A patterning process utilizing a nanoimprint lithography for fabrication of planar perpendicular patterned magnetic media

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A PATTERNING PROCESS UTILIZING NANOIMPRINT LITHOGRAPHY FOR FABRICATION OF PLANAR PERPENDICULAR PATTERNED MAGNETIC MEDIA

by
Robert Grove III

A Thesis
Submitted in partial fulfillment of the requirements of the Master of Science in Engineering Degree of The Graduate School at Rowan University October 21, 2005

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In Charge of Major Work

For the Major Department

For the College

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ABSTRACT

Robert Grove III
A PATTERNING PROCESS UTILIZING NANOIMPRINT LITHOGRAPHY
FOR FABRICATION OF PLANAR PERPENDICULAR
PATTERNED MAGNETIC MEDIA
2005
Dr. Robert Krchnavek
Master of Science in Engineering

This thesis describes the results of applied research in the area of patterned magnetic media. Current magnetic media is pushing the physical limits of magnetic bits by compressing them into very small spaces – a process that will eventually be hampered by the superparamagnetic effect. The superparamagnetic effect will require the magnetic media industry to find a modified method of storing magnetic bits. Perpendicular patterned magnetic media could be the method of choice for future generations of magnetic data storage. Patterning magnetic media allows bits to be stored in isolated magnetic islands instead of in a continuous magnetic surface, as is currently the case. Separating the bits increases signal to noise ratio and bit density at the same time. As the first step in fabricating patterned magnetic media, this research demonstrates the ability to pattern a 60 nanometer thick film of polymethyl methacrylate (PMMA) into 45 nanometer high pillars with a density correlating to 258 Gbits/in$^2$ over a 100 $\mu$m$^2$ area.
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CHAPTER 1 INTRODUCTION

1.1 The History of Magnetic Media

Information must be recorded. Whether carved into rocks, inked onto papyrus, penned onto paper, or stored in the hard drive sitting in a personal computer, it must be stored. Over the centuries the first three techniques have mostly been abandoned in favor of the last one. This is not surprising given the ease and density at which magnetic information can be stored. The industry is growing very rapidly. The typical American now generates around 100 gigabytes of data during his or her lifetime [1]. Most of this is stored on hard drives. In addition, hard drives have recently been finding their way into devices such as portable MP3 players, home entertainment systems, and systems for recording live television for later viewing. Adding to this demand are digital pictures, music, and movies that require vast amounts of storage space, usually on a hard drive somewhere. Even businesses need more storage capacity. Picture walking into a library and having to search through paper cards to find books, or walking into a grocery store and having to pay cash because you couldn't use a credit card. These types of business operations have also added to the demand for magnetic storage.

To keep up with this demand, the industry has been on a mission of steadily storing more information in less space. Figure 1.1 [2] shows the progress in areal bit density of hard drives from 1956 to 2004.
Areal bit density describes how close together bits on a hard drive are placed. The graph starts in 1956 when IBM introduced their first disk named the IBM 350. It had 50 platters with a diameter of 24 inches and stored 5 megabytes of information. The areal bit density was $2 \text{ kb/in}^2$ [3]. In 2005, Hitachi produced a hard drive using 5 platters with a diameter of 3.5 inches that stores 500 gigabytes of information. The areal bit density was $76 \text{ Gb/in}^2$ [4]. In less than 50 years areal bit density has increased over 7 orders of magnitude. In addition, platter size today is just over 2% of what is was in 1956. This feat was nothing short of amazing. In fact, the industry was so good at decreasing bit size during the 1990's that the magnetic storage capacity far outstripped demand. This forced the industry to consolidate. As a result hard drives were very inexpensive. Figure 1.2 [2] shows the
price per megabyte of storage for paper, semiconductor memory, and disk drives over the last 25 years.

The cost of all three has been decreasing, but magnetic memory storage actually became less expensive than paper in the late 90's. It now costs about a dollar per gigabyte and is far less expensive than paper or semiconductor memory. Storing information on paper is now over two orders of magnitude more expensive. Paper is very quickly becoming a storage method of the past. Magnetic storage is now the primary method of storing information. It is the driving force behind creating a more efficient technological future.

1.2 Conclusion

Knowing this, it is worth researching technologies that would make it possible to
continue the trend of increasing density illustrated in figure 1.1. Current methods of increasing density are nearing their end due to fundamental limits imposed on them by the laws of physics. On top of this, demand in the new millennium is once again very strong, putting a tremendous amount of pressure on the industry to increase disk capacity. The question is, can the trend continue? It is the goal of this thesis to answer that question.

Chapter 2 will describe the fundamental problem with increasing the density of magnetic storage. Chapter 3 will present a solution to the problem. And subsequent chapters will provide the details for implementing that solution. The end result will be a method of increasing magnetic storage density well beyond today's capabilities.
2.1 Chapter Overview

This chapter will lay the groundwork for understanding magnetic data storage. It will describe magnetic bits and how they store information. Next, their use in hard drives will be explained. The current demand for magnetic storage is continually increasing, requiring hard drives to store more information in the same space. To accomplish this, bit size must be scaled smaller. The current method of accomplishing this will be discussed along with the problem it will face in the near future. The chapter will conclude by proposing future methods of increasing storage density, focusing on a technique for storing bits on individual islands of magnetic media.

2.2 The Magnetic Bit

What is the definition of a magnetic bit? It is logical to assume it has something to do with magnetism. Hence the first word. The second word, bit, is defined by Google.com as "a small quantity." Putting the two together gives a fairly accurate definition of a magnetic bit. It is a small quantity of magnetism. This small quantity of magnetism is used to store information. Almost every kind of information imaginable is stored using magnetic bits. Everything from credit card numbers to the type of medication a person takes is stored this way.

Magnetic bits are made up of something even smaller, called grains. Grains are small amounts of metal that can be magnetized. In grade school there was a popular
experiment that many people did involving a nail, a battery, and a length of wire. As everyone knows, nails are not naturally magnetic. Putting one next to a paper clip would not cause the paper clip to stick to the nail. But the nail could be magnetized. If the wire was wrapped around the length of the nail, and then attached to each end of a battery, a current would flow through the wire. After a few minutes the wire could be removed from the nail and the nail would then pick up paper clips. What happened to the nail? Well, it turned into a magnet. But how? The answer lies in the electrons that make up the nail. Everyone knows that electrons have a charge. But a lesser known fact is that they also have a spin. Spin was discovered by Uhlenbeck and Goudschmidt in 1925 [5] when they proposed that an electron had angular momentum. Knowing that electrons have angular momentum, it can be seen from the Biot-Savart law (2.1) for a moving charge that charge with an angular momentum must be accompanied by a magnetic field.

\[ B = \frac{\mu_0}{4\pi} \frac{v*\sin(\varphi)}{r^2} \]  

(2.1)

In equation 2.1, \( B \) is the magnetic flux density, related to the magnetic field, \( H \), by the property \( B = \mu H \). The constant \( \mu_0 \) is the permeability of free space, \( v \) is the angular momentum of the electron, \( q \) is the charge of the electron, \( \varphi \) is the angle at which \( B \) is measured, and \( r \) is the distance at which \( B \) is measured. Simply put, electrons are spinning, and because of this spin they create a magnetic field, \( H \). In effect, they are like very tiny magnets. Their spin is what determines the direction of the magnetism. The wire around the nail oriented the average direction of all the electron spins in the nail the same way, creating an even bigger magnet. Similarly, magnetic grains house many spinning electrons. If the vector sum of all the spins in a grain does not equal zero, the grain, and
therefore the bit, will have a net magnetization.

But how is information stored using magnets? The information is stored in the transition from one bit to another. There are two possible situations that can occur when transitioning from one bit to another. Either the magnetic fields are aligned in the same direction, or they are not. For example, if the magnetic fields were aligned in the same direction, a bit value of 1 could be stored. And if the magnetic fields were opposing each other, a value of zero could be stored. A change in magnetization signifies a change in the bit stream. Stringing these magnetic transitions together allows large amounts of information to be stored in binary notation.

2.3 Current Method of Storing Magnetic Bits

Current disk manufacturing processes use a thin film of magnetic grains deposited on the surface of a platter to store the bits. All the grains are connected to each other, creating a continuous magnetic surface. The magnetic field of each grain is very weak because the grain is small. This makes sensing the field it produces impossible for current read heads. On top of this, single grains are influenced by the magnetic fields that surround them, making it easier for the grain to change its magnetization when it shouldn't. Therefore magnetic bits must be formed from a large number of grains. Current bits contain hundreds of grains each, with a general diameter ranging from 11-20 nm.

In order to write a bit, the head applies a magnetic field to the ferromagnetic platter. If the field is strong enough, it will magnetize the grains of a bit in one direction. The only thing that keeps the head from writing to adjacent bits during operation is the head geometry and the strength of the field the head produces. Adjacent bits are not
modified because the magnetic field of the head is not strong enough to permanently magnetize them.

Bits are read using a Giant Magnetoresistive (GMR) head that scans back and forth radially on the platter. It was introduced in 1997 by IBM. GMR heads are made possible by materials that change their resistance in the presence of small magnetic fields. The simplest way to envision a GMR head is to think of two magnetic layers of material separated by a non-magnetic layer of material. The magnetic layers are magnetized in opposite directions. In its natural state, this structure has a high resistance. If, however, the head encounters a magnetic field powerful enough to align both magnetic layers in the same direction (e.g. a magnetic bit), the structure's internal resistance decreases substantially. The magnetic direction of the bits is what causes the change in resistance in the GMR head. The resistance change measured by external circuitry is what differentiates 1's from 0's during reading. Before the invention of the GMR head, a Magnetoresistive (MR) head was used. MR heads were only capable of producing a 2.5% [6] change in resistance when reading bits. Current day GMR heads can produce a resistance change of over 13% [7]. The GMR head provided a significant improvement in sensitivity over the old MR heads and made separating the bit signal from the noise much easier.
2.4 Current Magnetic Hard Drives

Hard drives rely on magnetic bits to store information. The information must be organized in a smart manner in order to facilitate efficient storage and retrieval. To make this possible hard drives are divided into distinct areas. Figure 2.1 [8] illustrates the organization of a magnetic platter used in hard drives.

