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Hydrogen silsesquioxane (HSQ) for use in nano imprint lithography

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Hydrogen silsesquioxane (HSQ) for use in Nano Imprint Lithography

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ABSTRACT

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Hydrogen silsesquioxane (HSQ) for use in Nano Imprint Lithography
2009
Robert Krchnavek, Ph.D.
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Innovations are being researched, using materials science, in the areas of sub-100nm feature production. Current methods such as electron beam lithography (EBL), Extreme Ultra-Violet Lithography (EUV), and Nano-imprint lithography (NIL) are currently being studied to deliver a high throughput, low-cost process, and high field size for nano-lithography. EBL is a technique which can generate very small features (sub-10nm) but is a serial process which has undesirable time constraints. EUV is the latest generation of photo-lithography which can produce 35nm features, but has a limited area of exposure. NIL is a high resolution high throughput process, but still has time constraints with imprinter fabrication and pattern predictability. Important aspects of NIL are the creation of imprinters and the anti-adhesive layers used to protect the imprinters. Hydrogen silsesquioxane (HSQ) is a spin on dielectric with properties of a negative e-beam resist which can generate a SiO_2 like material. This can then be used as an imprinter for NIL work with significant process advantages over the standard technique for fabricating imprinters. HSQ has been observed to also have a time dependency factor during the electron beam process. For NIL to work effectively anti-stick layers are needed to ensure the correct designs are imprinted. Anti-stick layers such as F13, and Nanonex create a monolayer of atoms designed to reduce the effects of surface bonding on the nano-scale.

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CHAPTER I

Introduction

Nanolithography, or lithography at the nanometer scale, refers to the fabrication of nanometer-scale structures, meaning patterns with at least one lateral dimension between the size 1nm and less than 100nm. The semiconductor industry has been a leader in developing tools and techniques for nanolithography. The masked based lithographic tools and techniques used in the traditional semiconductor industry have entered the nanorealm (sub-100nm) and will contribute to nanotechnology development. This is true especially in the area of nano-electromechanical structures (NEMS), and for provision of the larger-scale supporting and connecting structures for molecular electronics and lab-on-a-chip systems. But, the new area of nanotechnology goes well beyond integrated circuit devices broadening into bioresearch, nano-particles, and mechanical properties of nano-materials.

The process behind the production of current integrated circuits involves shining UV light through masks onto a photosensitive resist then developing the sample thereby replicating the mask features in the photo resist. The wavelength of light limits the feature size which can be created. Current research in this area requires the creation of sub-70nm features using smaller wavelength electromagnetic radiation and other unique lithography techniques, such as electron beam lithography for mask generation [1] These techniques are contributing to higher costs for fabrication facilities in the next generation of integrated circuits and especially in bioresearch. For some of these applications,

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ultra-high resolution pattern replication over large areas will be critical for success. Photolithography, as used in the semiconductor industry, may satisfy the needs for some nano-scale applications. However, it is likely it will not be cost effective to handle large area reproduction needed in other avenues of nanotechnology. New techniques are being researched with the purpose of creating even smaller features over a large area with high output and thus keeping the cost, of new nano-features, lower. This thesis will begin with a brief review of the most common nano-scale lithography techniques to understand their strengths and weaknesses.

1.1 Photo-Lithography

Photo-lithography is a method used in semiconductor fabrication using light to replicate patterns. It uses light to transfer a pattern from a mask to a light-sensitive resist also known as a photoresist, placed on a substrate. The sample is then put through a series of processes which may include etching, metal deposition, and doping. In a complex integrated circuit a wafer can go through the photolithographic process up to 50 times. Figure 1.1 shows the depiction of a substrate with a resist that is exposed through a mask. Photo-lithography offers a large area exposure, which is limited to 15mm x 15mm, but you can't get >15mm without step and repeat, which creates errors[1].

Top View   Cross Section

Figure 1.1 Photo resist exposed through a mask, showing the removal

of the exposed material [2]

1.1.1 Photo-Lithography Procedure

The wafer (substrate) is first treated to remove contaminants and provide a suitable surface for applying the photoresist. A wafer is then spin coated with a photoresist. Photoresist is a liquid solution that uses the spin coating to produce a uniform thickness across the whole substrate. By changing the speed and acceleration you can vary the thickness of the resist.

The wafer is then "soft-baked" to drive off any solvent that may still be present. It is then placed on a mask aligner and exposed to an intense UV light. Positive photoresist becomes less chemically robust when exposed while negative photo resist becomes more chemically robust when exposed. Figure 1.2 shows a depiction of a photo resist material being exposed and developed, removing the positive photoresist, preserving the negative photo resist [1].

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Radiation
Mask
Photosensitive material
Substrate

Photosensitive materials properties change only where exposed to radiation

Spray substrate with developer solution

a) Positive resist, developer solution removes exposed material

b) Negative resist, developer solution removes unexposed material

Figure 1.2 the depiction of a substrate being exposed with the positive

resist being removed, while the negative resist is preserved [2]

In the etching step, a liquid or plasma chemical agent removes the uppermost layer of the wafer in areas not protected by the photoresist. After all this processing the photo-resist is ready to be removed. Either a liquid "resist stripper", which alters the resist so it no longer adheres, to the substrate, or

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oxygen plasma can oxidize the resist producing volatile components, which is called ashing. The pattern can also be lifted off, which is a process that involves depositing some material, commonly metal, and then stripping the resist off by chemical etching [3]. This is shown through figure 1.3. Other subsequent processing steps include dielectric formation, doping, semiconductor deposition and others. The details of these steps are not critical to this work and are readily available in numerous texts on semiconductor processing [1,2,3].

Figure 1.3 the process which the photo resists is removed revealing the transferred pattern [2]

1.1.2 Resolution

The projection of a clear image of small features onto a wafer is limited by the wavelength of the light used, and the ability of the reduction lens system to

capture enough diffraction orders from the illuminated mask. Current systems use light with wavelengths of 248 nm, which allow features down to 35nm [4]. The minimum feature size that can be projected can be represented by equation 1.1.

$$F = k * \frac{\lambda}{N_A}$$

(1.1)

Where F is the minimum feature size, k is the coefficient that encapsulates process-related factors, λ is the wavelength, N_A is the numerical aperture of the lens. With this equation we can see that decreasing the wavelength and increasing the numerical aperture the resolution can be increased. So we can get the smallest feature size by making lenses larger and bringing the wafer closer thereby increasing N_A. In addition, there is also a concern with the depths of focus, which can be seen in equation 1.2.

$$D_F = k * \frac{\lambda}{N_A^2}$$

(1.2)

The depth of focus restricts the thickness of the photo-resist and the depth of the topography of the wafer. To flatten the topography before high-resolution lithography a chemical mechanical polish is used. By increasing the numerical

aperture, N_A, you have the consequence of reducing the depth of focus. The focus and the error that comes from improper focus is shown in figure 1.4. If the focus is not correct the desired patterns will be distorted.

Figure 1.4 the depiction of light being focused, showing the error that can happen when not focused properly [2]

1.1.3 Extreme Ultra-Violet Lithogrpahy (EUV)

Traditionally, advances in optical lithography have relied on using shorter and shorter wavelengths of light, which can produce smaller features. Extreme Ultra-Violet Lithography (EUV) uses light with a wavelength of 193nm producing features of down to 35nm for exposure over a maximum field of 33mm². To expose large areas a process known as step and repeat is needed. This process goes to a point on the wafer, exposes, moves, exposes, and repeats

until most of the wafer is exposed. Unfortunately this increases the output time for a completed wafer and has an alignment synchronization issue, meaning that each end of the exposure needs to be lined up exactly to the next exposure area. This is the standard technique for ICs because individual ICs are rarely larger than 33mm². For other applications that may require high resolution over a large area (>33mm²) this is a challenging alignment issue. Figure 1.5 shows the components of a EUV Lithographer.

