condensed inside the impregnated oil rather than at the interface of oil and water. The answer to this question is negative due to the fact that for condensation to occur inside the oil according to the Eq(10), supersaturation should be reached inside the oil to decrease the free energy difference by Bulk free energy and on the other side , based on the Henry's law , the gas molecules can be dissolved in a solvent until saturation is reached . Drop can be condensed on the top of the post or on the oil layer. To determine which cases is preferable again, we can compare the surface energy corresponding to these case (considering the post geometry and oil properties) and the one which possess lower surface energy is more probable.

Until now we stablished the way to quantify the surface energy corresponding to the different cases. Here the three main cases are discussed in the order 1) micropost, 2) The gap between the pillars are filled by oils while the top post is exposed to air and 3) the oil completely cover the micropost and the water droplet initially condensed on the oil layer. Now let's derive the expression for surface energy corresponding to each cases (NOTE; we show the surface energy part by E to distinguish it from bulk or total free energy difference). Based on the definition of (r, Φ) we have:

$$E_2 - E_1 = A'\sigma_{LG} + A_p \left[\Phi(\sigma_{LS} - \sigma_{GS}) + (1 - \Phi)(\sigma_{LO} - \sigma_{OG})\right]$$

CASE III :

$$E_{1} = ((r - \Phi)\sigma_{OS} + \Phi\sigma_{OS} + \sigma_{OG}) A_{p} = (r\sigma_{OS} + \sigma_{OG}) A_{p}$$

$$E_{2} = A'\sigma_{LG} + A_{p} [(r - \Phi)\sigma_{OS} + \Phi\sigma_{OS}] + A''\sigma_{LO}$$

$$E_{2} - E_{1} = A'\sigma_{LG} + A''\sigma_{LO} - A_{p}\sigma_{OG}$$

Interesting to point that At case(III), by considering $A' = A_{\alpha\beta}$, $A'' = A_{\beta\gamma}$, $A_p = A_{\alpha\gamma}$ we reach to the same expression as (13) means that in this case the micropost properties are not considered and the behavior of condensed droplet depends on the properties of the oils.



Fig 13 a. Case(I) Water droplet on the micropost (Cassie state), b. Case(II) Gaps between posts are filled by oil (oil doesn't cover the top of the post, c. Case (III) the condensed droplet floats on the LIS

In this section, we tried to briefly introduce the condensation concept with regards to Gibb's free energy theorem. (Now by comparison the barrier energy between micropost and impregnated oil we can show which one is more preferable)

4.1.2 Comparing barrier energy

From classical nucleation theory, the work for cluster formation is given by (2), n is the number of molecules in the cluster and SR is the supersaturation, k is the Boltzman's constant, and E corresponds to the total interfacial energy of the cluster [1].

$$G - G_{0} = \Delta G = W(n) = -m\overline{R}T \ln\left(\frac{P}{P_{s}}\right) + E(\overline{R}: specific ideal gas constant)$$

$$PV = m\overline{R}T = nRT (\overline{R} = \frac{R}{molecular \ wight(mass / mole)})$$

$$W(n) = -nRT \ln\left(\frac{P}{P_{s}}\right) + E$$

$$N_{A}(Avogadro \ number) = \frac{number \ of \ molecules}{amount \ of \ matter(mol)} = \frac{N}{n}$$

$$K(Boltzmann \ Const) = \frac{R}{N_{A}} = \frac{Rn}{N} \Rightarrow nR = NK \ , \ SR = \frac{P}{P_{s}}$$

$$W(n) = -nRT \ln\left(\frac{P}{P_{s}}\right) + E \Rightarrow W(n) = -N.K.T \ .ln(SR)$$

For simplicity, the number of molecules in the cluster is shown by (n). Therefore:

$$W(n) = -nkT\ln(SR) + E$$
17

where v_m corresponds to the volume of a single molecule of condensate. Each cluster contains (n) number of condensate molecules. Therefore, adding the volume of molecules leads to the volume of the cluster:

n: number of condensate molecules in each cluster v_m : volume of each molecules $n.v_m = V$ (volume of cluster)

$$n = \frac{V}{v_m}$$
¹⁸

Since the shape of a cluster at the time of phase change occurring on the oil or substrate (heterogeneous condensation) is no longer spherical therefore by defining the shape factor both volume and surface area of the cluster should be modified.

