STABILITY OF SELF-ASSEMBLED MONOLAYER SURFACTANT COATING

IN THERMAL NANOIMPRINT

A Thesis

by

PATRICK GORDON LUNSFORD

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2010

Major Subject: Electrical Engineering

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Approved by:

Co-Chairs of Committee,	Xing Cheng
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ABSTRACT

Stability of Self-Assembled Monolayer Surfactant

Coating in Thermal Nanoimprint. (December 2010)

Patrick Gordon Lunsford, B.S., Texas A&M University

Co-Chairs of Advisory Committee: Dr. Xing Cheng
Dr. Haiyan Wang

High-resolution and low-cost fabrication techniques are essential for nanotechnology to overcome the commercialization barrier to benefit our society. Since its inception nanoimprint has become the ideal technology to fabricate dense sub-micron structures over large areas with low cost, which are important to many applications such as high-density storage disks and diffractive optical devices. The decade-long development in nanoimprint equipment has reached a point where large-scale manufacturing of high-density nanostructures are possible. However, there are a few remaining issues that need to be studied before the advent of commercial application of nanoimprint.

In this work we look at a pressing issue, long-term stability of the mold surfactant coating. It is important to understand the details of the surfactant wear during nanoimprint in order to limit defect density to a tolerable threshold in a high-volume manufacturing process. To study this we went through a nanoimprinting procedure and measured chemical and physical alterations in the coating. The surfactant wear information also helps to optimize the time interval for surfactant recoating to keep the

fabrication throughput as high as possible. In this paper we characterize the stability of two commonly used surfactants as well as prescribe a new technique for mold anti-adhesion.

Through this work we see that FDTS and OTS undergo significant degradation in air and gradual degradation by chain scission is observed during the nanoimprint procedure. It is also noted that an embedded anti-adhesion layer is effective for mold releasing.

ACKNOWLEDGEMENTS

First of all I would like to thank my family members who have lovingly supported me throughout all of my years in college. It is such a blessing having a family who is there for you.

I would also like to thank Dr. Xing Cheng, without his constant patience and help I would have never been able to achieve all that I have in engineering. I have always been so thankful for his guidance, and I do not believe I could have had a better advisor.

My research group was also very helpful during these past years. I would like to especially thank Hyunsoo, Huifeng, and Dehu. All of these men were very helpful whenever I had confusing results in the lab, or was uncertain of how to continue.

My thanks also go out to the rest of my committee, all of my professors, and the faculty in the Department of Electrical Engineering here at Texas A&M University. You all make Texas A&M one of the best colleges in the world.

Finally I thank God, the Father whom I have a relationship with through Jesus Christ. Although I have worked hard, I know nothing I have achieved would have been possible without God guiding my every step. It is such a blessing knowing I have a relationship with God, through Christ, by faith alone, and not of any works I have done, nor could do, but simply through His love and Grace.

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CHAPTER I

INTRODUCTION

Lithography is the heart of the electronic device fabrication process. There are many types of lithography processes that are currently being used, for example some of the most commonly used fabrication techniques are electron-beam lithography (e-beam lithography) and photolithography. For many years photolithography has been the most popular way to fabricate microelectronics. Although photolithography has been in use for many decades, it is now becoming increasingly difficult for photolithography to keep up with the higher and higher resolution features that are needing to be produced in order to stay on track with Moore's law.

In April of 1965 Gordon Moore stated "The complexity for minimum component costs has increased at a rate of roughly a factor of two per year".[1] Since then we have been able to double the number of transistors on an integrated circuit every two years, this is what is now known as Moore's law.[2] Using photolithography we have been able to follow that road map for the past 45 years. However as we approach smaller and smaller scale fabrication not only are prices of manufacturing with photolithography greatly increasing but the speed at which we are able to improve photolithography is decreasing. Although Gordon Moore inadvertently created a roadmap for the semiconductor industry to follow we have now reached a point where

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This thesis follows the style of Microelectronic Engineering.

we must create new processes to stay the course that was outlined so many years ago. Now that we are well into the nano age it is difficult for photolithography labs to keep up with the needs of small scale fabrication. While Intel Corporation, the company Gordon Moore co-founded, is able to produce 32nm devices, and do it on a large scale with their Core i7 processors, we know that using traditional 193nm lithography, an immersed deep UV photolithography process, we will be unable to produce 16nm features.[3]

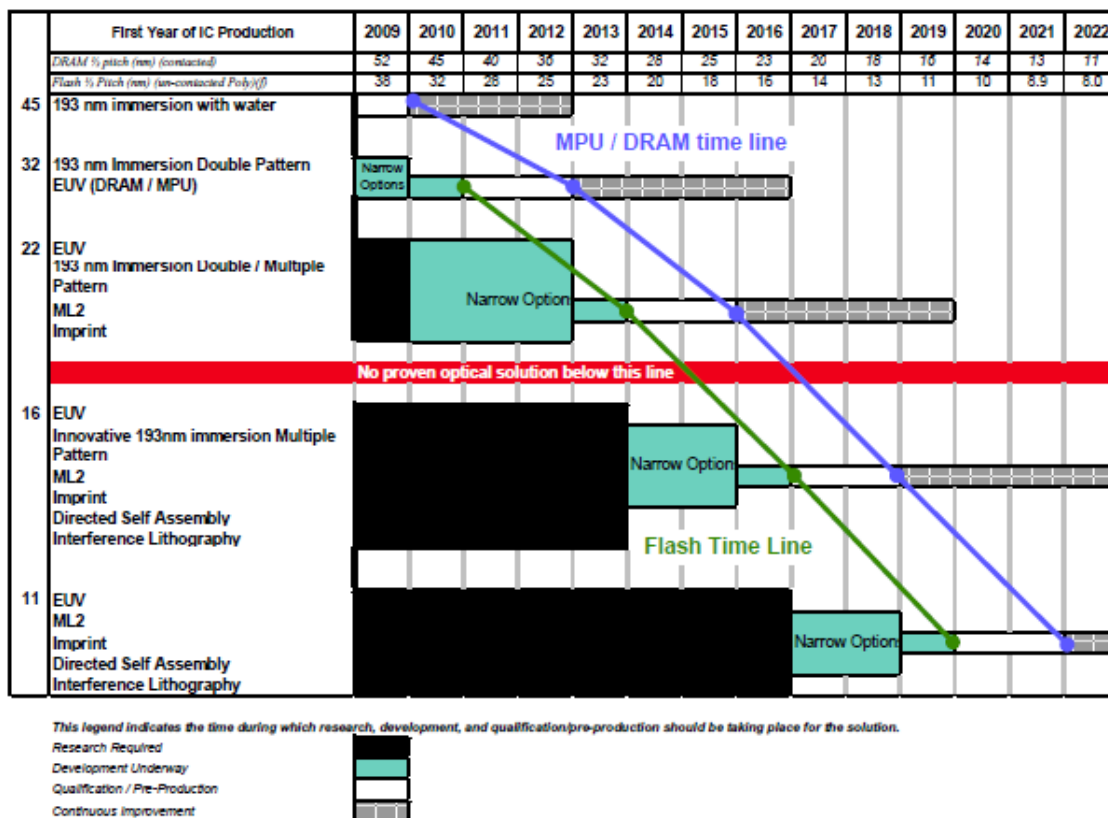| First Year of IC Production	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022
DRAM ½ pitch (nm) (contacted)	52	45	40	36	32	28	25	23	20	18	16	14	13	11
Flash ½ Pitch (nm) (un-contacted Poly)(f)	38	32	28	25	23	20	18	16	14	13	11	10	8.9	8.0

Figure 1.1: ITRS 2009

Looking at the International Technology Roadmap for Semiconductors[3] in Figure 1.1 we get a further understanding of what this roadmap looks like on a nanoscale, and the means by which it will be achieved. Currently we see that a deep UV 193nm immersion technique is used for 32nm scale production, and is feasible for 22nm features. However, once we are to produce on the scale of 16nm or below optical solutions will be obsolete. Optical lithography may became obsolete, but there are many techniques that are able to replace it. One very promising form of nanolithography is nanoimprint lithography (NIL). [4-5]

Before we delve into nanoimprint lithography it is imperative that we have a fuller understanding of NIL's superset, nanolithography. Nanolithography is the process used to fabricate structures that are on scale of less than 100nm.[6] Besides NIL there are currently many other types of nanolithography including photolithography, electron beam lithography,[7] edge transfer lithography,[8] and self-assembly.[9] We can use nanolithography to produce many useful structures, such as chemical detection sensors such as those used for cancer detection,[10] physical surface alteration, as well as many more. Also, this fabrication is very important in the production of solid state nanoelectronic devices. There are many applications for the small scale devices that are produced with nanolithography. Some of commonly researched areas of application include computer processors, solar cells, and organic light emitting diodes (OLEDs). There are many ways to produce the nanostructures used for such applications.