Figure 1.5 Components of EUV lithographer [6]

1.2 Electron Beam Lithography (EBL)

The practice of using a beam of electrons to generate patterns on a surface is known as electron beam lithography. The primary advantage of this technique

is that you can make features less than 10nm since the exposure isn't dependent on diffraction of light. This form of lithography has found wide usage in mask-making (for masks used in photolithography), low-volume production of semiconductor components, and research & development.

Figure 1.6 E-beam lithography exposure of resist [6]

A beam of electrons is focused and exposes certain areas of an e-beam resist. Depending on the resist used, positive or negative, the bonds are weakened or strengthened making certain areas on the sample more soluble. For instance, if you exposed a positive e-beam resist the bonds become more soluble and thus easier to etch away. This can be seen in figure 1.6. E-beam lithography is not suitable for high-volume manufacturing because of its limited throughput. The beam must be scanned across the surface to be patterned since pattern generation is serial. This makes for very slow pattern generation compared with a parallel technique like photolithography in which the entire surface is patterned at once.

1.3 Nano-Imprint Lithography

Nano-Imprint Lithography (NIL) is the production of nano-features by physically moving material into designated patterns. This requires the creation of an imprinter/mask, which is made through other various lithography techniques such as EBL. This imprinter is the negative of the pattern which is to be created. By pushing the imprinter into a pliable material a pattern can be made with nano-scale resolution. The size of the features that you want to create is nominally equal to the size of the features on the imprinter. There are two types of NIL which can be used: Hot Embossing and Step and Flash Imprint Lithography (SFIL). Hot Embossing involves heating polymers to a level at which they are easily pliable or semi-liquid, this can be seen in figure 1.10. The polymer is then physically moved to create a pattern. SFIL uses NIL and a photosensitive polymer with a low glass transition temperature (Tg).

Figure 1.7 Hot Embossing NIL Technique [7]

The NIL process has high throughput with high resolution. It begins with making the imprinter. This uses conventional techniques that determine the resolution NIL will be working with. There has also been research into using other materials, such as different metals for making imprinters [1]. When an imprinter is made, an anti-adhesive layer is placed onto the imprinter. The material being imprinted into can be a polymer, such as PMMA, because polymers can be made pliable at different temperatures. When the imprinter imprints, it is then cooled down to the region where the polymer is rigid and

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pulled from the sample giving a completed imprint. The greatest advantage to NIL is the large field size which can be produced with this process. NIL will be discussed more thoroughly in chapter 2 of this thesis.

1.4 Conclusions

The value of a technique comes from the resolution, throughput, cost, alignment, and field size which that technique can produce. Table 1.1 shows each technique's throughput, resolution, and field size which were discussed in the chapter. From this table NIL, which is greatly dependent on the imprinter features, is described as a high-throughput, high-resolution technique, and large field size.

Table 1.1 Lithography Technique's Throughput, Resolution, and Field Size

Technique	Throughput	Resolution	Field Size
Photo-Lithography	High	Low Resolution (35nm)	33mm²
Electron Beam Lithography	Low	High Resolution (5-20nm)	50-75 mm²
Nano-Imprint Lithography	High	High Resolution (5-20nm)	200 mm²

Chapter 2

Nano-Imprint Lithography

Nano-Imprint Lithography (NIL) is the production of patterns by physically moving material into designated patterns. This requires the creation of an imprinter/mask, which is made through other various lithography techniques such as EBL. This imprinter is the negative of the pattern which is to be created. By pushing the imprinter into a pliable material a pattern can be made at the nano-scale. The size of the features that you want to create is directly proportional to the size of the features on the imprinter. Hot Embossing involves heating polymers to a level at which they are easily pliable or semi-liquid. The polymer is then physically moved to create the pattern[7].

From figure 2.1 and the above paragraph, imprinter fabrication is a critical component of successful NIL. From Table 1.1, EBL is the only readily available tool to pattern the imprinter at the highest possible resolution. In this thesis I will discuss techniques for making imprinters at high resolution with a desirable anti-stick coating.

Figure 2.1 Hot Embossing NIL Technique [7]

2.1 Imprinter/Mask fabrication

In this thesis I am going to cover two different methods to fabricate a patterned imprinter using electron-beam lithography. The differences between the two processes are determined by the number of steps taken to make the imprinter. The basic theory on how to make the imprinters will be outlined.

2.1.1 SiO$_2$ Imprinter Fabrication

The first type, or standard, of imprinter manufacturing is used by producing a silicon dioxide (SiO$_2$) imprinter. The pattern is written into an electron sensitive resist known as polymethylmethacrylate (PMMA). The first

step is to spin on a layer of PMMA onto thermally grown SiO_2 with a Si substrate. For this thesis I used a bilayer method of e-beam lithography to create my patterns. This required using a lower weight of PMMA (100k) spun on first and having a higher weight of PMMA (950k) spun on over the lower weight. This allows for a small undercut on the developed samples as seen in figure 2.5. A pattern is then written into the imprinter using EBL. Next, the imprinter is developed to remove the written part of the PMMA. For the same exposure time the lower weight PMMA is exposed slightly more than the higher weight. This leaves a slight undercut when the PMMA is developed. Cr is deposited onto the sample landing on the exposed substrate. The imprinter is submerged in a chemical solvent to liftoff the PMMA leaving the metal on the substrate. The imprinter is etched down using an etching technique which removes the substrate faster than the metal deposited. This leaves an upraised pattern which can be used for imprinting purposes. Figure 2.2 shows the steps needed to create SiO_2 imprinter through electron beam lithography.

The nano-scale features can be made out of either Si or SiO_2, however SiO_2 seems to be a better choice [9]. Silicon is a crystalline structure. A crystalline material possesses a highly regular atomic arrangement along a particular plane. The plane can become weak and break if it is subjected to pressure which can happen to imprinters. SiO_2 does not have any crystal plane which can experience weakness in the presence of pressure. This is because it is an amorphous material when it is thermally grown. Therefore, a SiO_2-based imprinter is better suited for nano-imprint lithography.

Figure 2.2 An illustration of the steps that are involved with the fabrication of a

SiO$_2$ imprinter through electron-beam lithography [7]

Whether a resist is positive or negative plays a very important role in how that resist will be used. A positive resist such as PMMA is one that when exposed to electron irradiation, the polymer chains become fragmented. The fragments are a lower molecular weight and thus dissolve quicker in a developing solution. This leaves a positive tone pattern in the resist.

PMMA is one of the most widely used electron sensitive resists today. It is an ultra-high resolution, high current positive resist used for nanolithography. It has poor sensitivity and poor dry etch resistance. It sticks well to almost any surface, can be stored easily, is not white light sensitive, and gives very reproducible results [10]. ZEP is a very high resolution positive resist that like PMMA, is simple to use and gives reproducible results. Compared to PMMA it has the disadvantages of poor adhesion and undercut profiles [11]. I didn't use ZEP over PMMA because I wanted a good adhesive resist with a good undercut profile. Table 2.1 shows a comparison between electron beam resists available along with their resolutions and sensitivities.

Table 2.1 The resolution and sensitivity of positive electron sensitive resists

[7].

