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Study of demolding process in thermal imprint lithography via numerical simulation and experimental approaches

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STUDY OF DEMOLDING PROCESS IN THERMAL IMPRINT LITHOGRAPHY VIA NUMERICAL SIMULATION AND EXPERIMENTAL APPROACHES

A Thesis

Submitted to Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering

in

The Department of Mechanical Engineering

by

Zhichao Song
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To my parents, family and friends
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Abstract

The objective of present study was to analyze the mechanical behavior of polymer resist during the demolding process, such as stress distribution and evolution; distortion and tilt of microstructures in thermal imprint lithography, a new emerging technique in mass production of micro/nanoscale patterns. One of the most challenging technical issues for thermal imprint lithography is the structural damages during demolding process. Thermal stress, adhesion force and friction force all play important roles in determination of the success of demolding and it is crucial to understand the underlying physics in order to optimize the structure and process design.

In present study, we first studied the stress and deformation behavior of polymer during demolding by commercial finite element method (FEM) software ANSYS 10.0. Based on plane stress assumption, a 2-D model was created to represent one segment of the periodic structure. A 10 element Maxwell model was employed to describe the viscoelasticity of polymer resist. The normal demolding process was simulated and local stress was found to be concentrated at two locations: the corner of transition zone between patterns and residual layer and the contact region between patterns and releasing stamp. Parametric study was conducted and the influence of demolding angle, demolding rate, demolding temperature, friction coefficient and stamp geometry were all identified.

To verify the simulation results, we measured the force required to separate stamp from substrate (demolding force) at three different temperatures (25ºC, 70ºC and 100ºC) and the lowest value was shown at 70ºC, which implied the lowest mechanical resistance. Scanning electronic microscopy (SEM) images also confirmed that the imprinted patterns showed both better overall quality and sharper local profiles at 70ºC, which showed good agreement with simulation results.

In addition, we extended the FEM simulation to the demolding process of UV imprint lithography and injection molding. In UV imprint lithography, the residual stress was shown much
lower than the thermal imprint lithography; in injection molding, we predicted that local shear stress can be reduced up to 25% by building a 10 μm, 45° draft angle structure.
Chapter 1 Introduction

1.1 General Background

Micro/nanofabrication commonly refers to an ensemble of technologies used to fabricate structures at small scale (1-10000 nm), which can be integrated into complicated hierarchical systems. One of the most important micro/nanofabrication technologies is lithography, which enables the transformation of micro/nanoscale patterns to certain substrate, such as silicon, metal, polymer. Conventional lithographic methods, such as electron beam lithography, focused ion beam lithography, optical projection lithography, extreme UV lithography and X-ray lithography, have been widely used in the fabrication of integrated circuit (IC) chips [Guo et al., 2004], biomedical analytical instrumentation [Chen et al., 2001], polymer photonic devices [Guo et al., 2004] and so on; however, there are a lot of issues yet to be solved in these methods like the resolution; the cost of these conventional lithographic methods is also extremely high for most potential users. Thus, it is difficult to commercialize these conventional lithographic methods for the fabrication of micro/nano-electromechanical system (MEMS/NEMS) devices.

Recently, several alternative lithographic methods have been investigated, including microcontact printing, atomic force microscope (AFM) lithography, dip-pen lithography and nanoimprint lithography (NIL). Among them, nanoimprint lithography (NIL), which was firstly proposed by Chou’s group in 1995, has been put as one of the 10 emerging technologies that are likely to change the world, by MIT’s Technology Review, for its high resolution, high throughput and low cost. It has been illustrated that NIL has the capability of patterning sub-10 nm features in a thin layer of polymer resist [Chou et al., 1997], which is
much higher than traditional optical lithography. Large area pattern replication has also been realized by nanoimprint lithography and its in-parallel replication greatly improved the throughput, comparing with E-beam lithography [Heidari et al., 2000].

Despite the huge advantages, a couple of technical challenges remain in the NIL process: first, how to deform the polymer resist easily and fill micro/nanostructures on the stamp efficiently; second, how to reduce the mechanical resistance of separating the stamp from substrate, thus minimize the likelihood of structural damages.

The first issue is critical to the accuracy of pattern replication and the yield of the process can be enhanced by fast filling. The physical process involves polymer rheological behavior at elevated temperature, micro/nanoscale heat transfer, viscous driven and capillary driven flow and so on. Several groups have worked on the first issue. Polymer flow behavior was investigated by both experiments [Heydermann et al., 2001] and numerical simulation [Jeong et al., 2001]. Cavity filling modes were found and the underlying physics was studied for a better understanding of the process [Jeong et al., 2001; Rowland et al., 2004]. Parametric study was also performed for optimal process design, which enables fast replication of high quality patterns.

The second issue is crucial for the success of the NIL since most of imprint failures occur at the demolding stage and all-level mechanical and chemical interactions, such as thermal stress, adhesion and friction, chemical bonding involve and may contribute to the imprint failures. However, the study on the second issue is still lacking. Though some preliminary work has been done in this area recently [Worgull et al., 2005; Guo et al., 2007], fundamental study and systematic investigation of demolding, a process of separating the
stamp from substrate by overcoming all-level chemical and mechanical interactions between stamp and substrate formed by the process history and properties of materials involved.

1.2 Goal and Objective of This Study

The primary goal of this study was to study the mechanical behavior of imprinted poly(methyl methacrylate) (PMMA) resist during demolding in thermal imprint lithography. Basic rules of stress distribution and evolution were extracted from the results of finite element method (FEM) simulation and explained in the light of viscoelastic properties of PMMA and geometrical singularity of stamp. We investigated the influence of several process and geometrical parameters including demolding temperature, demolding rate, demolding angle and stamp aspect ratio. The influence of demolding temperature was studied by experiment and the results showed good agreement with simulation. Furthermore, we extended the simulation to the study of the ejection process in injection molding and the demolding process in step and flash lithography. For the injection molding, shear stress concentration and visible distortion of replicated polycarbonate microposts were observed. Particularly, we focused on the effect of mold insert geometries on stress concentration. Based on the simulation results, we predicted that stress in molded PC microposts could be significantly reduced by modifying sharp corners of the positive features on mold insert with a draft angle and the size and geometric dependence of the draft angle were analyzed. For step and flash lithography, simulation results showed much lower stress concentration than thermal imprint lithography, with identical stamp geometry.

In this thesis, we first gave a brief introduction of the basic background and major work of the thesis in chapter 1. Following the introduction chapter, we reviewed several
Important researches which have been done in related fields in chapter 2. In chapter 3, simulation methodology including governing equations, FEM modeling, material properties, and contact algorithm was discussed in detail. Chapter 4 and chapter 5 focused on the study of demolding in thermal imprint lithography from simulation and experiment, respectively. Simulation work was extended to study the demolding process in step-and-flash lithography and ejection process in injection molding in chapter 6 and chapter 7. Finally, we summarized the work of the thesis and proposed some future work in chapter 8.
Chapter 2 Literature Survey

Thermal imprint lithography, also known as thermal-nanoimprint lithography (NIL) was firstly proposed by Chou’s group [Chou et al., 1995, 1996]. It has been regarded as one of the most promising techniques in mass production of micro- and nanoscale patterns. Compared to the conventional lithographic methods, thermal imprint lithography has shown great advantages in following aspects. First, since patterns are transferred by the mechanical deformation of the polymer resist, the resolution of thermal imprint lithography is completely free from the limitations of conventional lithographic methods, such as light diffraction, beam scattering, and interference [Guo et al., 2001]. Second, as an in-parallel fabrication approach, thermal imprint lithography has shown incomparable advantages in pattern replication efficiency. Recently, large area of patterns (6 inch diameter wafer) with feature sizes down to 50 nm, separated by several hundreds of nanometers from the next feature has been imprinted [Heidari et al., 2000]. Despite several technical challenges remaining, the “in parallel” imprinting technique conceptually beats conventional “in sequence” lithography, which are both expensive and time-consuming. Third, different kinds of thermoplastic polymer and co-polymer are widely used as the resist layer in thermal imprint lithography. The commercial availability and low price of these polymers and co-polymers make thermal imprint lithography a cost-efficient lithographic method for mass production and the biocompatibility of polymer enables great potential in the biological applications [Guo et al., 2001].

Since the mid 1990s, numerous researches have been performed to improve thermal imprint lithography and various variants are developed [Chou et al., 1995; Colburn et al., 1999]. Meanwhile, for better understanding of the physical process of thermal imprint
lithography, several groups focused on the fundamental study on the mechanical behavior of resist during the molding and demolding process [Heyderman et al., 2000; H. D. Rowland et al., 2004]. Both experimental and numerical approaches have been employed; several rules and mechanisms of deformation and stress distribution were extracted, and underlying physics was discussed. Numerical simulation, particularly finite element method (FEM) has been proved to be a powerful tool in predicting the stress and deformation behavior of material at micro/nano scale [Hirai et al., 2001].

In this chapter, we review several significant advances of thermal imprint lithography (NIL) as well as its variants. Typical applications, like biological applications, polymer photonic device, are briefly introduced. We also focus on the previous researches in the study of polymer flow behavior during molding and defect analysis during demolding, which are closely related to the work presented in the thesis.

