

Pontificia Universidad Católica de Chile Physics Department

Wetting Properties of n-alkane thin films to understand the adherence mechanism of artificial membranes on silicon substrates

by

Diego Ignacio Díaz Díaz

Thesis presented to the Physics Faculty of the Pontificia Universidad Católica de Chile in partial fulfillment of the requirements for the degree of Master in Physics.

SUPERVISOR	:	Dr. Ulrich G. Volkmann (PUC, Chile)
CO-SUPERVISOR	:	Dr. Tomas P. Corrales (USM, Chile)
Correctors	:	Dr. Donovan Díaz (PUC, Chile)
Correctors	:	Dr. Griselda García (PUC, Chile)

August, 2017

Santiago, Chile ©2017, Diego Ignacio Díaz Díaz

Acknowledgements

Agradezco a SURFLAB UC por permitirme ser parte de su equipo de trabajo, en especial al profesor Ulrich Volkmann por su gran paciencia e interés al enseñar, a Tomás Corrales por su importante guía y consejos para la realización de este trabajo. A María José por su disposición a resolver dudas y enseñarme el arte de la limpieza de muestras. A Nicolás por involucrarme en este gran grupo de trabajo.

A mis padres por los valores inculcados y apoyo incondicional, el cual me permitió alcanzar mis metas y ser una mejor persona. A mis hermanos Sebastián y Camila que han servido como modelo a seguir y a mi sobrino Sebita que llegó al mundo a alegrar la vida de todos.

Quiero agradecer especialmente a Andrea Cid por ayudarme en un momento difícil de mi vida con su guía, paciencia y empatía. Me recibiste como un avión de papel roto al cual reparaste, le enseñaste a afrontar las embestidas del viento y echaste a volar otra vez. Ese avión sigue volando y lleva mis sueños y metas hasta lo más alto. Muchas gracias por todo.

Contents

A	ckno	wledgements	i
\mathbf{A}	bstra	uct	v
1	Inti	coduction	2
	1.1	Alkanes	3
	1.2	Dip-Coating	4
		1.2.1 Nanopatterns Morphology	5
		1.2.2 Coverage, velocity and morphology	7
	1.3	Contact Angle	8
		1.3.1 Contact angle calculation method	10
	1.4	Contact Angle Hysteresis	12
	1.5	Wettability models	12
	1.6	Artificial Membranes	15
2	Exp	perimental Setups	17
	2.1	Dip-Coater	17
	2.2	Dip-coater calibration	19
	2.3	Contact Angle Measurement Setup	20
	2.4	Analysis software ImageJ	23
	2.5	Atomic Force Microscopy	26
	2.6	Scanning Electron Microscope (SEM)	27
3	Res	sults and Discussion	29
	3.1	Influence of cleaning in Contact Angle	29
	3.2	Contact Angle dependence on withdrawal velocity	32
	3.3	Contact Angle in different directions	34
	3.4	Coverage vs. Velocity	34

	3.5	Contact Angle vs. Coverage		
	3.6	Alkane motion	38	
	3.7	AFM Measurements		
		3.7.1 Scanning of a sample immersed in water: Samples C3203,		
		C3240, and C3246 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots	42	
		3.7.2 Scanning after drop evaporation: Samples C3207 and C3204 .	46	
	3.8	Cassie Model	47	
	3.9	Contact Angle Hysteresis	49	
	3.10	Morphology of Single Phospholipidic Bilayers by Velocity-Controlled		
		dip-coating \ldots	50	
4	Con	clusions and Future Work	53	
Bi	Bibliography		56	

Abstract

In this work we present a study of the wetting properties of silicon samples coated with a single layer of n-alkane molecules that self-assemble perpendicular to the surface. The types of molecules studied here are n-alkane chains, mainly n-dotriacontane $(n-C_{32} H_{66})$, that were deposited on silicon substrates with a thin native silicon oxide layer (15Å). The thin films were prepared by Dip-Coating technique in a $C_{32} H_{66}$ /n-heptane solution. The techniques used to characterize these films are Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM).

In this research a contact angle setup was developed to measure wettability of submonolayer films. An influence of morphology and coverage on the contact angle was found. Moreover, alkane molecules migrate much like a reverse coffee-ring effect after drop evaporation, forming complex tail-like morphologies.

This research is relevant to understand alkane adhesion on silicon substrates, which is related with artificial membrane fabrication, which are used for biosensors applications. Micro-structured pattern like stripes could be applied as templates for other materials, especially considering the possibility of creating homogeneous surfaces with nanometer thick films.

Chapter 1

Introduction

Thin films have a wide range of applications in industrial processes in the semiconductors industry and biological applications. There are different types of thin films that can be made by Dip-Coating techniques, which are relevant to the area of nanotechnology and organic electronics.

In this work, we present research into contact angles for thin films that self assemble in different submonolayer coverage structures. The investigation of contact angles corresponding to coated samples gives us an idea of wetting control and properties of the surfaces. Therefore, such knowledge is very important for advances related to the conservation of resources such as water collection from the fog Camanchaca [1] and transport through hydrophobic gradients [2].

The thin films studied are made using dotriacontane (C_{32} H_{66} or C32) and are grown on Si/SiO₂ substrates. In this chapter we will make a review and description about this alkane; in particular their molecular ordering and morphology on silicon surfaces. Furthermore, we will explain a method to calculate the contact angle for a liquid on a surface, which is fundamental to undestanding the interactions in solid-liquid-gas interfaces, from the perspective of complete, partial or dry wetting properties.

1.1 Alkanes

Alkanes are a type of hydrocarbon structured through covalent bounds. They are composed of Carbon and Hydrogen, two of the most abundant atoms of nature. These compounds belong to what we call organic matter. Although the alkanes presented in this work are one of the simplest compounds in the nature, the complete understanding of their growth mechanism, structure and phase transitions is an important foundation for the analysis of more complex molecules.

In this investigation we used n-dotriacontane, which is a n-alkane distributed in lineal chain (See Figure 1.1) and can be adhered to silicon surfaces. These surfaces usually have a native oxide layer of ~ 15Å.



Figure 1.1: Chain molecules of n- C_{32} H_{66}

Alkanes are relevant for industrial applications such as prototype or model systems of more complex polymers and the fabrication of lubricants [2]. We can also find other types of structures with branched or ring form (See Figure 1.2).



Figure 1.2: Predominant types of molecular alkanes

According the characteristics of n-alkanes, we can mention their low reactivity and apolarity. This last quality implicates insolubility in water, i.e, hydrophobicity. It is possible to find these molecules in solid, liquid and gas states [3]. Solid states can be found in molecules with more than 20 atoms of Carbon at room temperature (293 K) present bulk crystallization due to London Forces. These attractive weak forces are a type of *Van der Waals* forces that exist owing to electron space charge interaction [4]. The magnitude of London forces depends on the molecular length and can affect thermodynamic features such as evaporation temperature of the material.

1.2 Dip-Coating

Dip-Coating is a coating technique for substrates that allows the creation of a thin film. The process consists in dipping a substrate into a solution, and then the sample is withdrawn with a set velocity. The coating can be created during the dive and withdrawal, because there is a dependency on the velocity, tipically at the soluton/air interface. When the substrate is withdrawn of the solution, the film grows as the solvent evaporates leaving behind the coating.

For many years dip-coating has been used for the fabrication of thin films. Actually, this is the oldest coating technique and holds some industrials applications such as grip to hand tools, such as pliers and clippers. Also, this technique is applied in sol-gel processes to make metal oxides, which are relevant in medicine, opto-mechanic and thin films for solar control applications [5].

In this work we use silicon surfaces as substrates coated with C32 dissolved in n-heptane (C_7H_{16}) , which acts as a solvent. The coating is produced within the solvent evaporation regime for low velocities [Figure 1.3] or the solution entraiment (Landeau-Levich-Deryaguin regime) [Figure 1.4] for high velocities [6,7].

The silicon substrates were cleaned cleaned using Tidswell method [8], that removes carbon impurities without affecting the oxide layer. This technique consists in the application of a solution of 70% sulfuric acid (28 mL H_2SO_4) and 30% hydrogen peroxide (12 mL H_2O_2) heated at 90°C over 30 min. However, we made some modifications to improve the method. Such improvements are the previous cleaning of the substrates with 2-propanol ($C3_{H8}O$) in order to remove impurities thourougly. Furthermore, the heating was performed during 40 min with the same goal.