Following is a discussion of the common processes used in nanolithography, along with a listing of their attributes and shortcomings. This dialogue will allow insight into the benefits of the main conclusion of this dissertation, surfactant wear information can allow the selection of self-assembled monolayer (SAM) coatings of highest durability for large-scale production utilizing the nanoimprint lithography process. As we will discuss further SAMs are used as an anti-adhesion coating on the surface of the nanoimprinting mold. In this we will also help support a prescription for a new mold releasing strategy we have come up with. First it is imperative that cover one of the most commonly forms of nanofabrication techniques for nanolithography. This is optical lithography, i.e. the previously discussed photolithography process that is approaching the end of its useful life.

Fabrication of nanostructures using photolithography uses a top-down technique, in other words it uses lithography to pattern nanoscale structures.[11] This is done using a mask to guide light onto and expose the thin photoresist coating. There are two types of photoresist, both positive[12] and negative[13] resist. The positive resist, when exposed to ultra violet rays, will be dissolved by a solvent. Conversely, solvents will dissolve the unexposed areas of negative resist because it becomes insoluble when exposed to light waves. In both cases, an exposure takes several seconds to complete and changes the chemical makeup of the photoresist to make them soluble or insoluble.

Most high end photolithographic facilities use chromium masks when exposing the photoresist. These masks have openings four times larger than the projected image dimension. Because of the expansion of light through the masks, photolithography is

limited and can only take us to 22nm. This can be further understood by looking at how we calculate critical feature size. Using the equation for critical dimension we are able to calculate the minimum feature size that can be produced with photolithography. The equation for critical dimension is:

$$CR = K_1 \cdot \frac{\lambda}{NA}$$
(1.1)

Examining critical dimension we see that it is limited by how small we can get λ, the wavelength of the light source being used, and NA, the numerical aperture of the lens. We can calculate NA as the product of refraction index and the incident angle. K_1 is a coefficient that takes into account several processing factors and can be on the range of 0.25 to 0.8. Another limiting factor for photolithography is that it is dependent on diffraction of light that we see in the Rayleigh equation. Because of the diffraction of light we see that depth of focus becomes a problem when we are working with very small feature sizes. To account for that we must look at the equation for depth of focus:

$$D_F = K_2 \cdot \frac{\lambda}{NA^2}$$
(1.2)

 Here K_2, alike K_1, is used for process related factors. The depth of focus limits the depth of topography on the wafer. From all of this information we see that once we reach a certain physical barrier there will no longer be a way to use light in order to complete nanolithography of 22nm features. Many of these problems are solved using nanoimprint lithography (NIL), [14-22] a process that will enable us to continue on route with the road map prescribed by Dr. Moore. As one can see from the critical feature

equation one way to decrease this minimum linear size is to shorten the wavelength of imaging light by using extreme ultraviolet light (EUV).[23] However, using EUV light will also require the use of new optics and photoresist with higher sensitivity.

Another limiting factor for photolithography is the time it takes to create the mask. Mask patterns are created by scanning beam lithography and a single mask can take up to 24 hours to create. There is an associated large cost incurred as each machine used in this process costs tens of millions of dollars. Because of these many time and cost limitations a new, more conventional technique to fabricate nanostructures is necessary. A valid option to replace the outdated procedure of photolithography is nanofabrication by means of molds and embossing, i.e. imprinting.

There are two major types of molding and embossing used to fabricate nanoscale structures, hard molds and soft, or elastomeric, molds. The general form of molding involves using a topographically patterned substrate to transfer a pattern onto the precursor. Imprinting, on the other hand, uses a flat polymer film as the base and then the mold, again generated by patterned topography, is transferred. Nanoimprint lithography is the form of embossing that will be the topic of focus in this discussion.

First let us cover the basics of elastomeric mold patterning using the soft lithography process.[24] This process involves preparing the soft mold using a liquid polymer precursor against the topographically patterned master. Typically elastomers are the polymers chosen to be used in order to copy the patterned master, with the most common successfully used elastomer being poly-dimethylsiloxane (PDMS). The reason PDMS is such a popular choice in nanofabrication is that it is unreactive toward

most types of materials to be patterned, it is not hydroscopic, has durable properties, is transparent to waves near 30 nm and its precursors are commercially available and inexpensive .[24] The fabrication of PDMS molds is so inexpensive that molds can become disposable. Being chemically inert allows PDMS to pattern many types of materials including polymers, precursors to carbons and ceramics, sol-gel materials, organic and inorganic salts, colloids, biological macromolecules, thiols, phosphonic acids, and silanes.

With all of these advantages for using PDMS in soft lithography it is also important to understand the limitations of PDMS. One of the major limitations we see in PDMS is its susceptibility to absorb nonpolar, low-molecular weight organic compounds such as toluene and hexane.[24] When PDMS absorbs these compounds it expands, swells, causing dimensional instability and adhesion to occur after polymerization of monomers. Because of these limitations there sometimes exists a need to eschew the use of PDMS and utilize other materials or even other processes like hard mold nanofabrication.

In order to create a hard mold reactive ion etching (RIE), wet etching, or electroplating is used to transfer the structure patterned in photoresist onto the substrate. These processes can be used to produce molds made of many materials including silicon, quartz, and metals, with silicon and quartz molds being the most typically fabricated and used. The resultant hard molds are then used to emboss structures onto the substrate through high pressure and relatively high temperature. An advantage to using hard molds of these materials is that they are stable at high

temperature, can retain nanoscale features under pressure, and are chemically inert to precursors used to mold polymers. Another useful attribute of the quartz mold is that it is transparent to many lengths of light waves. With this ability to transfer light through a quartz mold it is possible to align the mold to features on the substrate in a process called step-and-flash imprint, or UV imprint, lithography (SFIL). [25]

Step-and-flash imprint lithography first aligns the features optically through the quartz mold, and then once aligned photoinduces cross-linking of the molded liquid prepolymer. This cross-linking is brought about through UV exposure, also through the quartz mold. The prepolymer used in the process is a photocurable solution that is able to form onto the topography of the mold through applied pressure. When the prepolymer is exposed to UV light it polymerizes and hardens while inside the mold. The result is the substrate is coated with an inverse topography of the mold in use.

There are many advantages to this type of hard mold patterning aside from the ability for easy optical alignment. For instance SFIL uses a monomeric fluid with low viscosity (<5cPs), preventing incomplete mold filling. Although this is an advantage of SFIL, the UV-curable liquid, like that patterned in Fig 1.2, is not always completely displaced because of hydrodynamic forces. This problem can be avoided through careful procedure, making sure the mask and substrate are aligned perfectly, or by removing this layer through etching.
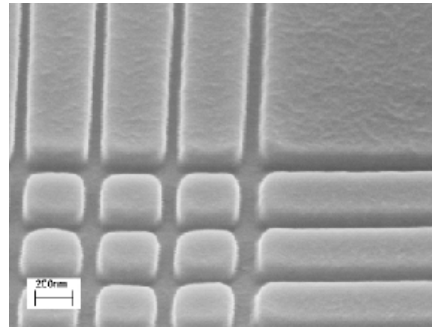
Figure 1.2: UV-curable epoxy silicon

Another important consideration with SFIL is the lifetime of the mold and what delays in fabrication a short mold lifetime may cause. An important factor in mold lifetime is the release layer. The release layer reduces the surface free energy of the mold, reducing the polymer cross-linking to the mold. A popular release layer is fluorinated silane but it can only withstand 100 patterns. Newer treatments are claiming to withstand 1500 imprints[26] but no conclusive research has been done to date. The dilemma of mold coatings with short lifetimes is also something run into with another type of hard patterns, thermal nanoimprint lithography (NIL).

Unlike SFIL, nanoimprint lithography uses pressure and heat to transfer the pattern from a silicon mold onto a thermoplastic polymer. The molds used for thermal nanoimprint are typically silicon, silicon oxide, and nickel. This mold must be coated with a SAM surfactant in order to prevent adhesion with the thermoplastic polymer, oligomer, film on the substrate. The coating procedure is done by immersion of the cleaned substrate into a bath of dilute solution at room temperature.[6] Typical thermoplastic polymers used for thermal nanoimprint lithography include poly-methyl

methacrylate (PMMA), polystyrene (PS), and polycarbonate (PC). With NIL 100mm

plates can be patterned in a single imprinting step, this along with the fact that

imprinting can be performed in less than one minute allows a very high throughput.