Resist Type	Resolution (nm)	Sensitivity ($\mu C/cm^2$)
PMMA	10	100
EBR-9	200	10
PBS	250	1
ZEP	10	30
AZ5206	250	6

2.1.2 Metal Deposition/Etching

Post processing transfers the pattern of nanoscale features that has been replicated in the resist to the substrate. Physical vapor deposition can use either evaporation or sputtering to deposit a layer of metal on a sample. Evaporation physically heats a metal until the point that it evaporates. It uses current transferred through the metal (or alternatively, an electron beam) to heat the metal up and the evaporated material deposits onto the sample. This is used for vertical deposition, meaning that the metal will not coat the sidewalls of the nano-scale features. This makes it easier to liftoff the resist without ripping the material from the substrate. This can be seen in figure 2.3(a). Figure 2.3(b) shows

sputtering deposition but, as can be seen, it also covers the side walls. This creates problems when removing the resist creating undesirable results.

Figure 2.3 The forming of deposited material by using (a) evaporation (b) sputtering physical vapor deposition [7]

Etching transfers the pattern in the resist to the substrate by removing the exposed material. Metal is used as a hard mask for the SiO_2. Metal is removed at lower rates than Si and SiO_2. This leaves the metalized sections raised higher than the exposed areas and thus allows for a complete three dimensional imprinter. Dry etching methods utilize plasma based techniques. The three basic ones are high pressure plasma etching, reactive ion etching (RIE), and ion milling [11]. These allow small features to be patterned and allow for high-aspect-ratio vertical structures. Unfortunately, dry etching provides less selectivity than wet etching. Selectivity is a property of etching that measures the ability with which the etchant can differentiate the masking layer (i.e resist) and the material that needs to be etched [6].

An etch can be isotropic or anisotropic. With an isotropic etch, the etchant removes the material in all directions at the same rate. With an anisotropic etch,

the etchant does not attack the material in all directions. An anisotropic etch can create vertical sidewalls [11].

2.1.3 Conclusion

Six steps are needed to create a SiO_2 imprinters . First, you thermally grow SiO_2 onto a silicon substrate and spin coat PMMA. Then a specific pattern is e-beam written into the resist. After the pattern is e-beam written the sample is then developed. When the sample is finished being developed Cr is evaporated onto the surface. Then a liftoff step is needed to remove the PMMA covered with metal. Finally, the metal pattern is used as a hard mask for etching producing an imprinter with raised features. Figure 2.4 shows a completed SiO_2 imprinter after it has gone through all six steps. This was created at Rowan University using e-beam lithography, utilizing PMMA and thermal metal evaporation. The resist was exposed with a point dose of 3fc on a Leo 1530 VP utilizing a Nano-Pattern Generating System (NPGS) program. The resist was removed and the sample was plasma etched with oxygen for 40 seconds to create 150nm high pillars 100nm apart utilizing an Oxford RIE.

Figure 2.4 A completed silicon dioxide imprinter with raised pillars created

at Rowan University

2.2 Anti-Adhesive Agent

One of the most important aspects of nanoimprint lithography is to prevent the polymer resist of the imprinted sample from adhering to the imprinter. If nanoscale sub-100nm features are being imprinted into a polymer resist, it is important to employ an imprinter with good anti-adhesive properties. If the surface energy of the imprinter is not sufficiently lower than that of the polymer resist layer there will be damaging effects. The polymer resist layer of the imprinted sample will tear and buckle. The nanoscale features of the imprinter could be destroyed. The features either collapse on the surface of the imprinter or get stuck in the resist of the sample being imprinted. Finally the resist can stick to the surface of imprinter. These effects can be prevented by applying an anti-adhesive agent to the imprinter. This would chemically alter the surface of the imprinter so that the surface energy would be greatly lower than the polymer resist layer on the imprinted sample. Thin fluoropolymer films were generated on microscale featured nickel stamps from a CH_4/H_2 plasma [12]. However they create a layer too large for nanoscale processing. A monolayer deposition is needed with nanoscale features so that the features are maintained and not covered up by the anti-adhesive coating. Other chemical coatings exist that are better suited for nanoscale features. Some are a hyper-branched perfluorinated polymer (HBFP) and tridecafluoro-(1,1,2,2)-tetrahydrooctyl-trichlorosilane (F_{13}-TCS) [11]. There will be more discussion on anti-adhesive layers in chapter 4.

2.3 Imprinting Process

There are two different nanoimprint lithography techniques: hot embossing and step-and-flash-imprint lithography (SFIL). They pattern a resist through physical deformation. However, they differ in the type of polymer resist used and the manner in which it is processed to preserve the replicated pattern. Heating and cooling steps are used with hot embossing to cure a thermoplastic resist polymer. SFIL uses a light source to cure a photo-curable polymer resist. Both are efficient techniques because of their parallel nature; however, there are several variables that need to be adjusted in order to produce defect-free and repeatable imprints. This thesis will discuss hot embossing NIL since that was the technique used for this research.

The imprinting process requires an imprinter, a sample to be imprinted into, and a press. Hot embossing NIL uses heat on the imprinting sample and drives materials such as PMMA into the glass transition region[7]. This is the region where the polymers become pliable. When the material becomes pliable it can be moved into desired features. Using this technique features can be created at the nano-scale using NIL.

After creating the imprinting mask, the mask is flipped over and aligned with the imprint sample. The sample is spin coated with a single layer of polymer resist such as PMMA. The imprinting sample is heated above the glass transition temperature, and comes in contact with the imprinter mask. Pressure is then applied and the imprinting material is moved due to the imprinting mask. The sample is then cooled down below the glass transition temperature. The imprinter

is released from the sample, and removed for further processing [7]. This can be seen in figure 2.1.

This is the most basic method of NIL, but can be problematic for post processing. The biggest problem is removing the small layer of polymer that is left on the sample. To remove the left over polymer a solvent solution can be used for a short amount of time to remove the material. If that polymer isn't removed the post processing can have problems depositing materials that attach to the substrate. This is because when the material is deposited it attaches to the polymer. When you liftoff the polymer the material that you want on the substrate is removed.

To solve this problem a bilayer of resists can be employed. With a bilayer the imprint can be wet etched to get an undercut. Then when the imprint goes through the liftoff process the deposited material will stay on the substrate.

A bilayer can be used so each layer of resist can be independently etched with different solvents. An isotropic wet etch of P(MMA-MAA) can be done using methanol or toluene. A wet etch or chemical etch of PMMA can be done using chlorobenzene or toluene to provide an undercut [13]. This can be seen in figure 2.5.

Figure 2.5 An illustration showing the functionality of a bilayer resist[11]

2.4 Conclusion

Nano-Imprint Lithography is the creation of patterns by physically moving material at the nano-scale level. NIL requires both a strong imprinter and good anti-adhesive coating to be effective. SiO_2 imprinter fabrication is the standard method for creating reliable imprinters but requires at least six steps for processing. Proper imprinting requires the use of reliable anti-adhesive coatings. Without an anti-adhesive coating nano-imprint lithography cannot be used as a useful lithography technique.

Chapter 3
Hydrogen silsesquioxane (HSQ)

The world today has seen a huge explosion in the area of storage and processing of electrical information. To keep up with the demand of larger capacity, faster processing speed, and lower prices, engineers have had to develop novel ways of creating features at the sub-50 nm scale. Typical high-resolution lithographic techniques, capable of creating sub-50 nm features, are often slow and expensive if the processed area is large. For example, patterned magnetic media for future hard drives may require 5 cm^2 of sub-50 nm features. Nano-imprint lithography (NIL) may provide the required resolution and process area, coupled with potentially low cost and fast turnaround, to produce future devices such as patterned magnetic media. In the previous chapter, the standard method of fabricating imprinters was reviewed. In this chapter, a new method is considered that significantly simplifies imprinter fabrication.