$$\begin{split} \psi &= shape \ factor \\ V &= \frac{\pi}{3} R^3 . \psi \ and \ A &= \pi R^2 . \psi \ (if \ the \ cluster \ is \ spherical \ then \ \psi = 4) \\ E &= \gamma A \Rightarrow \quad A &= \pi R^2 . \psi \quad , \quad R = \left(\frac{3V}{\pi \psi}\right)^{1/3} \quad , \ A &= \pi \left(\left(\frac{3V}{\pi \psi}\right)^{1/3}\right)^2 . \psi = \pi \psi \left(\frac{3V}{\pi \psi}\right)^{2/3} \\ E &= \gamma \pi \psi \left(\frac{3V}{\pi \psi}\right)^{2/3} , \quad V = n v_m \ , \quad \gamma \pi \psi \left(\frac{3n v_m}{\pi \psi}\right)^{2/3} \ , \ n^{2/3} . \gamma \pi \psi \left(\frac{3v_m}{\pi \psi}\right)^{2/3} = n^{2/3} \beta \\ \beta \\ \begin{cases} E &= n^{2/3} \beta \\ W(n) &= -n . K.T . ln \ (SR) + E \\ \alpha \end{cases} \\ W(n) &= -n \alpha + n^{2/3} \beta \end{split}$$

19

We can now write the nucleation work function as,

$$W(n) = -n\alpha + n^{2/3}\beta$$
²⁰

where, $\alpha = kT \ln(SR)$ and $\beta = \psi \pi \left[\frac{3v_m}{\pi \psi}\right]^{2/3}$. As mentioned above the surface energy acts as an energy barrier means that by passing this barrier the formation of a drop occurs spontaneously otherwise the cluster undergoes a shrinkage. To find this critical work or energy which should be dominated, we can take derivative from the energy equation with respect to the number of molecules (n). By obtaining the critical number and substitute the value in the energy equation, the energy barrier can be calculated as following:

$$W(n) = -n\alpha + n^{2/3}\beta$$

$$\frac{dW}{dn} = 0.0 \implies -\alpha + \frac{2}{3}n^{-1/3}\beta = 0. \implies n^{-1/3} = \frac{3\alpha}{2\beta} \implies n^* = (\frac{2\beta}{3\alpha})^3$$

$$W(n^*) = W^* = -n^*\alpha + n^{*2/3}\beta \implies -(\frac{2\beta}{3\alpha})^3\alpha + (\frac{2\beta}{3\alpha})^2\beta = -\frac{8}{27}\frac{\beta^3}{\alpha^2} + \frac{4}{9}\frac{\beta^3}{\alpha^2} = \frac{\beta^3}{\alpha^2}\frac{4}{27}$$

$$W^* = \frac{\beta^3}{\alpha^2}\frac{4}{27}$$

$$\alpha = K.T.\ln(SR) \implies \ln(SR) = \frac{\alpha}{K.T} = \frac{\alpha}{K.T} = \frac{2\beta}{3n^{*1/3}}\frac{1}{KT} \implies SR^* = e^{(\frac{2\beta}{3n^{*1/3}}\frac{1}{KT})}$$

21

 SR^* (saturation ratio requires to form a cluster by the critical size n^*

We establish that the energy barrier for nucleation in each state can be estimated from the critical supersaturation (SR^{*} required to cause nucleation of a critical cluster of size n*). SR^{*} is a function of β which in turn depends on the surface energy. Therefore, the system with higher surface energy (barrier energy) requires higher supersaturation ratio to dominate the barrier by bulk energy compensation or in other words, system has higher critical saturation at which nucleation takes place. Now, we can compare the systems based on this concept. For the first comparison states I and III are considered. To determine which one is more probable to occur the condition below should be satisfied:

$$\frac{E_{III}}{E_{1}} < 1 \text{ or } (system III should have less critical saturation ratio to be more probable})$$