![Figure 2.1 - Magnetic disk topology](image)

Hard drives partition bits into two main areas. The largest of these is called a track. Tracks are rings that circle the entire platter. In addition to storing bits they also store position information to let the head know how far it is from the center of the platter. Each track is separated into sectors. A sector is a segment of a track. If the head knows what track and sector it is in, it can more efficiently move to the area it needs to be in next. Inside the sectors are billions of magnetic bits tightly packed together. Disk manufacturers need to increase the number of bits in each sector to increase the capacity of the drive. This involves making the bits smaller so more of them can fit in the same space. Storing more bits in the same amount of space has been the primary goal of the magnetic media industry since it began.
2.5 Increasing Areal Bit Density of Hard Drives

The magnetic recording industry has been increasing areal bit density for over 50 years. As a result, areal density of hard drives has been on a logarithmic ascent. Today's densities are over 1000 times what they were in 1980. Over the last 50 years, the recording industry has relied on decreasing grain volume to increase areal density. If the volume of the grains used to record a bit is decreased, the same number of grains can be used while decreasing the overall size of the bit. But there is a fundamental problem with continuing to increase areal bit density this way and it will involve an answer that is much more difficult to implement than the GMR head. Eventually, it will make the current method of increasing areal density impossible by directly affecting the stability of each and every bit.

2.5.1 The Problem With Scaling

Many hurdles must be overcome to continue scaling magnetic bits even smaller. Among them are creating even more sensitive GMR heads, scaling those heads small enough to read the bits, and better error correction algorithms. But one problem sticks out above these because of how fundamental it is. If this problem is not solved, there will be no need to solve the others. That problem is the superparamagnetic effect. It is currently the only fundamental physical limit to increasing areal bit density. It has become very important to disk manufactures in recent years because of the increasing density of magnetic bits. Because magnetic bits are composed of magnetic grains which have electrons with ordered spins, each and every spin is constantly competing with Boltzmann's thermal energy, $k_BT$, to continue spinning in the direction it was forced to
during the write process. Now, the effect that $k_BT$ has on the spins is determined by the 
volume of the grain that houses them. The larger the grain, the less effect thermal energy 
has on it. When the volume of the grain shrinks, the bit becomes very susceptible to 
thermal energy. If the volume of the grains is reduced enough, thermal energy causes the 
grains to disorient themselves in such a way as to lose their overall magnetism. The 
superparamagnetic effect is governed by the following equation. 

$$\tau = \frac{1}{f_0} e^{\frac{\nu M_s H_C}{2 k_B T}}$$

(2.2)

In equation 2.2 [9], $\tau$ is the average length of time a bit will stay stable after being set, $f_0$ 
is the lattice vibration frequency, $\nu$ is grain volume, $M_s$ is spontaneous magnetization, $H_C$ 
is coercivity, $k_B$ is Boltzmann's constant, and $T$ is temperature. As the grain volume 
decreases, the exponential in this equation becomes smaller, causing the relaxation time to decrease. According to Wang [10], the linear dimension of the grains must be larger than $\sim 9$ nanometers or the bits will become unstable in a time shorter than would be suitable for long term data storage use. This corresponds to a longitudinal magnetic recording density limit of $40-70^1 \text{ Gbit/in}^2$.

There is a variable that could help increase the relaxation time of the bits while continuing to decrease grain volume. That variable is $H_C$, or coercivity. Coercivity is the strength of the magnetic field needed to magnetize the bits. Increasing coercivity would have the same effect as increasing volume. Research is being done to increase coercivity [11], but it is not certain if increased coercivity will be beneficial in the long run.

---

1 It may be noted from chapter 1 that Hitachi has already surpassed this limit. Although the details of how Hitachi implemented a $76\text{ Gbit/in}^2$ density are not mentioned, it is very likely they used Antiferromagnetically Coupled (AFC) media [12]. AFC media could extend longitudinal recording into the $100-200 \text{ Gbit/in}^2$ density range.
Increasing it does lead to longer relaxation times, but also creates other problems. As coercivity is increased, it becomes harder to magnetize the bits. This causes write times to increase because it takes more time to magnetize. Increasing the magnetic field requires more power, and slower writing speeds cause slower response times. Both of these things are very undesirable, so increasing coercivity probably won't be a good solution in the long run.

It is very clear that areal density must continue to increase. Chapter 1 presented the large demand for magnetic storage. The question is how can density increase beyond the superparamagnetic limit? In order to avoid the problem posed by the superparamagnetic effect, several modified methods of storing magnetic bits have been proposed. They are all in the research phase and have not been commercialized yet. It is time to take a look at these emerging methods.

2.6 Modified Methods for Increasing Areal Density

There are two distinct new methods for increasing areal bit density beyond the superparamagnetic limit. The first one is perpendicular magnetic media. Perpendicular magnetic media deals with changing the orientation of the bits and how they are written. It changes the structure of the bits in such a way as to avoid the superparamagnetic effect longer than would be possible using longitudinal recording techniques. The second technique is patterned magnetic media (PMM). It addresses how the bits are stored. PMM increases the Signal to Noise Ratio (SNR) when reading bits by separating them with non-magnetic material, thereby reducing transition noise which is a prominent source of error. A third method that will be discussed is combining both these techniques for a
2.6.1 Perpendicular Magnetic Media

One possible method of increasing areal bit density is changing the orientation of the bits. Currently, bits are stored horizontally. This means they are magnetized in a direction parallel to the surface of the platter. Figure 2.2 [13] illustrates the current method of writing bits horizontally.

The system uses an inductive write head consisting of a coil wrapped around a C shaped metal post for the electromagnetic, and another C shaped metal post for the receiving shield. Together they create a magnetic field from one end of the bit to the other, magnetizing the bit in the direction of the field. The darker block to the left is the GMR read head. Storing bits horizontally is space intensive. The bits are naturally longer than they are thick. This means that putting the bits end to end horizontally will take up much more room than standing them up on end like dominoes. Standing them up on end would automatically increase areal bit density. Figure 2.3 [13] depicts a method of storing bits perpendicularly.
As can be seen, some modifications are necessary to the write element. The shape of the write element must change from being symmetrically ring shaped to a much thinner single pole design in order to get the correct magnetic flux through the magnetic media. The flux path now has to be perpendicular instead of horizontal. This means that it must travel through the media to a conducting layer underneath and back up through the media to the other side of the write head. The write head design has the added advantage of recording with a deep gap field instead of a fringe field as in horizontal bit recording. This exposes the media to a magnetic field up to twice as strong [14] as would be possible when writing with a fringe field. Because the field is so much stronger, the coercivity of the media can be much larger. Larger coercivity allows for smaller grain size (refer to equation 2.2) which allows for higher areal bit density. Also, the volume of the grains can remain the same while at the same time taking up less space on the surface of the media. This is because the vertical orientation of the bits reduces the amount of area that is needed per bit on the platter. More of the bit is stored below the surface, keeping the volume the same. Perpendicular magnetic media is probably the most promising short term solution to the density problem.
2.6.2 Patterned Magnetic Media

Patterned magnetic media is yet another way of increasing areal density of hard drives. As was mentioned earlier, current hard disk platters are made of a continuous sheet of ferromagnetic grains. This means that all the bits are connected to each other. Patterned magnetic media is just the opposite. Each bit is its own magnetic island separated from other bits by nonmagnetic area all around it. With continuous magnetic platters, SNR is constantly a problem because neighboring bits interfere with the signal. This is because the only thing keeping the head from reading other bits is space. Bits must consist of a large number of grains to create a signal strong enough to stand out above the noise. Reducing bit size can only be done by reducing grain size because both the noise and the signal are reduced together, maintaining the same SNR. Granted, more sensitive heads have to be developed, but the GMR head has solved this problem for the time being.

But what if SNR could be increased while at the same time decreasing the bit size. PMM offers this possibility. If each bit is magnetically separated from the next, SNR would increase because of the absence of transition noise from one bit to the next. Increased SNR also means that the number of grains making up a bit could be reduced. PMM has the potential to be able to use one large magnetic grain to store a bit, giving a potential density increase of anywhere from 13-100 times that of longitudinal recording [15]. This could be done while at the same time avoiding the problems caused by the superparamagnetic effect. The major challenge PMM must overcome is finding a high resolution, parallel process of replicating patterns on magnetic media.
2.6.3 Perpendicular Patterned Magnetic Media

If both of these approaches increase areal density separately, why not use them together? Together these two techniques could be utilized to create areal densities up to 1 Tb/in² [16]. Combining these two approaches is the focus of this research. Individual magnetic bits have been demonstrated with limited success in the past, but most of the processing required to make them has been rather complicated. In addition, the final surface of the patterned media is sometimes very rough due to the processing it undergoes. Rough surfaces are undesirable for hard drives because the head flies about 25 nanometers above the surface of the platter at speeds up to 7200 RPM. A rough surface would force the head to fly much higher above the surface, making read/write operations difficult if not impossible. The advantage of the method used in this thesis lies in its simplicity. The magnetic media is prepared in advance, a resist layer is patterned on the surface of the media using NIL, and low energy ion bombardment is used to destroy the magnetization in regions unprotected by the resist. The resist is then rinsed away, leaving behind magnetically patterned bits with a surface roughness comparable to current hard drives.

2.7 Conclusion

Increasing areal density in the future will be more difficult. Continuing to scale bits by decreasing grain size will be hindered by the superparamagnetic effect. Perpendicular magnetic media provides near term density increases by allowing higher coercivity and smaller bit areas. Hitachi and other disk manufacturers are already heavily researching perpendicular media for use in hard drives. Although perpendicular magnetic
media will address density concerns for the near future, it cannot be a long term solution because it does not address the issue of degrading SNR. Perpendicular PMM is a long term solution because it increases SNR as well as density by separating bits into individual magnetic islands. It has the potential to increase storage density up to 100 times more than conventional longitudinal recording will permit [15].

The disadvantage to using Perpendicular PMM is that it requires a large area (> 60 cm$^2$) lithography technique with low defect density and high resolution. Fortunately such a lithography technique exists.

Nanoimprint Lithography (NIL) has been on the rise since its invention in 1995 by Chou [17]. It is a large area, high resolution method of replicating patterns on the nanoscale. It is commonly known to have a resolution of 10 nanometers, 5 times that of current day photolithographic systems. Recently Komag, the world's largest independent supplier of thin film-disks, used NIL to pattern the tracks on their magnetic media over an area of 100 cm$^2$ with a minimum feature size of 70 nanometers [18]. They have dubbed the technology Discreet Track Recording (DTR) and are already looking to license it to other manufacturers. If NIL could be used to pattern the actual bits of hard drives, much more space could be saved and bit densities as high as 1 Tbit/in$^2$ might be achieved [16].