3.1 Hydrogen Silsesquioxane (HSQ) Imprinter Fabrication

There are many ways of using EBL to create imprinters for the NIL process. One way is by using a positive resist and depositing metal. Removing the resist and etching the non-metal parts produces the desired result. On the other hand, a simpler alternative could involve a negative resist, such as Hydrogen Silsesquioxane (HSQ). HSQ is used as a spin on dielectric, but it does have some interesting properties that are useful in the area of NIL. HSQ is an SiO_2-like material which can be patterned using EBL [16, 17]. Its glass-like rigidity makes

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it a suitable material for imprinter fabrication. With this material we can eliminate two steps for imprinter manufacturing which will be seen further in this thesis.

Because HSQ acts as a negative resist and is a derivative of SiO_2, the final pattern of nano-scale features can be directly written into it [8]. The final pattern is written in the HSQ resist, developed, and post treated with heat.

HSQ displays some properties that enable it to be both a resist, and a robust enough material that can be used for the nano-scale features on an imprinter. It was purchased as a flowable oxide (FOX-12) from Dow Corning Inc. and dissolved in Methyl isobutyl ketone (MIBK) [11]. HSQ has a general molecular formula of

$$(HSiO_3)_{2n}, \; n = 2,3, \ldots \qquad\qquad (3.1)$$

Its initial molecular structure spun onto the substrate is shown in figure 3.1.

When the HSQ is spun onto the substrate it is in the caged form as seen in figure 3.1(a), but when it is exposed to electron irradiation, a network structure is developed. The final structure is more chemically and mechanically stronger than the initial structure. When areas are exposed to electron radiation (electron beam) they cannot be washed away with the developer [6].

Figure 3.1 (a) Structure of HSQ when it is spin coated onto Si. (b) HSQ structure when it has been thermally annealed or electron beam exposed [18].

Experiments show that the critical dose to produce semi-dense lines in HSQ is approximately 1400 μC/cm^2 [8]. Semi-dense refers to the proximity of patterns to each other. A dose of 1900 μC/cm^2 is needed for isolated lines. The contrast of HSQ was found to be 1.63 by measuring the remaining film thickness of 100 μm square pads over a dose ranging from 100 to 1000 μC/cm^2. With this moderate level of contrast you can expect to produce scumming and bridging, terms to mean areas not completely removed during post processing, with unexposed regions between dense lines [7]. One major downside to HSQ resist is that it experiences shrinking of the nano-features of approximately 20 to 25% between 375 to 800°C during the thermal treatment phase [7]. This suggests there will be a shrinking effect during the exposure to electron irradiation. The final downside is that HSQ has a short usable shelf life of 6 months. It must be refrigerated, and kept at low humidity in a non-glass container when being stored.

After the pattern is written in HSQ, it can be developed using sodium hydroxide (NaOH). The more concentrated the developer the rougher the surface will be [7]. After development the HSQ is subjected to a final heat treatment which strengthens the bonds promoting a defined network structure. The resulting HSQ structure is chemically similar to the SiO_2 structure used in the last method.

A negative, spin-coatable, inorganic silicon oxide resist known as hydrogen silsesquioxane (HSQ) [9] was employed to develop a new method of imprinter fabrication. Because HSQ is a negative resist the final pattern of nano-scale features can be directly written into it. This reduces the necessary steps of the PMMA process into a 3 step process as seen in figure 3.2. Deposition of a metal, liftoff, and etching, are eliminated in this new process. Essentially, the final pattern is written in the HSQ resist, developed, and post treated with heat.

Figure 3.2 An illustration of the necessary steps to create an HSQ-based

imprinter through electron- beam lithography [7]

HSQ has been shown to produce sub-10nm features. Experiments also showed that the critical dose to produce semidense lines is approximately 1400 $\mu C/cm^2$ [12]. While a dose of 1900 $\mu C/cm^2$ is needed for isolated lines. Unfortunately HSQ has a large downside and that is a short shelf life. Once the pattern is written in HSQ, it can be developed. HSQ can be developed simply using sodium hydroxide (NaOH) [14].

3.2 Time Dependency of Exposure for HSQ

Hydrogen silsesquioxane (HSQ) is used as a high-resolution, negative-tone, inorganic electron-beam resist for use in nanoimprint lithography. \In this work, the electron beam dose required for high-resolution (sub-50 nm) HSQ patterning is shown to be very sensitive to the time the sample has been at room temperature.

For example, a sample written with nano-scale features at constant e-beam dose will increase in size approximately 66% per hour of time at room temperature. The minimum feature size for a given dose depends on the ambient conditions the sample was stored in (air, nitrogen, and vacuum). Samples stored in vacuum are not exempt from the feature broadening. Long e-beam writing times for large-area patterning of nanoscale features will likely suffer from this time dependence unless the exposure dose is varied during the e-beam writing. These experiments relating the various ambient conditions and the minimum feature size under dose control are presented.

Studies have shown that over a week [1] and two week [13] long process, air has had an effect on the sensitivity and contrast of EBL patterned on HSQ. There have also been accounts of HSQ sensitivity changing over a smaller period of time, during the EBL process. In small periods of e-beam writing time, e.g. one hour, HSQ features showed a time dependency [23]. These findings prompted the following experiments. Investigating the effects that HSQ storage in different atmospheres has on the sensitivity of HSQ during hour-long sessions of EBL.

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3.3 Experiment

Three separate environments (air, nitrogen, and vacuum) were used to evaluate the time dependent exposure dose of FOX-12 HSQ [18] during EBL. The first test was in an air environment. A silicon wafer was cleaved into 10mm by 10mm squares using the technique shown in figure 3.3. They were spin coated with HSQ for 30s at 3000rpm using a Laurel Technologies spinner. The resulting thickness of the Fox-12 solution was 135 nm. The sample was then prebaked on a hotplate at 250ºC for 3 minutes. The HSQ was exposed in a Leo 1530VP Scanning Electron Microscope (SEM) fitted with Nanometer Pattern Generation System (NPGS) capabilities for EBL. The sample was exposed at 30KV with a beam current of 407.3 pA, and developed in a 1:3 ratio NaOH:DI water for 4 minutes and blown dry with nitrogen.

Figure 3.3 Silicon Wafer cleaved into 1mm by 1mm sections[7]

The nitrogen and vacuum samples were prepared in a glove box. The sample, HSQ, spinner, and hotplate were all placed in the glove box. Since house vacuum is half atmosphere, the glove box was purged three times with nitrogen to

reduce water molecules which may affect HSQ. For the nitrogen sample, the atmosphere in the glove box consisted of nitrogen. For the vacuum sample, the glove box was kept under vacuum. The same procedure for the air sample was repeated for the nitrogen and vacuum sample. After each sample was pre-baked, they were transported to the SEM in a container, with their respective atmosphere (air, nitrogen, or vacuum). The samples were removed from the container, placed on the e-beam writing stage using the sample holder shown in figure 3.4. They were then loaded into the SEM, which took approximately 20 seconds. This was the only time the nitrogen and vacuum samples were exposed to another atmosphere other than their ambient conditions before being place in the SEM vacuum. The SEM was then placed under vacuum to begin the e-beam writing process. The same e-beam exposure and development steps were used for each sample.