$$\frac{Ln(SR^{*})_{III}}{Ln(SR^{*})_{I}} < 1$$

$$\psi = (2 + \cos(\theta))(1 - \cos(\theta))^{2}$$

$$\frac{E_{III}}{E_{1}} = \frac{Ln(SR^{*})_{III}}{Ln(SR^{*})_{I}} < 1 = (\frac{\beta_{III}}{\beta_{I}}) < 1 \implies \frac{\beta_{III}}{\beta_{I}} = \frac{(\psi^{1/3} \cdot \gamma)_{III}}{(\psi^{1/3} \cdot \gamma)_{I}} = (\frac{\psi_{2}}{\psi_{1}})^{1/3} \cdot \frac{\gamma_{wo}}{\gamma_{wa}} < 1$$

$$system II : \gamma = \gamma_{wa}, \psi = \psi_{1}, \theta = \theta_{ws(a)}$$

$$system III : \gamma = \gamma_{wo}, \psi = \psi_{2}, \theta = \theta_{ws(o)}$$

The maximum value of ψ is (4) which corresponds to the spherical condensate (volume of sphere).

By knowing the contact angles of condensate on the surface in air and/or oil then the shape factor is obtained. Interesting to note that even if the ratio of interfacial tension is less than one, the shape factor ratio can be greater than one or vice versa. Therefore, determining which case is more favorable can be attributed to the contact angle and interfacial tension of condensate. The condition (III) is for the case when the oil cloak the condensate and subsequently the condensate is submerged into the oil and settle on the solid surface. If the spreading coefficient of oil on water in the presence of air $S_{ow(a)} < 0$. and the condensate doesn't completely spread on the oil $S_{wo(a)} < 0$. Then nucleation on the interface of oil-air is favorable than the case (I) If the following condition is satisfied, Eq. 23 [1]:

$$\begin{split} & \frac{E_{IV}}{E_{1}} < 1 \text{ or } \frac{\ln(SR^{*})_{IV}}{\ln(SR^{*})_{I}} < 1 \\ & G - G_{0}(surface part) = \sigma_{a\beta}A_{a\beta} + \sigma_{\beta\gamma}A_{\beta\gamma} - \sigma_{a\gamma}A_{p} \\ & \text{Surface free energy change} \\ & E_{IV} = \sigma_{a\beta} 2\pi R^{2}_{a\beta} (1 - \cos(\theta)) + \sigma_{\beta\gamma}2\pi R^{2}_{a\beta} \frac{\sin^{2}(\theta)}{\sin^{2}(\phi)} (1 - \cos(\phi)) \\ & \frac{\sigma_{\beta\gamma}\sin(\theta)}{\sin(\theta)} - \frac{(\frac{R_{\beta\gamma}\sin(\theta)}{\sin(\theta)})^{2}}{(R_{\beta\gamma}\sin(\theta))^{2}} & R^{2}_{\beta\gamma} \\ & - \sigma_{a\gamma} \pi R^{2}_{a\beta}\sin^{2}(\theta) \\ & \frac{\sigma_{a\beta}-\cos(\theta) + \sigma_{\beta\gamma}\cos(\theta)}{(R_{\beta\gamma}\sin(\theta))} & (R_{\beta\gamma}\sin(\theta))^{2} \\ & \frac{\sigma_{\beta\gamma}\sin(\theta)}{\sin(\theta)} \\ & force balance in x direction : \sigma_{a\beta}\cos(\theta) + \sigma_{\beta\gamma}\cos(\phi) = \sigma_{a\gamma} \\ & force balance in y direction : \sigma_{a\beta}\cos(\theta) + \sigma_{\beta\gamma}\sin(\phi) \\ & Base radios : R_{a\beta}\sin(\theta) = R_{\beta\gamma}\sin(\phi) \Rightarrow R^{2}_{\beta\gamma}\sin^{2}(\phi) = R^{2}_{I} \\ & E_{IV} = \pi\sigma_{\beta\gamma}R^{2}_{I}\cdot\xi \\ & \xi = \left[\frac{2(1 - \cos(\phi))}{(1 + \cos(\phi))} - \cos(\phi)\right] + \frac{\sin(\phi)}{\sin(\theta)} \left[\frac{2(1 - \cos(\theta))}{(1 - \cos^{2}e^{(1 - \cos(\theta))(1 + \cos(\phi))})} - \cos(\phi)\right] \\ & \xi = \left[\frac{2}{(1 + \cos(\phi))} - \cos(\phi)\right] + \frac{\sin(\phi)}{\sin(\theta)} \left[\frac{2}{(1 + \cos(\theta))} - \cos(\theta)\right] \\ & F = \left[\frac{2}{(1 + \cos(\phi))} - \cos(\phi)\right] + \frac{\sin(\phi)}{\sin(\theta)} \left[\frac{2}{(1 + \cos(\theta))} - \cos(\theta)\right] \\ & V = \frac{\lambda}{3}\pi R^{3}_{I} \Rightarrow R_{I} = (\frac{3V}{\lambda\pi})^{1/3} \Rightarrow R_{I}^{2} = (\frac{3V}{\lambda\pi})^{2/3} \\ & E_{IV} = \pi\sigma_{\beta\gamma}(\frac{3V}{\lambda\pi})^{2/3}.\xi \quad OR \quad \pi \quad \sigma_{\beta\gamma}(\frac{3V}{\lambda\pi})^{2/3}.\xi \Rightarrow \quad E_{IV} = \pi\sigma_{a\beta}(\frac{3V}{\lambda\pi})^{2/3}.\xi \cdot \frac{\sin(\theta)}{\sin(\phi)} \\ & \frac{e_{a\beta}\sin(\theta)}{\sin(\phi)} = \frac{\xi \cdot \frac{\sin(\phi)}{\sin(\phi)}}{(\lambda^{2}\psi)^{1/3}} = \frac{\xi \cdot \frac{\sin(\phi)}{\sin(\phi)}}{(\lambda^{2}\psi)^{1/3}} \Rightarrow \frac{E_{IV}}{E_{I}} = \frac{\xi \cdot \frac{\sin(\phi)}{\sin(\phi)}}{(\lambda^{2}\psi)^{1/3}} < 1 \end{aligned}$$