Not only can NIL pattern large plates but it can also pattern a variety of materials

including biomolecules, block copolymers, conducting polymers, and fluorescently

labeled polymers. Minimum patterning size of some of these materials is near 10 nm,

like the PMMA pits patterned in Figure 1.3, and unlike SFIL, optoelectronic devices

have successfully been manufactured using the NIL process. With nanoimprint surface

modification of polymer thin films has also been performed. Traditionally it is difficult

to create nanoscale surface morphology. However, NIL is an ideal technique for

surface morphology such as increasing surface strength, producing

superhydrophobic,[27] self cleaning, polymer surfaces and changing electrical properties

such as conductivity. The limitation of this important process was previously stated,

because of the high pressure and temperatures the nanoimprint molds must be recoated
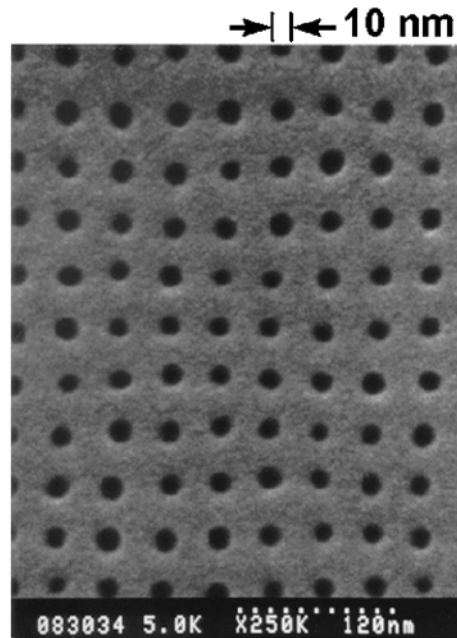
with surfactant after several imprints.

Figure 1.3: 10nm PMMA pits

Once surfactant coatings wear out there is an increase in defect levels in the imprinted devices over time. Since current NIL mold coatings have such a short lifetime and we lack understanding of the effects of nanoimprinting on the wear and degradation of surfactant coating for large-scale fabrication of polymer structures we need to look into how to create a fabrication technique that will allow fabrication output to increase. The purpose of this research is to study surfactant degradation after annealing and also nanoimprinting using surface characterization techniques.

CHAPTER II

THERMAL NANOIMPRINT LITHOGRAPHY

As we are studying the surfactant wear of coatings used for thermal nanoimprint lithography, it is important to understand the process that is thermal NIL. First we must have a mold, made of silicon or silicon oxide, as well as a substrate coated in thermoplastic polymer film. The nanoimprint mold is fabricated using a thermally grown SiO2 wafer by reactive-ion etching. The nanoimprint mold is coated with FDTS or OTS by soaking molds in a dilute FDTS or OTS solution in heptane for 10 minutes. After this preparation of the mold a typical nanoimprinting procedure is followed. The mold, and the substrate coated with thermoplastic polymer film are aligned and heated, to 175° C for 5 minutes. Next cooling takes place, and the substrate is detached from the mold, and the nanostructures are produced in the polymer film. When the surfactant coating has worn out, this final step requires more a physical force in order to detach the two, causing defects in the polymer as it sticks to the mold. This process is outlined in Fig 2.1.

Silicon or silicon oxide mold

Thermoplastic polymer film

Substrate

Heat to melt polymer &
apply high pressure

Mold-substrate separation
after cool down

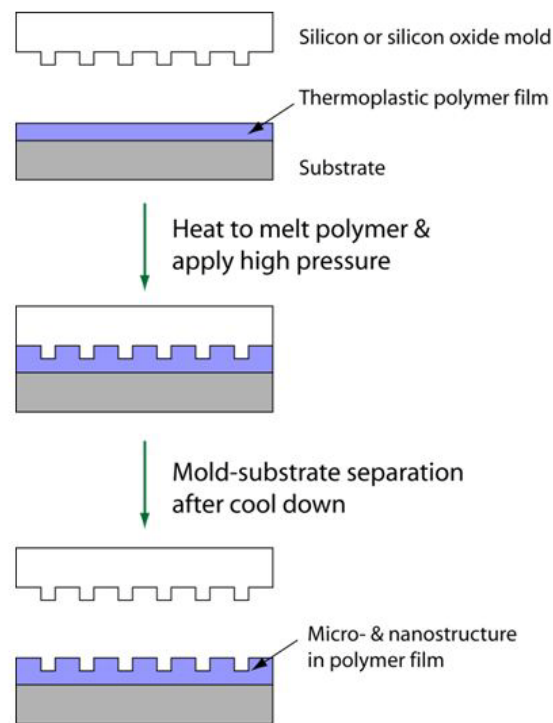Micro- & nanostructure
in polymer film

Figure 2.1: Thermal nanoimprint

Another type of thermal nanoimprint is roll-to-roll imprinting (Fig 2.2). Roll-to-roll nanoimprint and its variations are practical for creating ordered micro- and nanostructures on large objects used in daily life.[28-31] For instance this type of NIL could be used to coat glass used on a skyscraper in order that the building would have self cleaning features. This would allow the building owner to not need to hire people to clean the building. Roll-to-roll works by rolling a substrate, plastic is typically used, through an impression roller and a Gravure cylinder. The Gravure cylinder is what is used as the mold, and imprints features into the resist as it rolls through. Unfortunately, with roll-to-roll, over time the resist layer might degrade in the heated environment.
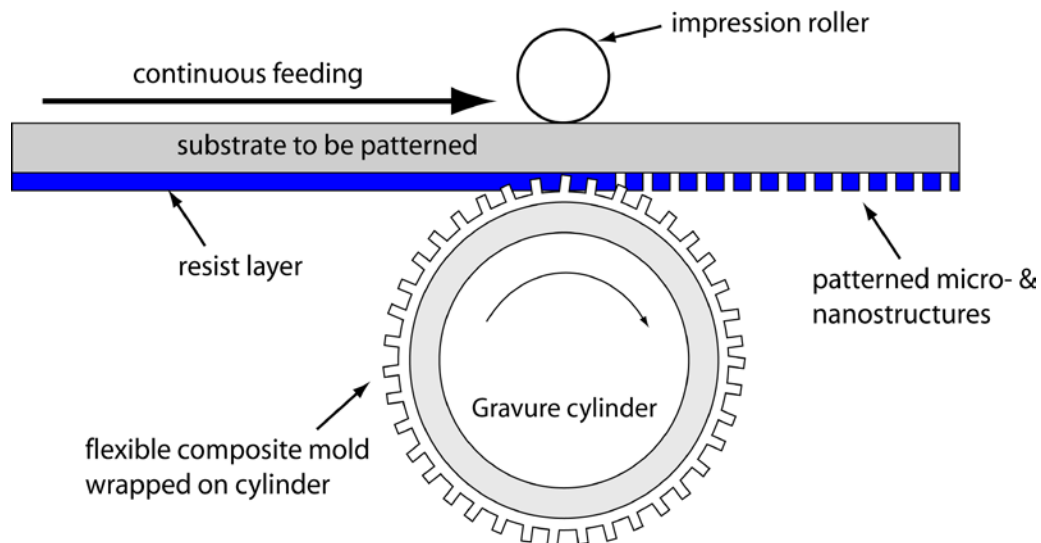
Figure 2.2: Roll-to-roll patterning

For our sample preparation we ran a thermal stamp nanoimprint with the OTS, and FDTS surfactants. After the nanoimprint was complete the mold surfaces were investigated. Another way we analyzed surfactant degradation was to do thermal annealing in air. For thermal annealing, molds with FDTS and OTS surfactant coatings were heated on a hot plate for specific times at various temperatures in order to understand degradation in an ambient environment. The mold surfaces after annealing were investigated using goniometry and x-ray photoelectron spectroscopy.