The structure formed by alkanes over silicon has been studied using atomic force



Figure 1.3: Evaporation Regime: The solvent evaporates leaving behind the coating.

microscopy, elipsometry an X-ray diffraction [9-12]. These analysis showed that the C32 molecules on silicon surface self-assemble in multilayers. As shown in the Figure 1.5, where we have 2 layers of molecules with their long axis parallel to the substrate [12]. These parallel bilayers are followed by layers with molecules with their long axis perpendicular to the substrate.

In our experiment, we form a single perpendicular layer of C32 by dip-coating from a solution with 15mg of C32 disolved in 20 mL of n-heptane. The solute and solvent concentrations were made in accordance with M. Bai *et al.* [13][14][15], who made thin films through manual dip-coating at low velocities. Their research demostrated that for lower concentrations up to 20mg of C32 disolved in C7, the thin films on substrate do not present more than one perpendicular layer of ~ 4.2 nm.

1.2.1 Nanopatterns Morphology

Although M. Bai *etal.* had controlled the C32 concentration dissolved in nheptane, they could not quantitatively control the withdawal velocity during dipcoating because it was made manually with velocities slow enough to produce almost no bulk material in the film. However, T. Corrales *et al.* [16] studied the nanopatterns formed in the perpendicular layer of C32 films with controlled speed, using the C32 concentration described by M.Bai. Therefore, it was possible to determinate speed ranges where one can see the presence of nanopatterns named as *Dragonflies* and



Figure 1.4: Landeau-Levich-Deryaguin Regime: The coating does not depend on the evaporation but also the liquid dragged up due to velocity.



Figure 1.5: C32 molecule on the native oxide layer of a silicon surface followed by parallel bilayer of 1.2 nm and a pill of perpendicular layers of 4.3 nm.

Stripes [Figure 1.6], which define a relation between C32 coverage and withdrawal velocity.

T. Corrales's dip-coating experiments considered a speed range of 0.007 mm/s $\lesssim v \lesssim 1.7$ mm/s. Figure 1.6 shows SEM (scanning electron microscopy) images for Dragonflies and Stripes. We can see at $v \leq 0.17$ mm/s that molecules present a branched structure or dentritic named *dragonflies*. At $v \approx 0.25$ mm/s, the dragonfly length increases, particularly in the direction parallel to the withdrawal velocity. Otherwise, for v = 1 mm/s there are nanopatterns with *Stripes* form parallel to the withdrawal direction.



Figure 1.6: Scanning Electronic Microscope images (SEM) that show the mophologies of C32 films for different velocities. a) 0.03 mm/s, b) 0.08 mm/s, c) 0.17 mm/s, d) 0.25 mm/s e) 0.5 mm/s f) 1mm/s. (Image from [16])

1.2.2 Coverage, velocity and morphology

Coverage means the percentage of coating of some compound on the substrate. For the case of C32 on silicon there is a interdependence between 3 important aspects: Coverage, withdrawal velocity and morphology[16]. Figure 1.7 show the presence of dragonflies for the range of withdrawal velocities 0.007 mm/s < v < 0.25 mm/s, where one can note a critical speed of $v_c \sim 0.15$ mm/s corresponding to the lowest coverage of the measurements. This inflexion point represents a transition between evaporative and Landau-Levich-Deryaguin regimes. Above $v \sim 0.25$ mm/s, the morphology shows a radical change and by initiating the stripe phase.

There are two regimes in the Figure 1.7 that describe the alkane adhesion on the silicon. The first is the evaporation regime (for $v < v_c$), where C32 film is formed when the heptane evaporates after substrate is withdrawn from the solution, and no liquid film forms in the substrate. The second Regime is the *entrainment regime* or regime I($v < v_c$), within which the increasing speed entraints more solution in the withdrawal direction and thus the alkane concentration grows during the solvent evaporation. This is named Landau-Levich-Deryaguin (LLD or regime II) speed dependent regime. Here a liquid film is formed and depends sensitively on



Figure 1.7: Relation between withdrawal speed and coverage of a silicon substrate. From ~ 0.25 mm/s the stripe structure regime is initiating. There are two important regimes distinguished for the formation of the film: 1) evaporative and 2) entrainment. (Image reproduced from [16])

the withdrawal velocity, because film thickness h varies with speed according to $h \propto v^{2/3}[6]$.

One can see in Figure 1.7 a third regime: *The gravity-limited entrainment regime*. This regime despite the number of measurements displayed suggests the speed is not high enough to entrain more solution, hence a limit is reached and the coverage remains constant. Furthermore, substrates only have a half of their area covered by stripes, showing it is possible to achieve similar coverages between high and low velocities.

1.3 Contact Angle

The Contact Angle (CA) is the angle formed by a liquid upon contact with a surface. This is related directly with the wetting characteristic, that is, the way a liquid flows on a surface. Therefore, one can distinguish certain angles in order to determinate whether or not a surface has a degree of affinity with a liquid. When the liquid is water, one can define a surface as hydrophilic or hydrophobic considering a range of contact angles.

The CA measurement allows insight into the surface modification brought about by certain thin films deposition techniques, by noting the wetting variations. The importance of CA is valuable for characterizing coating paintings, herbicides deposited on the leaf surfaces to prevent insect pests in plantations [18].

It is necessary to introduce Young's equation to describe the wettability of thin films. This equation lets one understand the meaning of why water has a CA higher for hydrophobic surfaces than for hydrophilic. If a drop of water wets a solid surface, there are two posibilities: 1) the liquid totally spreads out on the surface (contact angle $\theta_c = 0^\circ$); or 2) the solid is not completely wet and one drop forms an ellipsoid or semisphere and so exists a finite CA. For the second case, we have three contact phases: solid, liquid and vapor [Figure 1.8], thus the Young equation relates CA with surface tension forces at the three-phase-line: liquid-vapor γ_{LV} , solid-vapor γ_{SV} and the interface solid-liquid γ_{SL} :

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos(\Theta_c) \tag{1.1}$$



Figure 1.8: a) Interaction of surface tension forces at the three phase-line in a solid surface. b) Surface tension forces in a system with three different liquids (Image from [18]).

If the surface tension force at solid-vapor is higher than the surface tension at the solid-liquid ($\gamma_{SV} > \gamma_{SL}$), then the left side of the Young equation (1.1) will be positive and therefore $\cos(\Theta_c)$ will be positive leading to a CA smaller than 90°. A positive CA describes a hydrophhilic surface. Otherwise, if the solid-vapor interface is energetically less favorable than solid-liquid ($\gamma_{SV} < \gamma_{SL}$), then the CA will be higher than 90° because $\cos(\Theta_c)$ is negative. This case describes a hydrophobic surface . Figure 1.9 illustrates both the described cases.

 2α



Figure 1.9: a) hydrophilic surface with water contact angle less than 90° ; (b) hydrophobic surface with water contact angle greater than 90° and (c) superhydrophobic surface with water contact angle larger than 150° (Image from ref. [19]).

1.3.1 Contact angle calculation method

Contact angle calculation requires an adequate setup and methodology. Figure 1.10 illustrates the method used in this work, considering a 2 μ L 2-D droplet on a silicon surface. The idea behind this method is to fit a circumference around the droplet. The following description will show the demostration of the values of angles 1, 2, 3 and 4, and their relation with the contact angle (θ_c).