Accordingly, we can also compare cases (IV and III) together to investigate the possibility of nucleation on the oil interface as well as within the oil medium.

$$\frac{E_{IV}}{E_{III}} < 1 \quad ; \frac{E_{IV}}{E_{III}} = \frac{\pi \gamma_{wo} (\frac{3V}{\lambda \pi})^{2/3} . \xi}{\gamma_{wo} \pi \psi (\frac{3V}{\pi \psi})^{2/3}} = \frac{\xi}{\lambda^{2/3} \psi^{1/3}} \qquad \Rightarrow \frac{E_{IV}}{E_{III}} = \frac{\xi}{(\lambda^2 \psi)^{1/3}} < 1$$

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By comparing the surface energies in each of the states I, II, III and IV and based on the ratio of surface tension and corresponding contact angles between the interfaces - a regime map is determined [1], which demarcates the various regions where nucleation may occur.

24



Fig 14 b. shows nucleation conditions in the oil that is preferred over nucleation in vapor. c. The map demonstrating nucleation conditions at the interface of oil and air that is preferred over nucleation at the interface of solid and air. d. The map showing where nucleation condition is preferred at the interface of oil and air over nucleation within the oil for different surface wettablities.

4.1.3 Nucleation inside the oil.

This section considers the possibility of nucleation within an immiscible oil. Nucleation rates for oils are found to be like those in air for identical super saturation conditions. A question such as whether the vapor get supersaturated in the liquid when it is subcooled below the dew point, is discussed here. This allows us to examine whether homogenous nucleation is feasible irrespective of the nature of lubricating liquid.

To understand this better lets, employ Henry's law, $Cs = H_v P_v$, where H_v is the Henry's constant of solubility in vapor at a given temperature, the partial pressure at a given temperature, T_v and Cs_v , is the maximum volume of vapor absorbed per unit volume. One expects the amount of dissolved vapor to decrease with increase in temperature. Cs gives us the theoretical limit of the amount of dissolved vapor that may be present at a given temperature. When we sub-cool, the liquid we have lesser dissolved vapor than the theoretical limit which results in the liquid being under-saturated without no prospect of being super saturated as calculations for Cs using Henry's law limit the maximum solubility. Homogenous nucleation thus is unlikely given the unavailability of adequate dissolved vapor in the liquid for the process of nucleation to be initiated. As the temperature increases inside the liquid the molecules tend to leave the liquid due to the high kinetic energy to provide the equilibrium condition and when the temperature is decreased the solubility of vapor molecules increases inside the liquid. However, there is a limitation for such an increase until the solution reaches the saturation condition. We can conclude that nucleation occurs at the air-oil interface or on the other words any condensed droplets were generated as a heterogeneous condensation at the air-oil interface layer not within the bulk oil.