CHAPTER III

INSTRUMENTATION AND TESTING

In order to understand why surfactant coatings have such a short lifetime and the overall effects nanoimprinting has on these silanes we need to fully understand how the monolayers break down. We did this by, first, better understanding current polymer coatings, OTS and FDTS, and where scissions may take place in nanoimprint. The most important information to consider when studying surfactant wear is the chemical makeup of the surface coating and the surface property change such as surface energy. In Figure 3.1 we can see how FDTS degrades when undergoing thermal nanoimprint or thermal annealing. This degradation is characterized by surface energy analysis, a KSV CAM system was used to understand change in surface energy. Also, with x-ray photoelectron spectroscopy (XPS), change in chemical makeup was determined. Finally SEM was used to characterize nanoimprinted structures.
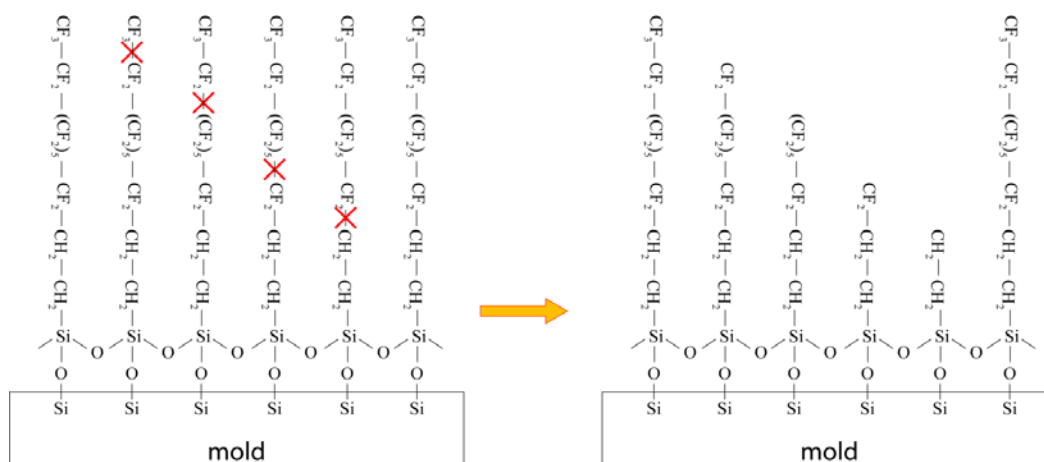
Figure 3.1: Surfactant scission

The first attribute of the surfactant coatings we looked at was the surface tension, and how it changed over time due to different temperatures. In order to study this feature we used a KSV Contact Angle Measurement System goniometer. The KSV CAM measures the contact angle of H2O on the surface of the mold. Looking at the intersection of liquid, gas, and solid in Figure 3.2 we see the contact angle, θ, which helps us understand wetting. This is helpful because the contact angle is related to surface tension, γ, of the substrate.
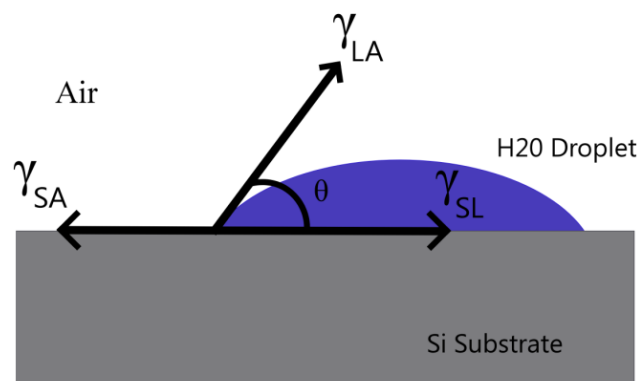

Figure 3.2: Contact angle calculation

In order to use the goniometer, after annealing or imprinting the mold, the Si mold is loaded onto the CAM system and water droplets placed on the surface and an black and white image is acquired. Software determines the contact angle by looking at the change in black and white pixels. The surface tension of the substrate is then calculated:

$$\gamma_{LA} \cdot Cos\,\theta = \gamma_{SA} - \gamma_{SL} \qquad (3.1)$$

After surface energy was calculated, when studying annealing, samples were further processed and contact angle measurements were taken again to see how the surface energy changed over time.

Another technique used was x-ray photoelectron spectroscopy, this is used to analyze the chemical makeup of the mold surface. An XPS creates an ultra high vacuum environment, and focuses an x-ray on the mold being studied. Electrons in surface molecules can be ejected by absorbing high-energy X-ray photon. The emitted photoelectrons have characteristics energies that is related to the type of the source atoms and its local binding environment . Because there is an ultra high vacuum we are able to measure the binding energy of the ejected photoelectrons. These binding characteristics can reveal the chemical composition at the surface.

CHAPTER IV

SURFACTANT COATINGS

4.1 Common Surfactants

Two typical NIL anti-adhesion mold coatings used for NIL are perfluoro-decyl-trichlorosilane (FDTS) and octado-decyl-trichlorosilane (OTS). Coatings are chosen for their low surface energy, this allows the mold to be more easily released from the polymer after the imprinting process. FDTS is a type of mono-alkyl-tri-chloro-silanes (MTS) and has a surface energy of 12 mN/m. Once we have FDTS we need to coat the SiO_2 mold in order to form the anti adhesion layer, this process can be followed in Figure 4.1. First FDTS is mixed with the solvent and the chlorine group is changed to an OH group, or is hydroxilated. Next the hydroxilated FDTS is absorbed by the oxygen from the molds surface of the SiO2. Finally the hydrogen from the hydroxilated FDTS and the oxygen from the SiO_2 becomes water and is removed in a dehydrolyzing process. As this occurs on the surface the monolayer is formed on the surface of the mold, and we have an anti-adhesion coating in place.
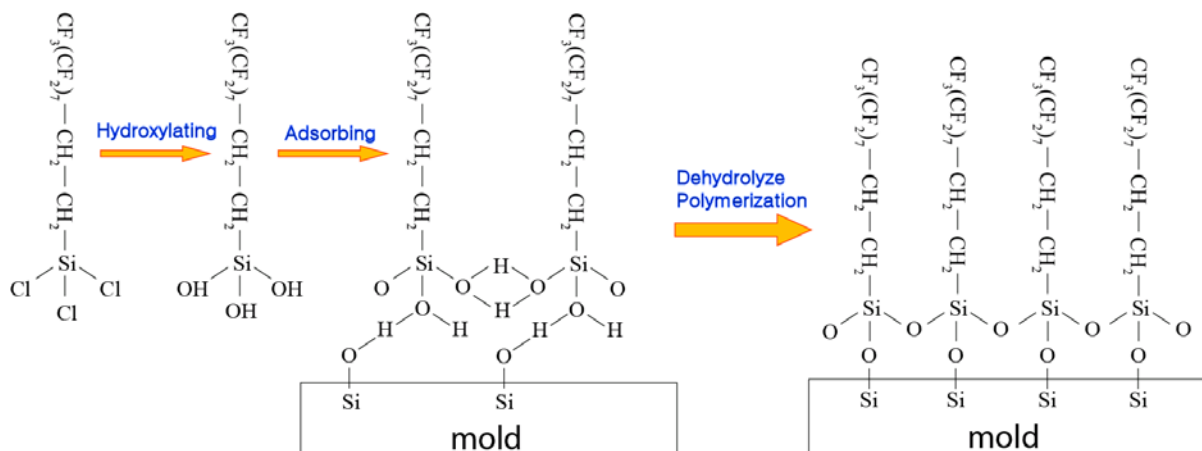
Figure 4.1: FDTS solvent coating

4.2 OTS

We wanted to characterize the wear of the most commonly used, in nanoimprint, mold surfactants so we studied perfluoro-decyl-trichlorosilane and octado-decyl-trichlorosilane. The first thing in addressing surfactant wear in nanoimprint is to understand the mechanism through which surfactant coating degrades. The stability of PTFE-like coatings on nickel template and their interaction with polymer resists during hot embossing have been reported.[32] This focuses on the stability of self-assembled monolayers on mold materials and their interaction with polymer resists during nanoimprint. The SAMs on a mold surface and their thermal behavior are probed initially by the surface-analysis technique of studying contact-angle measurement.