Figure 3.4 an illustration of a top-down, and side view of the Sample

holder designed for EBL [7]

Additional samples were made and stored in air, nitrogen, and vacuum for 8 hr,
24 hr, 48 hr, and 120 hr time periods to determine the impact of longer-term
storage on feature size. During that time they were not tampered with, they just
sat in their atmospheres for extended periods of time. After the 8 hr time period
was up, the sample was transported and placed in the SEM as described earlier.
The sample was e-beam written with the same pattern as the previous samples and
developed. This was duplicated for the 24 hr, 48 hr, and 120 hr time periods.

The pattern for electron-beam writing, shown in Figure 3.5, was designed
with a range of point doses from 20-59 fC (520-1534 $\mu C/cm^2$). The pattern
consisted of a grid of five squares by eight squares, each 100 μm ×100 μm in size
and 50 μm apart. Each square was exposed with a different point dose, yielding
an array of dots with a pitch of 400 nanometers. These dimensions were chosen
to eliminate proximity effects between the different doses. This pattern was e-

beam written in the HSQ five times, each 15 minutes apart. The finished HSQ sample was imaged on the 26 fC pattern for each time it was run to determine the change in pillar diameter over time. 26 fC was used since it was known to be a dose that gives a pillar that won't be under or over exposed.

Figure 3.5 E-beam patterns which was written in HSQ

For the first experiments I processed the HSQ in air ambient prior to EBL. Moving the sample from processing to the NPGS/SEM took 15 minutes before the sample was placed in the vacuum chamber. The e-beam writing did not commence until 15 minutes after the sample was placed in the chamber - this includes pumping time, focusing, current determination, and planar mapping. The samples were e-beam written for an hour and took 15 minutes to develop and post process. The longer-term samples were moved in the same way, and then went through the same development and post processing. All samples were sputter

coated with approximately 10 nm of gold for subsequent imaging to determine the feature size. Using the SEM, the feature diameters were determined at a 26 fC point dose looking straight down on the sample to determine feature size. The same experiments were run for both nitrogen and vacuum atmospheres for spinning and pre-baking.

3.4 Results

All measurements were taken from the 100μm × 100μm area at the 26 fC dose point. This 26 fC dose point was chosen because of previous e-beam writing experience obtained for NIL purposes [7]. All the samples showed an increase of pillar diameter over the one hour writing time. Fifteen points were taken from the 26 fC area at each 15-minute marker, up to 60 minutes. The zero time in the figures 3.10, 3.11 and 3.12 represent the time the first e-beam written pattern started. This would be after all pre-processing, mounting, and setup. The fifteen minute marker was the start of the same pattern written on a different part of the sample fifteen minutes after the previous sample had started. This continued for the full hour and is consistent through all the samples. Figure 3.6-3.9 shows scanning electron micrographs of the samples after e-beam writing and post-processing and figure 3.10 shows the 26 fC feature size as a function of e-beam writing time for the three different atmospheric conditions (air, nitrogran, and vacuum). Each graph point is the mean of 15 data points.

Figure 3.6 SEM views of E-beam written pillars in HSQ

Figure 3.7 The increase in pillar diamater of an e-beam written pattern with pre-processing in air, a) at 0 minutes, b) 15 minutes, c) 30 minutes, d) 45 minutes, e) 60 minutes.

Figure 3.8 The increase in pillar diamater of an e-beam written pattern with pre-processing in nitrogen, a) at 0 minutes, b) 15 minutes, c) 30 minutes, d) 45 minutes, e) 60 minutes.

Figure 3.9 The increase in pillar diamater of an e-beam written pattern with pre-processing in vacuum, a) at 0 minutes, b) 15 minutes, c) 30 minutes, d) 45 minutes, e) 60 minutes

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The sample in air showed the most increase over the writing time. The first 26 fC area (noted as the zero time) had a mean diameter of 31 nm, while the final 26 fC area (noted at the 60 minute mark) showed feature sizes of 53 nm in diameter.

The samples ran in nitrogen showed a slower increase, compared to air, over the hour period. The first 26 fC area showed the features to be approximately 30 nm in diameter, while the last 26 fC area showed feature sizes of 47 nm in diameter.

The samples ran in vacuum showed the same rate of increase of pillar diameter, compared to nitrogen, over the hour period but they started at a smaller feature size. The first 26 fC area showed the features to be about 28 nm, while the final 26 fC area showed feature sizes of 45 nm.

It can be seen that the smallest feature sizes over time correspond to pre-processing under vacuum, while air ambient conditions yield larger features. We can also see that the first 26 fC dose, corresponding to a time of 0 minutes, for all three conditions has approximately the same feature size. This leads to the conclusion that the mechanism affecting HSQ sensitivity occurs over time but also depends on the conditions used to prepare the films for writing.

These experiments produced a great deal of data, which can be seen in the appendix. Diameter size was taken on individual pillars and a graph was made of mean pillar diameter over a period of time with time as the X-coordinates and pillar diameter as the Y-coordinates. This was made with all atmospheres and

placed on the same graph to help analyze the data, this can be seen in figure 3.10, figure 3.11, and figure 3.12.

figure 3.10 Mean pillar diameter of HSQ processed in Air, Nitrogen, and

Vacuum for an e-beam writing time of 60 minutes

figure 3.11 Variance of pillar diameters of 60 minute e-beam time, top most

HSQ in Air, middle in Nitrogen, bottom in Vacuum

We next consider the samples prepared to determine the effects of longer-term storage. Figure 3.12 shows the change in feature size (pillar diameter) for samples prepared in air, nitrogen, and vacuum. A range of points was used giving us a mean for the size of the features (pillar diameter). This graph shows a larger feature size for samples kept in air, with a decrease in size for nitrogen and the smallest size from the vacuum samples. We see the feature size increase and eventually levels out at a saturation point. From Figure 3.3 we see that keeping the samples in vacuum during pre-processing yields a smaller change in feature size over time periods up to 120 hr. However, even an 8 hr delay in processing produces feature sizes that are 58% larger than films that are processed immediately after being prepared.

figure 3.12 Mean pillar diameter of HSQ processed in Air, Nitrogen, and Vacuum for up to 120 hours, with fifteen points averaged for each data point.

The problems with HSQ involving sensitivity have been explored by [12], [19], and [20]. There is evidence to suggest that HSQ can be affected by small contaminants, which are absorbed in the HSQ layers. These contaminants impede the network formation of HSQ during exposure [12]. For the air process, contaminants are readily available, especially the presence of water, and oxygen. The vacuum sample should have fewer constituents that may affect the sensitivity but as pointed out earlier, the house vacuum used in this work was not a strong vacuum. Probably one of the most surprising results is the nitrogen sample. The nitrogen gas (99.998%, H_2O <5 ppm, O_2 <5 ppm) has low water content and should have fewer contaminants than the vacuum sample, but even the nitrogen sample exhibited the time-dependent sensitivity. These results show a need for great care during the time of soft bake to exposure.

3.5 Conclusion

HSQ is a spin-coatable dielectric that can be used for imprinter fabrication in NIL. Utilizing HSQ imprinter production some steps used in standard imprinter fabrication can be eliminated. In these experiments we have shown the sensitivity of HSQ in different atmospheric environments. Pre-processing in air seems to reduce the sensitivity of HSQ more than nitrogen and vacuum, which give the least amount of difference when utilizing EBL. During a 1 hour e-beam writing session, the feature size can easily increase by 60%. The results are even worse if there is a delay between sample preparation and e-beam writing, going over a 100% increase in feature size. Contaminants are likely a factor in the

processing of HSQ, and can affect the outcome of e-beam written features over time. From this we learn that for reliable EBL results, pre-processing of HSQ in vacuum or nitrogen is recommended to reduce the increase in feature size over e-beam writing time and samples should be e-beam written immediately after preparation. Further control of feature size may require time-dependent dose control [18].