Let AF be the arc that represents a droplet with diameter b and height h, fitted to a circunference with a ratio r. \overline{DA} and \overline{CD} are tangents to the circunference. We call \angle CAD α and therefore:

$$\overline{DA} \perp \overline{AB}; \overline{DC} \perp \overline{CB}$$

$$\Rightarrow \angle CAB = \angle BCA = 90^{\circ} - \alpha, \text{ but } \overline{AB} = \overline{BC}$$

$$\Rightarrow \triangle ABC \text{ isosceles and } \angle CAB = \angle BCA = 90 - \alpha$$

$$\Rightarrow \angle ACD = \alpha; \ \angle ABC = 180^{\circ} - \angle CAB - \angle BCA = 180^{\circ} - 90^{\circ} - (90^{\circ} - \alpha) = 10^{\circ}$$



Figure 1.10: Schematic of the method used to calculate θ_c of water droplet on a surface. A circumference is set around of droplet and the curvature radius is measured.

$$\Rightarrow \angle EAB = 180^{\circ} \cdot 90^{\circ} \cdot 2\alpha = 90^{\circ} \cdot \alpha$$
$$\Rightarrow \angle CAE = -90^{\circ} \cdot 2\alpha = 90 - \alpha - (90^{\circ} \cdot 2\alpha) = \alpha$$
$$\therefore \angle 1 = \alpha; \ \angle 2 = 90^{\circ} \cdot \alpha; \ \angle 3 = \angle 4 = \alpha$$

Using the definition of θ_c and according to Figure 1.10 one obtains $\theta_c = 2\alpha$. Thus, we have by Pitagoras:

$$r^{2} = \left(\frac{b}{2}\right)^{2} + (r - h_{1})^{2} \tag{1.2}$$

$$\iff b^2 = 4[r^2 - (r - h_1)^2]$$
 (1.3)

$$\iff b = 2\sqrt{r^2 - (r - h_1)^2} \tag{1.4}$$

Thus, the relations for b and r are obtained, and α can be solved via the following function:

$$\tan(\alpha) = \frac{h_1}{\left(\frac{b}{2}\right)} = \frac{2h_1}{b} \tag{1.5}$$

$$\iff \alpha = \arctan(\frac{2h_1}{b}) \tag{1.6}$$

$$\iff \theta_c = 2\arctan(\frac{2h_1}{b}) \tag{1.7}$$

Therefore, measuring the height h_1 of droplet and the radius *b* applied to equation 1.7, one can calculate θ_c .

1.4 Contact Angle Hysteresis

Contact Angle Hysteresis (CAH) is a phenomenom related to the wetting of surfaces by droplets of liquids. It finds importance for industrial applications such as slipping droplets, evaporative self-assembled and coating techniques [19]. The understanding and control of CAH is relevant to the analysis of the properties of surfaces which are modified in order to improve operation of industrial system such as ink-jet-printing, fiber coatings and immersion litography[20].

When a droplet is injected on a surface with a specific injection velocity, the contact angle grows up to a maximum equilibrium value, where one can measure the static contact angle described by the Young's equation. That angle is called The Advancing Contact Angle θ_A [Figure 1.11] and if we do the reverse process, a minimum contact angle can be measured and is named the Receding Contact Angle θ_R . Also, a droplet on a vertical surface or tilted can present a θ_A and θ_R because of the deformation caused by gravity. Thus, CAH is defined as the difference between θ_A and θ_R [21].

1.5 Wettability models

Wettability can give us information about the affinity of a surface with some liquid. Chemical composition and morphology of the surface influences the wettability, such that there exist models to describe this phenomenom for certain surfaces: Wenzel and Cassie model.

The Wenzel model describes rough homogenous surfaces, where the roughness of the deposition increases the surface area of substrate and by geometry contributes to the hydrophobicity.[22]. When the surface is homogeneous and flat one can see a



Figure 1.11: Distinct methods to estimate CAH. Left: Substrate and droplet tilted 90. Right: Water pump injecting liquid and forming several distinc θ_A .

classic static or Young's contact angle (CA). However, a real surface has an Apparent CA (θ^*) given by the tangent between the liquid-vapor interface and the apparent contact line on the solid surface. For Wenzel model, θ^* is defined by the following equation

$$\cos(\theta^*) = r\cos(\theta_c) \tag{1.8}$$

where θ_c is the Young's CA and r the roughness ratio given between the real and apparent surface area. In this case the liquid penetrates into the grooves of a rough surface [Figure 1.13].



Figure 1.12: A: The liquid penetrates into the groves (Wenzel model). B: Air pockets are trapped underneath the droplet becoming an additional surface (Cassie-Baxter model)

If the liquid does not penetrate into the grooves, one must apply the Cassie equation to define θ^* [22]:

$$\cos(\theta^*) = f_1 \cos(\theta_1) + f_2 \cos(\theta_2) \tag{1.9}$$

where f_1 and f_2 are the area fraction corresponding to two different surface potentials or chemistries in the sample θ_1 and θ_2 are the intrinsic contact angles for the two component mentioned. If instead there is a solid surface with air pockets underneath the droplet between the grooves and substrate, one can consider the CA for air as $\theta = 0^{\circ}$ and equation (1.9) becomes:

$$\cos(\theta^*) = f_1 \cos(\theta_1 + 1) - 1$$
 (1.10)

In summary, equation (1.9) represents the Cassie Model and 1.10 Cassie-Baxter Model. The first model is applicable to thin films throughout this work, because there are two components with differenciable chemistries (the silicon surface and the C32 monolayer). Therefore, the CA for this type of surfaces can be understood as an average between the two CA for each component [22].



Figure 1.13: Cassie model for a surface with two different chemical composition

1.6 Artificial Membranes

Lipid membranes are fundamental compunds found within living organisms, regardless of whether they are simple structures such as bacteries or multicelular organisms. These membranes allow the selective transference of ions, cell recognition and wall division between neighboring cells to delimit organs and protect the DNA.

Artificial membranes can be useful to detect diseases, toxines in food and environmental hazards, because they can allow the insertion of esential molecules, e.g molecules. Therefore, they form an important tool for the field of biosensors.

1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC), is a fosfolipid with formule C_{40} H_{80} NO_8P . It has a hidrophilic polar head and a hydrophobic apolar body (alkane) as shown in Figure 1.14. A few years ago, an artifitial fosfolipidical membrane with DPPC was made[23]. Retamal *et al.* reported a lipidic bilayer on a hydrated silicon support on chitosan, which is a porous and hydrophilic sugar used for the humectation of DPPC. This process is illustrated in Figure 1.15.

Knowledge of the adhesion properties of alkanes could help us to understand how the deposition of DPPC functions. Also, it is interesting to know the alkane stability on a silicon surface after wetting because it could be a support, considering its hydrophobic properties for water accumulation.



Figure 1.14: Molecular structure of DPPC



Figure 1.15: Artificial membrane on a silicon substrate with chitosan and DPPC deposited on the top.

Chapter 2

Experimental Setups

In this chapter, we will explain the experimental setup used throughout this work to measure CA of thin films of C32 with no more than one perpendicular layer. The samples were made via velocity controlled dip-coating technique and analized with Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM), which are important in order to study some aspects of the obtained surfaces such as coverage and morphology. Below is a brief review of thin films growth and charaterization techniques.

2.1 Dip-Coater

The coating of samples with n-alkane molecules was made using a PTL-MMB01 dip-coater located in SURFLAB UC. Figure 2.1 shows this equipment and components. The equipment can control the withdrawal speed of the substrates and the traveled distances. The range of speeds can be selected between 1 mm/min and 200 mm/min, for withdrawal from submersion.

The machine features also an oven to regulate temperature up to a maximum of 200° . However, dip-coating was performed at room temperature. The oven has dimensions of 280 mm L x 280 mm W x 280 mm H and inside samples were fabricated. Figure 2.2 shows the inside of the oven, where the structure is moved upwards or downwards by a pulling wire whose movement is controlled by a motor (Stepping Motor).

We made 66 samples in total for this work, with 6 samples for each velocity. We worked with 11 velocities: 1, 2, 4, 7 10, 50, 100, 125, 150 and 200 mm/min where the first four are considered low speeds and the five last are high speeds (10 mm/min

CHAPTER 2. EXPERIMENTAL SETUPS



Figure 2.1: First dip-coater setup. Sample Holder allows inmersion of two samples at the same time.



Figure 2.2: Inside the oven where dip-coating occurs. The temperature range can be selected between 50° C until 200° .

is an inflection point). Each dip-coating process generates twin samples for each velocity, i.e, one sample to measure CA and other to calculate coverage of a thin film from SEM images.

Some problems with sample holder of the dip-coater were encountered, because it held two samples very distanced from each other, complicating the inmersion of the substrates in the glass with a solvent of only 20 mL. For this reason, a more comfortable and simple setup was installed. The idea was to inmerse two substrates at the same time in a solution of C32, because each pair was required to have the same growth conditions. Besides, in the case of fabricating several samples it was necessary that dip-coating took little time because the evaporation of heptane is know to increase the concentration of C7-C32 solution affecting coverage. Figure 2.3 illustrates the installed modification.