The first contact-angle measurement studied OTS at 300° C over a period of an hour of annealing this can be seen in Figure 4.2. Initially a drastic decrease in contact angle after annealing at 300°C is observed when in an ambient oxygen rich

environment. After the initial large drop in contact angle, the angle decrease

continuously as annealing progresses. This shows that the surface energy of the mold

coating would not be lasting very long, and would be a limiting factor in large scale
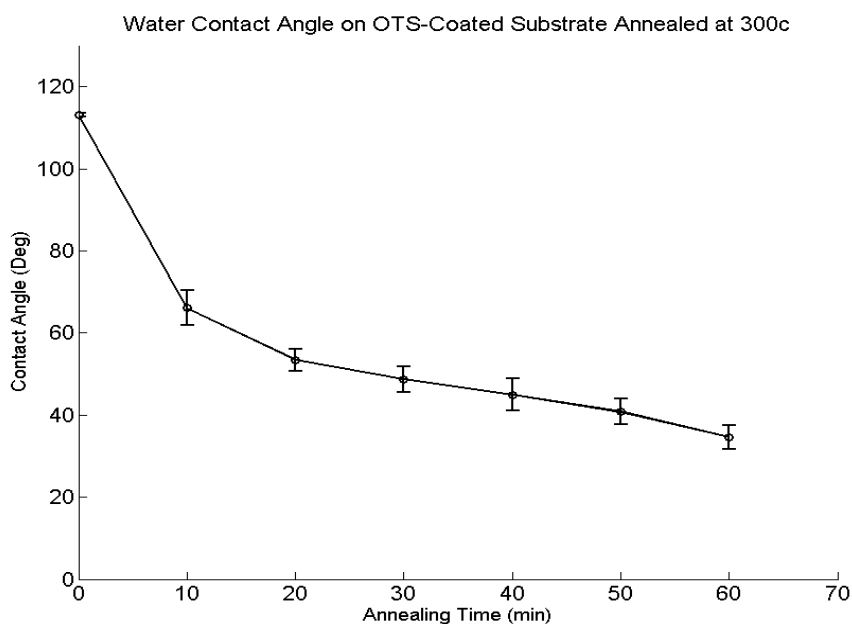
nanoimprint like roll-to-roll.

Figure 4.2: OTS contact angle measurements after 300° C anneal

This decrease in surface energy is further inspected by understanding the

bonding energy on the surface, calculated using XPS. For OTS measurements with

XPS we annealed at 300°C for 30 minutes. After this annealing we saw that the C1s

spectra (Figure 4.3) had almost completely leveled off, indicating that there was very

little carbon left on the surface. Also we saw a large increase in the O1s spectra (Figure

4.4) this is possibly changing the results from what we would expect to see in a typical

nanoimprint environment. Also we see a shift in the O1s peak, from these results we can see that the carbon bonds in OTS are breaking down and possible bonding with oxygen (e.g., C-OH, C=O) occurred.
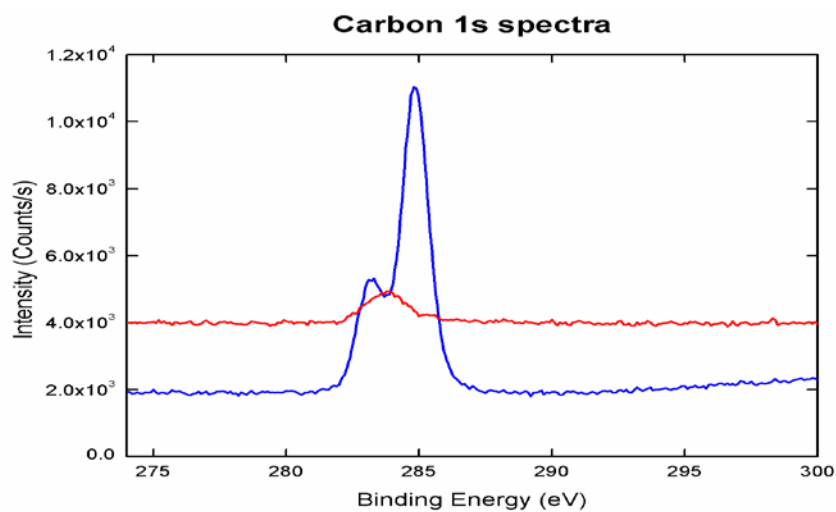

Figure 4.3: Binding energy spectra of OTS before (blue) and after (red) anneal for C1s
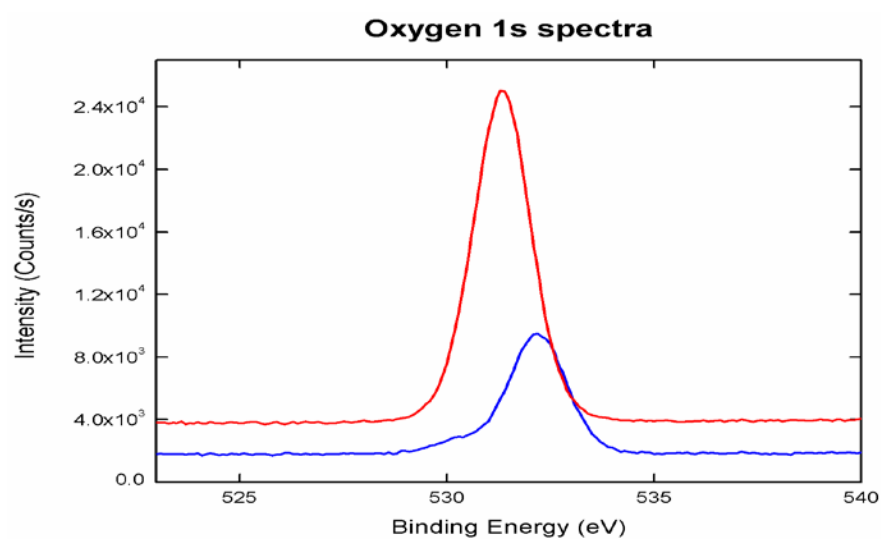

Figure 4.4: Binding energy spectra of OTS before (blue) and after (red) anneal for O1s

After we reviewed OTS surfactant degradation through thermal annealing, in air, we found it also important to study what degradation would occur during nanoimprinting. In order to understand the effects of heat we ran several imprints at 50°C intervals. Looking at these binding energies we see that there are much better results when considering the oxygen bonding, and carbon scissions. We see that OTS C1s peak intensity decreases only slightly as nanoimprint temperature increases (Figure 4.5). Another important find is that O1s peak position does not change, so there are no C=O or C-OH formations (Figure 4.6). OTS degradation is much less than that annealed in air, possibly due to the shielding from oxygen by PMMA during nanoimprinting.
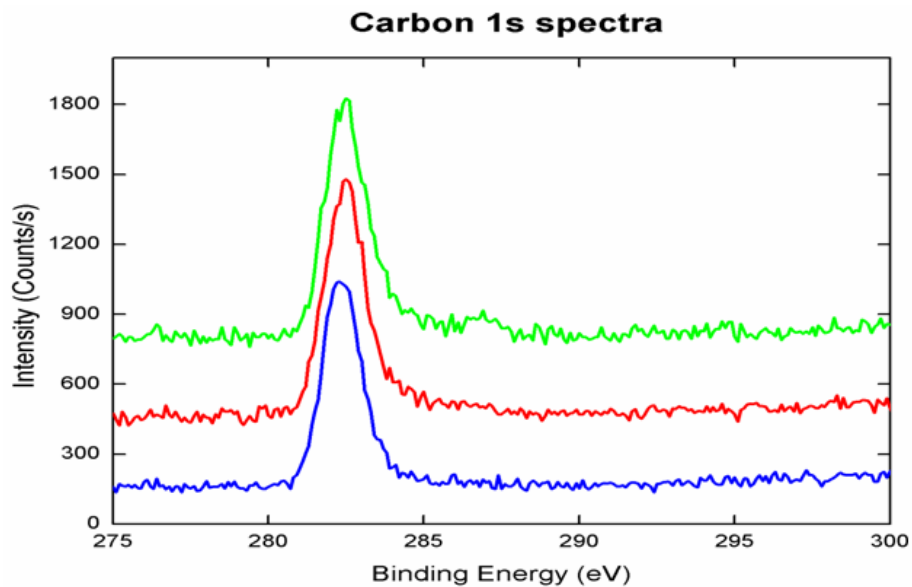