NIL has the potential to make mass production of perpendicular PMM a reality. This research patterns perpendicular magnetic media using NIL. The focus of the research was on perfecting the NIL process for this specific application. To clarify NIL and what it entails, the next chapter has been devoted to the understanding of NIL.
3.1 Chapter Overview

Chapter 2 concluded that Perpendicular PMM had the potential to be a long term solution to the problem of increasing areal bit density of hard drives. It described Perpendicular PMM and the advantages it provided in SNR. It also noted the biggest drawback to PMM. PMM requires a large area, high resolution method of patterning the magnetic media. NIL was proposed as a possible solution to this drawback. This chapter provides the background necessary to understand the NIL process and the specific methods of implementing it in this research.

3.2 Introduction

NIL is a relatively new technique for transferring nanoscale patterns onto a substrate. It has two distinct advantages over current photolithographic techniques. Those advantages are better resolution coupled with the ability to pattern large areas. Currently it is lacking the speed of photolithography, taking on the order of minutes instead of seconds to pattern samples. As research continues, pattern replication times will no doubt fall as processing techniques are refined and better stamping techniques are discovered. The other important feature that makes NIL a contender for patterning PMM is the fact that, like photolithography, it is able to pattern complex non periodic patterns, which is essential for patterning hard drives. Figure 3.1 illustrates the NIL process.
First, a substrate is coated with a polymer, usually a thermopolymer. A thermopolymer is very rigid at temperatures well below its glass transition temperature. But at temperatures approaching the glass transition temperature, it becomes moldable. To mold the polymer, a hard surface with an embossed pattern called an imprinter is pressed into the polymer. The imprinter and polymer are heated to around 70° C above the glass transition temperature of the polymer to soften it. As the polymer softens, it is forced to conform to the embossed pattern on the imprinter. Once the polymer has completely conformed to the imprinter, everything is cooled to let the polymer solidify. The imprinter is then removed from the polymer, leaving an impression of the imprinter.
in the polymer.

This process requires several items. It requires a machine to control the contact of the two surfaces, an imprinter to transfer the pattern into the polymer, a coating on the imprinter to keep it from adhering to the polymer, and a recipe that specifies the imprinting conditions. Each item is crucial to successful imprinting. Following is a more detailed explanation of each.

### 3.3 The Imprinting Machine

The imprinting machine is responsible for forcing the imprinter into the sample. Figure 3.2 [19] is the imprinting machine made in-house for Rowan University by Dan Marks.

![Imprinting Machine](image)

**Figure 3.2** - (a) A model drawing of an imprinting machine. (b) A photograph of an imprinting machine.

The frame is constructed of stainless steel. Mounted to the back of the frame is a pneumatic press filled with nitrogen for applying imprinting pressure. Mounted to the bottom of the press is a white block of Macor® and an aluminum imprinting block with
holes in it. Another set of blocks is mounted to the base of the machine. Looking at figure 3.2b will reveal that the Macor® blocks are inserted between the imprinting blocks and the rest of the machine. This is because Macor® is a machinable glass ceramic with a low thermal conductivity of 1.45 W/m-°C, making it ideal as a thermal insulator to protect the seals in the pneumatic press from the high temperatures the imprinting blocks are exposed to. The Macor® improves heating and cooling response time by limiting the mass of metal that is heated. Both the Macor® and the aluminum blocks are attached with room temperature vulcanizing (RTV) adhesive.

Looking closer at the imprinting blocks reveals 5 small holes in them. The 3 larger holes are for the resistive heater cores used to heat the blocks. The two smaller holes are for thermocouple feedback for the controllers. Both the heaters and the thermocouples tie into a controller box which is used to coordinate the imprinting process. It turns the pressure on and controls the imprinting temperature. Figure 3.3 [19] is a picture of the controller box used in this research.

![Controller box used for imprinting.](image)

The top and bottom block heaters are controlled separately by individual heater controllers on the right. This allows the bottom and top blocks to be heated to different
temperatures if necessary. A digital meter displays the pressure being applied to the block, and a timer is used to regulate imprinting time. Air and water cooling were used to cool the imprinting blocks, but cooling was performed manually.

3.4 The Imprinter

The imprinter is the patterned substrate used to transfer a pattern into samples. It is made via lithography. The original imprinter must be made by a lithographic process other than NIL. Photolithography can be used in some instances if nanoscale resolution is not needed. But if very high resolution is needed, imprinters are generally created via electron beam lithography (EBL). This section describes the processing involved for fabrication of EBL imprinters, focusing on two specific methods. The first method, described in section 3.4.3, illustrates the standard way of making SiO₂ imprinters via EBL. It was the primary method of creating imprinters at Rowan prior to this research. It was not used in this research because the equipment necessary to perform the processing was not available in-house. It was succeeded by a second method, described in section 3.4.4. The concepts of both these methods are described in this chapter, leaving the details of the implementation of the second method entirely to chapter 4.

3.4.1 Sample Cleaning and Spinning

Substrates were cleaned using a mechanical force. Methanol was applied to the substrate and a lint free cloth was used to wipe it off. Blow drying the sample after cleaning was not necessary because the methanol evaporates almost immediately. Once the samples were cleaned, they were spin coated with an e-beam resist using a Laurell Technologies spin coater. After spinning, the samples were pre-baked to drive off the
solvent. Then they were patterned via EBL.

3.4.2 Electron-Beam Lithography

A modified scanning electron microscope (SEM) is used to perform EBL. EBL is the process of taking the electron beam of the SEM and directing it in a specific pattern predetermined by user input to pattern a material that is sensitive to electrons. This material is called a resist. A pattern can be transferred to the resist by exposing it to the electron beam of the SEM. This exposure changes the molecular properties of the resist. When the resist is developed, the unexposed part is rinsed away by the developer leaving behind the e-beam pattern. This type of resist is called a negative resist. The process also works in reverse, using what is called a positive resist. Using a positive resist would result in areas that were exposed to the electron beam being removed after developing while the rest of the resist was left intact.

EBL is a slow lithographic process due to its serial nature, but has a high resolution because of the electron beam it utilizes. IC manufacturers use EBL for fabricating high resolution optical masks for the photolithography used in IC production. Likewise it can be used to create imprinters for NIL. EBL requires an SEM that allows external control of the beam by independent hardware and software. This hardware and software coordinate to control the movement of the electron beam in the SEM. The EBL equipment used in this research was purchased from JC Nabity Lithography Systems in Bozeman, Montana (jcnabity.com). The SEM was a LEO 1530 VP.

3.4.2.1 Focusing the Electron Beam for EBL

High resolution EBL requires the electron beam to be focused at every pattern
written on a sample. Unfortunately the focal distance changes from point to point on a sample. This is because the stage and sample are not completely perpendicular to the beam. Moving to a different point on the sample requires refocusing the electron beam. Unfortunately, focusing the electron beam also exposes the resist. To avoid having to focus the beam near points where an imprinter pattern is desired, the plane of focus is predetermined, and future focal points are predicted using the equation of that plane. Creating an accurate focal plane is the most important issue when performing EBL. It can be generated by focusing on 4 to 5 points around the edge of the sample and fitting those points to a focal plane that the EBL software will automatically use to determine future points of focus. It is important that the fit of the plane have an RMS error under 1 nanometer. Higher error will result in the beam not being focused enough to pattern at high magnification (1000x). In this way the EBL software is able to set the focus of the beam automatically at every point a sample is written, without having to pre-expose the resist.

When collecting the points for the plane, scratch the surface of the sample all around the edges to create something to focus on. Good spin coated samples do not have anything to focus on naturally. Focus on the scratches at a magnification of no less than 300,000x. Find the same types of scratches to focus on. Different scratch types have different heights, and different heights will cause the focal plane to be inaccurate. Now that EBL has been explained, the previous method of creating EBL imprinters will be described.
3.4.3 Silicon Dioxide Imprinters

Silicon Dioxide (SiO$_2$) imprinters are by far the most prevalent type of imprinters used in NIL. There are two main reasons for this. First, until recently, they were the easiest type of imprinter to fabricate. The processing techniques used to create them have been around for many decades. They are well known and understood. Second, SiO$_2$ is well known for its large compression strength. This strength is the main reason it is attractive as a material for creating NIL imprinters. The pressures used for imprinting require an imprinter material that is able to withstand them. These two strengths have made SiO$_2$ a dominant material in imprinter fabrication. Figure 3.4 illustrates the process of creating SiO$_2$ imprinters using PMMA as the patterning resist.

![Diagram of the process of creating SiO$_2$ imprinters](image)

**Figure 3.4 - Creation of SiO$_2$ imprinters**

The process starts with a silicon substrate on which an oxide has been grown. PMMA is spun onto the substrate. Next, the resist is e-beam written. After e-beam...
writing is complete, the resist is developed and a thin layer of metal is evaporated onto
the surface to protect the substrate from reactive ion etching. The rest of the resist is then
rinsed away and a reactive ion etch is performed to remove the material in between the
metal pattern. This transfers the desired pattern in the oxide of the substrate. This method
of creating imprinters was never used in this research because a reactive ion etcher was
not available in-house for transferring the pattern into the oxide. As a result a different
method of creating imprinters had to be used. Hydrogen Silsesquioxane (HSQ) provided
the means to fabricate EBL imprinters without using a reactive ion etch.

3.4.4 Hydrogen Silsesquioxane Imprinters

Hydrogen Silsesquioxane (HSQ) is a spin on glass made by Dow Corning. Its
molecular form is HSiO₃/₂. In its cured state it is very close to SiO₂, giving it a large
compression strength. Amazingly, HSQ can be used as a negative tone e-beam resist.
This means it can be directly e-beam patterned and used as an NIL imprinter without
having to transfer the pattern into another material. This saves a lot of time and requires
less equipment, making HSQ imprinters very convenient. All of the imprinters created for
this thesis were fabricated using HSQ. Figure 3.5 illustrates the process of creating HSQ
imprinters.
A SiO$_2$ substrate is spin coated with HSQ. After spinning, the sample is e-beam written with a pattern via EBL. The HSQ is developed, leaving behind the pattern exposed on it by the electron beam. The HSQ is cured to harden it into a structure similar to SiO$_2$, and it is ready for use as an imprinter. Working with HSQ was an integral part of accomplishing the goal of this thesis. HSQ is difficult to work with because it is constantly forming Si-O bonds that reduce the dose necessary to e-beam write it. Much research was performed to determine the best way to e-beam write HSQ to produce consistent results. This work is presented in chapter 4 where a time dependent approach to e-beam writing HSQ is presented. The details of the specific process by which HSQ imprinters were created for this thesis are presented there.