Figure 2.3: Image of dip-coater inside oven.

2.2 Dip-coater calibration

To calibrate the dip-coater, a comparison between the experimental velocity and the value given by the dip-coater was made, which was calculated measuring the time that the sample holder needs to travel a distance of 10 cm. Figure 2.4 shows a calibration graph that compares theoretical and experimental velocities in order to determine the precision of the dip-coater.

The straight line fitted in the graph has a slope very close to 1, which indicates that the programmable velocities of dip-coater are reliable. Also, the dispersion asociated to experimental velocity are so low and we cannot see them in the graph



Figure 2.4: Set velocity (dip-coater) vs experimental velocity(manually calculated). The straight line 0,9903 x-0,99956 fits almost perfect to the measured points of the graph.

Dip-Coater Value(mm/min)	Experimental measured velocity(mm/min)	Error
200	196,2	$\pm 1,2$
175	174,1	\pm 1,5
150	147,8	\pm 1,7
125	121,1	$\pm 0,8$
100	98,5	\pm 1,1
75	72,7	$\pm 0,4$
50	48,3	\pm 0,3
25	$24,\!3$	\pm 0,2

(Table 2.1).

Table 2.1: Data of velocities calculated for dip-coater, with their respective dispersions.

2.3 Contact Angle Measurement Setup

During this work, two type of setups were used to inject water droplets onto C32 films. This was because of the need to form droplets in the most symmetrical way possible in order to measure adecuately the CA. First, we manually injected water with a pipette using volumes of 2-5 μ L. From this range we decided to choose the volume of 2μ L, so that drops had less risk of flowing out from the silicon substrate

[dimensions of $1 \times 0.5 \ cm$]. All drop images were processed with the image analyzer program ImageJ to verify simetry and estimate CA. The procedure for estimating CA will be explained in the next pages.

Basically, our experiments consist of injecting ultrapure water onto the substrate containing a previously deposited thin film of C32, then to take an image with a microscope camera to measure the droplet's CA. It was very important to use a reflecting surface (metallic surface, e.g iron in this case) behind the sample in order to enhance the contrast and differentiate the droplets contour.

If a surface is wetted manually with a pipette, as in our first experimental setup, the symmetry of the droplet is affected, in such a way that the CA on the left and the right side could be different. This is shown in the Figure 2.6. Therefore, in this situation it would be difficult fit a circle and describe the change in wettability of the substrate. The pulse of the free hand can provoke the liquid to spread unevenly on the surface, because the motion of the hand can add additional energy to the water thus deforming the droplet [Figure 2.7].



Figure 2.5: Image from ImageJ. The drop appears symmetric.



Figure 2.6: Image from *ImageJ*. Droplet is affected by the motion of pipette due to the pulse.

The setup visualized in Figure 2.8 was used in order to gently place the droplet over the substrate and obtain an acceptable symmetry. Here the pippete can be displaced vertically using a lab jack.



Figure 2.7: Image of setup used to measure CA.



Figure 2.8: Left:Back setup with micrometric screw. Right: Front image of sample holder forCA setup.

Underneath the sample a goniometer was installed in order to rotate it and measure angles in different directions. Thus, one can test whether CA is relatively constant and non direction dependent for the films investigated, at least for this type of film. Figure 2.9 shows the goniometer on the sample holder.

2.4 Analysis software ImageJ

To Calculate CA the equation (1.7) was used. Experimentally is measured with our setup the height and radius of the droplet. These parameters were calculated with ImageJ, a multifunctional program for image processing which can be used to measure segments and coverage of samples.

As mentioned, in section 1.3.1, a circumference around the droplet was fitted to its contour [Figure 2.9]. When the adecuated curvature radius was fitted, one can measure the diameter and height of the droplet. Then, equation (1.4) was used to relate curvature radius and height with the droplets's CA (see Figure 1.10).



Figure 2.9: Circumference fitting in ImageJ

Diameter and height were measured using the tool *straight*. These measurements are in pixels, thus we must apply the conversion factor to convert in milimeters.



Figure 2.10: Left: Measurement of diameter of the droplet. Right: Measurement of height of the droplet.

ImageJ also allows the measurement of coverage or percentage covered of the surface by alkane. In this case, an image binarization (*Binarize* function) is performed in order to calculate the number of white pixels or pixels covered by nanopatterns and thus to determine the fraction of total counts in the image. Pixilated images can be seen in Figure 2.11.

After the binarization, one can select an area of interest and make a crop (crop



Figure 2.11: Left: SEM image of sample C3247 without the respective binarization. Right: Same sample after binarization with siftware ImageJ.

function). Then, the white(area covered) and black (area not covered) pixel distributions are obtained by using the Histogram function (Proccess \rightarrow Histogram). Figure 2.12 shows some amounts for the function, where *Count* represents total counts (pixels) of the zone selected and *Mode: 0 (number)* the pixels (white pixels) covered by alkane (stripes). The ratio *Mode/Count* give us the fraction of the surface coated for stripes.



Figure 2.12: Histogram function in ImageJ with distrubution of pixels.

2.5 Atomic Force Microscopy

Atomic Force Microscopy(AFM) is an essential characterization technique for nanoscopic research. AFM consists basically in scanning the sample surface with a sharp tip attached to a cantilever and measuring the interaction forces between the tip and the sample. The measured forces are attractive and repulsive and depend on the distance between tip and the sample within either constant height or constant force mode [25]. A laser beam is focused on a cantilever, which presents a deflection proportional to the surface forces that act on the tip. The reflected beam is detected by a photodetector consisting of four quadrant photodetector which indicates the position of the laser spot [Figure 2.13].



Figure 2.13: a) Typical setup for AFM. b) Lennard-Jones Potential that is used to describe the interaction forces between tip and sample. Image reproduced from [19]

There are three scanning modes for AFM: Contact, Intermittent and non-contact mode. For Contact mode, the tip is dragged across the sample surface in the repulsive regime. A feedback loop keeps the interaction constant and the detector converts the position of the reflected laser in a signal, which provides the contrast of the image. However, non contact mode keeps the vibration of cantilever constant. In this mode, there is no contact with the sample and the vibration is near to resonance frequency of cantilever. Non-contact mode is preferably used for samples susceptible to degradation such as biological and organic thin films. In this work the Intermittent or (Tapping mode) was used to scan the thin films. This mode consists in the intermittent contact of the tip with the sample and thus the repulsive regime exists when the tip touches the surface. The tip is scanned over the surface maintaining a constant amplitude

2.6 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM) is a type of SPM (Scanning Probe Microscopy) based on the scanning of a conductive surface using an electron beam. The basic idea is as follow: These electrons are emitted via termoionic emisions obtained by heating a tungsteng filament. Then the electrons are accelerated in a potential ranging between 0.2 kV to 50kV (electron gun) and focused with magnetic lenses, which also generate a beam as fine as possible in order to maximize the resolution. Also, deflector coils [Figure 2.14] focus and deflect the beam, probing the sample. Electrons lose energy after the interaction with sample atoms, releasing Secondary Electrons (SE), Auger Electrons(AE), Backscattered Electrons(BE) and X-rays.



Figure 2.14: Schematic of SEM. The interaction between the electrons and the sample releases secondary electrons, Backscattered electrons and X-rays.

In this work we measured SE's, which were recollected using a Everhart-Thornley detector. This detector projects the intensities on a screen with a Cathod Ray tube (CRT) to make the images (Currently this is made with a flat screen). A Scilintator inside a Faraday cage attracts SE's when a low voltage is applied. The SE's result from inelastic scattering because of the interaction between the electron beam and the electrons of the sample, whilst BSE can also be generated by elastic scattering.

Chapter 3

Results and Discussion

This chapter will present the results for CA measurements between water and thin films of C32, as a function of film coverage and withdrawal velocity. The approach was to examine correlations among these 3 variables (CA, coverage and withdrawal velocity), for 66 samples coated using the dip-coating, for which 33 samples were investigated for CA measurements and 33 samples analyzed with SEM to estimate surface coverage. During each dip-coating 2 substrate are pulled out of the solution in such a way that the solvent on the sample surface evaporates while the sample is pulled. Velocities from 0.16 mm/s to 3.3 mm/s were investigated using a dip-coater PTL-MM01 with a concentration of 15mg of C32 disolved in 20 mL of C7.