Figure 4.5: XPS spectra of C1s for OTS after PMMA nanoimprint for 30 minutes at 250oC (blue), 300oC (red) and 350oC (green)
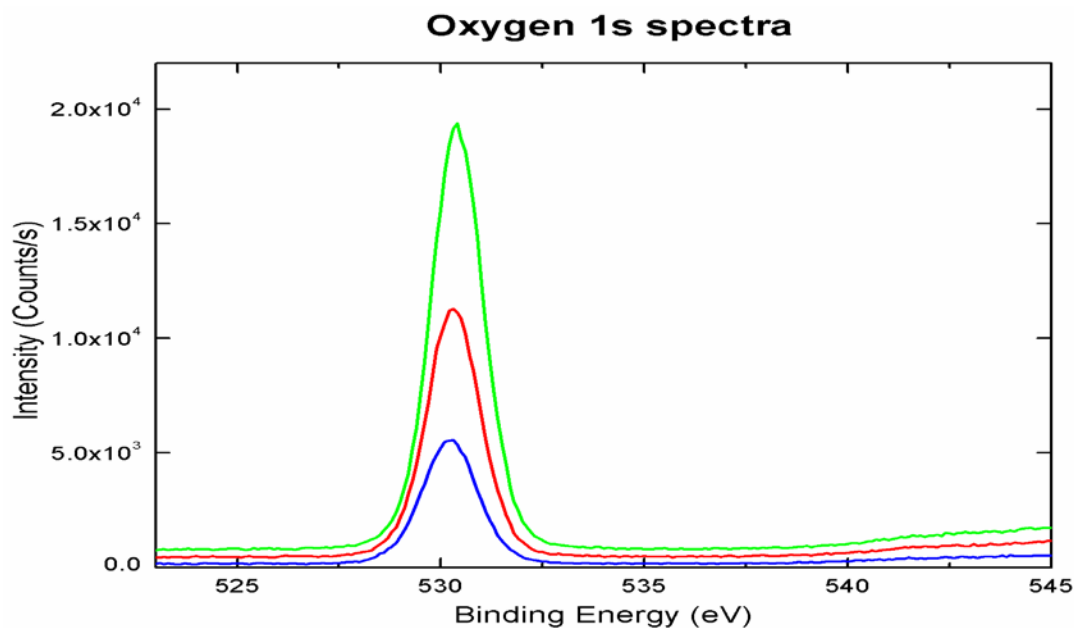
Oxygen 1s spectra

Figure 4.6: XPS spectra of O1s for OTS after PMMA nanoimprint for 30 minutes at 250oC (blue), 300oC (red) and 350oC (green)

OTS is not a very reliable surfactant coating for anything in a heated environment for a long time. Therefore this coating would not be very useful for roll-to-roll thermal nanoimprint. Although we saw better stability with stamp and print nanoimprinting, there is still oxygen bonding on the surface of the mold.

4.3 FDTS

Another of the common surfactant coating for thermal nanoimprinting is perfluoro-decyl-trichlorosilane. To investigate the surfactant wear of FDTS we ran similar tests to those ran on OTS. We began with studying the surface energy, collected using the CAM system, then used to x-ray photoelectron spectroscopy to analyze binding energy on the surface.

When the contact angle of OTS was measured we saw a large decrease, after only 10 minutes. Because of these results we expected similar results with FDTS however, when looking at contact angle measurements in Figure 4.7 we noticed small change in the contact angle over time . In fact, even after several hours of annealing at 350°C we never saw the same decrease in contact angle that we saw with OTS. Even after 60 minutes, we only saw a very small change in surface energy, as the contact angle only changed by 1°. This led us to believe surfactant wear was not very rapid with an FDTS coating, and annealing was continued for ten hours. Even after observing such low degradation after such a long time, we knew contact angle measurement may be misleading because the contact angle may still be large after FDTS degradation due to remaining fluorinated groups on mold surface.
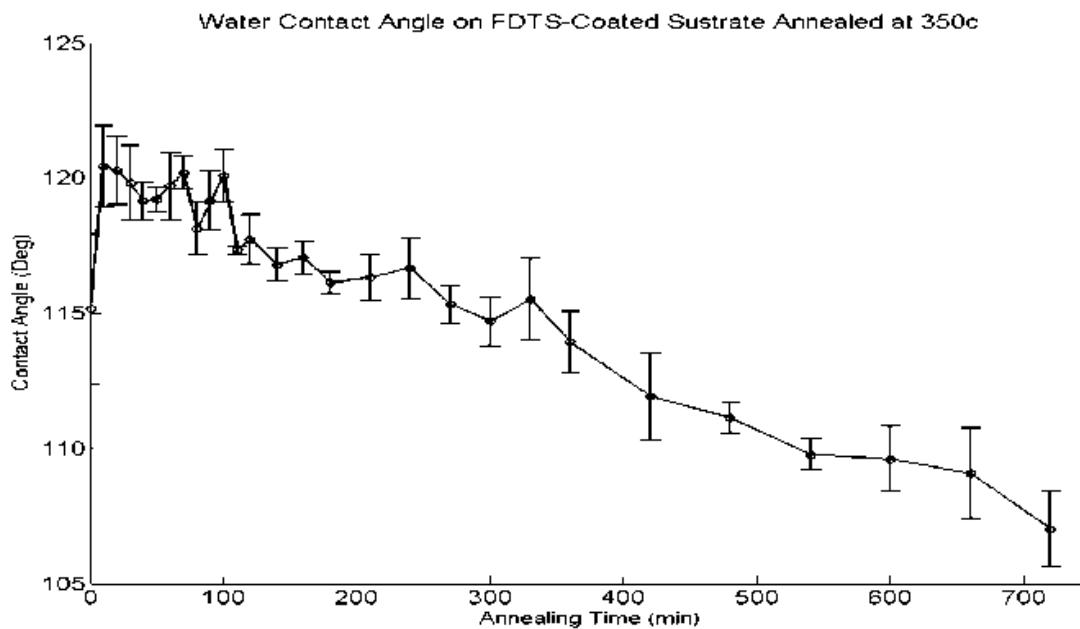

Figure 4.7: FDTS contact angle measurements after 350° C anneal

To better understand how this may occur we looked at where scissions take place on the dehydrolized FDTS molecule. As scissions occur on the surface we see that the FDTS tail does in fact have fluorinated groups remaining, these can be viewed in Figure 3.1. Through this we understood that although the Fluorine bonds were breaking they were not displaced from the substrate causing contact angle measurement results to be misleading. The fluorine groups on the end of the tail, are what made it appear as though there was small change in contact angle measurement. As we are studying these fluorinated groups we need to evaluate the binding energies on FDTS after annealing.

There is a large decrease of F1s peak after annealing, the decrease observed here indicates significant fluorine loss after thermal anneal (Figure 4.8). Very similar to the OTS results we also see an increase of O1s peak and shift of peak position may be contributed to both increased exposure of the substrate due to chain scission and the formation of C=O and C-OH groups (Figure 4.9). Another interesting result is the change in carbon binding viewed from x-ray photoelectron spectroscopy (Figure 4.10). From the Carbon 1s spectra we can see that the CF3 group is completely gone after thermal anneal. There is also a large drop in CF2 peak after two hours of annealing. However, (CH2-CH2)-CF2 peak remain unaffected by the thermal anneal process. The change of C1s peaks indicates gradual chain scission over time.
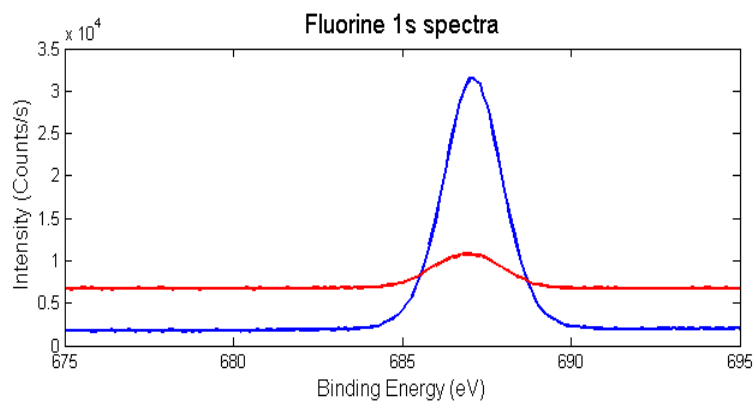
Figure 4.8: Binding energy spectra of FDTS before (blue) and after (red) anneal for F1s
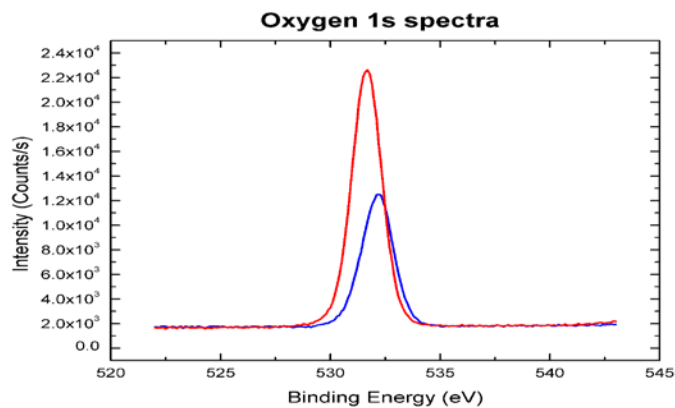