This points to a theory that when a vapor is introduced in the liquid film, it gets diffused and mixes with the liquid and thus even the continuous supply of vapor species in the oil is not able to supersaturate the oil and it stays under-saturated.

4.2 Dew collection

To gain insight to the mechanisms which likely to take place after condensation it is worth mentioning that depending on the droplet growth rate on the oil surface and spreading velocity rate of oil on the water a drop can stay float and partially wet the oil or submerged within the oil (cloaking). Droplet growth on the oil surface is induced by two mechanisms 1) diffusion 2) coalescence. Because of the difference in vapor concentration close to the drop surface and far from the surface and by diffusion mechanism a drop can adsorb the vapor molecules and grow while in the coalescence the two drops are brought close to each other by an external force and then the oil film between the two-adjacent drop can be ruptured by the intermolecular force (Van der waal) and disjoining pressure which in the latter is a function of viscosity of the oil. Increasing the viscosity delays the rupturing compared to the low viscosity oil and droplet grows by diffusion is more probable. Now the question can be posed here is that in which cases drops can grow faster. In case of the non-cloaking oil, the two mechanisms of diffusion and coalescence both contribute in droplet growth while in the cloaking case we already showed that it is unlikely that the vapor molecules reach supersaturation within the oil and coalescence plays an important role.

One of the main objective of this study is to measure the amount of dew collected by designed textured surfaces. Here we pay attention to the behavior of water droplets after condensation specifically the motion of droplets on the LIS. The gravity (weight of the droplet) acts as a driving force while viscos dissipation induced by viscosity of oil and velocity gradient plays as a resistant force. To quantify these forces, it is worth mentioning that the mass center of the droplet starts moving by inclining the surface and the contact line between water and oil gets a certain value however the oil points attached to the bottom of the textured have zero velocity. Therefore, in both oil layer with thickness h_o and water drop with mass center height of h_w shear stresses are formed and the magnitude of these shear stresses at the contact line of oil-water should be same.

$$\tau_{w} = \mu_{w} \frac{\partial u}{\partial y} \quad \mu_{w} \frac{V - V_{i}}{h_{w}}, \ \tau_{o} = \mu_{o} \frac{\partial u}{\partial y} \quad \mu_{o} \frac{V_{i} - 0}{h_{0}}$$

$$\tau_{w} = \tau_{o} \Rightarrow \frac{V - V_{i}}{V_{i}} = \frac{\mu_{o}}{\mu_{w}} \frac{h_{w}}{h_{o}} \Rightarrow \frac{V}{V_{i}} = 1 + \left(\frac{\mu_{o}}{\mu_{w}} \frac{h_{w}}{h_{o}}\right)$$

$$25$$

Since the value of the parenthesis is greater than one it depicts that the interface velocity of oilwater has negligible velocity leading to the rolling water droplet instead of sliding. The velocity found by the scaling analysis is used in making the force balance for a drop rolling on the oil. Considering the steady state - viscos flow (ignoring the inertia term) and noting that the gradient of shear stress would be zero since the velocity gradient was assumed to change linearly, then viscos dissipation term dissipates the motion of droplet induced by gravity. Hence the driving force (weight) should be balanced by opposite force coming from the dissipative energy and pinning force. If a drop possesses the same advancing and receding contact angle, then the whole system is in balance while in hydrophobic surfaces the advancing and receding contact angles are not the same (advancing>90 and receding <90) then projection of the surface tension forces on the surface creates the driving force and surface applies the opposite force on the droplet called pinning force equal and in the opposite direction of deriving force.



Fig 15 Schematic of water droplet rolling on a lubricant-impregnated surfaces 26

The maximum velocity is obtained when the surface is placed vertically [103]. Also, the velocity is inversely increases by oil viscosity. If the oil cloaks the condensed droplet, then inertia and gravitational as well as viscous dissipation can be neglected. Cloaking can lead to decreased efficiency by depletion of impregnated oil as well as contaminate the condensed drops.