Chapter 4

Study of Anti-Adhesive Coatings for NIL

This next part of the thesis will be about the 3 anti-adhesive coatings used for NIL. The coatings were put on imprinters and then imprinted using hot embossing techniques. Along with the coated samples, experiments were done with no anti-adhesive coatings applied, this was used as the controlled test. These experiments were done to determine the anti-stick coating that will give the largest percentage of desired pattern.

4.1. Experiment

Silicon substrates were used, and cleaved into 10mm × 10mm parts using the techniques in figure 3.3. HSQ FOX-12 was spun 30s at 2500rpm using a Laurel Technologies spinner. All sample preparation was done in a vacuum box allowing for the smallest feature size electron beam written. This was done due to the conclusions made in chapter 3. The resulting thickness of the Fox-12 solution was 100nm. The samples were moved to a LEO 1530 and e-beam written with the NPGS software.

The NPGS software utilizes CAD, which allows for the easy creation of various polygon shapes. A 100µm × 100µm square was created with NPGS allowing for many polygon shapes to be written serially. Figure 4.1 shows the pattern created, with 14 squares at different point doses, and finally a large triangle allow for an asymmetric pattern.

Figure 4.1 Pattern created using NPGS software and e-beam written into HSQ

The SEM was set to 30kV making the beam current around 403.7 pA. The pattern in each of the squares was a series of pillars with a center to center, line to line distance of 50nm. This means the electron beam sits at one point for .0006 seconds, and then moves 50nm along a horizontal line and repeats. When the beam comes to the end of the line the beam moves vertically 50nm sits and then moves horizontally in the other direction. When the beam is moved over the whole area the pattern is repeated for all 14 sets. The triangle is finished at the end. Each square was done at different point doses, which determines the amount of time the beam sits at each point. Figure 4.2 shows the pillars created with a 26fc point dose.

Figure 4.2 HSQ imprinter with center to center, line to line, of 50nm and a

height of 100nm

After the e-beam process the samples were developed using a 1:4 ratio of

NaOH and DI water. They were placed in the solution bath for 4 minutes leaving

the e-beam written pattern behind. They were then baked at 400° C for 2 hours to harden the HSQ into a SiO_2 like material. One sample was left with no anti-adhesive coating as a control test. Two were coated with F13, one at room temperature and the other heated. The final sample was coated with Nanonex NRX-100, which was done at Columbia University.

4.2. tridecafluoro-(1,1,2,2)-tetrahydrooctyl-trichlorosilane (F$_{13}$) Heated and Non-Heated Process

It is necessary for an imprinter to have an anti-adhesive coating to decrease the surface energy of the imprinter. This lowers the surface energy below the polymer resist surface energy on the imprinted sample and reduces the amount of polymer torn from the sample. F_{13} forms a covalent bond with Si, SiO_2, or HSQ but releases hydrochloric acid gas. This can be seen in figure 4.3. Because the covalent bond is so robust the coating is not removed after every imprint.

figure 4.3 The bonding of F_{13}-TCS to a Si or SiO_2 substrate through the

elimination of HCl [21].

Both imprinters were hydroxylated in nitric acid for 3 minutes. This is necessary for creating a surface that will react with the F_{13} and form a strong bond to the substrate. After hydroxylation, the imprinter was blown dry with a stream of pressurized nitrogen. If there were any streak marks present on the imprinter, this step was repeated since the area with streaks is not hydroxylated. The imprinter was transferred to the glove box after it was hydroxylated, rinsed in DI water, and blown dry. A pair of tweezers, pipette, a hot plate, a beaker, and two larger petri dishes were placed in the glove box. Also a bottle containing the F_{13} and a bottle of hexane were taken out of vacuum storage and placed in the glove box.

At this point, the rest of the coating process was performed in the glove box. Chlorosilanes present in the F_{13} react in the presence of a small amount of water, quickly polymerizing forming large chain aggregates. These would have formed on the imprinter making a non-monolayer coating. Therefore, the reaction was done in an anhydrous environment created by the glove box. Typically, a water content of less than 1 ppm is desired [7]. A vacuum was pulled in the glove box and nitrogen was pumped in. This was completed three times. Three psi of nitrogen was steadily pumped into the glove box with a small vacuum pulled allowinfg for a constant flow of nitrogen when the reaction was run.

The imprinters were placed in the center of larger 90 mm diameter petri dishes. One petri dish was placed on the hotplate and allowed to heat up to 250ºC. After 10 minutes elapsed, 65 µL of F_{13} was released into the side of the petri dish [7]. The petri dish was covered with the top to contain the F_{13}. The other imprinter was placed in a Petri dish, the F_{13} was placed in the dish, and the top was placed. The samples were left on the hotplate for 2 hours to complete the reaction. At the end of 2 hours, the imprinters were taken out of the petri dish and soaked in hexane for 1 minute. This is done to remove the excess F13, and not polymerize with atmosphere. The samples were taken out of the hexane and allowed to dry. Then the samples were taken out of the glove box and put in sample holders.

4.3. Nanonex

The final imprinters were coated with a layer of Nanonex put on by a Nanonex Ultra-100. This was done by Columbia University and sent back to Rowan University.

The Ultra-100 is designed to be used for nanoimprint mask treatment for release, surface adhesion promotion, MEMS NEMS anti-stick coating, micro and nano fluidic channel surface treatment, all-purpose UV-Ozone cleaning, resist stripping, as well as UV curing in vacuum or gas environment [22].

4.4. Imprinting Process

Once the samples were coated with an anti-adhesive coating they were ready to be used as imprinters. PMMA, with a molecular weight of 100K, was spun on to 20 silicon samples, dimensions 14mm × 14mm. The PMMA was spun for 30s at 3500 rpm, giving a height of 65nm. The imprint samples were made with larger dimensions so there would be no interference by the PMMA build up on the edge of the silicon substrate. If the built up resist on the sides is higher than the nano-features then the features will not imprint into the PMMA. This can be seen in figure 4.4.

Figure 4.4 (a) Sample that has edge bead that won't allow the nano-features to reach the PMMA (b) Sample with large area substrate which allows the nano-features to imprint into PMMA [11]

The samples were put into the Rowan made NIL imprinting press which is shown in figure 4.5. The press was designed to work with a control box, which can be seen in figure 4.6 [11]. The features of this press involve active heating and active cooling, this allows the imprint to be cooled right after imprint. This is important so the nano-features that are imprinted will stay solid immediately after

imprinting. This was designed to increase throughput by reducing the cooling time needed for the process to be completed.

Figure 4.5 NIL Press made at Rowan University

Figure 4.6 Control box used to control Imprinting Press [11]

The imprint samples were placed on the bottom plate and held on by double sided carbon tape. The samples were then blown with nitrogen to remove

any airborne particles that might interfere with the imprinting. The imprinter with no anti-adhesive coating was placed onto the imprint sample and a piece of carbon tape was placed on the non-polished side. When the top press comes into contact with the tape it will adhere to the imprinter allowing the imprinter to lift off the sample when done.

When the imprinter is placed on the imprint sample the heaters are activated and brought up to 180°C. The glass transition temperature of PMMA is $T_{g,PMMA} = 105$ºC which is the temperature that PMMA starts to become gel-like. After the press plates have been brought up to 180°C nitrogen is pumped into the press which brings the top plate down starting the imprinting process. The nitrogen was pumped in at 30psi.