2.1 Thermal Imprint Lithography Process

The process of thermal imprint lithography is schematically shown in Figure 2.1. It consists of three steps: molding (include preheating), cooling, demolding, which altogether determine the accuracy of pattern replication and strength of replicated patterns. During the molding step, a stamp with desired micro/nano structures is pressed into a substrate coated with a thin layer of polymer resist, which is heated above its glass transition temperature. After conformal molding, the stamp/resist/substrate assembly is cooled down below the glass transition temperature of the resist, with pressure hold. Finally, the pressure is released and the stamp is separated from the replicated patterns.
2.1.1 Development of Thermal Imprint Lithography and Its Variants

Chou et al. initially proposed the technique of compression molding in a thin resist coated on substrate by hard mold insert, followed by anisotropic etching to transfer pattern through the entire resist thickness. Combine with a lift-off process, metal patterns with a feature size of 25 nm and a period of 70 nm were fabricated. This work was published in Science in 1996, in which Chou et al. predicted the great potential of thermal imprint lithography as a high throughput lithographic method for manufacturing integrated circuits and other nanodevices. They also pointed out sub-10-nanometer resolution can be achieved by further development [Chou et al., 1995; Chou et al., 1996].

In 1997, Chou et al. further developed the thermal imprint lithography. They fabricated 10 nm diameter and 40 nm period holes in PMMA on gold and silicon substrate, and 6 nm diameter and 65 nm period holes in PMMA on silicon substrate. With this new technique, they fabricated nanocompact disks with 10 nm features and 400 Gb/in² data density, which is three orders of magnitude higher than current CDs and they read back the
data successfully by a silicon scan probe [Chou et al., 1997].

In thermal imprint lithography, polymer resist layer needs to be heated above its glass transition temperature so that the polymer can be deformed easily. However, due to the mismatch of thermal expansion coefficients, thermal stress is generated during the cooling process, which may lead to structural failures. Also, the high molding temperature results in inevitable long thermal cycle time. Khang et al. developed a room-temperature thermal imprint lithography based on solvent sorption treatment on polymer resist layer [Khang et al., 2000]. Instead of heating the polymer above its glass transition temperature, they added solvent to the polymer to reduce the viscosity of the polymer, experiment results showed that the mold features and imprinted features have the identical size and no patter distortion is inspected.

Application of hard mold insert has the key advantage of high resolution, however, the high pressure required to deform the resist may lead to the fracture of mold and substrate. In order to prolong the lifetime of mold insert and ensure the pattern quality, Khang et al. used a flexible film (~100μm) mold made of fluoropolymer material with the surface energy as low as 15.6dyn/cm. SEM and AFM images of polymer surface imprinted were taken to check the uniformity of pattern depth at four different regions on the sample and result showed excellent uniformity of 147±3 nm [Khang et al., 2004].

Another well-known variant of thermal imprint lithography, developed by Willson’s group, in University of Texas, Austin, is called step-and-flash imprint lithography (SFIL) [M. Colburn et al., 1999]. In the SFIL process, an organic transfer layer is firstly coated on substrate. Then, a surface treated, transparent template with pattern structures is closely
aligned to the substrate. Once in proximity, a drop of low viscosity, photopolymerizable, organosilicon solution is introduced into the gap, which is filled by the capillary action of the solution. After contact, the structure is exposed to UV light, which cures the photopolymer and creates a solidified, silicon rich replica with low surface energy. Finally, the template is separated from substrate after UV curing is completed. Compare to thermal imprint lithography developed by Chou’s group, the SFIL process is implemented at room temperature and requires low pressures only up to 100 KPa. Experimental results have shown excellent pattern fidelity with resolution down to 60 nm.

For micro- and nanopatterning on functional polymers, low molding temperature and operation pressure is often desirable. To solve these problems, polymer inking, which is known as a reverse-nanoimprint lithography, was reported by Bao et al. in 2003. They spin coated a thin polymer film on a patterned mold on selective surfaces by different type of surface coating. Then under suitable temperature and pressure condition, the polymer on protruded surfaces of mold was transferred to the substrate and a positive image of the mold was obtained [Bao et al., 2003].

Recently, Gao et al. proposed a novel imprint method, air cushion press (ACP) [Gao et al., 2006]. Compare to widely used method, solid parallel plates press (SPP), air cushion press showed much better pressure uniformity. Through comparison experiment, air cushion press shows immunity to backside dust and minimizes the affected area of the dust particles trapped between substrate and stamp; while solid parallel plate press showed tremendous stress concentration in the cases above. And compare to solid parallel plates press, air cushion press has much smaller thermal mass, thus faster the imprint process.
2.1.2 Application of Thermal Imprint Lithography

The high resolution, high throughput and cost-efficient capability of thermal imprint lithography enable it to be widely used in both academic and industrial applications, which require precise patterning. In this section, we briefly introduce several of the new applications.

2.1.2.1 Biological Application

It is well known that the reduction in sizes and volumes in miniaturized bio-systems such as “lab-on-a-chip” can improve the efficiency, throughput and cost dramatically, thus help the biological applications, such as diagnostics and drug screening, also the research on genomics and proteomics. The key issue is how to fabricate micro- and nanofluidic devices in order to minimize the bio-systems. Even though traditional, silica-based microfabrication process can be used, the intrinsic disadvantages like the high cost and complicated procedure determine that it cannot be widely used. However, as an emerging high resolution, high throughput and low cost lithographic method, thermal imprinting based technique may play an important role in fabrication of micro- and nanofluidic devices as well as direct molding in polymers.

Guo et al. imprinted a nanochannel template into a very thin layer of resist, which is coated on a cover slip [Guo et al., 2003]. Because of the limitation of resist supply, structures on the nanochannel are not completely filled and enclosed channel structures are built. By controlling the initial thickness of polymer resist layer, enclosed channels with desired size can be achieved.

Falconnet et al. combined nanoimprint lithography (NIL) and molecular assembly patterning by lift-off (MAPL) together and produced streptavidin patterns with feature size
down to 100 nm [Falconnet et al., 2004]. Pyrex plate sputter-coated with 12 nm transparent Nb$_2$O$_5$ was used as substrates. Then, the substrate was spin-coated with a thin film of 125 nm of PMMA. They imprinted a stamp into preheated thin PMMA layer after preheating and removed the residual PMMA in protrusion areas in sequence by O$_2$ plasma. After that, the pattern was dipped into an aqueous solution PLL-g-PEG/PEG-biotin. Finally, they removed the left PMMA by lift-off process and replaced with non-functionalized PLL-g-PEG/PEG and streptavidin showed selective absorb behavior on the pattern as expected. The proposed approach showed great advantage in minimizing the change of exposure of those complex and delicate bio-molecules to the organic solvent or other harsh conditions.

Park et al. developed a fabrication method to modify local chemical properties on surface by a process sequence of thermal imprint lithography, vapor phase deposition and lift-off. AFM/LFM images clearly demonstrated the chemical patterns of fluorinated silane on the feature size as small as 25 nm half-pitch [Park et al., 2005]. To solve the contamination on the background surface area, which is associated with the lift-off process, a modified process was proposed by performing surface modification before imprinting. Through the comparison of AFM/LFM images and fluorescence micrographs, it was found that contamination on the background surface area was dramatically reduced, though not completely eliminated.

2.1.2.2 Polymer Photonic Device

Because of the high resolution and high throughput, thermal imprint lithography can be applied in the fabrication of polymer photonic devices and waveguide devices, which involves the replication of periodic features in the submicron regime.
Seecamp et al. successfully fabricated low refractive index passive optical devices via thermal imprint lithography [Seecamp et al., 2002]. They imprinted diffraction gratings, waveguides and one dimensional photonic structure in PMMA and PS respectively. The pattern transfer was found to be accurate to the 10 nm level. PMMA diffraction gratings showed less than 3% variations of their periodicity over area of 5×5 mm²; PS rib waveguides and 1 dimensional photonic structure also showed acceptable results in experiments.

Micro-ring resonator device is another important optical application of nanoimprint lithography. Chao et al. developed two methods to fabricate polymer microring devices based on thermal imprint lithography [Chao et al., 2002]: one was direct imprint in polymer films; the other involved a template filling process. The optical measurement demonstrated a filtering behavior of microring resonators with a Q factor as high as 5800.

Wang et al. directly patterned organic light-emitting structures at submicron resolution [Wang et al., 1999]. Both small molecules and polymer-based light-emitting structures are patterned via thermal imprint lithography. Comparison experiment of luminescence efficiency indicated that thermal imprint lithography did not lead to degradation of the optical property.

2.2 Polymer Flow Behavior in Molding

Molding is a process to transfer the stamp patterns into the polymer resist by deform the resist mechanically above its glass transition temperature. In order to ensure the accuracy of pattern replication, minimize the built-up stress, reduce the residual layer thickness and prolong the lifetime of stamp, etc, it is essential to understand the polymer flow behavior in molding and determine the optimal molding parameters, thus facilitate the conformal molding.
To find out the deformation mechanisms during molding, extensive researches have been performed by both molding experiments and numerical simulations.

2.2.1 Experimental Study on Polymer Flow Behavior in Molding

This section reviews those representative works done via experimental methods to study the polymer flow behavior in molding.