4.3 Results

The Fig.16 depicts relation between SR^* and contact angles between water- air and water-oil [1]. The plot shows that SR^* for nucleation of water on textured surface (salinized with OTS) in air is higher than textured surfaces (salinized with OTS) impregnated with selected different oils, that implies that for nucleation to occur on surfaces coated with OTS will require more time and higher



Fig. 16 Plot between critical supersaturation ratio (SR*) for nucleation for variable contact angles of water on the solid surface in presence of air and oil as a function of surface wettability in air $\Theta ws(a)$, in oil $\Theta wo(o)$. Plot also shows SR* for nucleation of water on a OTS surface in air and OTS surface immersed in different oils. SR* is highest for OTS.

 $\Delta T_{subcooling}$ as compared to the oil impregnated on the OTS textured surfaces. In the foolowing study, oils that require lower *SR** compared to OTS coated surface is used to study formation and collection rate on them.

4.3.1 Results on microposts sample

In this section, experimental data for calculating nucleation rate is showed for different surfaces and based on the data (Fig. 17) it can be noticed that $\Delta T_{subcooling}$ for unimpregnated surface is remarkably higher than all the LIS cases. So, it can be concluded that at the first step, LIS is more preferable than unimpreganted surface. For example, the $\Delta T_{subcooling}$ difference between BMIm and unimpregnated surface is 76% which depicts that there is faster nucleation for BMIm.



Fig. 17 Plot between ΔT subcooling (K) and surfaces (OTS coated textured surface, OTS coated surface with different oils impregnated). Plot shows when nucleation occurred after reaching the dew point. $\Delta T = T$ nucleation-Tdp

This behavior can also be predicted from free energy difference calculations (equation set 15), such that, for BMIm is $-2.01*10^{-03}$ J and for unimpregnated is $-1.57*10^{-06}$ J (Table 4 oil properties). The Fig. 18, shows the number of droplets being formed on the surface with respect to time, droplet count for BMIm is higher than unimpregnated surface. Also, comparing the performance of ethyl

cinnamate (ΔE =-1.64* 10⁻⁰² J) with respect to unimpreganted, it is theoretically and experimentally proved to be better than unimpreganted surfaces. According to the following equations:

$$J[m^{-3}s^{-1}] = \rho Z J \exp\left(\frac{-\Delta G_{barrierenergy}}{K_B T}\right)$$
$$\exp\left(\frac{-\Delta G_{barrierenergy}}{K_B T}\right): The probability of occuring condensation$$
$$K_B T: Thermal energy \quad , \quad \rho: The number of nucleation sites per unit volume$$

The free energy difference gives a direct relation to the nucleation rate, i.e. higher energy difference gives lower nucleation rate. To present a comparison between two LIS cases, here considered, Ethyl cinnamate(EC) and 1-Chloronapthalene (1-CN), the ΔE for EC is -1.64* 10⁻⁰² J whereas for 1-CN is ΔE =-1.2860304* 10⁻² J saying nucleation between these two cases, will happen sooner on EC as the energy difference barrier is lower than compared to 1CN. In the Fig. 17, the $\Delta T_{subcooling}$ for 1-CN (3.6K) is higher than compared to EC (1.5K).



Fig. 18 Plot shows droplet count with respect to time. Here, different oils are considered to compare the increase in droplet count within a frame, 1CN is 1-Chloronapthalene, EC is Ethyl cinnamate.

The Fig. 19, shows the water formation and collection data on microposts (OTS coated) and microposts(OTS coated) immersed in different oils. It can be seen the amount of water formation and collection for unimpregnated surfaces is lower than LIS. To make a firm conclusion for comparison of LIS case, here BMIm and EC, the water formation is higher for BMIm than for EC, reason being the nucleation energy barrier.



Fig. 19 Plot shows water formation and collection on $10\mu m$ posts. Unimpregnated surface is OTS coated 10 μm textured surface and others are OTS coated textured surfaces immersed in different oils.

Also, when compared for water collection, EC has more amount of water than BMIm because the viscosity of BMIm is higher than EC, thus concluding high viscosity results in lower shedding velocity. Compared to 1-CN that has less viscosity, the shedding is greater than BMIm, EC. The collection rate also depends on the nucleation rate, therefore, when the nucleation rate is higher, the collection rate is higher as well.

To select the best performing oil in terms of water collection, EC has better collecting rate because the viscosity of EC is lower than BMIm, even though considering its higher nucleation energy barrier than BMIm. The nucleation in EC leads to droplet growth, further shed off the surface due to gravity and thus collection is higher. Whereas, in BMIm, the amount of water getting formed is being held for collection due to the high viscosity of the oil.