The two plates were left for 4 minutes and then the active cooling is started. Tap water flows through the NIL press which drops the temperature down to 50°C in 10 seconds. This leaves the PMMA with the desired imprint. The nitrogen pressure is then flowed through the opposite input of the NIL device with the result of separating the imprinter from the imprint. This is repeated 4 more times with the imprint samples, coated with gold and analyzed with the SEM. This process was repeated with the imprinters coated with non-heated F_{13} and Nanonex.

4.5 Results

After imprinting, the samples were coated with 5nm of gold using a sputtering system, and put into the SEM. Five imprints were done with each imprinter with different coatings; no anti-adhesive agent, F_{13} non-heated, F_{13} heated, and Nanonex. Each imprint had five areas with 26fc point dose, with 50nm center to center, line to line spacing.

4.5.1 Nanonex Coated Imprinter

Figure 4.7 shows the imprint from a Nanonex coated imprinter.

Figure 4.7 SEM image of a imprint from Nanonex coated imprinter

The darker areas are the desired holes as seen in figure 4.8, while the white areas have been ripped up by the imprinter exposing the substrate as shown in figure 4.9.

| | 30nm | EHT = 10.00 kV | Signal A = InLens | Date :5 Feb 2007 |
| Mag = 251.55 K X | ├────┤ | WD = 4 mm | Photo No. = 3186 | Time :18:22:15 |

Figure 4.8 Darker areas of figure 4.7, showing the holes which were created

from the pillars of the Nanonex coated imprinter

200nm
Mag = 32.55 K X |⊢———|

EHT = 10.00 kV
WD = 4 mm

Signal A = InLens
Photo No. = 3184

Date :5 Feb 2007
Time :18:21:16

Figure 4.9 White areas of Nanonex imprint which have been ripped up

exposing the substrate

The imprint photos were imported into matlab. Matlab code was developed to determine the area of the images that had the desired pattern. The images went into matlab as a grey scale matrix with each pixel having a grey scale value between 0-1. With the number 0 indicating black while 1 indicates white. This can be seen in figure 4.10.

Figure 4.10 Second Imprint of nanonex transformed with matlab code to determine the area which has not been ripped up during imprint

The pixels of the imprint with the desired pattern were changed to 0, while the pixels of the imprint with undesirable patterns were changed to 1. The imprint images were transferred into matlab with a pixel resolution of 800 x 800. This gives 1 pixel the same area as 125 nm^2. This is 4 times the size of the desired individual patterns. The area of the imprint with the non-desirable patterns has a higher grey scale value than the areas with desired patterns. The area with desired patterns had a grey scale value between .4-.5. All pixels with a grey scale value above .55 were changed to 1, while all pixels below .55 were changed to 0. The pixels that are black (or grey scale value 0) were divided by the total number of pixels in the image. This gives an idea of the percentage of

area with the proper imprint. Figure 4.11 shows an imprint with desired features and less desirable imprints. The darker areas have the desired features, while the whiter areas show less desirable features. Appendix A shows the matlab code used for these experiments.

Figure 4.11 Area's in the image whiter with a grey scale value closer to 1 are less desirable imprint, while darker areas of the image show desired imprint.

The matlab image is enlarged, and the area of desired imprint is determined. This is repeated for each imprint done at 26fc point dose.

Figure 4.12 Original picture of imprinter next to the matlab image

The first imprint of every imprinter had no area of desired features. This is due to the fact that all of the anti-adhesive coatings are self cleaning, which means all airborne particles that aren't under the coating will not be covalently bonded to the imprinter and are easily removed by becoming trapped in PMMA during imprinting. In essence, the first imprint of all the imprinters does not contain any nano-features (e.g. contaminents or dust). This is from the natural impurities found in air which fall onto the imprinter but don't adhere due to the anti-adhesive coating. After the first imprint all the contaminants are pulled by the gel-like PMMA. So, the first imprint will have a higher amount of contaminants. Figure 4.11 was from the second imprint of the Nanonex coated imprinter. Each sample has a total of five 26fc point dose areas. The next figures show imprints 3, 4, and 5.

Figure 4.13 Third Imprint of nanonex with matlab image to determine the

area which has not been ripped up during imprinted

Figure 4.14 Fourth Imprint of nanonex with matlab image to determine the

area which has not been ripped up during imprinted

Figure 4.15 Fifth Imprint of nanonex with matlab image to determine the area which has not been ripped up during imprinted

From these images we get a percentage of desired features. Figure 4.12 shows that 96.98% of the pixels were changed to black. Figure 4.13 shows that 97.81% of the pixels were changed to black. Figure 4.14 shows that 98.03% of the pixels were changed to black. Figure 4.15 shows that 99.14% of the pixels were changed to black. This was done for each imprint done with the 26fc point dose. The mean and variance was produced and graphed which can be seen in figure 4.16.

figure 4.16 graph of mean percentage and variance of proper imprint vs. the

number of times imprinted using Nanonex

4.5.2 Non-heated F13 Coated Imprinter

The process to coat the imprinters with non-heated F13 is identical to heated F13, except they are not heated with a hotplate. The imprinters are placed in the petri-dishes and sit for the same amount of time as the heated process. The first imprint showed no results since F13 coatings are a self cleaning process. Figure 4.17 shows the second through fifth imprints.

a.)

b.)

c.)

66

d.)

Figure 4.17 a.) Second Imprint and matlab image for non-heated F13 b.) Third imprint and matlab image c.) Fourth imprint and matlab image d.) Fifth imprint and matlab image

From these images we get a percentage of desired features. Figure 4.17 (a) shows that 94.42% of the imprint was successfully transferred to the imprint. Figure 4.17 (b) shows that 82.05% of the imprint was successfully transferred to the imprint. Figure 4.17 (c) shows that 67.96% of the imprint was successfully transferred to the imprint. Figure 4.17 (d) shows that 52.78% of the imprint was successfully transferred to the imprint. This was done for each imprint done with the 26fc point dose. The mean and variance was produced and graphed which can be seen in figure 4.18.

Figure 4.18 graph of percentage of proper imprint vs. the number of times

imprinted using Non-heated F13

4.5.3 F13 Heated Imprinter

The same process was taken for the heated F13 coated imprinter. The first imprint showed no results since F13 coatings are a self cleaning process. Figure 4.19 shows the imprints from the heated F13 coating.

d.)

Figure 4.19 a.) Second Imprint and matlab image for heated F13 b.) Third imprint and matlab image c.) Fourth imprint and matlab image d.) Fifth imprint and matlab image

From these overlays we get a percentage of desired features. Figure 4.19 (a) shows that 95.53% of the imprint was successfully transferred to the imprint. Figure 4.19 (b) shows that 92.55% of the imprint was successfully transferred to the imprint. Figure 4.19 (c) shows that 85.06% of the imprint was successfully transferred to the imprint. Figure 4.19 (d) shows that 76.84% of the imprint was successfully transferred to the imprint. This was done for each imprint done with the 26fc point dose. The mean and variance was produced and graphed which can be seen in graph 4.20.

Figure 4.20 graph of percentage of proper imprint vs. the number of times imprinted using heated F13

4.5.4 Non Coated Imprinter

The same process was taken for the non-coated imprinter. The first imprint showed no results, the imprinter completely ripped up the coating on the sample. This can be seen in Figure 4.21 and 4.22.

Figure 4.21 Imprint of non-coated sample, no nano-features

Figure 4.22 Imprint sample with no anti-adhesive coating

4.6 Conclusions

From these results a graph was created showing the percentage of usable nano-features versus the number of imprints made with the different anti-adhesive coatings. This can be seen in figure 4.23.