Heyderman et.al observed the top view and the height profile of PMMA pattern, which is not completely transferred due to insufficient molding time [Heyderman et al., 2000]. Then, they increased the molding time gradually and observed the PMMA pattern at each step. By comparing the pattern geometry and height profile at different step during molding, they concluded that for stamp with simple and periodic cavities, filling mode is as follows: First, the filling starts from the edges of cavity and polymer climbs up the cavity walls. Then, polymer inside the cavity region prior to embossing is pushed by squeeze flow of polymer and fills the central region of cavity. Finally, circular hole in the central region, governed by surface tension shrinks until eventually disappears; (Sometimes, the circular hole will not disappear as a result of air trapped in); for stamp with complex and irregular cavities, at low pressure, polymer deformation may follow the same mode as the stamp with simple and periodic cavities; however, at high pressure, mounds of PMMA may be formed within the stamp cavities and then forced up.

Rowland and King focused on the microcavity filling behavior with polymer film of sufficient thickness such that polymer supply is not limited [Rowland and King, 2004]. They measured the polymer replicates by Atomic force microscopy (AFM) and Scanning electron microscope (SEM) with various stamp geometries and at different imprint conditions. Single-
peak deformation was observed in 30μm width cavities, while dual-peak deformation dominated by viscous flow and probable shear thinning behavior occurred for cavities of 50μm and 100μm, which indicate the dependence of polymer filling modes on pattern groove scale. Dual-peak deformation was observed at low temperature, because viscosity is high and polymer flow is largely restricted; single peak deformation was observed at high temperature, because viscosity is low and two peaks merge into one peak very fast. And the overall height of the deformation increases faster at high temperature, also because of the low viscosity.

Shen et.al embossed a silicon mold insert with circular openings of 100, 120 and 200μm in diameter into a 500μm thick polycarbonate substrate [Shen et al., 2002]. They studied the influence of embossing temperature, embossing time and applied pressure on the replicated patterns by measuring the height and curvature of the microlens. They concluded that temperature dependent viscosity and surface tension play important roles in the determination of pattern profile. As embossing temperature increases, viscosity of polymer flow decreases dramatically and facilitates the filling process; the “buckling” phenomenon observed by Heydermann also disappears at high temperature due to the decrease of surface tension. The height of microlens increases linearly, as a function of applied pressure, while the curvature of the microlens is independent on the applied pressure. Both the height and curvature of microlens increases with time and gradually reaches a steady-state height.

Juang et.al investigated the dependence of replication accuracy and molded-in stress on process conditions, for isothermal and non-isothermal embossing [Juang et al., 2002]. They concluded that for isothermal embossing, replication accuracy and molded-in stress are strongly dependent on process conditions, which must be balanced with cycle time in order to
achieve good replication and low molded-in stress; for non-isothermal embossing, excellent replication can always be achieved as long as embossing is completed, because local high temperature can be achieved. In isothermal embossing, the flow pattern resembles a biaxial extensional flow. For non-isothermal embossing, the polymer flows upward along the wall of the mold feature, followed by being compressed downward and squeezed outward.

Martin et.al focused on the mechanical recovery of PMMA resist in the central region of micro-scale structure replicated [Martin et al., 2003]. The height and width of recoveries are measured by atomic force microscopy (AFM) statistically. The mechanical recoveries increase as imprint force increases, until a critical force above which the recoveries dramatically decrease to zero. Authors believe that the mechanical recoveries are not due to elastic deformation of mold insert, but a relaxation of elastic stress stored in the resist during imprint.

2.2.2 Simulation Study on Polymer Flow Behavior in Molding

Numerical simulation is an important tool to predict the stress and deformation behavior of polymer resist during molding and find the optimal process conditions. Finite element method (FEM) simulation is the most widely used tool in stress and deformation analysis in molding; computational fluid dynamic (CFD) code based on finite difference method and finite volume method is also a powerful tool to simulate the filling behavior of polymer flow. Linear elastic model, non-linear elastic model, viscous fluid mold are employed by different researchers to describe the mechanical properties of polymer resist above its glass transition temperature. In this section, we review the simulation studies on polymer flow behavior during molding and correlate them to experimental results.
To understand the effects of capillary force and width of stamp groove on flow behavior at embossing stage. Jeong et.al simulated the filling behavior of polymer flow by computational fluid dynamics (CFD) code, CFD-ACE, based on the finite volume method [Jeong et al., 2002]. In simulation unsteady incompressible flow with free surface is solved by full Navier-Stokes Equation. High order nonlinear boundary conditions are imposed on free surface in order to simulate surface tension. Simulation results show that concave region during cavity filling is formed by capillary force and without corners of cavities can not be completely filled without surface tension. Width of stamp groove is dominant in determination of topography of polymer flow. The simulation results are compared to experimental observation from Heyderman and show excellent agreement.

Hirai et.al simulated the deformation of thin polymer film in nanoimprint lithography by the commercial finite element method (FEM) software MARC [Hirai et al., 2001]. A rubber elastic model, 2-parameter Mooney-Rivlin model was employed to describe the non-linear stress-strain behavior of PMMA above its glass transition temperature. Systematic simulation results reveal that not only high aspect ratio, but also low aspect ratio patterns require high pressure for a complete filling, while the pressure is minimized when the aspect ratio is around 0.8. Pressure required for complete filling is strongly dependent on the initial thickness of polymer resist film. It can be reduced up to 70% by increasing the film thickness from the depth of stamp structure to the triple of structure depth. These results were theoretically explained by the non-linear deformation mechanism of the polymer and agree well with the results of related experimental inspections.

In order to capture the underlying physics of polymer flow from the nanometer to
millimeter length scale and examine geometry and thermo-physical process quantities affecting cavity filling and reveal the process design rules for nanoimprint lithography, Rowland et.al simulated the polymer deformation process with free/moving boundary by a Galerkin finite element program GOMA [Rowland and King, 2005]. They defined three non-dimensional parameters: capillary number of polymer flow \( (Ca=\frac{\eta v}{\sigma}) \), the directional flow ratio \( W/hi \) and the polymer supply ratio \( S/hr \). Capillary number determines the viscous flow versus capillary driven flow, the directional flow ratio predicts single or dual peak flow and the polymer supply ratio determines shear dominant Stokes flow versus squeeze flow. All the previous researches on the flow behavior and cavity filling modes are characterized by these three parameters. In another publication from Rowland et.al, they investigated the polymer flow and mold filling process of NIL for embossing tool having irregular spacing and sizes, and focused on the geometric quantities governing cavity filling order, polymer peak deformation and global mold filling time. The same simulation tool, finite element multi-physics code GOMA is used and simulation results revealed that individual cavity characteristic volume determines filling orders in non-uniform hot embossing; Global filling time is governed by the characteristic size and volume of the maximum cavity with a quadratic dependence.

Young analyzed the polymer flow behavior during the imprinting by a model based on viscous fluid [Young et al., 2005]. Young believed that the relaxation effect is very quick for the temperature several degrees above the glass transition temperature, thus, no elastic effect would be left in the resist. He found that, for a constant imprint rate, the pressure does not change much at the beginning and rises to a higher value as the tool base touches the polymer.
Also, the wave-like polymer front was also predicted.

Juang et al. simulated the polymer flow at isothermal and non-isothermal conditions by finite element method (FEM) software DEFORM [Juang et al., 2002]. The study showed that for the isothermal embossing, flow pattern predicted from simulation with a slip boundary condition is more accurate than that with no-slip boundary conditions. And the simulated results showed a fairly good comparison with experimental observations for non-isothermal embossing.

2.3 Study of the Demolding Process

Demolding is a process to overcome all levels of chemical (adhesion force) and mechanical interactions (residual stress) between stamp and substrate formed by the process histories during molding and cooling, which strongly depends on material properties. During demolding, resist at the interface experiences friction and adhesion forces (acting along and perpendicular to the interface, respectively), which result in a significant change in the stress distribution in the resist layer as demolding proceeds. Resist deformation is determined by the relative magnitude of the local stress to the yield stress of the resist. When the local stress in resist domain is higher than its mechanical strength, plastic deformation, even structural collapse may occur during the demolding process, as shown in figure 2.2. However, compare to the extensive researches on polymer deformation in the molding process, study on the demolding process is still lacking, even though several groups have performed exciting work on different aspects of the demolding process.

2.3.1 Surface Treatment – Anti Adhesion Coating

To understand the effect of self-assembled monolayer in minimizing adhesion
between stamp and polymer resist. Tallal et.al measured the contact angle of different liquids drop on stamp surfaces with different anti adhesion coating [Tallal, 2006]. To represent the overall interaction between stamp and polymer resist in demolding, Approach-retract tests are conducted by AFM nano-indentation and force curve during loading-unloading process is record. The experimental results showed that force needed to pull off AFM tip from polymer surface can changed by nearly one order of magnitude with and without anti sticking coating. Polycarbonate shows lower adhesion than PMMA and NEB with identical anti sticking coating and Optool is a better anti sticking coating material than Fots, because the adhesion is weaker with the Optool surface coating.

![Figure 2.2](image.png)

Figure 2.2 (a) Typical imprint failures of imprinted PMMA patterns and (b) silicon stamp

Similar to the work performed by Tallal, Cameron et.al employed the variable temperature chemical force microscopy and measured the pull-off force of AFM tips, silanized with four different self-assembling monolayers, from thin polymer film, at a series of temperatures [Cameron et al., 2006]. By Comparing the force required to remove AFM tips at different conditions. Measurement results showed that the silanized substrates are hydrophobic, as a result of formation of organosilane Self-assembling monolayers and the surface tension decreases monotonously verse contact angle, thus lead to low adhesion force.
Temperature dependent adhesion force measurement results indicate that the pull-off force increases versus the temperature. Particularly, at the glass transition temperature, both non-hydrofluorinated tips and long-chain hydrofluorinated tips show substantial increase of adhesion force, while short-hydrofluorinated tips show slight increase.