This chapter also presents an AFM study of some samples in order to describe the behavior of nanopatterns after water evaporation and during wetting. Finally, the Cassie Model is considered in order to explain the wetting properties of the samples.

3.1 Influence of cleaning in Contact Angle

Within this study we realized the importance of substrate cleaning for the CA measurements. As described previously, the Tidswell method was used. At first the cleaning effectivity was measured using a Very High Resolution Ellipsometer (VHRE). This instrument measures the change in ellipticity induced by a contamination, with respect to a perfect clean Si/SiO_2 substrate. The polarizing angle obtained was compared with a reference value for a clean silicion surface depending on ellipsometer configuration [18]. Afterwards, our cleaning method was verified with CA measurements. Si known to be hydrophilic, with a CA less than 90°, which is a reference for which to to compare results. Whereas if there is more dirt on

the substrate, CA will be higher, because the water is not only in contact with silicon but also with impurities. Table 3.1 shows the improvement related to cleaning, decreasing CA for silicon substrate as a function of time.

Date 2015(Bachelor thesis)	Contact Angle $(^{o})$
March	32.3
April	26.4
April	18.03
May	14.2
May	9.5
May	9.6
June	<5
June	<5

Table 3.1: CA results for Si O_2 /Si-substrate show how our cleaning process improved with practice. A volume of 2 μ L of ultrapure water was used for all samples.

Figure 3.1 shows a graph of the data of table 3.1. One can see how CA amount decreases as our method improved The difference between initial and final CA's obtained as shown Figures 3.1 and 3.2. Our final cleaning protocol assures a final CA of 0°, which is an acceptable and expected amount for clean silicon. Because the CA's measured in this work for our dip-coated samples are relatively low, it was particularly important to obtain such clean surfaces.



Figure 3.1: The graph shows how we improved the silicon cleaning over time.



Figure 3.2: Droplet of $2\mu L$ on Si/SiO₂ surface without cleaning. CA measured was 32° .



Figure 3.3: 2μ L of ultrapure water on clean silicon. The water wets the surface almost completely, forming a flat film of water, so CA is to low to be measured (~ 0°). Red arrow indicates the liquid film.

3.2 Contact Angle dependence on withdrawal velocity

Wetting measurements was performed using ultrapure water (from Merck) on 33 silicon substrates coated with dotriacontane. The water volume used was $2\mu L$ to avoid that liquid wets the edges of samples. Silicon substrates (100) had a rectangular form of $0.5x1cm^2$ with approximattely 0,4 mm thickness and dimensions. The sample was placed with the withdrawal direction perpendicular to the camera's axis.

Wetting results as a function of velocity are shown in Figure 3.4. As expected, the tendency was very similar to T. Corrales *et al.* results [Figure 1.7]. Theoretically, it would be expected that CA vs velocity has the same trend as coverage vs velocity because C32 is hydrophobic, i.e, if we have a higher alkane concentration then the surface becomes more hydrophobic and CA would be expected to increase.

Figure 3.4 presents 11 CA's corresponding to velocities for the range 0.017 mm/s $\lesssim v \lesssim 3.3$ mm/s. One can observe a critical or minimum CA ($\theta_{cr} = 10.81^{\circ}$) at v = 0.83 mm/s, which is not an expected result, because there was not a minimum



Figure 3.4: Graph shows the dependency of CA with the withdrawal velocity. The range of velocity went from 0.017 mm/s to 3.3 mm/s. The dotted line represents a parametric point connector that draws a smooth curve through the points. This point connector is called B-Spline and does not pass necessarily through the original points. Red dots are dragonfly patterns and blue dots stripes.

coverage dependent of the velocity (C(v)) for this angle. It was expected that minimum CA should coincide with the minimum C(v), because this sample contains less hydrophobic material than others. Therefore, this suggests CA is not only dependent on withdrawal velocity but also on morphology, considering θ_{cr} belongs to the regime of stripe formation and $C(v_{cr})$ to dragonfly regime (according T.Corrales *et al.* v_{cr} = 0,15 mm/s as shown in 1.2.2), which shall be discussed further on in this chapter.

Below v_{cr} , wettability increases with v in the presence of regime I and LLD. In the evaporation regime, the samples are less hydrophilic with $\theta \sim 21^{\circ}$ at v= 0,017 mm/s, which is the lowest velocity and highest C(v) Above v_{cr} , where CA increases with v, there exist a predominancy of stripe morphology. Therefore, considering that the CA for cleaned silicon surface is 0° , we can firmly say that our nano-patterns visibly change wwettability properties of the solid substrate surface

3.3 Contact Angle in different directions

When we estimate CA, it is important to know its anisotropy, that is, to verify if wettability is the same in all directions. For example, if a sample is horizontally rotated on the sample holder by some angle, would CA be the same? To study this effect in thin films of C32, CA was measured in two focus directions of the camera: 0° (perpendicular to withdrawal direction during the dip-coating) and 90° (parallel to withdrawal direction during the dip-coating). Seven withdrawal velocities were selected in the range between v= 0,017mm/s and v= 3,3 mm/s. Firstly, the perpendicular direction was tested for which every surface was measured with a volume of 2μ L of ultrapure water.

CA was measured for high velocities ($v \ge 0.083 \text{ mm/s}$) in the directions mentioned (Figure 3.5). Clearly, in perpendicular direction the CA is higher than for the parallel orientation, but we can see at 1.67 mm/s and 3.3 mm/s a smaller difference between the measurements for each orientation. In general, there is a shift between the directions because we had to focus the camera when the sample was rotated. Therefore, during that refocus time the water evaporates and CA decreases.

According the aspect described before, we assume that CA differences with direction is not a real effect because the first direction measured will be always greater than second. The experiment was performed using an inverse order (first parallel direction and after the perpendicular) and the result was reversed, which suggests an evaportation effect. CA also depends on water volume, considering that the surface energy could vary affecting the curvarture radius of the droplet.

3.4 Coverage vs. Velocity

To verify coverage and uniformily of the thin films, the data for coverage with respect to velocity was plotted. In this work, velocities higher than T. Corrales *et al.* [15] were used, where dip-coating had a maximum of 1.67 mm/s. Thus, the focus of this part of the study was to investigate coating behaviour for high deposition velocities. Firstly, SEM images from Figure 3.6 were analyzed. This Figure shows a set of images with morphologies of nanopatterns for different withdrawal velocities.



Figure 3.5: CA in two orientations. We can see perpendicular direction presents higher CA than parallel direction





In the Figure 3.6 we can see for $v \le 0.17$ mm/s that molecules form a monolayer of predominantly dragonfly structure. However, for $v \gtrsim 0.83$ mm/s these nanopatterns seems more extended in the withdrawal direction of the substrate, and they try to align parallel to this direction with stripe morphology. Such dipcoating experiments have never been formed before at such a high velocity as 3.3 mm/s as shown in Figure 3.6 f), which presents stripes almost perfectly aligned. Figure 3.7 shows coverage vs velocity according to the data obtained. This trend is very similar to Figure 1.8 for the velocity range of T.Corrales et al. The surface coverage minimum in both graphs is basically the same (coverage $\sim \%12$) at $v_{cr} \sim 0.17$ mm/s, which constitutes the critical velocity where liquid film is pulled from the bulk solution. Below v_{cr} , in the regime I, the amount of deposited material on silicon decreases with v, but above v_{cr} increases as was expected. T.Corrales et al. controlled velocities up to a maximum of v = 1.7mm/s and set the GLE(Gravity-limited entrainment) regime in the range of $1 \text{mm/s} \lesssim \text{v} \lesssim 1.7 \text{mm/s}$ where it was assumed that coverage would be constant. However, the results of this work show that since $v \sim 1.7 \text{mm/s}$ the coverage increases with v and thus this range belongs to LLD (Landau Levich Deryaguin) regime. Therefore, one can know at least the LLD regime exists for $1.7 \text{mm/s} \lesssim \text{v} \lesssim$ 3.3 mm/s until coverage(C(v)) reaches a maximum in ~50%. There is also a plateu for C(v) because gravity sets a velocity limit (v_{limit}) where is impossible to drag more solution, so GLE must occur below a v_{limit} located at $v \gtrsim 3.3$ mm/s.