3.5 The Mold Release Coating

After creating imprinters, it is essential to apply a mold release coating (MRC) to them. The MRC prevents the imprinter from adhering to the sample during imprinting.
This is an unavoidable problem when imprinting nanoscale features. The MRC becomes more important as feature size shrinks because dense features provide more surface area for the polymer to adhere to. To prevent this, a low surface energy monolayer is covalently bound to the surface of the imprinter.

3.5.1 Van der Waals Forces

To understand why a MRC is necessary, it is important to first understand what causes polymer to adhere to an imprinter. Any two molecules that come in contact with each other are subject to van der Waals forces. Van der Waals forces are intermolecular in nature. This means that they occur between two molecules, not inside a molecule. It is important not to confuse van der Waals forces with covalent bonds in molecules. Two atoms that share valence electrons are said to be covalently bound. For example, in SiO₂, silicon and oxygen are covalently bound. Silicon has 4 valence electrons, it needs four more to completely fill its outer shell. It gets those 4 electrons from oxygen. Figure 3.6 illustrates this bonding.

![Figure 3.6 - SiO₂ surface](image)

Four oxygen atoms share 1 electron each with silicon fill its outer shell. This is a covalent bond. It is not Van der Waals forces.
Van der Waals forces include molecular interactions that do not share valence electrons. These forces include dipole-dipole interactions and dispersion forces. Dipole-dipole interactions are relatively weak compared to dispersion forces and therefore will not be covered in this description. The other forces, dispersion forces, are a result of electrons orbiting around a nucleus. To illustrate how dispersion forces work, picture a symmetric H₂ molecule which is neutral in charge. Both hydrogens share their valence electron to create a covalent bond between the two atoms. It can be thought of as a single entity with a neutral charge.

The electrons are orbiting around the nuclei in this molecule. And even though the average charge of the H₂ molecule is neutral, it can polarize at any time. In order for the H₂ molecule to polarize, both valence electrons would have to be at one end of the molecule, creating a charge imbalance across it. This would cause a momentary dipole in the molecule.

Now suppose this H₂ molecule is joined by another H₂ molecule whose electrons happen to be dispersed evenly over the molecule.
As the two molecules come together, the dipole in the H₂ molecule on the left would attract the valence electrons of the molecule on the right, inducing a dipole in that molecule also.

Of course an instant later the polarity of the left molecule would be completely reversed due to the fact that the electrons are constantly moving. But this new polarity would again be transferred to the molecule on the right. In this way the polarity of the molecules would always stay in sink.

This transfer of polarity produces a constant attractive force between the two molecules. Negative charge attracts positive charge, positive charge attracts negative charge. This attractive force will continue to exist until the molecules move away from each other due to a larger external force. This phenomenon is called van der Waals dispersion forces. There isn't an actual exchange of electrons, just an attraction between electrons unevenly dispersed across the molecules. Van der Waals forces cause the polymer to adhere to the imprinter during imprinting.

3.5.2 Reducing van der Walls Forces

Because van der Waals forces cause the polymer to adhere to the imprinter, it is in the interest of better imprinting to reduce them. Van der Waals forces can be greatly reduced by carefully selecting what molecules come into contact with each other. If
molecules with weak dipoles can be attached to the imprinter, polymer adherence could be reduced. The ability of a molecule to create a dipole depends greatly on the size of the molecule and how many valence electrons it has. The smaller the molecule is, the weaker van der Waals forces are. Similarly, the more valence electrons a molecule has, the weaker the van der Waals forces are. This is because the probability of unbalanced electrons in a small atom with a large number of valence electrons is much less likely than in a larger atom with few valence electrons. It turns out that molecules with very low van der Waals forces have already been identified.

The C-F bond is the most stable bond found in organic chemistry (~485 kJ mol⁻¹) [20]. Due to the large number of valence electrons it has and the way they overlap, it has a very low polarizability [21]. As a result, it has very weak van der Waals forces. It was predicted by Zisman [22] that a surface composed only of -CF₃ groups would have the lowest surface tension at around ~6 dyn/cm. Through experimentation, Bailey [23] later demonstrated the actual surface tension of this surface to be close to 12 dyn/cm. In comparison, PTFE, better known as Teflon®, has a surface tension of 18 dyn/cm. If the surface of an imprinter was completely covered in -CF₃ molecules, its surface tension, or van der Waals forces, could be greatly reduced, thus preventing it from adhering to the polymer. This technique was used in our research. A thin monolayer of fluorocarbons was covalently bound to the surface of the imprinter. The details of that process follow.

3.5.3 Substrate Cleaning for MRC Application

Imprinters to be coated with a MRC were cleaned using a two step process. First, they were placed in a beaker of dichloromethane for 15 minutes to degrease them. This
eliminated any oils that could have been present on the surface. After 15 minutes the imprinters were taken out of the dichloromethane and placed in a piranha solution consisting of 3 parts sulfuric acid to one part hydrogen peroxide. This was placed on a hot plate at 70° C for 20 minutes. The piranha etch removed any strongly bound impurities from the surface. Lastly, the imprinters were rinsed with DI water and blown dry with nitrogen.

3.5.4 Surface Preparation

Fluorocarbons do not naturally bind to the surface of SiO₂. There must be a mechanism for attaching them to the surface, much like the glue on the back of wallpaper. One mechanism uses a trichlorosilane (TCS). The TCS is attached to one end of the fluorocarbons to facilitate bonding to the surface of the SiO₂. Unfortunately the TCS cannot bond to the SiO₂ until the surface of the SiO₂ has been prepared to receive it. Figure 3.6 is a top view of an SiO₂ surface.

![Figure 3.6 - SiO₂ surface](image)

It consists of silicon atoms with four oxygen atoms bound to each one creating a tetrahedral structure. To make it possible for the TCS to bond to the SiO₂, the surface of the SiO₂ must be hydroxylated. Hydroxylation breaks apart Si-O-Si bonds and replaces them with 2 Si-OH bonds. Hydroxylation was accomplished by placing the imprinter in
nitric acid for 5 minutes. After it was removed from the nitric it was rinsed with DI water, then acetone, and blown dry with nitrogen. Exposing the SiO$_2$ substrate to nitric acid resulted in the following chemical reaction.

$$HNO_3 + SiOSi + H_2O \rightarrow HNO_3 + 2SiOH$$  \hspace{1cm} (3.1)

This produced a surface covered in OH groups. Figure 3.7 depicts a hydroxylated surface.

![Figure 3.7 - Hydroxylated SiO$_2$ surface.](image)

### 3.5.5 The Coating Process

The process for applying the MRC [24] utilized a trichlorosilane (TCS) as the intermediary for covalently binding the -CF$_3$ molecules to the surface of SiO$_2$. The fluorinated TCS used in the reaction, Tridecafluoro- \((1,1,2,2)\)-tetrahydrooctyltrichlorosilane (F13-TCS) was purchased from the American division of Gelest.

The reaction took place in a passivated\(^2\) petri dish with a small hole in the cover for inserting the F13-TCS. The petri dish, a hot plate, and the necessary chemicals were placed in a nitrogen atmosphere dry box. This reaction required a vapor phase deposition of the F13-TCS. The hot plate was set to 250$^\circ$C with the petri dish and imprinters on it.

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\(^2\) The petri dish was passivated using the same process before coating imprinters in it. This was done to prevent the glass of the petri dish from using up all the F13-TCS and leaving none for the MRC on the substrates.
These were allowed to sit for 10 minutes to let the temperature stabilize. At this point 100 μl of F13-TCS was inserted through the hole in the petri dish and a glass cover slide was immediately placed over the hole to prevent it from escaping the petri dish. The reaction was allowed to continue for 1 ½ hours. After this time, the petri dish was taken off the hot plate and allowed to cool. The imprinters were rinsed in anhydrous hexanes to remove any excess F13-TCS from the surface. This completed the process.

3.5.6 The Chemical Reaction

There are two competing ideas as to what is the best chemical reaction for applying this MRC. The first idea comes from [24], and requires that the reaction chamber be very dry (< 1 ppm water). The second idea comes from [25] and utilizes water in the reaction to attach the F13-TCS to the SiO₂ surface. During the course of this research, both reactions were performed to determine which one performed better when imprinting. The two reactions are described below.

3.5.6.1 Dry Reaction

The dry reaction is inhibited by water. It is illustrated in figure 3.8 [24].

![Figure 3.8 - Dry MRC reaction](image-url)
In the absence of water, the TCS molecule reacts with the surface of the SiO$_2$. At the surface, the chlorine molecules and the OH groups react to form Si-O-Si bonds and hydrochloric acid in the following reaction.

$$SiCl_3 + 3 SiOH \rightarrow Si(OSi)_3 + 3 HCl$$  \hspace{1cm} (3.2)

If water is present it will react with the TCS molecule in the reaction

$$SiCl_3 + 3 H_2O \rightarrow Si(OH)_3 + 3 HCl$$  \hspace{1cm} (3.3)

making it impossible for the TCS molecule to bond to the SiO$_2$ surface via the chlorines.

To facilitate this type of reaction, the process was performed in a very dry atmosphere (< 1 ppm water) as was specified in [24]. A simple calculation can be performed to determine the ratio of F13-TCS molecules to water molecules.

The number of water molecules in the petri dish will be determined first. The molecular weight of nitrogen is 14.01 kg/kmol. The density of room temperature nitrogen gas at sea level is 1.25 kg/m$^3$. The volume of the petri dish was 1.57 x $10^{-4}$ m$^3$. Knowing these three things the number of nitrogen molecules inside the petri dish can be calculated.

$$\frac{1.25 \text{ kg \, m}^{-3}}{14.01 \text{ kg \, kmol}^{-1}} (1.57 \times 10^{-4} \text{ m}^3)(6.023 \times 10^{26} \text{ molecules \, kmol}^{-1}) = 8.4369 \times 10^{21} \text{ nitrogen molecules}$$  \hspace{1cm} (3.4)

Knowing the number of nitrogen molecules, the number of water molecules can easily be calculated at 1 ppm.
Next, the number of F13-TCS molecules will be determined. The molecular weight of F13-TCS is 481.55 g/mol. The density of F13-TCS liquid is 1.818 g/cm³. The number of F13-TCS molecules is therefore,

$$\frac{1.818 \text{ g}}{481.55 \text{ g/mol}} \times 6.023 \times 10^{23} \text{ molecules} = 227,386 \times 10^{15}$$ \hspace{1cm} (3.6)

This gives a ratio of almost 27,000 to 1 in favor of the F13-TCS. It is therefore very unlikely that water kept the chlorines from reacting with the surface of the SiO₂.