2.3.2 Demolding Simulation and Experiment

In order to find proper methods to reduce shrinkage of molded parts and minimize demolding forces, thus avoid damages of microstructures during demolding. Worgull et al predicted the stress distribution during large area embossing by finite element simulation [Worgull et al., 2006]. Based on the stress analysis, they concluded that, in order to avoid inhomogeneous pressure distribution in polymer flow and achieve uniform shrinkage, it is critical to bound the pattern area artificially with frames. Simulation results showed that non-uniform shrinkage over the whole pattern area can be relaxed obviously by this method. Simulation results also showed that, during imprinting, outer structures are always exposed to higher stress than central structures, thus, it reduces the stress value in pattern area greatly to create additional structures surrounding pattern area to protect it.

Guo et.al pointed out the thermal stress due to the mismatch of thermal expansion coefficient and friction/adhesion on the interface were two main reasons which may lead to structural damages during demolding [Guo et al., 2006]. They calculated the thermal stress using a finite element method (FEM) software ABAQUS/Standard and proved that stress in pattern area can be released by building stress barrier at the edge of the stamp. They correlated the adhesion force and the surface energy of the two contact surfaces quantitatively by an empirical formula based on elasto-plastic contact, which was proposed by Pollock et.al
in 1978. To minimize the surface energy, thus reduce the adhesion and facilitate the demolding process, PTFE coating was applied on the nickel mold insert. Experimental results showed that typical demolding defects like pull-up and damaged edge can be reduced.

Analysis of the demolding process in micro injection molding is also significant for the study in nanoimprint, because of the extremely similar process and conditions. Fu et al. also believed that there are two factors that possibly lead to demolding failure: shear stress during demolding due to the contact pressure and thermally-induced stress due to cooling. Based on the isotropic thermal shrinkage assumption and pressure-volume-temperature relation of the resist, they theoretically derived a critical temperature for demolding, below which there is no contact on mold insert-resist interface and demolding force is zero. By analyzing the stress evolution during demolding, they concluded that the moment most possibly subject to breakage during demolding is always the onset of demolding [Fu et al., 2006].

M. Worgull et al. characterized the friction force during the demolding process by a rate-controlled tensile test [Worgull et al., 2006]. They concluded that the demolding is determined by the static friction between mold and polymer, which is responsible for the structural damages during demolding. They investigated several process parameters which may influence the friction considerably: First, the demolding force increases as molding temperature increases, since polymers flow more freely at higher molding temperature and fill the surface roughness of mold more easily, thus form strong adhesion and mechanical interlock. Second, the higher molding pressure gives lower demolding force. They explained the result from the pressure dependence of thermal expansion coefficient. With higher
molding pressure, the thermal shrinkage is smaller, thus the residual thermal stress is lower. Third, they found that anti-sticking coating may decrease the demolding force dramatically, by minimizing the surface tension and roughness.

Even though a lot of significant researches have been performed, the mechanical response of the polymer resist during demolding under various molding and demolding conditions in thermal imprint has not been fully understood. An in-depth and systematic study on the demolding process will allow for determination of process conditions, stamp geometries, and material selections, which will lead to low stress and deformation in the polymer resist layer and thus the success of demolding. And in the thesis, we focus on the issues mentioned above and try to find solutions to them thus improve the process and stamp design for thermal imprint lithography.
Chapter 3 Simulation Methodology

Finite element method (FEM) softwares have been widely used as powerful and reliable tools in mechanical analysis of micro-electromechanical system (MEMS) devices under various conditions. In this chapter, we describe the simulation methodology used in this work in detail, including geometrical modeling, boundary conditions, meshing, material properties, process conditions and governing equations.

![Figure 3.1 2D finite element method (FEM) model of a Si stamp/PMMA resist/Si substrate assembly](image)

3.1 Mold Creation

Figure 1 shows a two-dimensional (2-D) FEM model of a Si stamp/PMMA resist/Si substrate assembly and the boundary conditions are shown. The depth of recessive area on the silicon stamp is 5μm and the aspect ratio of the feature is 1:2. Both the residual PMMA layer and the silicon substrate have identical thickness of 5μm. The recessive area on the stamp is fully occupied by PMMA resist. The plane stress assumption is adopted to simplify
the simulation because the perpendicular motion of resist to the substrate surface during demolding is negligible.

### 3.1.1 Boundary Conditions

The bottom surface is constrained on all three freedoms and a symmetric boundary condition is applied on the centerline in order to reduce the calculation time. Since the PMMA resist is spin coated on silicon substrate, the PMMA/Si substrate interface is defined as glued interface, no stress and displacement discontinuity is allowed; on the other hand, the interface between the silicon stamp and replicated PMMA pattern is set to be slip-allowed, however, no penetration and separation on normal direction is allowed. These boundary conditions can be justified considering the fact that an anti-sticking coating is usually applied to the stamp surface in order to reduce adhesion to the resist while increased adhesion is preferred between the PMMA resist and Si substrate.

Uniform pressure of 10 MPa is applied on top surface of the stamp during the cooling process to compensate the thermal shrinkage during cooling and ensures the dimensional accuracy of replicated patterns; during the demolding step, the pressure is released and a vertical displacement of 6 μm is applied on the stamp, at a demolding rate of 0.05 μm/s. For the cooling process, we are only interested in the final profile of Von Mises stress distribution in replicated PMMA patterns, 1 sub-step is defined. For the demolding process, 1000 sub-steps are defined, which will allow for convergence within 25 iterations (up limit of ANSYS program) for each sub-step of 0.1s (tracking time, not CPU time), in order to acquire enough information for stress evolution analysis.
3.1.2 Element Type and Meshing Detail

Two types of different structural elements are employed in the simulation: PLANE42 and VISCO88. PLANE42 is a 2-dimensional, 4-nodal linear structural element and VISCO88 is a 2-dimensional, 8-nodal quadratic structural element. In the simulation, PLANE42 is assigned to linear elastic material – silicon and VISCO88 is assigned to PMMA, which is defined to be viscoelastic material.

Since we focus on the stress analysis in PMMA, the element size in the PMMA domain is set to be 0.1 μm and the element size in silicon domain is set to be 0.2 μm. Due to the irregular geometry of the stamp and resist domain, free mesh is applied.

3.2 Material Properties

3.2.1 Silicon – Linear Isotropic Elastic Model

Silicon has been widely used in micro/nanofabrication due to its outstanding optical, mechanical and thermal properties. Particularly, silicon exhibits perfect tensile and compression strength as high as 7 GPa with low toughness, thus we assume both the silicon stamp and substrate to be linear isotropic elastic. Also, the temperature and rate dependence of the material properties are neglected because the melting point of silicon (~ 1400°C) is much higher than the temperature range of thermal NIL process(< 200°C). In the simulation, Young’s modulus, Poisson’s ratio and thermal expansion coefficient of silicon are input as constants 128 GPa, 0.28 and 2.5e-6/°C, respectively [Basic Mechanical and Thermal Properties of Silicon, Virginia Semiconductor, Inc].

3.2.2 PMMA – Viscoelastic Material

Compared with the silicon stamp and substrate, the dependency of the PMMA
response on temperature and load rate cannot be ignored. Since we focus on the stress and deformation analysis in the PMMA domain, the constitutive equations of PMMA are particularly important. In previous FEM simulations of polymer molding, non-linear elastic models, like Mooney-Rivlin model were used to describe the mechanical properties of polymer resist [Hirai et al., 2001]. However, the Mooney-Rivlin model was proposed to predict non-linear mechanical behavior for rubbery elastomer and is not suited to describe the viscoelasticity of polymers, which is not only temperature-dependent, but also time-dependent [Kolmpen, 2005]. Thus, in this simulation a 10 element Maxwell model was used to accommodate the time-dependent thermal and mechanical properties of PMMA.

### 3.2.2.1 Viscoelasticity

Viscoelasticity refers to material behavior that exhibits both viscous and elastic characteristics when undergoing plastic deformation. Viscous materials resist shear strain linearly with time when a stress is applied; elastic materials deform instantaneously when a stress is applied and recover immediately once the stress is released. In the viscoelastic model, both viscous (dashpot) and elastic elements (spring) are included.

### 3.2.2.2 Molecular Background

Previous researches have shown that the origin of polymer deformation lies in the capability to adjust their chain configuration on a molecular level by rotation around single covalent bonds in the main chain [Kolmpen, 2005]. This freedom of rotation is, however, controlled by intra-molecular (chain stiffness) and inter-molecular (inter-chain) interactions. Together these interactions give rise to an energy barrier that restricts conformational changes of the main chain. The rate of conformational changes, i.e. the molecular mobility, is
determined totally by the thermal energy available in the system. Increasing of the thermal energy increases the rate of change which, on a fixed time scale, allows for larger molecular rearrangements and, thus, accommodation of larger deformations. Since thermal energy is determined by temperature, there will be a relatively strong relation between temperature and mobility, and thus also with macroscopic deformation (in fact polymers are known for their pronounced temperature dependence). In addition to this, there is also a strong influence of stress on molecular mobility since polymers allow for "mechanical" mobility when secondary bonds are broken by applying stress. Last but not least, the molecular mobility at certain load and temperature is also time-dependent, which is known as “creep”. The behavior is governed by two characteristic relaxation mechanisms: the glass transition and the reptation process [Kolmpen, 2005]. On short time scales the response is solid-like since only limited molecular rearrangements are possible. With increasing time scales, the size of the conformational changes increases, ultimately resulting in unbounded segmental diffusion at the glass-rubber transition. Large scale motion of polymer chains is, however, inhibited by physical entanglements that can be envisaged as temporary cross-links. At this stage the polymer effectively behaves like a rubber, whereas at even longer times, reptation enables main-chain-diffusion (entanglements are dissolved), and the polymer behaves as a fluid (melt).