Figure 4.9: Binding energy spectra of FDTS before (blue) and after (red) anneal for O1s
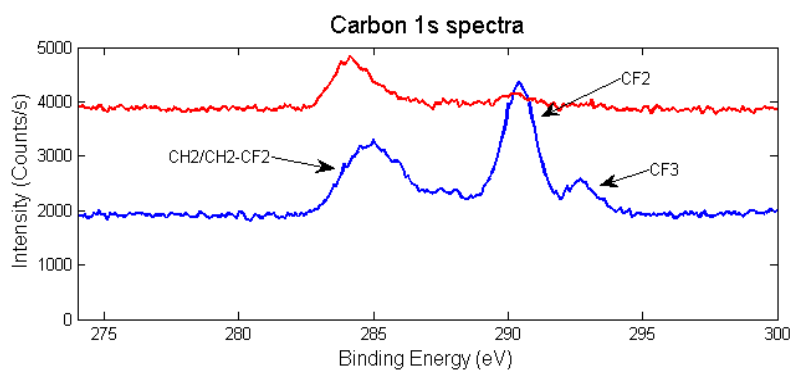

Figure 4.10: Binding energy spectra of FDTS before (blue) and after (red) anneal for C1s

Looking at the same binding energy level, carbon 1s, after nanoimprint as opposed to thermal annealing we see a large change. As we observe from Figure 4.11 when in nanoimprint, the ratios among different C1s species do not change. At this temperature, FDTS loss mainly comes from the detachment of the loosely adsorbed FDTS molecule as seen in PMMA spectra. It is also understood that chain scission is not observed after nanoimprinting.
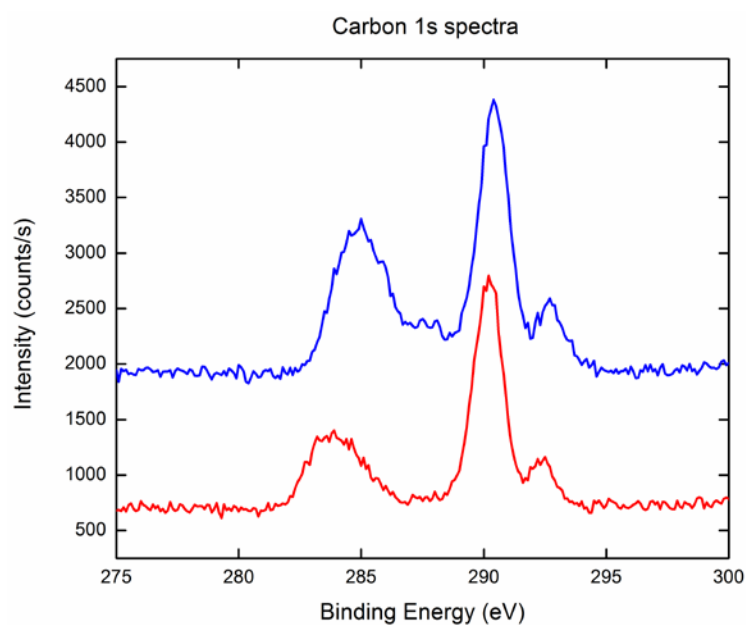

Figure 4.11: XPS spectra of FDTS before (blue) and after PMMA nanoimprint for 2 hours at 250 °C (red)

To further confirm this we wanted to also study the surface of PMMA after it was imprinted using NIL with FDTS coated mold. Results were as we suspected, C1s and F1s spectra indicate that the molecule is entirely transferred from FDTS to the

PMMA surface after nanoimprint at this temperature (Figure 4.12, Figure 4.13). This shows that the FDTS is not being completely absorbed on the mold surface, and is then becoming attached to the PMMA surface.
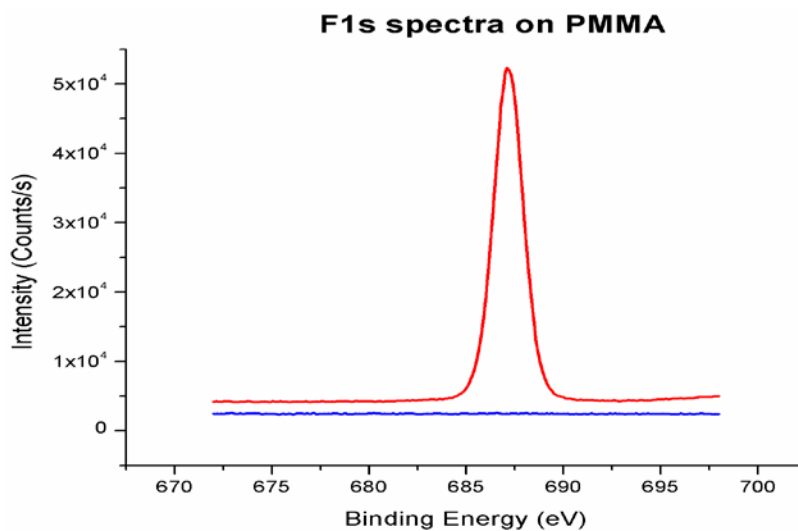

Figure 4.12: XPS spectra for F1s of PMMA surface before (blue) and after (red) nanoimprint at 200 °C for 30 minutes (FDTS)
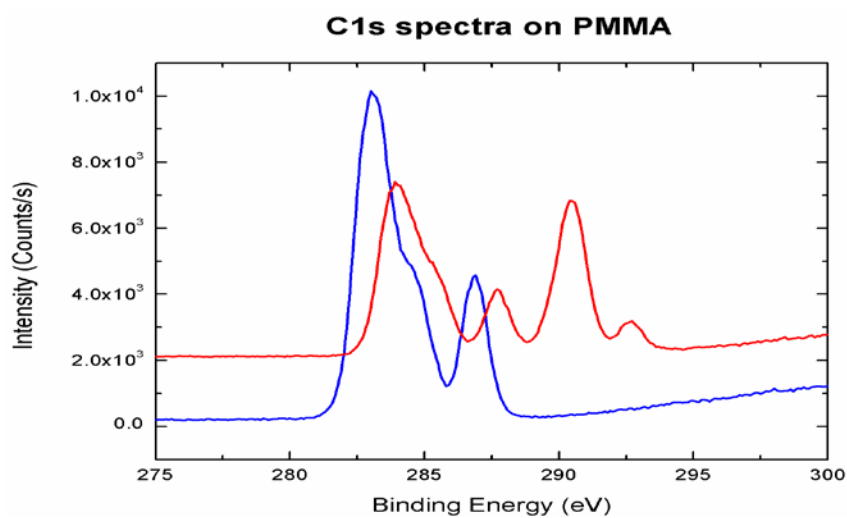

Figure 4.13: XPS spectra for C1s of PMMA surface before (blue) and after (red) nanoimprint at 200 °C for 30 minutes (FDTS)

4.4. Conclusion of Thermal NIL with Surfactant Coating

After both annealing and imprinting FDTS and OTS we have been able to understand the process of surfactant degradation. We see that FDTS and OTS undergo significant degradation when annealed in air and gradual degradation by chain scission is observed. Although they both undergo significant degradation, FDTS has much better temperature stability than OTS. For both, much less degradation occurred in nanoimprint as compared to samples annealed in air was observed due to the shielding of oxygen species in nanoimprint. This observation lead to the conclusion that OTS or FDTS are good enough for conventional thermal nanoimprint, and we will be able to expect a fairly long lifetime on mold in conventional nanoimprint because of the lack of oxygen in that environment. But they are not suitable for large-area roll-to-roll thermal nanoimprint in an ambient environment because the mold is exposed to air at constant high temperature thus surfactant degradation can continuously occur.

CHAPTER V

A NEW STRATEGY

5.1 Embedded Anti-Adhesion

There is an obvious problem with surfactant wear in an ambient environment that

needs to be taken care of for large-area imprinting. Typically the mold releasing agent,

normally surfactant coating, is located on the surface of the mold. This is a problem

because this thin coating is in constant exposure to any other agent in the environment.

In order to overcome the inevitable mold surfactant degradation, we can place the mold

releasing agent into the resist formula and no surfactant coating on mold surface is

needed! After heating, the surfactant molecules in resist migrate to the surface as

illustrated in Figure 5.1. This forms an anti-adhesion layer between the mold and the

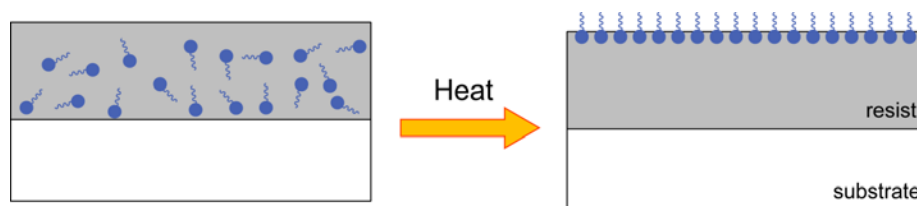nanoimprint resist.