Figure 3.7: This graph shows the dependency of C(v) with velocity for our data. The dotted line represents a parametric point connector called B-Spline. Red stars corresponds to dragonflies and Blue dots are stripes.

3.5 Contact Angle vs. Coverage

It was seen before that there is a dependency of CA with v, i.e, a very similar trend to Figures 1.8 and 3.4. It is known that C(v) depends on v, so it is expected that CA has some relation with C(v). Figure 3.8 shows the CA versus Coverage. One can see for the case of dragonflies (red stars), wettability decreases with the amount of C32 deposited on the surface, reaching a maximum for $\theta \sim 22^{\circ}$. However, for stripes (blue dots), firstly CA decreases until θ_{cr} and then starts to increase with C(v) there after.



Figure 3.8: Relationship between contact angle and the coverage. Red dots represent dragonfly structure and black dots stripe patterns.

There is an interesting aspect to discuss with respect to Figure 3.8. One can see for similar CA's there are different C(v)'s, even at the maximum C(v): v = 0.017mm/s and v= 3.3 mm/s which are the highest and lowest v, showing $\theta \sim 15,4^{\circ}$ and $\theta \sim 22^{\circ}$ respectively. This suggets CA is not only dependent on covered area but also the morphology can affect the wettability of the substrate. Therefore, there apparently exists a particular tendency for the case either stripe or dragonfly, but we do not know exactly what aspect of morphology can affect the surface properties.

3.6 Alkane motion

In this work, 33 samples were analyzed using SEM for measuring coverage. However, an interesting phenomenom related to the wet samples was observed. After the water evaporated, the SEM images showed an apparent alkane motion: Nanopatterns were displaced and reorganized leaving a depletion zone. Figure 3.9 shows the effect of the 2μ L water drop on dragonfly morphology. One can observe a rim where the contact line was initially located. After the evaporation of the droplet a depletion



zone appeared and a rearrangement of C32 molecules around the rim.

Figure 3.9: The water droplet leaves a rim after evaporation. Outside this rim, dragonflylike nanostructures are observed, while within the rim, regions with a different type of pattern emerge along with bulk crystals. Between the dragonfly region and the interior of the rim, a depleted region is observed. This region suggests a de-pinning of the contact line and a dynamic rearrangement of the molecules during drop evaporation.

The same effect was reproduced using sample (C3204^{*}) as shown in Figure 3.9. After drop evaporation, the molecules had migrated to the center of the area where the sessile drop was placed, much like a reverse coffee-ring effect. Coffee-Ring-Effect consists of a ring formation at the edge or perimeter of a coffee drop after evaporation and it takes place because the liquid evaporating from the edge is replenished by liquid from the interior [25]. In our case, there is a pinning of the contact line of the drying drop followed inwards for a depletion zone of alkane and then, a circular zone covered with alkane. At the bottom right of the Figure 3.10, dentritic structures change to thinner forms as if it there were a detachment.



Figure 3.10: The top image shows that the water droplet leaves a rim after evaporation. The white rectangula zone represents a zoom of the top image. The last three images corresponds to a zoom of the middle image divided in three zones. Outside of the rim, dragonfly-like nanostructures are observed, while within the rim, regions with a different types of patterns emerge along side bulk crystals. Between the dragonfly region and the interior of the rim, a depleted region is observed. This region suggests a de-pinning of the contact line and a dynamic rearrangement of the molecules during evaporation. The dotted line represents the contact line of the droplet.

This suggests that water had moved underneath the C32 nanostructures increasing its mobility, then the hydrophobic C32 was likely to have been relocated inside the droplet-SiO₂ interface. It would be the same logic if one thinks in the macroscopic case such as shown in Figure 3.11. If a silicon surface covered with C32 macrocrystals is wetted, one can expect C32 to move toward liquid-air interface. Therefore, one can assume the same phenomenom happens once water provocates the de-pinning of the C32 molecules.



Figure 3.11: Left: Silicon surface with undissolved C32 before the wetting. Right: Silicon surface with undissolved C32 after wetting. C32 moves towards surface of water droplet.

One can see in Figure 3.12, specifically in the image at the bottom right, the change in dragonfly structure, reorganizing and forming a net. Evidently, one can assume that the CA measured was an initial CA considering the effect of water evaporation as long as the molecules are totally removed from the substrate in a certain time duration. The number of molecules depends on the area covered by liquid and also should affect wettability of surface. In some regions inside the zone where the droplet was injected we found more regions with reorganized molecules forming a net (see Figure 3.10). Apparently, C32 is not anchored strongly to the Si O_2 /Si substrate and the water can move underneath the thin film (to enter to the C32-Si O_2 /Si interface) because silicon is hydrophilic.

3.7 AFM Measurements

The alkane motion was also studied with AFM before and after wetting of thin film. The idea was to understand how molecules are removed by the water. For this the wetting was considered in two ways: 1) Scanning of a sample immersed in the water and 2) Scanning after the drop evaporation.

The first way basically consisted in the scanning with AFM in tapping mode of a dry sample and after which the sample surface was filled with water to repeat the measurement. Then, one can analyze the behavior for high and low withdrawal velocities and thus dragonfly and stripe morphology. The second method was only



Figure 3.12: The top image shows an interface between dragonfly and a type of alkane net generated by the water. Bottom left: Zone where nanostructures were not in contact with water. Bottom Right: Zoom around the net generated due to the interaction with water .

a common scanning probe with a dry substrate after the wetting.

3.7.1 Scanning of a sample immersed in water: Samples C3203, C3240, and C3246

The two samples C3203 and C3240 were analyzed underwater. Such samples have the velocities 0.33 mm/s and 3.3 mm/s respectively, which present high coverages (at least 50%). High coverages involve the presence of more nanostructures interacting with water.

Figure 3.13 shows images for sample C3203. The dry sample is on the left image and the right image is the sample dipped in water, (five minutes after the immersion).

The image shows a zoomed out view of the wetted sample. One can see in this zone how the morphhology of the nanostructure changes as a result of an alkane detachment from the substrate. There is an important change in the the film height and clearly the molecules moved because of the presence of water.



Figure 3.13: Left: Dry sample with a extended dragonfly morphology. Right: Sample immersed in water.

Changing the zone scanned (Figure 3.14), appear the nanostructures seen in the dry sample, but apparently thinner. Also, one can see at the right image $(50x50\mu m)$ how the C32 detaches, leaving behind incomplete dragonflies. This image is a zoom to (15umx15um) of the image on the left and gives one an idea about the rearrangement of C32 molecules under water. In General, it was difficult to scan this type of images with water as sometimes the tip of the AFM cannot attach itself properly or approached correctly on the sample and causing interference in the resulting image.



Figure 3.14: Left: Sample C3203 after the inmersion with nanostructures thinner. Right: Left image zoomed where one can see a detachment of C32.

Next, we wanted to find out what happens to samples fabricated at high velocities (v>100mm/s), particularly those with the highest coverage and the presence of stripes. Figure 3.15 corresponds to sample C3246 made at v= 2.5mm/s, before (left) and after (right) its immersion in water. Here one also can see the detachment and aglomeration of C32, which loses its initial structure and increases its height. This suggests a possible molecules stacking during contact with water. Moreover, in some zones measured one could not find redepositions of material which was removed. Thus, it is possible to say the thin film was fully detached from the substrate after a certain time, at least for t>5 minutes.

For v= 3.3 mm/s, sample C3240 which presented stripe morphology. Figure 3.16 shows images in intervals of 5 minutes with the sample under water. At image *a*) there are stripes before wetting and one can see how height increases with time. Actually, dry nanostructures have a initial height of 5 nm aproximately above which changes up to 20 nm in contact with water. However, the stripes size and separation also tended to modify themselves since alkane lines became thinner with increasing distance from each other. Therefore, it appears to be that they are stacked due to the presence of water, which changes the height and the coverage of the thin films.



Figure 3.15: Left:Dry Sample C3246 with stripes. Right: C3246 after immersion with presence of C32 aglomeration with increased height above 6 nm and stripes with more height.



Figure 3.16: Nanopatterns evolved under water. Stripes become thinner and after 2 hours the height grows above 25 nm.