Figure 4.23 Percentage of proper imprint vs. the number of times imprinter was imprinted (◇Nanonex, △ F13 Heated, ☐ F13 Non-heated)

From this graph and table 3.1 we see that Nanonex had the largest percentage of the imprint properly transferred during the NIL process. In fact Nanonex gets cleaner the more it is used. This does not mean that the imprints

are this exact, but this clearly shows that Nanonex will give the cleanest imprints over time.

	% of Proper Imprint No Coating	% of Proper Imprint F13 Heated	% of Proper Imprint F13 Non-Heated	% of Proper Imprint Nanonex
1st Imprint	0	0	0	0
2nd Imprint	0	95.53	94.42	96.98
3rd Imprint	0	92.55	82.05	97.81
4th Imprint	0	85.06	67.96	98.03
5th Imprint	0	76.84	52.78	99.14

Table 3.1 Imprint averages of F13 heated, non-heated, and nanonex

Chapter 5

Conclusions

New and innovative ways to create nano-features have been discussed in this thesis. Photo-lithography, X-ray Lithography, and E-beam Lithography all have advantages and challenges. Nano-imprint Lithography has the potential to be a high-resolution, high-yield tool used to create nano-features. There are many challenges with NIL. This thesis discussed the problems with manufacturing imprinters and anti-stick coatings for NIL.

From this thesis the study of HSQ has shown that the processing atmosphere is important to the desired EBL features. This work has demonstrated how HSQ features increased in size for a given e-beam dose depending on the atmosphere involved in pre-processing. By keeping the samples in vacuum during the pre-processing, desired features can be better achieved for the purpose of imprinter production for NIL.

Anti-adhesive coatings are a very important part of the NIL. This thesis has shown the effects of imprinters with no anti-adhesive coatings. By using anti-adhesive coatings such as F13 and Nanonex, features can be properly created with NIL. This thesis has also shown that Nanonex is the best coating for the desired imprint giving the largest properly imprinted area.

HSQ is currently being used in processing, materials, and medical research [24,25,26,26]. It is used widely for its ability for high resolution high throughput manufacturing and is a candidate for sub-22nm production. This research shows

that HSQ can replace previous methods of nano-lithography techniques, and should be used for future NIL production.

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Temperature Nanoimprinting Using Release-Agent Spray-Coated Hydrogen

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APPENDIX

```matlab
clear
I=imread('13.bmp');
;Matlab code to import imprinted image
whos
I=rgb2gray(I);
I=im2double(I);
imshow(I)
;Digitize image to 800 x 800 pixels , check the pixel grey scale
;If pixel grey scale above .55 then put to grey scale value of 1
; else put grey scale value of 0
M=800;
for i=1:M
   for j=1:800
      if I(i,j)>.55
         I(i,j)=1;
      else
         I(i,j)=0;
      end
   end
end
;export new image as digital image
imshow(I)
N=0;
for i=1:M
   for j=1:800
      if I(i,j) == 1
         N=N+1;
      end
   end
end

N=N/(M*800)
```

**Matlab code used to transfer SEM into grey scale image and
determine the area of the image that has the desired imprint.**

```matlab
;This matlab code will take raw data and create graph of average for 5 points
;Input raw data for graphing
a=[0];
b=[99.14
   99.19
   99.24
   99.09
   99.04];
c=[98.03
   98.23
   98.41
   97.83
   97.65];
d=[97.81
   98.01
   97.61
   98.25
   97.37];
e=[96.98
   97.48
   96.48
   97.98
   95.98];

;Create graph with the mean of points given
Time = [1, 2, 3, 4, 5];
AirMean = [mean(a), mean(b), mean(c), mean(d), mean(e)];
AirSTD = [std(a), std(b), std(c), std(d), std(e)];

p=polyfit(Time, AirMean, 6);
bestAir=polyval(p,Time);

set(0,'defaultaxesfontsize',16);
;Create figure of new graph
figure(1);
errorbar(Time, AirMean, AirSTD, 'd');
hold
plot(Time, bestAir)
xlabel('Number of Imprints');
ylabel('Percentage of proper imprint');
axis([0, 6, 0, 100])
```

Matlab code used to create graphs for mean and standard deviation of nanonex, used to make graphs for heated and nonheated F13.

Raw Data for HSQ Pillar Diameters

Air (nm)	0 minutes	15 minutes	30 minutes	45 minutes	60 minutes	8 hrs	24hrs	48 hrs
	31	36	38	45	53	58	64	71
	30	37	37	45	53	59	64	71
	31	38	37	46	54	58	66	72
	30	33	38	47	52	58	64	71
	30	35	38	44	52	59	65	70
	32	34	37	45	51	57	63	70
	31	34	39	43	54	57	63	70
	30	38	39	45	54	58	65	71
	32	37	39	46	53	57	64	73
	32	36	38	47	53	59	64	72
	31	36	37	43	52	57	66	71
	29	37	38	43	53	58	64	71
	32	36	39	45	52	57	63	69
	29	38	37	46	54	59	65	69
	31	33	38	47	53	60	64	70

Nitrogen (nm)	0 minutes	15 minutes	30 minutes	45 minutes	60 minutes	8 hrs	24hrs	48 hrs
	30	33	37	43	47	52	61	66
	31	34	37	43	47	54	62	65
	29	33	38	43	46	52	61	66
	29	32	38	42	46	51	61	66
	31	33	37	42	47	51	64	67
	32	34	37	44	47	52	60	68
	32	32	37	43	48	53	60	66
	31	32	36	42	47	53	61	64
	30	34	36	43	47	51	62	66
	30	31	36	43	48	54	62	65
	29	33	37	42	48	55	63	66
	30	32	37	43	47	56	60	64
	31	34	37	42	46	54	59	67
	31	34	38	43	46	52	61	67
	29	33	36	44	47	52	60	65

Vacuum (nm)	0 minutes	15 minutes	30 minutes	45 minutes	60 minutes	8 hrs	24hrs	48 hrs
	28	31	33	39	45	47	51	53
	30	30	33	39	45	47	50	52
	30	32	33	39	45	45	50	54
	28	30	34	38	44	46	50	54
	28	30	32	38	46	47	51	53
	27	33	32	40	46	48	49	53
	27	31	33	40	47	49	50	53

30	31	32	39	47	47	49	52
28	32	34	40	45	46	51	52
28	31	33	39	44	46	52	52
28	30	33	38	43	47	52	54
30	32	34	38	43	47	49	53
27	31	32	39	47	48	50	53
27	31	32	40	43	49	51	54
30	31	33	38	44	48	51	55

Raw Data for Percentage of Proper Imprint

Nanonex (number of imprints)	1st	2nd	3rd	4th	5th
	0	99.14	98.03	97.81	96.98
	0	99.19	98.23	98.01	97.48
	0	99.24	98.41	97.61	96.48
	0	99.09	97.83	98.25	97.98
	0	99.04	97.65	97.37	95.98

F13 Heated (number of imprints)	1st	2nd	3rd	4th	5th
	0	95.12	92.43	85.12	76.37
	0	95.29	92.76	85.19	76.11
	0	95.99	92.12	85.67	76.89
	0	96.02	91.54	84.78	75.98
	0	94.57	93.03	86.24	76.93

F13 Non-Heated (number of imprints)	1st	2nd	3rd	4th	5th
	0	94.11	82.54	67.73	52.43
	0	94.29	82.33	67.13	52.5
	0	94.67	82.49	67.48	52.67
	0	94.23	82.01	67.81	52.11
	0	93.98	81.79	67.01	53.09