3.5.6.2 Semi-dry Reaction

The semi-dry reaction utilizes water to bond the fluorocarbons to the surface of the SiO₂. Figure 3.9 [26] illustrates this reaction.

The reaction proceeds from left to right. It starts with the hydroxylated SiO₂ surface in the presence of water vapor. As the F13-TCS molecules precipitate to the surface, they react
with the water according to equation 3.3. This forms silanes on the end of the F13-TCS molecules in place of the TCS. The silanes then react with each other and the hydroxyl groups on the SiO₂ surface according to the condensation reaction

\[ \text{SiOH} + \text{SiOH} \rightarrow \text{SiOSi} + \text{H}_2\text{O} \quad (3.7) \]

to produce a covalently bound fluorocarbon monolayer on the surface of the SiO₂.

This reaction was encouraged by allowing more water vapor in the reaction chamber. A dry box purged three times with nitrogen was used to create a reaction atmosphere significantly more humid than in reaction one. Unfortunately the exact water content of this reaction chamber was not known because sensors were not installed on the box. However, using sodium benzophenone ketyl \[27\], it was determined that the water content was above 10 parts per million. How much above 10 parts per million could not be determined.

Some reasonable estimates can be made as to the amount of water present in the reaction atmosphere. Room temperature air saturates at a water content of 17.3 g/m³. The density of room temperature air at sea level is 1.25 kg/m³. This means that the relative humidity of air at room temperature is 100% when water constitutes 1.4% (17.3g/1.25kg) of the molecules. It is reasonable to assume that purging the dry box three times with nitrogen could reduce the relative humidity down to 1%. If this assumption is correct, the corresponding number of water molecules in the atmosphere would only be 0.14% of the total number of molecules. This corresponds to a water content of 1400 parts per million. Repeating equations 3.4-3.6 from the dry reaction shows that the ratio of F13-TCS molecules to water molecules would then be 19. Therefore the probability that the TCS molecules were reacting according to equation 3.3 would be much higher.
3.5.7 Experimental Data

The following table summarizes the experimental data conducted during research on the MRC reaction. Each imprinter is listed by its ID along with the type of reaction used to attach the MRC. The imprinting results are then summarized with each imprint ID listed to the right.

<table>
<thead>
<tr>
<th>Imprinter ID</th>
<th>Reaction</th>
<th>Imprinting Result</th>
<th>Imprint ID's</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000</td>
<td>Dry</td>
<td>Minimal Adhesion</td>
<td>4404,4405,4406</td>
</tr>
<tr>
<td>4001</td>
<td>Semi-dry</td>
<td>No Adhesion</td>
<td>4458,4461,4463</td>
</tr>
<tr>
<td>4002</td>
<td>Dry</td>
<td>No Adhesion</td>
<td>4472,4475,4476</td>
</tr>
<tr>
<td>4003</td>
<td>Semi-dry</td>
<td>Minimal Adhesion</td>
<td>4515,4516,4517</td>
</tr>
<tr>
<td>4004</td>
<td>Dry</td>
<td>No Adhesion</td>
<td>4508,4511,4512</td>
</tr>
<tr>
<td>4005</td>
<td>Semi-dry</td>
<td>No Adhesion</td>
<td>4506,4509,4510</td>
</tr>
<tr>
<td>4006</td>
<td>Dry</td>
<td>No Adhesion</td>
<td>4521,4522,4523</td>
</tr>
<tr>
<td>4007</td>
<td>Semi-dry</td>
<td>Minimal Adhesion</td>
<td>4527,4529,4530</td>
</tr>
<tr>
<td>4008</td>
<td>Dry</td>
<td>Minimal Adhesion</td>
<td>4531,4533,4535</td>
</tr>
<tr>
<td>4009</td>
<td>Semi-dry</td>
<td>No Adhesion</td>
<td>4537,4538,4539</td>
</tr>
</tbody>
</table>

3.5.8 A Note on Keeping Chemicals Dry

The hexanes and F13-TCS come packaged under nitrogen. The hexanes must be dry because they are used for removing excess F13-TCS from the surface of the imprinter. If they contain water, it will polymerize the F13-TCS according to equation 3.3. This could possibly bond the excess F13-TCS to the surface of the imprinter, obscuring small features. To prevent this, type 4A molecular sieves [28] were put directly into the hexanes to keep them dry.

Because the F13-TCS polymerizes in the presence of water, it must also be kept dry. Failure to keep it dry could render it useless for future MRC reactions. Molecular
sieves cannot be used in the F13-TCS because it immediately undergoes an irreversible chemical reaction in the presence of water. The only way to keep the F13-TCS dry is to keep it away from water in the first place. This can be accomplished by keeping chemicals in a dry box or vacuum chamber with desiccant. In this research all chemicals were kept in a vacuum chamber with desiccant under static house vacuum.
3.5.9 Conclusion

During this research both a dry and a semi-dry chemical MRC reaction were performed to see which one prevented polymer from adhering to the imprinter better. Although these two methods were tested against each other, no difference in imprint quality was noted. Both worked equally well in keeping the polymer from adhering to the imprinter. While a measurement of the density of F13-TCS molecules bound to the imprinter surface would have provided a more quantitative analysis of the success of each reaction, a simple imprinting test provided sufficient information as to which reaction could be used to avoid adhesion. In addition, further experimenting with water content and the quantization of F13-TCS molecules on the surface of the imprinter would have been a research topic of its own, falling outside the scope of this thesis. Although both reactions essentially result in the same chemical bond, it is likely that excessive water would cause reaction 3.3 to dominate, facilitating mass polymerization of F13-TCS molecules to each other via reaction 3.7. Large groupings of F13-TCS molecules bound to each other would make deposition of a monolayer very difficult. It is therefore safer to minimize the amount of water present during the reaction. This research merely suggests that the atmosphere does not have to be extremely dry (< 1ppm) to facilitate a successful MRC coating.

3.6 Imprinting

Once a MRC has been applied to the surface of the imprinter, it can be used in imprinting. The imprinting process consists of coating a sample with polymer and using the imprinting machine to press the imprinter into it. The process is very dependent on the
preparation techniques and imprinting variables. This section describes those preparation techniques and processing variables and how they were specifically used in this research.

3.6.1 Sample Preparation

One of the most basic items in the imprinting process is the polymer. This research used 2% 100K PMMA in chlorobenzene from Microchem in all experiments. A major problem during this research was polymer contamination. It was discovered that the solvent in the polymer dissolved the plastic pipettes that were being used to transfer the polymer out of the bottle. This caused the polymer to change to the point of promoting adherence between the polymer to the imprinter. As a result, the use of plastic pipettes was discontinued and an elementary method of determining the quality of the polymer was used to safeguard against using contaminated polymer. Contaminated polymer changes color. Therefore a spun sample of suspect PMMA would be compared to the color of a good sample of PMMA to see if there was any difference in the color. This test was an easy check to determine if the PMMA was contaminated.

Spinning a clean, uniform layer of polymer onto the substrate is very important. The substrates should be cleaned before spinning using one of the methods described in section 3.4.1. Samples are spin-coated using a commercially available thin film spinner. The spinner is started and accelerates from 0 to the desired spin speed in 5 seconds. During the acceleration, a few drops of the polymer are deposited onto the substrate. The sample is spun for 30 seconds. Figure 3.10 [29] illustrates the typical spin curve for the 100K PMMA used in this research.
A thickness of 60 nanometers was used for all experiments. This corresponded to a spin speed of 2700 RPM. After spinning samples they were baked to drive off the solvent for 10 minutes in an oven at a temperature of 170° C. Samples were then ready for imprinting.

### 3.6.2 Imprinting Variables

Imprinting is the final step in NIL. Simple squeeze flow theory can be utilized to determine how long a periodic pattern will take to imprint. Although squeeze flow theory has traditionally been associated with macroscopic flow, some groups have started to test its validity in nanoscale flow situations [30]. There are four things that effect imprinting time. They are: stamp width, polymer height, polymer viscosity, and imprinting pressure. Figure 3.11 illustrates the first two.
For a periodic structure, stamp width is a measurement of the width of the raised area of the imprinter from one periodic cavity to the next. In the case of figure 3.11, that distance is split equally on each side of the cavity. In this work, stamp width will be treated as a constant because the imprinter geometry is predetermined. Polymer height is split into two parameters, \( h_0 \) and \( h_r \). The initial spin height of the polymer is denoted as \( h_0 \). The polymer height after imprinting is denoted as \( h_r \). Viscosity and pressure are the last two variables. Viscosity is a measure of the rate at which the polymer flows when acted on by a force, and pressure is the force that causes the polymer to flow. All of these variables are put into equation 3.8 which was taken from classic squeeze flow theory and tested empirically by [30].

\[
    t_f = \frac{\eta(T) S^2}{2 \, p} \left( \frac{1}{h_r} - \frac{1}{h_0} \right)
\]  

In equation 3.8, \( t_f \) is the time required to fill the pattern (optimum imprinting time), \( \eta \) is the viscosity of the polymer, \( T \) is temperature, \( S \) is the stamp width, \( p \) is the imprinting pressure, \( h_0 \) is the initial height of the polymer, and \( h_r \) is the height of the polymer after imprinting. Using this equation, the effects of viscosity, pressure and polymer height on imprinting time can be described.
3.6.2.1 Polymer Viscosity

Equation 3.8 shows that viscosity is directly related to imprinting time. Higher viscosity causes imprint time to increase. But what affects viscosity? The most prominent variable is temperature. Viscosity is inversely related to temperature. Lower temperatures increase viscosity of polymers. Early in this research imprinting was done at temperatures around 70° C above the glass transition temperature of the polymer. This was taken from [31] to be a good starting point. It was discovered later on that higher temperatures were necessary to reduce the viscosity of the polymer enough to allow for successful imprinting. Viscosity is very sensitive to temperature. According to [30], a 20° C drop in the temperature can increase imprinting time by a factor of 5. This means that an imprint that took 2 minutes would take 10 minutes. For this reason it is necessary to imprint at temperatures around 100° C above the glass transition temperature of the polymer. At the same time, care must be taken to avoid destroying the polymer with heat. At temperatures higher than 100° C above the glass transition temperature the polymer starts to break down, ruining the imprint.