Fig. 20 Plot shows area being covered by droplet on different surfaces (OTS coated textured surfaces and OTS coated surfaces immersed in different oils).

From the Fig. 20, the area covered by water droplet is similar for BMIm and EC, showing that even after coalescence the shedding of droplet is being difficult for BMIm due to the viscosity. But for EC, the droplet growth is similar to BMIm but resulting in higher collection due to lower viscosity that is promoting ease of mobility. From the Fig. 19, it is evident that more water formation happens when there is lower nucleation energy barrier. In other words, according to the classical nucleation theory, the rate of nucleation slows exponentially with the height of the free energy barrier.

4.3.2 Results on nanograss sample

This part of the experiments is done using nanograss samples (coated with OTS) and nanograss (coated with OTS) samples immersed in different oils to study the difference in performance of surfaces when compared to microposts.



Fig. 21 Plot water formation and collection on nanograss sample. Unimpregnated surface is OTS coated nanograss textured surface and others are OTS coated textured surfaces immersed in different oils.

Firstly, the similar trend was noticed in formation and collection of water with respect to unimpregrnated samples and LIS, refer Fig. 21. The formation and collection is higher in LIS, additionally the behavior of EC is justified to be higher than BMIm due the reason of viscosity as stated in the previous section. The free energy difference with BMIm is lower as compared to unimpregnated nanograss sample and also oils like EC. Yet, the formation and collection is higher due to the effect of viscosity.

4.3.3 Comparison between microposts and nanograss samples

Comparing the results for water formation on microposts and nanograss, Fig. 22, it is noticed that

the water formed is higher for all the cases in nanograss. This behavior is due to the geometry, where microposts hold less amount of oil as compared to nanograss textures. From table 3, Φ parameter, gives the areas occupied by silicon and rest of the area available for oil to be impregnated.

Sample	а (width) µm	b (spacing) μm	h (height) μm	$\Phi = 0.25 \Pi a^2 / (a+b)^2$	$1-oldsymbol{\phi}$
Microposts	10	10	10	0.196	0.804
Nanograss	0.05	0.1	10	0.087	0.913

Table 3. Sample texture dimensions, comparison between Φ parameter

As calculated, in nanograss around 91% of the area is available for oil whereas for microposts its 80%. Some of the oils considered in the study have high vapor pressure and therefore by the time the process of condensation to start, the oil would evaporate. In table 4, the oils highlighted have high vapor pressure.



Fig. 22 Plot shows comparison between water formation on 10 μ m posts and on nanograss textured samples. There are some oils with no data because they have high vapor pressure and thus evaporates before the condensation process could start.

4.4 Conclusion

To sum up, the LIS is for the oils that have following properties: low vapor pressure, non – cloaking oil, immiscible with water, low viscosity. In the study, it has been concluded that cloaking oil results in low water collection, but interestingly, Olive oil is a cloaking oil and has demonstrated the highest collection rate compared to other oils considered. This study can further be implemented for the oils that are used for daily use cooking and therefore safe for the health, to extract water from the thin layer of air above the surface.

Oils	ρ	Vapor	v	γωο	γoa	γwa	S _{wo(a)}	S _{ow(a)}	Θ_{wa}	Θ_{wo}
	(g/ml)	pressure	(cSt)	(mN/m)	(mN/m)	(mN/m)	(mN/m)	(mN/m)		
		(mmHg)								
Perfluorodecalin	1.9	6.25	2.7	56.6	19.3	72.2	-109.5	-3.7	31.3	138.5
Tetradecane	0.8	6.8E-3		52.2	26.6	72.7	-98.3	-6.1	32.3	132
Decane	0.7	1.002		52.0	23.8	72.7	-100.9	-3.1	24.5	144.6
Dodecane	0.7	8.8E-2	1.3	52.8	24.9	72.7	-100.6	-5.0	30.5	135.7
1-CN	1.2	2.9E-2	2.9	40.7	42.1	71.3	-70	-11.5	30	118.8
Ethyl cinnamate	1.0	3E-05		21.4	37.9	39.3	-22.8	-19.9	32.0	77.7
BMIm	1.4	3E-05	34.1	13.7	37.0	42.0	-18.7	-8.7	18.6	101.8

Table 4 Properties of oil

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