Figure 5.1: Anti-adhesion migration due to heat

5.2 Zonyl

The candidate we chose for this application was zonyl (Figure 5.2). zonyl is a

fluorinated compound with self cleaning characteristics, these characteristics include a

low surface energy so it will be promising for anti-adhesion. Another important

characteristic is that this compound can be added into the nanoimprint resist solution

without a problem. Also, zonyl is amphiphilic, it can migrate to the surface of PMMA

thin film during annealing, thus forming a surface layer that prevents polymer adhesion

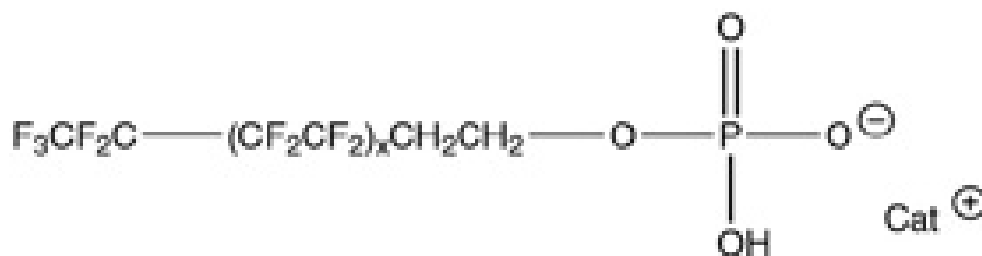to mold surface during nanoimprint.

Figure 5.2: Zonyl molecule

When using zonyl for this new strategy, there is no need for surfactant coatings

on the mold surface, thus completely relieving surfactant degradation issues. Typically

after a nanoimprint you must physically detach the mold from the substrate, which can

cause service damage to the resist. After nanoimprinting with an embedded anti-

adhesion molecule we experience the mold automatically separating from the substrate.

This shows that the anti-adhesion properties of the zonyl resist solution have much

better anti-adhesion qualities. The removal of mold surfactant coating makes the whole

process highly compatible with roll-to-roll nanoimprint in an ambient environment.

One thing that is important to look at is how this surface handles thermal

annealing, and also nanoimprint. There were two very promising results from these

tests. First of all after a thermal anneal we saw a slow increase in the contact angle of the zonyl solution. This is a very promising outcome, as both FDTS and OTS saw a decrease in their wetting ability after thermal annealing. Another encouraging result, is that after a thermal NIL we saw that the zonyl coated substrate had an increase in the contact angle by 15°.

5.3 Embedded Anti-Adhesion Conclusion

The contact angle measurements were so promising that we wanted to also look at the SEM results in order to see if the features also turned out well after imprinting with this new NIL strategy. From SEM we see that high fidelity pattern transfer with low defect density is achieved in nanoimprint using zonyl (Fig 5.3). In this case there is no surfactant coating on mold, showing that such anti-adhesion strategy is highly effective. If there was no zonyl in PMMA, we would see many defects formed during mold releasing due to strong mold-PMMA adhesion, such as the defects seen in Figure 5.4.
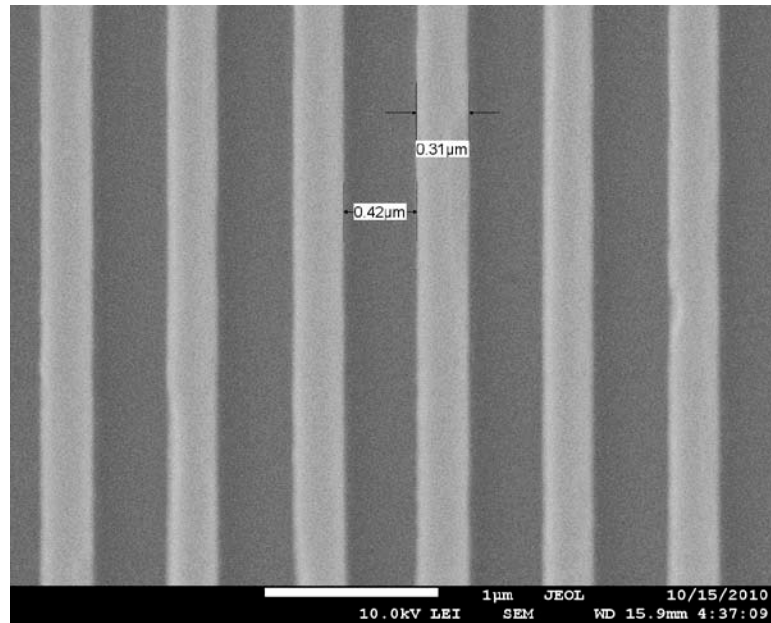
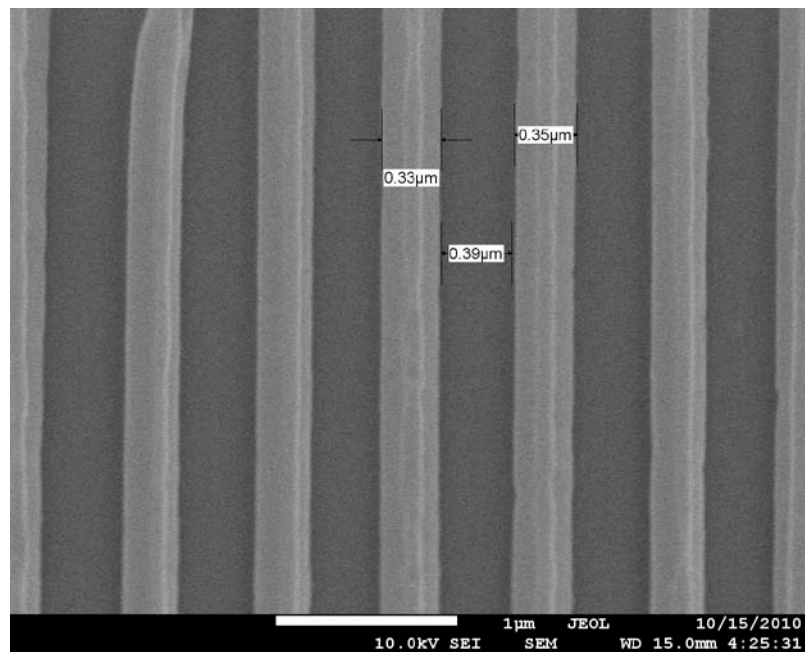Figure 5.3: SEM image of dense grating lines in PMMA with Zonyl

Figure 5.4: SEM image of PMMA grating without Zonyl

CHAPTER VI

CONCLUSIONS

High-resolution and low-cost fabrication techniques are essential for nanotechnology to overcome the commercialization barrier to benefit our society. Since its inception, nanoimprint has become the ideal technology to fabricate dense sub-micron structures over large areas with low cost, which are important to many applications such as surface modification and diffractive optical devices. As surfactant coatings are an important part of the nanoimprinting process, it is imperative to understand the entirety of their degradation.

We see that FDTS and OTS undergo significant degradation in air and gradual degradation by chain scission is observed. Although they both undergo significant degradation, FDTS has much better temperature stability than OTS. Both FDTS and OTS suffer degradation under nanoimprint conditions, but less degradation than the samples annealed in air was observed due to the shielding of oxygen species. Through this degradation we see the detaching of physically absorbed surfactant molecules from mold and their embedding in polymer surface. This surfactant degradation is so great that it is a very practical issue for large-area nanoimprint in an ambient environment. Adding surfactant (zonyl) into resist formula is a highly effective way for mold releasing. This will enable nanoimprint without the need for mold surfactant coating, thus particularly useful for continuous nanoimprint for large-scale manufacturing of surface nanostructures in an ambient environment.

There are many ways to extend this work into further research. A more in depth characterization by FTIR and Raman techniques to identify the chemical bonds after annealing and nanoimprint would be helpful in further explaining what chemicals remain on the surface of the substrate. It would also be beneficial to do a quantitative analysis will be carried out to establish a model to predict the lifetime of SAM coating for nanoimprint. This can be done by investigating mold surfactant degradation rates at different temperatures. With this we could better prescribe the best mold surfactant coating to be used in large-scale nanoimprint. Other alternative anti-adhesion techniques, such as embedded anti-adhesion, avoid SAM degradation issues. Finally a better understanding of surfactant stability in UV-curable nanoimprint would be beneficial. All of these further studies would help to produce a fabrication strategy that could further increase throughput of nanostructures produced through NIL.

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