3.6.2.2 Pressure

In equation 3.8, pressure is inversely related to imprinting time. A decrease in pressure results in an increase in imprinting time. Pressure provides the force to make the polymer flow into the pattern. If inadequate force is applied, the polymer will not be completely forced into the cavities of the imprinter. An example of this can be seen in figure 3.12. An imprinter was forced into a sample with a pressure of 5 PSI. This was not enough pressure to completely pattern the sample, resulting in a partial imprint. When the
experiment was repeated with a pressure of 20 PSI, the entire surface was patterned.

Figure 3.12 - Imprint with inadequate pressure.

A possible explanation for this effect is that the polymer buckles under the heat and pressure of the imprinting process. From inspection in an SEM, it was noted that the patterned areas of figure 3.12 are raised above the level of the smooth areas. This would suggest that as the polymer buckles, it is forced into the cavities of the imprinter in random areas. In this case applying more pressure would force the buckles to compress into a smooth plane again. This type of result can be avoided by carefully regulating pressure.

3.6.2.3 Polymer Height

Imprinting time is inversely related to the square of the final polymer height. This means that imprinting requires more pressure as polymer thickness decreases for the same imprinting time. This is most likely due to polymer adhesion to the substrate and imprinter surfaces, which increasingly affects polymer flow as \( h_f \) decreases. This also
affects imprinting into thinner polymer layers, which also takes more time.

3.6.3 Cooling

Cooling is the last step in the imprinting process. Cooling sets the imprint permanently in the polymer. If the pressure is removed prior to cooling, the polymer will flow back into a smooth surface and the imprint will be lost. During the course of this research air and water cooling were both used. Water cooling is by far the quickest method, cooling samples from 200° C to 34° C in 45 seconds. But air is acceptable when water is not available. It is important to cool the imprint well below the glass transition temperature of the polymer before removing the pressure to allow the polymer to solidify enough to retain the imprint.

3.7 Nanoimprint Lithography Weaknesses

NIL is not without its disadvantages. One disadvantage is the fact that NIL usually requires heating and cooling. Heating and cooling cause the imprinted polymer to expand and contract, causing it to deform. This has caused many researchers to switch to a process called Step and Flash Imprint Lithography (SFIL) [32]. SFIL does not require heating and cooling, but is somewhat more complicated to perform. SFIL uses a uv curable etch barrier which is not removable with a solvent. The advantage of the etch barrier is that it has a very low viscosity because it is a liquid at room temperature. The SFIL process is fundamentally the same as NIL, except that a light source is added. The imprinter stamps the substrate just as in NIL, but also exposes the uv resist to uv light at the same time. This causes the resist to harden. Because the etch barrier is liquid at room temperature, it does not have to be heated during imprinting. This allows imprinting
without any heating or cooling which eliminates resolution problems due to thermal distortion.

As was mentioned earlier, NIL also requires a MRC. While MRCs are fairly commonplace today, they can sometimes be difficult to implement. This is especially true when the imprinter is made out of some material other than SiO$_2$ because most of the processes known for applying MRCs are tailored for SiO$_2$ substrates. Despite its weaknesses, NIL has a lot of strengths that make it very suitable to PMM.

3.8 Previous Work

Much preliminary research was done by Marks [33] in the area of patterned magnetic media using NIL. The primary goal of [33] was to imprint closely packed holes into PMMA and sputter magnetic material (Permalloy) on top of the polymer. The polymer was then stripped from the surface, leaving behind small dots of Permalloy. This substrate was then tested to determine its magnetic properties. The hope was to be able to sense magnetism in the small Permalloy dots and do magnetic testing to see if they would be suitable for future magnetic storage applications. The Permalloy ended up being too magnetically soft to be tested using magnetic force microscopy (MFM). Work done for [33] provided the imprinting machines used for part of the imprinting in this research. In all, two machines were created; One for small area imprinting, and another for very large area imprinting. The machine created for large area imprinting can be seen in section 3.3. The small area imprinter was essentially a smaller version of the large one. Neither of these machines had active cooling, a feature greatly desired when imprinting because it reduces the cycle time. Therefore another imprinting machine was developed in parallel
with this work by two undergraduates students, Brian Balut and Ray Odgers. It was scaled one size up from the small machine to provide more pressure and active cooling using water.

3.9 Conclusion

This chapter covered the methodology behind NIL and the specific methods by which it was implemented for this work. It covered the necessary requirements and design of the imprinting machine. Next, methods of fabricating imprinters were discussed. Creating imprinters on SiO₂ and HSQ was explained. This research focused on HSQ imprinters because they did not require a reactive ion etch, something that was not available during this research. After discussing imprinters, the chapter went on to describe the importance of a mold release coating. The details of the MRC process were explained as well as the experiments with two different chemical reactions for the process. The results of the experiments were that both chemical reactions did equally well in promoting polymer separation from the surface of the imprinter. No difference in imprinting ability was noted. After covering the specifics of the mold release coating, the imprinting process itself was explained. Sample preparation was described and the importance of imprinting variables was discussed. Finally, the chapter closed with the weaknesses of NIL and a brief explanation previous work on this topic.

Before using NIL to fabricate PMM, a convenient method of creating imprinters had to be discovered. A method of creating imprinters which did not involve a reactive ion etch was necessary due to equipment limitations. To facilitate this, a relatively new technique for creating imprinters using HSQ was studied. Over time it became apparent
that HSQ was somewhat difficult to work with. During the process of perfecting this
technique, a time dependent method of e-beam writing HSQ imprinters was discovered.
The next chapter is devoted to the research that developed a method of fabricating HSQ
imprinters for PMM and specifically to the time dependent aspect of the process.
CHAPTER 4 A TIME-DEPENDENT APPROACH TO E-BEAM WRITING

DENSE PATTERNED IMPRINTERS WITH HSQ

4.1 Chapter Overview

Chapter 3 described the NIL process and how it was implemented for this research. This chapter will focus on one aspect of the NIL process, imprinter fabrication. Imprinter fabrication was a huge obstacle to this work because the traditional method of fabricating imprinters utilizing a reactive ion etch could not be implemented due to the lack of a reactive ion etcher. Therefore a newer method of fabricating imprinters with HSQ was implemented. In the process of learning this technique a time dependent method of e-beam writing HSQ was introduced to reduce the inconsistency observed when fabricating these imprinters. The details of that method are set forth in this chapter.

4.2 Introduction

Hydrogen Silsesquioxane (HSQ) is a well known spin on glass in the semiconductor industry. This is mainly because it has been tested as a low-k dielectric for separating layered interconnects in MOSFETs [34]. Interestingly enough, it can also be used as a negative tone e-beam resist. Many academic research groups are now using HSQ to create imprinters via e-beam lithography (EBL) for Step and Flash Imprint Lithography (SFIL) [35]. One of the reasons for the interest in HSQ as an imprinter fabrication material is that it eliminates a separate pattern transfer step required by current methods of imprinter fabrication. There are only three steps required to fabricate HSQ
imprinters: EBL, development, and curing. While HSQ does reduce processing steps, it
also introduces a problem. It is constantly changing and must be refrigerated to slow the
change. EBL is not performed at refrigerated temperatures. Therefore the HSQ is
undergoing change during EBL. This results in very inconsistent experiments with HSQ.
Therefore working with HSQ requires an understanding of this change and a method of
controlling it. First, an explanation of the change is in order.

4.2.1 Molecular Changes in HSQ

HSQ has the molecular form HSiO$_{1.5}$. It shares 12 oxygens with 8 silicons. Figure 4.1
depicts an HSQ molecule.

![Figure 4.1 - HSQ in its preprocessed form.](image)

Attached to each silicon is three oxygens and a hydrogen. Silicon desires four bonds to be
stable, so this structure is stable. The problem is that hydrogen bonding is not very strong.
Therefore in the presence of water the following reaction occurs.

$$SiH + H_2O \rightarrow SiOH + H_2$$  \hspace{1cm} (4.1)

This allows adjacent silanols to undergo a condensation reaction just as in the MRC
reaction to form Si-O-Si bonds according to the equation.
In addition to the Si-O-Si bonding taking place, a competing reaction causes adjacent silicons to bond together according to equation 4.3.

\[ SiH + SiH \rightarrow Si_2 + H_2 \]  

(4.3)

In this way an HSQ starts to form an imperfect SiO₂ structure as soon the thermal energy is high enough for HSQ to form bonds and extract water out of the atmosphere. Figure 4.2 [36] illustrates this structure.

Many Si-O-Si bonds form with some direct Si-Si bonds forming (thick black lines in figure 4.2) when HSQ is unrefrigerated. The formation of these bonds is what causes HSQ to constantly change during EBL.
4.2.2 E-beam Writing HSQ

HSQ is a negative tone e-beam resist. It crosslinks when exposed to an electron beam to forms Si-Si bonds (equation 4.3) much faster than it would normally. This crosslinking makes it possible for patterns to be written on it. After e-beam writing, the sample is developed in NaOH to rinse away all HSQ molecules that did not covalently bond to each other. This leaves behind the pattern written by the electron beam. Unfortunately these bonds start forming naturally at room temperature in the presence of water. This causes the amount of bonds to be changing as a function of time. As a sample sits at room temperature it forms the bonds that would have been made by the electron beam. Therefore as bonds are formed, the necessary exposure to the electron beam decreases. In effect, this makes the aggregate energy that the sample is exposed to during e-beam writing higher, causing overexposed designs. This made it evident that when e-beam writing HSQ, the exposure had to be changed with time.

4.3 Experimental Details

Fabricating HSQ imprinters consisted of e-beam writing HSQ on an SiO$_2$ substrate and curing the substrate to promote the transformation from HSiO$_3$ into SiO$_2$. EBL using HSQ was not consistent. Some samples would be overexposed while others were not exposed enough. Every detail of the EBL process was examined to determine inconsistencies in processing. After careful analysis of processing parameters, it was proposed that the processing window of samples was too broad. Sample processing was completed within 6 hours of removing the HSQ from the refrigerator. To determine the exact effect processing time had on samples, timed experiments were performed.
Afterwards, the samples were analyzed to determine the sensitivity of HSQ to time.

\textbf{4.3.1 Sample Preparation}

Samples were cut from 6 inch silicon wafers into $1.5 \text{ cm} \times 1.5 \text{ cm}$ squares. The squares were cleaned using a mechanical clean. Methanol was applied to a lint free cloth and the substrate. The cloth was used to clean the substrate employing a quick circular mechanical action. This was continued for several seconds until no visible dirt or foreign material was present. The methanol evaporated from the surface fast enough that it did not have to be actively removed. After cleaning the substrate, HSQ in Methylbutylisoketone (MIBK) was spun onto it at 1500 RPM for 30 seconds. The HSQ was purchased from Dow Corning under the name FOX-12. This produced a resist thickness of 140 nm. The sample was then put on a hot plate for 3 minutes at $240^\circ \text{C}$ to drive off the solvent.