3.7.2 Scanning after drop evaporation: Samples C3207 and C3204

For past drop evaporation, one can find a similar behaviour with the last method, probably due to the time interaction between liquid and alkane. The velocities 0.067 mm/s and 3.3 mm/s were studied because the coverage is high both with dragonfly and stripe morphology, respectively. Sample C3204 was analyzed in SEM, in an attempt to find the same net structure as found with AFM. As one can see in figure 3.14 a), there is a kind of net formed by alkane, which is the same structure seen in SEM (Figure 3.9 and 3.12). The images were made in the site where liquid was injected.



Figure 3.17: Left: Sample C3204 after immersion with presence of a net or agglomeration of nanostructures. Right: C3204 after immersion with presence of nanostructures much like a tails or nanofibers .

In Figure 3.17b) it is possible to see the formation of alkane tails or nanofibers in a zone near to the net structures. It is very interesting to observe the height measured for this type of morphology, which is greater than the perperdicular layer (4.3 nm), exceeding 25 nm. Tailed structures in alkanes have been reported previously by Denkov et. al research [26], but only considering compounds with 14-20 carbons.

Denkov *et.al* controlled deformation of hydrocarbon droplets dispersed in aqueous surfactant solution changing cooling rate. The deformation found was triangular or rhomboid with tails. Curiously, thin films of dry C32 at room temperture after several months show a similar change in the nanostructures, which start gathering into rhomboid bulks. Figure 3.18 shows SEM images of rhombid shapes of alkane molecules and and tails seen in AFM to compare with structures formed in Denikov





Figure 3.18: Comparison between the tails found and the Denikov experiments. a) Rhomboid shapes in thin films of C32. b) Sample C3204 in a different zone from Figure 3.17 c) The same zone than b) but with the scale 3x3d) hydrocarbon with triangular shape and tails in the edges seen with an optical microscope. Scale bar in d): 50 μ m.

3.8 Cassie Model

An explanation of the wetting properties of the thin films of C32 can be considered through the Cassie model, as the samples are chemically heterogeneous (substrate and film). Previously stated the CA that was measured is really an apparent contact angle θ^* , such that the cosine was applied to the measured CA of figures 3.4 and 3.8 to verify the consistency with the model.

Figure 3.19 shows cosine of the CA measurements with respect to deposition velocity. This is the inverse curve of figure 3.4 with the critical velocity v_{cr} marked by a dotted straight, where there is an inflection and then a decrease of cosine (θ^*) for



Figure 3.19: This graph shows the cosine of apparent CA in a range from 0.017 mm/s to 3.3 mm/s. The dotted line is a B-Spline parametric point conector that marks the critical velocity Vc.

the stripe regime. One can see in the figure 3.20 the cosine of the apparent contact angle versus coverage, which can be grouped in two regimes which depend linearly on coverage. This is consistent with the Cassie equation for a flat surface that is chemically heterogeneous, because the increase of coverage implies a higher hydrophobic material concentration on the substrate. Therefore, γ_{SV} (surface tension for solidvapor interface) falls improving the wettability which explains the negative slope for the dotted lines.

According to the behavior indicated before, we suspect that the separation in two regimes is due to morphological differences that emerge from the dip-coating preparation conditions, e.g patterned stripes ($v \ge v_{cr}$) or dentrites ($v \le v_{cr}$). Actually, this offset can be caused due to slight density differences between a stripe or a slowly coated dragon-fly structure.



Figure 3.20: Cosine of apparent contact angle versus initial coverage. There are two regimes separated by preparation velocity or resulting morphology (dragonflies and stripes).

3.9 Contact Angle Hysteresis

This section presents the results regarding contact angle hysteresis (CAH) for thin films of C32. The idea was to find a considerable variation in CAH that would imply a change in the perpendicular layer. The samples used for this measurements have a coverage above 40% corresponding to high velocities and consequent the stripe regime.

The samples corresponding to C3210 (2.5 mm/s) and C32136(3.3 mm/s) were wet with a stepper motor controlled NE-1002X Programmable Microfluidics Syringe Pump (from New Era Syringe Pump). Firstly, a little volume of water was injected, after which it was pumped off at rate of 30 uL/min to produce a final volume of 15 uL. When the desired volume was completed, the maximum CA or advancing contact angle (θ_a) was measured. Then, the water withdrawal was performed at the same rate as injection, measuring the minimum CA or receding contact angle (θ_r). The cycle was repeated 3 times and then an average of the angles was calculated. Figure 3.21 shows the moment where θ_a and θ_r are achieved.

The process of pumping and withdrawal of the water lasted a few minutes. This



Figure 3.21: Left: Advancing Contact Angle. Right: Receeding Contact Angle.

process showed that the variation of CAH was not enough to assume an important nanostructures movement, which would imply a remarkable change in the coverage (Figure 3.22). However, the AFM results showed previously that one can see a C32 detachment after 5 minutes at least, but only after hours such detachment is considerable. Therefore, hysteresis at least is consistent with the time required to provoke a notorious arrangement of the C32 molecules. The 3 cycles are shown in the figure 3.22, where red dots represents the left CAH, which changes from 23.6° (first cycle) to 26.7°(third cycle).

3.10 Morphology of Single Phospholipidic Bilayers by Velocity-Controlled dip-coating

An additional experiment was made in order to understand the adhesion or formation of phospholipid bilayers. In this section, the possibility of self-assembling single bilayers of DPPC over SiO_2/Si substrates by dip-coating at controlled velocities will be shown. The idea of the control of preparation conditions such as evaporation rate, concentration of the solution or withdrawal velocites are very important in the formation of self-assembled patterns supported by some solid surface.

For this experiment, we used 15 mg of DPPC disolved in 20 mL of chloroform for the preparation of samples by dip-coating. The velocities used were 0.017 mm/s, 0,17 mm/s and 3.3 mm/s. Every velocity was scanned by AFM to describe morphology and height of the deposited material.

The samples studied were humected with 20 μ L of ultrapure water and chilled at



Figure 3.22: θ_a , θ_r and CAH for 3 cycles performed with a syringe pump.

2 during 15 min before the AFM measurements. Figure 3.22 shows the sample made using a low velocity v = 0.017 mm/s. One can observe the presence of a network of cluster which coincide with the height of a bilayer (6 nm) [23]. If one increases the velocity above a critical velocity, one can observe the formation of circular cluster with a height of 5 nm approximately as shown in figure 3.24.



Figure 3.23: Sample made using a low velocity (1 mm/s) by dip-coating technique. One can see a structure much like a net of clusters.



Figure 3.24: Sample made using a high velocity (200 mm/s) by dip-coating technique. It is possible to observe the formation of circular clusters.

Chapter 4

Conclusions and Future Work

Thin films of C32 were fabricated using dip-coating technique at a controlled velocity and we have studied its wetting properties via contact angle measurements. The idea was to find a correlation of the contact angle with coverage or withdrawal velocity. The velocities achieved went from 0.017 mm/s to 3.3 mm/s using twin samples for each coverage.

The samples prepared with velocity controlled dip-coating are silicon substrates with a native oxide layer (~15Å). The substrates are cleaned by Tidswell method which involved removing the impurities (organic material) with a piranha solution and after are treated with ultrasonic bath. This method gave reproducible hydrophilic substrates with $\theta_c \sim 0^\circ$. The substrates are stored in extra pure water and then dipped in a solution of 15 mg of n-Dotriacontane(C32) crystals disolved in 20 mL of n-Heptane(C7).

We have developed an experimental setup to measure contact angle for our samples. The method to calculate this angle consists in wetting the surface with a droplet of 2 uL (extra pure water for chromatography from Merck). After wetting we fit a circle and estimate CA through the curvature radius. Besides, we installed a goniometer to study CA in different orientations according to the position of the sample with respect to the camera. A total of 66 samples were used, 33 for SEM analysis and 33 for wettability measurements.

The CA vs withdrawal velocity curve is very similar to Coverage versus velocity as we expected. However, the minimums in coverage and CA do not coincide at the same velocity. We find a CA minimum at v = 0.83 mm/s and for Coverage at v = 0.17 mm/s, which is in coincidence with T.Corrales *et al.* results [15]. Therefore, the samples do not have the maximum wettability with the lowest coverage. This suggests that wetting is not only depend on coverage but also on morphology.