3.2.2.3 10-Element Maxwell Model

Different models, such as Maxwell model, Kelvin-Voigt model and Standard Linear Solid Model, are widely used to predict stress-strain responses of materials under various loading conditions. The viscoelastic behavior is comprised of elastic and viscous elements, as
the linear combinations of sprints and dashpots. Each model differs in the arrangement of the elements.

The elastic component is molded by a spring of elastic modulus \( E \) and the viscous component is molded by a dashpot of viscosity \( \eta \). The constitutive equations are as follows:

\[
\sigma = E \varepsilon \quad \text{(spring)} \quad \text{(Equation 3.1 a)}
\]

\[
\sigma = \eta \frac{d \varepsilon}{dt} \quad \text{(dashpot)} \quad \text{(Equation 3.1 b)}
\]

The Maxwell model can be represented by a purely viscous dashpot and a purely elastic spring connected in series, as shown in figure 3.2. The constitutive equation is expressed as following:

\[
\frac{d \varepsilon_{\text{total}}}{dt} = \frac{d \varepsilon_D}{dt} + \frac{d \varepsilon_v}{dt} = \frac{\sigma}{\eta} + \frac{1}{E} \frac{d \sigma}{dt} \quad \text{(Equation 3.2)}
\]

![Figure 3.2 Schematic of Maxwell model (linear combination of spring and dashpot)](image)

The generalized Maxwell model, also known as Maxwell-Weichert model is the most widely used model to describe the mechanical response of viscoelastic material. It takes into account the stress relaxation not a single time, but a distribution times. The model can be built with as many Maxwell model as are needed to describe the viscoelastic behavior accurately. (Figure 3.3)

Deformation up to the yield point is governed by at least one, but usually more than one relaxation mechanisms. Each of these mechanisms has its origin at the molecule level
and is activated by time and temperature. The viscoelastic deformation is commonly described by a Boltzmann single integration representation in its relaxation form,

$$\sigma(t) = \int_{-\infty}^{t} E(t-t')\dot{\varepsilon}(t')dt'$$  \hspace{1cm} (Equation 3.3)

The time-dependent modulus $E(t)$ can be captured by a mechanical model with a sufficient number of elastic and viscous elements. The elastic modulus of the spring-dashpot system (Maxwell model) can be expressed as follows.

$$E(t) = \sum_{i=1}^{10} E_i \exp(-\frac{t}{\tau_i})$$  \hspace{1cm} (Equation 3.4)

Here, $\tau_i = \eta_i / E_i$ refers to the relaxation time of the $i^{th}$ Maxwell element. The strain rate dependence is neglected, thus relaxation time of each Maxwell element and corresponding elastic modulus is determined by fitting the elastic modulus vs. time curve at $110^\circ\text{C}$ from experimental measurement with Equation 3.4 [Worgull et al., 2006] and input as constant which are shown in table 3.1.

3.2.2.4 Time-Temperature Superposition and Williams-Landel-Ferry (WLF)  \hspace{1cm} Equation

Usually, the viscosity of liquid shows strong temperature dependence. The viscosity
of liquid tends to decrease as the temperature increases. There exist several models to express this phenomenon, such as exponential model, Arrhenius model, Williams-Landel-Ferry (WLF) equation and Seeton fit. In this work, we used the WLF equation which is widely used for predicting polymer melting. The WLF equation can be expressed by equation 3.5.

\[
\log a_r = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)} \tag{Equation 3.5}
\]

\[
C_1 = \frac{4}{3 \cdot 2.3} \frac{T_A}{T_A - T_g}; \quad C_2 = T_g - T_A \tag{Equation 3.6}
\]

Here, \( T_g \) is the glass transition temperature of PMMA and \( T_A \) is the temperature for the secondary transition of PMMA, which roughly equals to \( 0.75T_g \). \( z \) refers to the coordination number of a segment smaller by 2 than that of an ordinary molecule. For our simulation, \( T_g \) is 110°C; \( C_1 \) and \( C_2 \) are 12.796 and 74.787, respectively, which were also determined by systematic dynamic mechanical analysis at different temperature and master curve fitting, by Worgull et al [Worgull et al., 2005].

![Table 3.1 Elastic modulus and relaxation time for each Maxwell model in the simulation](image)

<table>
<thead>
<tr>
<th>Element Number</th>
<th>Relaxation Time (s)</th>
<th>Normalized Elastic Modulus (E/E₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4345.6</td>
<td>0.0057752</td>
</tr>
<tr>
<td>2</td>
<td>1.0734</td>
<td>0.15835</td>
</tr>
<tr>
<td>3</td>
<td>0.02363</td>
<td>0.16223</td>
</tr>
<tr>
<td>4</td>
<td>83.983</td>
<td>0.020769</td>
</tr>
<tr>
<td>5</td>
<td>1.66036E6</td>
<td>0.0031756</td>
</tr>
<tr>
<td>6</td>
<td>3.9778E-6</td>
<td>0.10456</td>
</tr>
<tr>
<td>7</td>
<td>0.21832</td>
<td>0.19654</td>
</tr>
<tr>
<td>8</td>
<td>7.0342</td>
<td>0.086638</td>
</tr>
<tr>
<td>9</td>
<td>8E-5</td>
<td>0.13355</td>
</tr>
<tr>
<td>10</td>
<td>0.00154</td>
<td>0.12741</td>
</tr>
</tbody>
</table>

\( E_0 = 2.41E6 \text{ (Pa)} \)
3.2.2.5 Equations of State

The basic goal of equations of state (EOS) is to accurately describe experimental PVT data, i.e. specific volume as a function of temperature and pressure, from which further physical properties such as thermal expansion coefficient and compressibility can be derived at various conditions of pressure and temperature. There are two types of EOS: empirical descriptions and those based on theoretical considerations. Tait Equations of state are typical empirical description of the specific volume as a function of pressure and temperature, expressed as equation 3.7 [M. Schmidt et al., 1997],

\[ V(P,T) = V(0,T) \cdot \left\{1 - C \cdot \ln\left[1 + \frac{P}{B(T)}\right]\right\} \]  \hspace{1cm} (Equation 3.7)

Temperature-dependent parameter \( B(T) \) is called Tait parameter and can be described by an exponential expression as equation 3.8,

\[ B(T) = B_0 \cdot \exp(-B_1 T) \]  \hspace{1cm} (Equation 3.8)

Both \( B_0 \) and \( B_1 \) are constants. The zero-pressure isobar \( V(0,T) \) can be described by a first or higher order polynomial (equation 3.9) or exponential expression (equation 3.10),

\[ V(0,T) = C_0 + C_1 T + C_2 T^2 + C_3 T^3 \]  \hspace{1cm} (Equation 3.9)

\[ V(0,T) = V_o \exp(\alpha_o T) \]  \hspace{1cm} (Equation 3.10)

For most polymers, the constant \( C \) turns out to be universal and equal to 0.0894 [P.Zoller, 1989].

An analysis in terms of the scaling parameters \( P^*, V^*, T^* \) of the Simha-Somcynsky EOS has resulted in a modified Tait EOS that takes into account the slight temperature and pressure dependence of \( C \) as well as the pressure dependence of \( B \) [R. K. Jain et al., 1989]. The Simha-Somcynskey EOS theory is based on a quasi-lattice theory where the molecules,
consisting of \( n \) chemical repeat units, \( n \)-mers, with molecular weight \( M_r \), are divided into \( s \) equivalent segments, \( s \)-mers, with molecular weight \( M_0 \) that occupy only a fraction \( y \) of the lattice sites. Each chain has \( 3c \) external volume-dependent degrees of freedom and the intersegmental potential is based on the 6-12 potential in the square-well approximation. The fraction of lattice vacancies, is characterized by \( h = 1 - y \). Assuming a random mixing of vacant and occupied sites of equal size, the number of vacancies disordering the system is determined by the minimization of the Helmholtz free energy for an equilibrium system. For polymers, contributions from terminal groups become negligible as \( s \) tends to infinity and the flexibility ratio \( 3c/s \) is generally assigned as the value of 1. The Simha-Somcynsky EOS can be written in terms of two coupled equations 3.11 (a) and (b)

\[
\frac{PV}{T} = [1 - 2^{-1/6} y(y\bar{V})^{-1/3}]^{-1} + \left(\frac{2y}{T}\right) \cdot (y\bar{V})^{-2} \times [1.011(y\bar{V})^{-2} - 1.2045] \quad \text{(Equation 3.11 a)}
\]

\[
\left(\frac{s}{3c}\right) \left[\left(\frac{s-1}{s}\right) + y^{-1}\ln(1-y)\right] = \frac{V}{6T} \cdot (y\bar{V})^{-2} \times [2.409 - 3.033(y\bar{V})^{-2}] + [2^{-1/6} y(y\bar{V})^{-1/3} - 1/3] \times [1 - 2^{-1/6} y(y\bar{V})^{-1/3}]^{-1} \quad \text{(Equation 3.11 b)}
\]

where \( \tilde{P} = P/P^* \), \( V = V/V^* \), \( T = T/T^* \) are the reduced PVT variables and \( y\bar{V} \) is the reduced cell volume. \( P^* \), \( V^* \) and \( T^* \) are the characteristic scaling parameters that are determined from PVT equilibrium melt data and contain the molecular characteristics or the structural characteristics of segment, as equation 3.12 (a), (b) and (c).