\textbf{4.3.2 E-beam Writing HSQ}

\textit{4.3.2.1 Pattern Description}

Thirteen $100 \mu \text{m} \times 100 \mu \text{m}$ patterns were e-beam written on each substrate. The thirteen patterns were arranged in a non-symmetric fashion to make identifying individual patterns easier. Figure 4.3 shows the order of the patterns.
The design of each pattern was a 100 nanometer pitch crosshatch as is illustrated in figure 4.4. The pitch of horizontal and vertical lines was kept the same.

4.3.2.2 Method

E-beam writing was performed using a LEO 1530VP SEM equipped with the Nano Pattern Generation System (NPGS) software and hardware from JC Nabity Lithography Systems in Bozeman, Montana (jcnabity.com). Patterns were written at two different doses. The dose started high and was reduced to compensate for the changing nature of HSQ. Experimenting with different doses revealed the correct reduction in dose to compensate for the formation of bonds. The correct dose for patterns 1-6 was a line dose of 4.29 nC/cm. The correct dose for patterns 7-13 was 4.14 nC/cm. After writing the patterns, the sample was removed from the SEM and developed in a 0.25 M aqueous solution of NaOH for 2.5 minutes. It was then put in a furnace for 2 hours at 410° C to complete the formation of Si-O bonds.
4.3.2.3 EBL Timing Constraints

Unfortunately, specifying the dose of an EBL HSQ experiment without explaining the timing constraints will only work for short EBL sessions. As the session becomes longer, time has a larger effect on the results making the timing of the experiment critical. Upon starting an experiment, HSQ was taken out of the refrigerator and spun onto the cleaned substrate. It was then put on a hotplate for 3 minutes to drive off the solvent. This process took 7 minutes. At this point the sample was ready for EBL. General setup of the microscope for EBL took 30 minutes. The EBL process itself took 50 minutes to complete. It was performed in two equally timed sessions. 25 minutes after the session started the dose changed to the reduced value. After writing the sample, it was developed. Time between the end of writing and developing was 10 minutes. 5 minutes after development the sample was put in the furnace to be cured.

4.3.3 Sample Analysis

After all processing was completed the sample was observed in a SEM. The first, middle, and last patterns were chosen as good points to observe the effects of time. Patterns 1, 7, and 11 were monitored for changing exposure. To determine exposure, the width of the crosshatch lines was measured. The results from this measurement were used to find the correct time dependent dose for EBL.

4.4 Results

Experiments were geared towards reversing the effects of time on HSQ EBL sessions. After writing half of the patterns, the dose was changed by decreasing the original dose by a percentage and writing the rest of the patterns.
Figure 4.5 illustrates a sample written with a constant dose. The line width of patterns 1, 7, and 11 steadily increases from 17 to 23 nanometers. Patterns 1, 7, and 11 were monitored while decreasing the dose to compensate for natural bonding effects. The result was a sample that was evenly exposed over all three patterns. Figure 4.6 illustrates a sample that was written with a time dependent dose.

Figure 4.6 - Changing dose pattern. From left to right: patterns 1, 7, and 11. Feature size stays constant at 15 nm wide.

In this sample when patterns 1, 7, and 11 were examined no difference in line width was seen. All lines measured a constant 15 nanometers. The imperfections seen on the left side of figure 4.6 are surface bound polymer that attached itself to the imprinter during an imprinting experiment. It is not exposed HSQ.

This experiment provided test data on HSQ exposure doses that suggests a time
dependent dose equation should be used for EBL sessions greater than one hour. Using this data it was concluded that the required dose should be reduced by 3% every 50 minutes. Since chemical bonding of silicon molecules in HSQ necessitated the time-dependent dose, and since chemical bonding often happens at an exponential rate, it was logical to represent the dose reduction is an exponential decay. The exponential equation to represent this assumption is straightforward. Using equation 4.4 during EBL sessions to set the dose produced evenly exposed patterns over an EBL session of 50 minutes.

\[ D(t) = D_0 e^{-\alpha(t-t_0)} \]

where \( \alpha = 0.037/hr \)

This equation worked for this research. However, further validation of its exponential nature is still necessary.

### 4.4.1 Experimental Data

The following table summarizes the data gathered during research on the time-dependent approach to e-beam writing HSQ. Each imprinter is listed by its ID along with the dose used during EBL. To the right of the dose the resulting line width of the features on patterns 1, 7, and 11 is specified in nanometers. Finally, the dose type is specified.

<table>
<thead>
<tr>
<th>Imprinter ID</th>
<th>Dose</th>
<th>Line Width of 1,7,11 (nm)</th>
<th>Dose Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1065</td>
<td>4.29 nC/cm</td>
<td>17.1, 20.3, 23.2</td>
<td>Constant</td>
</tr>
<tr>
<td>1066</td>
<td>4.29/4.14 nC/cm</td>
<td>15.1, 15.3, 15.1</td>
<td>Time-dependent</td>
</tr>
<tr>
<td>1067</td>
<td>4.29 nC/cm</td>
<td>17.2, 20.1, 23.3</td>
<td>Constant</td>
</tr>
<tr>
<td>1068</td>
<td>4.29/4.14 nC/cm</td>
<td>15.1, 15.0, 15.0</td>
<td>Time-dependent</td>
</tr>
<tr>
<td>1069</td>
<td>4.29 nC/cm</td>
<td>17.2, 20.0, 23.1</td>
<td>Constant</td>
</tr>
<tr>
<td>1070</td>
<td>4.29/4.14 nC/cm</td>
<td>15.2, 15.1, 15.3</td>
<td>Time-dependent</td>
</tr>
</tbody>
</table>
4.5 Conclusion

HSQ has a shelf life of six months, and thus must be viewed as an ever changing chemical. Timing of longer EBL sessions using HSQ must be closely controlled to achieve consistent results. Although fabricating imprintsers with HSQ does eliminate a separate pattern transfer step, it does not mean that they will be easier to fabricate. Due to the molecular makeup of HSQ, it will always be difficult to handle. Special attention must be given to the timing of the experiment and the proper dose as a function of time necessary to compensate for Si-O and Si-Si bonds constantly forming in HSQ. Although a time dependent method of e-beam writing HSQ will not solve all the problems associated with using HSQ, it is a start to producing more consistent imprintsers with it in the future. A time dependent EBL method should reduce many of the inconsistencies seen in this research.

Chapters 3 and 4 were devoted to describing NIL and imprintsers fabrication. Now that these two processes have been introduced, their role in patterning magnetic media can be explained. The use of all the techniques discussed in the last two chapters was necessary to accomplish this goal. Chapter 5 will be devoted to the patterning process for fabrication of continuous surface patterned magnetic media.
CHAPTER 5 THE PATTERNING PROCESS FOR FABRICATION OF PLANAR PERPENDICULAR PATTERNED MAGNETIC MEDIA

5.1 Chapter Overview

The previous two chapters were devoted to introducing NIL. NIL was the method used to pattern magnetic media for this research. This chapter describes the details of patterning perpendicular magnetic media using NIL. The process of imprinting a crosshatch pattern onto a magnetic substrate will be described, and the chapter will conclude by presenting the results of this work.

5.2 Introduction

As was noted in chapter 2, the superparamagnetic effect will eventually make continued scaling of magnetic bits impossible. The equation governing the superparamagnetic effect is repeated again for clarity.

$$\tau = \frac{1}{f_0} e^{-\frac{\mu M_s H_c}{k_B T}}$$  \hspace{1cm} (5.1)

In equation 5.1, \(\tau\) is the average length of time a bit will stay stable after being set, \(f_0\) is the lattice vibration frequency, \(v\) is grain volume, \(M_s\) is spontaneous magnetization, \(H_c\) is coercivity, \(k_B\) is Boltzmann's constant, and \(T\) is temperature. The volume \(v\) of the grains can be seen in the numerator of the exponential in equation 5.1. Changing \(v\) has a direct effect on relaxation time. Relaxation time is very sensitive to volume. Reducing grain size by \(\frac{1}{4}\) can reduce the relaxation time by a factor of over 28,000. This emphasizes how
powerful the superparamagnetic effect can be. The superparamagnetic effect is forcing designers to come up with different ways of storing magnetic data.

One method of countering the superparamagnetic effect is by separating bits into individual magnetic areas. This is called patterned media. The separation of bits with non-magnetic areas in between increases SNR. This increased SNR reduces the necessary number of grains needed per bit, and ultimately increases data density without sacrificing reliability.

This research employed a hybrid method of increasing bit density by combining both patterned and perpendicular magnetic media. Using NIL, a layer of PMMA was patterned into individual pillars on top of a perpendicular magnetic media sample from Hitachi. The purpose of the pillars was to protect the magnetic media from demagnetization.

After patterning, the magnetic sample would be exposed to ion bombardment to destroy the magnetization of the media not protected by the PMMA pillars. Simulations done by Hitachi had indicated that if the pillars could be made 70 nanometers high, they would sufficiently protect the magnetization of the media from the ions. Figure 5.1 illustrates this process.
If the energy of the ions was low enough, they would destroy the magnetization of the sample without physically etching the surface of the media. After rinsing away the PMMA, a planar surface of magnetic bits would be left behind. Figure 5.2 illustrates the desired magnetic surface after ion bombardment and PMMA removal.

The advantage of this method is that it produces a substrate with a surface roughness comparable to current magnetic hard drives. This allows the read head to fly close to the surface at high speeds, making data storage and retrieval possible. Many methods of patterning magnetic media require a physical etch, which does not leave behind a planar surface. This forces the read head to fly further above the surface to avoid contact with
the media, making read/write operations very difficult. This chapter describes the details of the NIL process used to pattern the PMMA on top of the magnetic media.

5.3 Experimental Details

Imprinters were created according to the process described in chapter 4. The crosshatches had a pitch of 50 nanometers. The dose for the 50 pitch pattern was 2.17 nC/cm and a time dependent approach using equation 4.4 was used during the EBL process. Figure 5.3 is a SEM picture of the resulting HSQ imprinter.