Coverage vs CA showed a particular behaviour for each type of nanostructure and one can see similar CA's for different coatings. Also, although the hydrophilicity in general decreases with the amount of material on the substrate as we expected, there is an inflection point at C(v) = 32.8% affecting the tendency. This suggests again that morphoplogy can conditionate wetting properties.

For the case of CA measurement with the sample rotated, we believe that the wettability variation is resulting from the time delay caused by the re-focusing after sample rotation. During the focusing of camera, the water evaporates decreasing the volume of the droplets anchored on the substrate. Therefore, we assume a constant CA for any direction achieved with rotation (isotropic behavior).

It was found that by changing the withdrawal velocity from a solution of DPPC dissolved in chloroform, one can obtain a single phospholipid bilayer with different morphologies. We find that the structures obtained by pulling from solution using a high velocity (3.3 mm/s), which belongs to the Landau-Levich regime, one obtains circular clusters of around 5 nanometers in height. Using a low velocity (0.017 mm/s), these clusters merge forming a network of clusters with a constant height which matched the bilayer height (~6 nm) [23]

The alkane motion on the substrate was studied next. Here it was found that the adhesion of C32 on silicon surface is not as we expected, because this moves by effect of water during the pinning of the contact line. As alkanes are hydrophobic, we discard the disolution in water. SEM images(sample C3204) show that after drop evaporation, the molecules migrate to the center of the area where the sessile drop was placed, much like a reverse coffee-ring effect. Also, appeared new structures like nets resulting from a rearrangement of alkane molecules. Firstly, It was understood that the molecules molecules moved on the top of droplet surface, which means a change in the surface energy that increases CA, but this should be instantly or seen with the time as a notorious CA variation. The AFM measurements demonstrates that the alkane needs a considerable time to detach from the substrate, which discards the theory about instant motion of molecules on the top drop surface (water-air interface) because we would expect the decreasing of wettability during the time. Two type of measurements were made with AFM for samples with high coverages: 1) Scanning of th sample immersed in water; 2) Scanning after drop evaporation. With the first method we scanned patterned stripes at v = 3.3 mm/s and it was found a thinning of the nanostructures. Besides, the average height grows with the time even above 2 hours from 6,93 nm to 39,69 nm. This suggest a stacking of C32 molecules that changes the coverage on the substrate. For low coating velocities in the evaporative regime, dragonflies lost their shape and aglommerate into higher stacked structures than the original thin film (h > 20 nm).

Sample C3204 (v = 0.033 mm/s) was scanned as described in point 2). It was found that the original patterns (dragonflies) restructure forming complex tail-like morphologies after drop evaporation. As well as in SEM images one could observe a kind of net formed by C32 near to the tails zone.

Finally, the wetting properties were shown to be consistent with the Cassie model for a chemically heterogenous surface. The cosine of apparent contact angle decreases linearly with the coverage in two separated regimes as seen in the respective plot, defining a critical velocity at $v_{crit} = 0.83$ mm/s. In the case of Hysteresis experiments, contact angle hysteresis did not present a significant variation after three cicles of pumping and withdrawal of water, for high velocity samples C3210 (v = 2.5 mm/s) and C32136 (v = 3.3 mm/s). This proves that alkane molecules need a considerable time to move and change the initial coverage as was found from the AFM images post wetting and drying.

Future works must focus on further AFM studies in liquid. Thus, we could know all conditions that influence the formation of tails and understand the dynamic of the alkane rearrangement. In addition, for the two regimes seen in Cassie model, we must verify with X-Ray measurements the existence of small differences in lattice parameters or structural density.

Bibliography

- Kyoo-Chul Park, Shreerang S. Chatre, Siddarth Srinivasan, Robert E. Cohen, Gareth H. McKinley . Langmuir, 2013, 29 (43), pp 13269–13277
- [2] F. T. Malik, R. M. Clement, D. T. Gethin. W Krawszic A. R Parke. Bioinspir. Biomim.(2014)9(3) 031002.
- [3] Vollhart K., Schore N., Organic Chemistry Structure and Function, W.H Freeman and Company, Third Edition 1999.
- [4] Lamoreaux S.K, Casimir forces: Still surprising after 60 years, Physics Today, February 2007, p.40-45.
- [5] S.S. Kanu, R. Binions. Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences. The Royal Society, 2009.
- [6] Landau L.D, V.G Levich. Acta Physicochim. URSS 1942, 17, 42.
- [7] Deryaguin, B. Acad. Sci. URSS 1943, 39, 1.
- [8] Tidswell, I.M; Ocko, B.M; P. S.; Wasserman, S. R.; Whitesides, G. M.; Axe, J. D. X-ray Specular Reflection Studies of Silicon Coated by Organic Monolayers (Alkylsiloxanes). Phys. Rev. B 1990, 41, 1111–1128.
- [9] U.G Volkmann, M.Pino, L.A. Altamirano, H.Taub, F.Y Hansen, J. Chem. Phys.116, 2107 (2002).
- [10] S. Trogish, M.J. Simpson, H. Taub, U.G Volkmann, M. Pino, F.Y. Hansen. J. Chem. Phys. 123, 154703 (2005).
- [11] H.Mo, S. Trogisch, H. Taub, S. N. Ehrlich, U.G. Volkmann, F.Y Hansen and M. Pino. Phys. Stat. Sol. 201, 2375-2380 (2004).

- [12] H. Mo, H.Taub, U.G Volkmann, M. Pino, S.N Ehrlich, F.Y Hansen, E. Lu, P. Miceli, Chem. Phys. Lett. 377 (2003), 99-105.
- [13] M.Bai, S.Trogisch, S. Magonov, H. Taub, Ultramicroscopy 108 (2008) 946-952.
- [14] M.Bai, K. Knorr, M.J. Simpson, S. Trogisch, H.Taub, S.N. Ehrlich, H. Mo, U.G. Volkmann, F.Y Hansen, EPL 79 (2007) 26003.
- [15] "Flow Induced Growth of Striped Alkane Monolayers", M.Bai, H.Taub, A. Diama, K.Knorr, U. Volkmann, F. Hansen, APS 2008 (Oral Session).
- [16] Tomas P. Corrales, Mengjun Bai, Valeria del Campo, Pia Homm, Piero Ferrari et al. ACS Nano, 2014, 8 (10), pp 9954–9963.
- [17] Hans-Jürgen Butt, Karlheinz Graf, Michael Kappl. Physics and hemistry of Interfaces. WILEY-VCH, Third, Revised and Enlarged Edition 2013.
- [18] Latthe, S. S., Terashima, C., Nakata, K., Fujishima, A. Molecules, 19(4), 4256-4283 (2014).
- [19] Eral, H. B., Oh, J. M. a, Colloid and polymer science, 291(2), 247-260 (2013).
- [20] Yuan, Yuehua, and T. Randall Lee. "Contact angle and wetting properties." Surface science techniques. Springer Berlin Heidelberg, 3-34 (2013).
- [21] Lafuma, A., Quéré, D. Nature materials, 2(7), 457-460 (2003).
- [22] Sigmund, W. M., Hsu, S. H. Cassie-Baxter Model. Encyclopedia of Membranes. Springer Berlin Heidelberg, 310-311 (2016).
- [23] Maria J. Retamal, Marcelo A. Cisternas, Sebastian E. Gutierrez-Maldonado, Tomas Perez-Acle, Birger Seifert, Mark Busch, Patrick Huber, Ulrich Volkmann. J. Chem. Phys. 141, 104201 (2014).
- [24] Harlang G. Tompkins Eugene A. Irene. Handbook of Ellipsometry. William Andrews Publishing, 2005.
- [25] "Atomic Force Microscopy, Scanning Nearfield Optical Microscopy and Nanoscatching Application to Rough and Natural Surfaces", G. Kaupp Springer-Verlag Berlin Heildelberg 2006..

- [26] Yunker, P. J., Still, T., Lohr, M. A., Yodh, A. G. (2011). Suppression of the coffee-ring effect by shape-dependent capillary interactions. Nature, 476(7360), 308-311.
- [27] Denkov, N., Tcholakova, S., Lesov, I., Cholakova, D., Smoukov, S. K. Nature 2015, 528(7582), 392-395.