\[
P^* = q_z \varepsilon^*/(sv^*) = (z - 2)\varepsilon^*/v^* \quad 3c/s = 1 \quad \text{(Equation 3.12 a)}
\]

\[
V^* = (N_A/M_0)v^* \quad \text{(Equation 3.12b)}
\]

\[
T^* = q_z \varepsilon^*/(ck) = 3(z - 2)\varepsilon^*/k \quad 3c/s = 1 \quad \text{(Equation 3.12c)}
\]

Where \( q_z \) is the number of inter-chain nearest neighbors or intermolecular contact
sites in quasi-lattice of coordination number \( z = 12 \), \( N_A \) is Avogadro’s number and \( k \) is the Boltzmann constant. \( \nu^* \) and \( \varepsilon^* \) are defined by the intersegment potential as the repulsive and hard core volume and the maximum attractive energy or potential minimum respectively. The molecular weight of the segment \( M_0 \) can be calculated from the scaling parameters as equation 3.13.

\[
M_0 = (R/3) \cdot T^* / (V^* \times P^*)
\]  
(Equation 3.13)

In our simulation, we employ the PVT diagram in the definition of thermal expansion coefficient of PMMA. As the pressure is held constant during the cooling process, we ignore the pressure dependence of thermal expansion coefficient and focus on the temperature dependence. As determined by the experimental measurement of Worgull et al., thermal expansion coefficient is expressed in terms of three order polynomial function of temperature as following,

\[
\alpha(T) = (5.183 \times 10^{-5}) - (1.221 \times 10^{-6})T + (2.99 \times 10^{-8})T^2 - (1.012 \times 10^{-10})T^3
\]  
(Equation 3.14)

### 3.3 Process Assumption

Several assumptions are made in order to simplify the simulation.

First, we assume that the mechanical behavior of both silicon and PMMA at the simulated scale is governed by the equations of continuum mechanics, in which we consider all object to be continuous. Properties such as density, pressure, temperature, and velocity are taken to be well-defined at "infinitely" small points, defining a REV (Reference Element of Volume), at the geometric order of the distance between adjacent molecules of fluid. Properties are assumed to vary continuously from one point to another, and are averaged over values in the REV.
The Knudsen number (Kn), which is defined as the ratio of the molecular mean free path length (λ) to a representative physical length scale (L) (Equation 3.15), is useful to determine whether statistical mechanics or the continuum mechanics formulation of fluid dynamics should be used.

\[
Kn = \frac{\lambda}{L} = \frac{K_B T}{\sqrt{2\pi\sigma^2} PL}
\]  

(Equation 3.15)

Here, \(\lambda\) is the mean free path of fluid, \(L\) is representative physical length scale, \(K_B\) is Boltzmann’s constant, \(T\) is the temperature, \(\sigma\) is the particle diameter, and \(P\) is total pressure. Chan and Horn proposed that the Reynolds description of the drainage process for organic liquids appears to be very accurate down to film thickness of about 50 nm [D. Y. Chan et al., 1985]. They also showed that the continuum hypothesis breaks down, as the film thickness is less than about ten molecules thick. The dimensions of a polymer molecule-chain are usually characterized by the radius of gyration, \(R_g\), which can be calculated by equation 3.16.

\[
R_g = 0.012M^{0.583} \text{ (M – molecular weight)}
\]  

(Equation 3.16)

Since the molecular weight of PMMA used in the experiment is 25,000g/mol, we obtain the \(R_g\) value of 4.4 nm, which is much less the scale of the features on the pattern (5000 nm). As a result, we believe that continuum hypothesis holds and finite element method is still valid.

Second, we assume microcavities on silicon stamp are initially completely filled by the PMMA flow at the molding temperature. Even though the polymer filling process is a challenge in imprinting, several groups have shown that proper combination of process parameters such as molding temperature, molding pressure, ensures perfect polymer filling.
In addition, no air is trapped inside the microcavities and buckling phenomenon due to surface tension is ignored.

Third, the flow stress during molding is ignored. The residual stress in PMMA consists of two parts: flow stress and thermal stress. We assume that flow stress in molding is much less than the thermal stress generated due to the mismatch of thermal expansion coefficient during cooling, as well as the shear stress at the stamp-resist interface during demolding which results from the thermal stress and adhesion. This assumption can be justified by results of the temperature-dependent residual stress measurements at polymer-silicon interfaces, where negligible residual stress was revealed at the temperature above $T_g$ of the polymer [Wang et al., 2000].

Fourth, there is no heat transfer between different components during cooling, but cooled down at an identical cooling rate. This point can be justified by the high thermal conductivity of silicon ($149 \text{ W/m·K}$) and the small scale of stamp/resist/substrate assembly ($\sim 10 \mu\text{m}$).

Fifth, sliding is allowed at vertical interfaces between stamp and resist, but no separation and penetration are allowed. This point can be justified by surface treatment of anti-adhesion coating. However, the thermal shrinkage during cooling process is compensated by the high pressure applied during cooling, thus the PMMA is always in hard contact with silicon stamp during the whole process; no penetration and separation will occur.

Finally, we assume that all the material properties are isotropic. Since the polymer chain length of PMMA is much smaller than the representative scale of feature structure of
stamps, the orientations of PMMA molecules are distributed randomly, thus, the material properties are isotropic.

3.4 Governing Equations

In this study, a computational method based on an implicit algorithm is employed and in this section we will introduce the equations governing the solving process.

3.4.1 Continuity Equation

A continuity equation is an equation of conservation of mass. The law of conservation of mass states that the mass of a closed system of substances will remain constant, regardless of the processes acting inside the system. An equivalent statement is that matter can not be created nor destroyed, although it may change form. Equation 3.17(a) and (b) are the integral and differential form of the continuity equation, respectively.

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = \frac{d \rho}{dt} + \rho \nabla \cdot \mathbf{v} = 0 \quad \text{(Equation 3.17 a)}
\]

\[
\int_{V(t)} \int \frac{\partial \rho}{\partial t} dV + \int_{s(t)} \rho \mathbf{v} \cdot nds = 0 \quad \text{(Equation 3.17 b)}
\]

Since we do not consider the influence of gravity in the simulation, the density in equation 3.17 (a) and (b) is assume to be constant and the equation can be simplified as following,

\[
\nabla \cdot \mathbf{v} = 0 \quad \text{(Equation 3.18 a)}
\]

\[
\int_{s(t)} \mathbf{v} \cdot nds = 0 \quad \text{(Equation 3.18 b)}
\]

3.4.2 Navier-Stokes Momentum Equation

The Navier-Stokes momentum equation describes the relation of momentum transfer and conversation. It states that the increment of momentum in a closed domain equals the
momentum that enters the domain through the surface. Equation 3.19 (a) and (b) are the integral and differential form of Navier-Stokes momentum equation, respectively.

\[
\iiint_{\Omega(t)} \frac{\partial}{\partial t} (\rho v_i) dv = \iiint_{\partial \Omega(t)} \rho f_i - \iiint_{\partial \Omega(t)} (\rho v_i v_j - \sigma_{ij}) n_j ds \quad \text{(Equation 3.19 a)}
\]

\[
\frac{\partial v_i}{\partial t} + v_j \frac{\partial v_i}{\partial x_j} = \frac{dv_i}{dt} = \frac{1}{\rho} \frac{\partial \sigma_{ii}}{\partial x_i} + f_i \quad \text{(Equation 3.19 b)}
\]

### 3.4.3 Strain-Displacement Equations

Strain-Displacement equations describe the basic relations between displacement and strain, which are shown as equation 3.20 (a) – (f).

\[
\varepsilon_x = \frac{\partial u}{\partial x} \quad \text{(Equation 3.20 a)}
\]

\[
\varepsilon_y = \frac{\partial v}{\partial y} \quad \text{(Equation 3.20 b)}
\]

\[
\varepsilon_z = \frac{\partial w}{\partial z} \quad \text{(Equation 3.20 c)}
\]

\[
\gamma_{xy} = \frac{1}{2} \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \quad \text{(Equation 3.20 d)}
\]

\[
\gamma_{xz} = \frac{1}{2} \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right) \quad \text{(Equation 3.20 e)}
\]

\[
\gamma_{zx} = \frac{1}{2} \left( \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) \quad \text{(Equation 3.20 f)}
\]

### 3.4.4 Strain Compatibility Equation

Strain compatibility equation is based on the consideration of the continuum assumption. When we analyze the strain-displacement behavior of a small 3-D element, we must ensure the continuity of material before and after deformation. Equations 3.21 (a) – (f) are first derived by Saint-Venant from the strain-displacement equation.
In summary, to obtain the stress distribution by finite element method (FEM), first, the force load is transferred to strain load, then displacement load by constitutive equation and strain-displacement equation, respectively. Then, the continuity equations and strain compatibility equations are solved by finite element method (convert differential equation to linear equation group) and calculate the displacement for each element. Finally, the strain and stress for each element are derived from displacement data by strain-displacement equation and constitutive equation in sequence.