![Figure 5.3 - Top view of a 50 nm pitch crosshatch HSQ imprinter.](image)

5.3.1 Imprinting Parameters

Silicon substrates with a thin magnetic film were cleaned using methanol and a mechanical rub to remove surface contaminations. They were spin coated with 100K molecular weight (MW) PMMA at 2800 RPM for 30 seconds, leaving a 60 nanometer layer of polymer on the substrate. The PMMA was purchased from MicroChem as 2% PMMA in chlorobenzene. After spinning, the samples were put in an oven at 170° C for 10 minutes to drive off the solvent.
Imprinting was done with a pneumatic imprinting press equipped with heating and rapid cooling. The force used to imprint was 12.41 lbs. Taking into consideration the size of the patterned area on the imprinter, the pressure was 53,376 psi, assuming that un-patterned areas of the imprinter were not touching the polymer. Imprinter and sample were held to the press using carbon tape. The imprinter was pressed into the sample at the specified pressure and heated to 190° C. When temperature stabilized, imprinting time started. Samples were imprinted for 3 minutes. After 3 minutes, the system was water cooled to 34° C. Cooling took 2 minutes. After cooling was done, the pressure was removed and the imprint was complete.

5.4 Results

The imprinter was able to successfully pattern polymer on the surface of the magnetic sample. Figure 5.4 is a picture of crosshatch imprint with pillars about 30 nanometers high and 50 nanometers apart. This equates to an areal bit density of 258 Gbits/in².

![Figure 5.4 - Left: side view of an imprint with 50 nm pitch pillars. Right: top view of an imprint with 50 nm pitch pillars.](image)

From past experiments a residual layer of 15 nm of polymer has been observed...
underneath the visible pillars in figure 5.4, giving a total polymer thickness of 45 nanometers at the peaks.

5.5 Discussion

It is not certain that 45 nanometers of polymer will be enough to protect the magnetic surface from further processing to magnetically pattern the surface. According to prior measurements, 70 nanometers of polymer would be needed to protect the surface. Unfortunately, a 70 nanometer thickness was unachievable and will be discussed below.

5.5.1 Imprint Thickness Problem

Imprint depth was 30 nanometers with an hr of 15 nanometers. A question arises as to why the pillars are not at least as tall as the original polymer thickness of 60 nanometers. Figure 5.5 is a SEM picture of a real imprint, illustrating the flow of polymer out from under the imprinter.
To the right, the edge of an imprinted crosshatch can be seen. Moving to the left, the darker area is raised as a result of massive flow out from underneath the imprint. Even further to the left polymer flow is still visible, but on a diminished scale. The massive flow observed near the edge of the imprint does not reach this far. At first this massive flow out from underneath the imprinter was thought to be the effect of high polymer viscosity due to inadequate temperature during the imprinting process. This idea was quickly dismissed, however, when temperatures in excess of 200°C failed to eliminate the problem. Higher temperatures could have been used, but only at the risk of having the polymer break down. Therefore other possible reasons for the height discrepancy were explored.

Previous work [37] suggests that this lack of height is caused by a side effect of e-
beam writing HSQ. A solid film of HSQ gets exposed underneath the pattern seen on top of the imprinter. Figure 5.6 [37] illustrates this situation.

![Figure 5.6 - Exposed HSQ buildup underneath the pattern.](image)

This exposed HSQ underneath the pattern reduces the net height of the imprinter features. During imprinting, it forces the polymer out the sides of the imprint instead of creating taller pillars.

A second theory is that the crosshatch pattern does not allow sufficient flow throughout the design to facilitate complete filling of the pattern cavities. It restricts the flow of polymer by forcing it into segmented compartments, thus eliminating flow between the cavities of imprinter. As a result, flow between compartments is non-existent. Thus the polymer takes the path of least resistance and flows out the sides of the pattern instead of completely filling the cavities. If either of these situations was the cause of the shallow imprint, a different imprinter pattern could be the answer to the problem.

### 5.5.2 A New Pattern Design

The crosshatch pattern requires a large exposure dose because of the larger volume of the design (almost 50% of the patterned area). It is quite likely that the solid film exposed underneath of the pattern is a function of the dose. By reducing the necessary dose for patterning the HSQ, the thickness of the film should also be reduced. To test this theory, the design of the pattern was changed to look similar to figure 5.7.
If an imprinter with closely packed pillars like the one in figure 5.7 was used for imprinting, star shaped pillars connected to each other through narrow channels of PMMA would be formed in between the imprinted holes in the PMMA on the surface of the magnetic media. These star shaped pillars could then protect the surface from magnetic destruction just as the pillars had in the crosshatch design. Although the final product would be continuous magnetic bits, they would only be connected to each other through narrow channels of magnetism. It is likely that this configuration of bits would still increase SNR by being almost magnetically separate, while still allowing deep imprints to be formed. This pattern also has the advantage of allowing flow between the pillars, unlike the crosshatch design.

This design was tested, and initial results look promising. Figure 5.8 is an imprint using an imprinter similar to the one illustrated in figure 5.7.
This imprinter design moved a lot of polymer into the cavities of the imprinter while at the same time evacuating more polymer out from underneath the imprinter pillars. The result was a continuous imprint that created star shaped pillars connected to each other through narrow channels of PMMA. The final height difference from the top of the pillars to the bottom of the pits was estimated at 50 nanometers using a SEM. This experiment suggests that an imprinter design of separate pillars may imprint higher aspect ratio features than a crosshatch design, allowing for a deeper overall imprint.

5.6 Conclusion

Successfully imprinting patterned magnetic media depends heavily on finding the right pattern for imprinting. At high densities, polymer flow becomes a major factor for successful imprinting. A pattern that restricts flow more than is necessary will be harder to imprint than a more continuous design. But understanding flow and designing the best
imprinter is a research topic in and of itself. The goal of this research was to pattern magnetic media with a crosshatch pattern. This was successfully accomplished at a bit density of 258 Gbits/in$^2$. While the desired polymer height of 70 nanometers was not achieved, much was learned about the imprinting process and successfully imprinting samples. This knowledge will be used to create better imprinters that will allow deeper imprint depths.
CHAPTER 6 CONCLUSION

6.1 Chapter Overview

This research fabricated individual PMMA pillars on a perpendicular magnetic media surface using nanoimprint lithography. It proved that a thin film of polymer could be patterned on top of a magnetic surface into areas dense enough to become individual magnetic bits. Along the way several noteworthy findings were made. These findings helped speed the process of patterning the magnetic media along. Although magnetic results were not obtained as of the writing of this thesis, a solid groundwork was laid for further testing of planar surface patterned magnetic media. The end result of this thesis was a 50 nanometer pitch PMMA patterned magnetic sample that was sent away for ion bombardment processing to isolate the bits magnetically. The following sections summarize the progress made and the obstacles that had to be overcome to make this possible.

6.2 Imprinter Fabrication

Although HSQ has been used before by several groups to create stamps for NIL and SFIL, the instability of the material has never been addressed. HSQ is very unstable at room temperature, changing hourly. This research investigated a method of obtaining more consistent results when e-beam writing HSQ. Through this research, it was found that a time-dependent method of e-beam writing HSQ must be implemented during long (> 10 minutes) sessions. This
is because of the molecular Si-Si bonds forming in HSQ. During the course of an hour, the EBL dose had to be altered by 3.6% to compensate for the formation of these bonds. From this observation a time dependent dose equation for e-beam writing HSQ was obtained. Equation 6.1 is the first of its kind to be reported in any literature involving e-beam writing HSQ and should serve as a fundamental building block for future research into time dependent methods of EBL using HSQ.

\[ D(t) = D_0 e^{-\alpha(t-t_0)} \]

(6.1)

where \( \alpha = 0.037/hr \)

6.3 Mold Release Coating

During this research a widely accepted method (documented in [24]) of applying a mold release coating to imprinters was used. An experiment was performed to see if imprinters performed better with an MRC applied in a dry atmosphere (< 1 ppm water) or a humid atmosphere (> 1400 ppm water). From this experiment it was observed that although a different chemical reaction bonds the MRC to the surface in each case, the quality of imprinting from each imprinter was the same. This would suggest that water vapor at this concentration does not harm the quality of the MRC. The MRC seems to be fairly robust to different humidity conditions up to the semi-dry level established in this research. Most likely both chemical reactions are acceptable during the application of this MRC. However, excessive water will more than likely cause the mold release molecules to polymerize into large groups, making deposition of a monolayer very difficult. For this reason it is safer to keep water content to a minimum during this reaction.
6.4 Dense Magnetic Patterning with NIL Using HSQ Imprinters

Nanoimprint lithography has become a strong competing force for patterning large areas at a high resolution. However, it is not understood as well as many other lithography techniques, such as photolithography. This is a marked disadvantage for NIL because it makes it harder to fully exploit its strengths and weaknesses. As a result, progress is slow when implementing NIL in specific applications such as patterned magnetic media. This research coupled NIL with a fairly new technique for creating imprinters to perform the difficult task of patterning planar dense magnetic media using a mold release coating not well researched for use with HSQ. Combining this set of processes to pattern planar surface magnetic media has never been done before. This was groundbreaking research that had many challenges along the way. The first challenge was learning how to fabricate HSQ imprinters. The second challenge was determining the best method of applying the MRC. The third challenge was understanding polymer flow and using imprinting variables wisely to produce quality imprints. In light of these challenges significant progress was made towards the goal of fabricating dense patterned planar magnetic media. The end result was an imprinted sample with a pillar height of 45 nanometers and a pitch of 50 nanometers. This equates to an areal bit density of 258 Gbits/in². While the polymer thickness obtained was not the desired 70 nanometers, it still represents major progress towards the overall goal. The imprinting process has been mastered, and imprinting time reduced to under 6 minutes per imprint. Patterning planar surface perpendicular magnetic media was an overall success.
CHAPTER 7 FUTURE RECOMMENDATIONS

Future work should focus on increasing the thickness of the patterned polymer from 45 nanometers to 70 nanometers. This defect is most likely a result of the imprinter. A possible reason that the imprinter did not produce 70 nanometer pillars is the observation made by [37] of a difference in measured feature height from the middle of the imprinter to the edge. Methods of creating imprinters without this defect must be studied. Going back to older techniques used to create SiO$_2$ imprinters would be a possible way of removing this defect. Another possible reason for the inadequate patterning height is the actual pattern of the imprinter. A crosshatch pattern tends to restrict the flow of polymer during imprinting. Restricted flow could result in most of the polymer being pushed out the sides of the pattern instead of filling the cavities to the fullest extent. A flow enhancing pattern should also be researched to determine if it will help increase the aspect ratio of the imprint.
REFERENCES


<http://www.hitachigst.com/hdd/research/recording_head/pr/index.html>