3.5 Contact Algorithm

Since high stress concentration and deformation occur near the interface between stamp and resist, the contact algorithm becomes an important element type option in analysis. ANSYS 10.0 offers five different contact algorithms: pure penalty method, augmented Lagrange method, pure Lagrange multiplier method, Lagrange multiplier on contact normal and penalty on frictional direction and internal multipoint constraint method. In this study, we
employed the augmented Lagrange method for the calculation of contact status and stress. As described in ANSYS documentation, augmented Lagrange method is an iterative series of pure penalty method that uses a “spring” to represent the mechanical interaction between two contact surface and the spring stiffness is called contact stiffness. Compare to pure penalty method, augmented Lagrange method is expected to lead to better conditioning and is less sensitive to the magnitude of contact stiffness. The Lagrange multiplier & penalty method and pure Lagrange multiplier method enforce zero penetration when contact is closed, which does not satisfy the simulation requirement. The Internal multipoint constraint method is used in conjunction with bonded contact to model several types of contact assemblies and kinematic constraints, while the interface in the simulation is slip-allowed. And in the simulation, augmented Lagrange method has not led to any convergence problem.
Chapter 4 Demolding Simulation in Thermal NIL

4.1 Introduction

Despite the great potential in mass production of micro/nanodevices, there are several technical challenges remaining in thermal imprint lithography and the structural damages during demolding process is one of the most challenging issues. In this chapter, we focus on the micro/nanomechanics in the polymer resist domain and the stamp/resist interface at cooling and demolding steps in thermal imprint lithography. Finite element method (FEM) simulations based on a 2-D symmetric model were performed to analyze the stress evolution and distribution of PMMA patterns for cooling and demolding steps. In order to find the effects of different parameters, we simulated the identical process with various demolding rate, demolding temperature, demolding angle and stamp aspect ratio; the underlying physics is also discussed.

4.2 Mechanical Behavior of PMMA Resist during Normal Demolding

To understand the mechanical behavior in the PMMA resist layer as well as at the stamp/resist interface during demolding, we firstly simulated a normal demolding process in thermal imprint lithography. For stamps of both single symmetric structure and multiple symmetric structures, the rules of stress concentration and evolution were extracted from the simulation results.

4.2.1 Stress Analysis in Normal Demolding for Stamp of Single Symmetric Structure

In this section, we simulated the normal demolding process for the stamp of single symmetric structure shown in Figure 4.1. The demolding temperature was 70°C and the stamp was normally displaced from replicated patterns at a demolding rate of 0.05μm/s.
Figure 4.1 (a) shows the evolution of the Von Mises stress in the PMMA resist during the demolding process. The maximum stress in the PMMA layer at each demolding time is highlighted. Note that a different stress scale bar was used for 2.516 s because the stress at this demolding time is much higher than the rest. The stress is concentrated at two different locations in PMMA. The first location is at the corner of transition zone between the PMMA pattern and the residual layer and the second location of stress concentration is near the contact region between the replicated patterns and the stamp moving up as demolding proceeds. Different from previous simulation by Guo et al., in which the stress in PMMA resist concentrates only near the contact region with a Ni mold insert, our simulation results clearly show that the stress concentration also exists at the transition zone between the residual layer and replicated structure. This is attributed to the application of visoelastic model in description of PMMA in our simulation. The thermal stress generated during cooling will not relax immediately, but follow multi-relaxation mechanisms, each governed by a certain relaxation time. Thus, the residual stress at the corner between the residual layer and the replicated structure remains over the entire demolding process.

Figure 4.1 (b) plots the highest local stress at both locations as a function of demolding time. The yield stress of PMMA at 70°C is shown as a horizontal line. At the beginning of demolding, the highest local stresses at both locations increase dramatically and reach the first maximum value, decay rapidly to a constant value, and then, just before demolding completes, slightly increase again and show the second maximum stress. The stress near the contact region with the moving stamp is always slightly higher than that at the transition zone, which is again due to the time-dependent relaxation behavior of PMMA.
However, since the high stress in the PMMA structure exceeding the yield stress is narrowly confined to the contact zone with the moving Si stamp, we cannot predict based on this simulation result that a catastrophic failure, i.e. partial or total ripping of the PMMA structure, will occur. However, this result is in turn an indication that, as the width of a structure becomes smaller, (as the aspect ratio increases) it becomes more difficult to achieve demolding without a structural damage.

The second maximum stress appearing just before the end of demolding in the highest local stress versus demolding time curve is due to the strong geometrical confinement against the tendency of PMMA to deform by the relaxation. Even though the second maximum stress is much lower than the first maximum stress for normal demolding, it becomes significant for a large offset from normal demolding or for structures far away from the centerline, which will be discussed in the next sections. Nevertheless, the existence of the second maximum stress indicates that a structural failure can also occur at the end of the demolding process and this may account for the stretched structures often observed in the imprinted polymers.
The stress generated in the Si stamp during cooling and demolding is in the range of ~200MPa, also concentrating at the structural corners. However, the stress in Si is still far below the yield stress of Si (~7GPa). Considering the high Young’s Modulus value of Si (~130GPa), deformation in the Si stamp structure is expected to be very little. Thus, our discussion only focuses on the stress and deformation in the PMMA resist layer.

4.2.2 Stress Analysis in Normal Demolding for Stamp of Multiple Symmetric Structures

The stamps used in thermal imprint lithography normally contain more than a single structure, usually periodic structures. Thus, we extend the simulation to stamps with multiple structures in order to understand mechanics of demolding for different locations deviated from the symmetry center. Figure 4.2 (a) plots the Von Mises stress evolution in the PMMA resist layer as the demolding proceeds. Also included are the highest local stress values near each contact interface, from symmetric centerline to edge. Similar to the previous simulation results, the stress concentrates locally both at the corner of transition zone between the replicated patterns and residual layer, and near the contact region between the patterns and moving stamp. However, different highest local stress values are revealed depending on the relative distance to the symmetric centerline.

Figure 4.2 (b) shows the evolution of the highest local stress for all three corners. Similar to previous simulation result, the highest local stress shows two maximums, the first at the beginning and the second right before the demolding ends. Comparing the stress values at three different locations, the maximum is revealed at the microstructure furthest from the centerline while the stress values for the inner two edges are low and almost identical to each other. In agreement with the previous simulation results, this result also indicates that an
auxiliary structure added outside the active structures can act as a stress barrier protecting active inner structures.

Figure 4.2 (a) Von Mises stress evolution in PMMA resist during normal demolding for stamp of multiple symmetric structures and (b) the highest local stress versus demolding time for three different locations

Considering a certain microcavity located away from the symmetry center, our simulation result shows that high stress appears at both sides of the walls of the microcavity, although the stress at the outer wall is higher relative to that for the inner wall. This is in contrast with previous FEM simulation result [Guo et al., 2007], in which stress is concentrated only at the sidewall close to the centerline of the whole structure and a micro gap was formed between the replicated structure and the outer wall of the mold insert. This discrepancy occurs due to two different assumptions taken for the simulation. First, no-separation boundary condition was applied between the PMMA layer and the stamp surface for our simulation. Second, the stress is instantaneously relaxed upon detachment of resist from the mold insert wall using the linear elastic assumption for the resist layer in previous simulation [Guo et al., 2007]. In a practical imprinting process, a pressure is applied during cooling in order to keep the dimensional stability of the molded structure. Experimentally, no measurable discrepancy in dimensions between the stamp structure and the imprinted pattern.
has been reported for micro- and nanoscale imprinting. On the other hand, an anti-sticking coating usually applied for the stamp surface will make it easier for part of the resist adjacent to the stamp surface to be detached from the stamp surface because it is difficult to achieve a perfect surface coating which completely removes the adhesion of the resist to the stamp surface. In all, we can speculate that the real situation will be between the two cases. In addition, the result also implies that the viscoelasticity of PMMA and the adhesion and friction at the interface play important roles in stress analysis in demolding.

4.3 Parametric Study of Demolding

The success of demolding is determined by the material properties, stamp geometries, surface treatment, and process conditions. In this section, we focus on the influence of several important parameters, such as the friction coefficient on the interface of replicated PMMA and silicon stamp, demolding rate, demolding angle, demolding temperature and the aspect ratio of the stamp. We extract the dependence of different parameters and explain them by underlying physics mechanisms.

4.3.1 Influence of Demolding Angle

Demolding angle is a critical angle in thermal imprinting lithography since absolutely normal demolding is extremely difficult to achieve. Thus, the influence of demolding angle on the stress level in the PMMA resist layer during demolding was studied in order to determine the maximum allowed misalignment from the normal demolding. For that, we simulated non-normal demolding of the single structure by applying a displacement of the stamp at different tilt angles from the normal to the stamp surface. Figure 4.3 shows the highest local stress as a function of the demolding time for different demolding angles up to
4.6°. As the demolding angle increases, the local highest stress increases over the entire
demolding process. At $\theta = 4.6°$ the highest local stress in PMMA lies above the yield stress
almost the entire demolding process.

Figure 4.4 shows the highest local stress as a function of demolding angle determined
at the first and second maximum. Despite a slight increase, the first maximum stress does not
show a strong dependence on the demolding angle; however the second maximum stress
increases significantly with the demolding angle. This is understandable because, as the
demolding proceeds, the PMMA resist layer in contact with the moving stamp experiences a
cumulative compression by the stamp wall in the horizontal direction. Particularly, for the
demolding angle larger than 4°, the second maximum stress even exceeds the first maximum
and become the dominant factor in demolding failures. In this case, highly stretched PMMA
replica in the direction of the demolding angle is expected to achieve.

4.3.2 Influence of Demolding Rate

For the laboratory scale imprinting of micro- and nanostructures, demolding is usually
performed manually utilizing a sharp razor blade and the whole demolding process takes
place for relatively a short duration, in many cases within seconds. Since it difficult to control
the demolding rate accurately using the manual demolding method, the demolding rate has
not been considered as an important parameter for achieving good imprint results. However,
an accurate control over the demolding rate is now made possible using an automatic
demolding unit equipped with a precision strain sensor. Thus, we studied the influence of
demolding rate on the evolution of the Von Mises stress during normal demolding of the
single symmetric structure, which is shown in Figure 4.5.
However, as we discussed in previous section, it is extremely difficult to achieve absolutely normal demolding; thus, it is more significant to study the influence of demolding rate on the evolution of Von Mises stress during the demolding process with a certain angular offset. We simulated the demolding process with a demolding angle of 2.3°, at different demolding rates. Figure 4.6 shows the contours of the normalized Von Mises stress.
distribution, at the first maximum, which is normalized by the yield stress of PMMA at 70°C. At the demolding rate of 0.005 μm/s, PMMA is totally undergoing elastic deformation; at the demolding rate of 0.05 μm/s, yielding occurs at the corner of the transition zone between replicated PMMA pattern and residual layer; at the demolding rate of 0.5 μm/s, the plastic deformation area expands, which means the likelihood of structural failures increases.

In general, local stress in PMMA domain is a monotonously increasing function of demolding rate. Particularly, at the lowest demolding rate of 0.005 μm/s, the highest local stress in the PMMA resist layer is below the yield stress over the entire demolding process. This can also be explained by the viscoelastic property of the PMMA resist because the low demolding rate allows for a quasi-static demolding process and enough time for the residual stress in PMMA to be relaxed. However, the use of the low demolding rate will significantly reduce the yield of the thermal imprint lithography. Thus, the optimized demolding rate needs to be balanced in such a way that minimizes the process cycle time while at the same time does not lead to any structural damage during demolding.

Figure 4.5 The highest local stress as a function of demolding displacement for different demolding rates

In general, local stress in PMMA domain is an monotonously increasing function of demolding rate. Particularly, at the lowest demolding rate of 0.005 μm/s, the highest local stress in the PMMA resist layer is below the yield stress over the entire demolding process. This can also be explained by the viscoelastic property of the PMMA resist because the low demolding rate allows for a quasi-static demolding process and enough time for the residual stress in PMMA to be relaxed. However, the use of the low demolding rate will significantly reduce the yield of the thermal imprint lithography. Thus, the optimized demolding rate needs to be balanced in such a way that minimizes the process cycle time while at the same time does not lead to any structural damage during demolding.
4.3.3 Influence of Friction Coefficient

The frictional shear stress on the interface between silicon stamp and replicated PMMA patterns is one of the most important reasons that lead to structural damages in thermal imprint lithography. It is determined by the normal stress and the friction coefficient. Previous studies have shown that the friction coefficient of stamp surface can be reduced by surface coating. In this section, we focus on the effect of friction coefficient on demolding quantitively.

Figure 4.7 shows the highest local stress as a function of demolding time, with different friction coefficient of 0.1, 0.2 and 0.3. Simulation results indicate that the highest local stress, particularly the first maximum at the start of demolding, is strongly dependent on the friction coefficient. When the friction coefficient is 0.1 or 0.2, the first maximum of highest local stress is much less than the yield stress of PMMA at given temperature, which means the replicated PMMA is undergoing elastic deformation and no structural damages will occur; however, when the friction coefficient is 0.3, the first maximum of the highest local stress increases up to 77MPa, which is much higher than the yield stress (23MPa). Furthermore, the time interval with the highest local stress higher than the yield stress is
increased from 0 to 7 seconds, as a result, structural failures may occur when the friction coefficient is 0.3.

There are several methods that can be used to reduce the friction, thus facilitate the demolding process. The first and mostly used method is anti-sticking coating. Since the surface tension of the stamp can be reduced dramatically by the deposition of self-assembled monolayer, not only the friction coefficient, but also the normal force, partially the adhesion force, can be reduced. However, the lifetime of anti-sticking coating remains a challenging issue for the commercialization since the effective limitation of anti-adhesion coating is under 50 cycles. The second method is to reduce the surface roughness in order to minimize the surface area and eliminate the mechanical interlock between stamp and polymer resist. The last method is to release the holding pressure in cooling process. As we analyzed, during cooling process, the polymer resist tends to shrink, however, the volumetric shrinkage is compensated by the holding pressure, which deforms the polymer resist mechanically. By

![Figure 4.7 The highest local stress verse the demolding time for the demolding process with different friction coefficient on interface ($\mu=0.1, 0.2, 0.3$)](image)

There are several methods that can be used to reduce the friction, thus facilitate the demolding process. The first and mostly used method is anti-sticking coating. Since the surface tension of the stamp can be reduced dramatically by the deposition of self-assembled monolayer, not only the friction coefficient, but also the normal force, partially the adhesion force, can be reduced. However, the lifetime of anti-sticking coating remains a challenging issue for the commercialization since the effective limitation of anti-adhesion coating is under 50 cycles. The second method is to reduce the surface roughness in order to minimize the surface area and eliminate the mechanical interlock between stamp and polymer resist. The last method is to release the holding pressure in cooling process. As we analyzed, during cooling process, the polymer resist tends to shrink, however, the volumetric shrinkage is compensated by the holding pressure, which deforms the polymer resist mechanically. By
releasing the pressure in cooling process, a slight gap can be generated between silicon stamp and replicated PMMA due to the mismatch of thermal expansion coefficient, thus the stamp can be separated from replicated pattern without any mechanical resistance. However, the control of gap size and uniformity can be a new challenge, particularly when the feature size scales down to sub 100 nanometers.

4.3.4 Influence of Demolding Temperature

Temperature is one of the most important parameters in thermal imprint lithography not only for the polymer flow in molding process, but also for demolding since the thermal stress, the friction and adhesion forces and the mechanical strength of resist are all strongly dependent on temperature. For example, the thermal stress is linearly proportional to the temperature drop between molding and demolding, since thermal expansion coefficient is assumed to be constant. The temperature dependence of the yield stress of PMMA and friction coefficients between silicon stamp-PMMA resist interface with anti-sticking coating, were taken from literatures, which are shown in Table 4.1. Yield stress at different temperatures was calculated, based on linear interpolations of the experimental results by Quinson et al. The friction coefficients between PMMA resist and silicon stamp with anti-sticking coating were assumed to be slightly smaller than the friction force microscopy results by Hammerschmidt et al. The friction coefficient shows the trend of linear decreasing from the β relaxation (20-30°C) to glass transition temperature (110°C). The rough estimation would cause an error in absolute values of local stress, however, it is expected that the overall trend would hold.
Figure 4.8 shows the stress distribution in PMMA resist at the 1st maximum for different demolding temperature at different demolding temperatures from 40°C to 100°C. Both the overall stress and highest local stress in PMMA resist increase as demolding temperature decreases, the highest local stress in PMMA at demolding temperature of 40°C is as high as 175MPa, while the highest local stress at demolding temperature of 100°C is 53MPa. The simulation results achieve agreement with our theoretical analysis.

However, the deformation behavior of the replicated patterns is determined by, not only the absolute stress, but also the yield stress of PMMA at the demolding temperature. The experiment result indicates that the yield stress of PMMA decreases linearly from room temperature to right below glass transition temperature. Figure 4.9 plots the highest local stress as a function of demolding time for 40°C, 70°C and 100°C, with the yield stress at each temperature highlighted.

Since the yield stress shows the same trend with the absolute local stress, we normalize the local stress by the yield stress at the each demolding temperature. When the normalized stress is above 1, material yielding occurs and structural damages may happen. Figure 4.10 shows the normalized stress distribution at the first maximum for different temperatures. At 70°C, normalized stress distribution shows the least plastic deformation area;

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>40</th>
<th>55</th>
<th>70</th>
<th>85</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield Stress (MPa)</td>
<td>35.39</td>
<td>28.26</td>
<td>22.88</td>
<td>18.16</td>
<td>14.51</td>
</tr>
<tr>
<td>Friction Coefficient</td>
<td>0.5</td>
<td>0.4</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 4.1 Temperature dependence of yield stress of PMMA and friction coefficient between PMMA and silicon
while both at high demolding temperature (100°C) and low demolding temperature (40°C), larger plastic deformation area is plotted. Figure 4.11 shows the highest normalized stress at first maximum as a function of demolding temperature, which also shows the minimum at 70°C.

\[
\begin{align*}
\sigma_{\text{max}} &= 175\text{MPa} \\
T &= 40^\circ C \\
t &= 5.168s
\end{align*}
\]

\[
\begin{align*}
\sigma_{\text{max}} &= 115\text{MPa} \\
T &= 55^\circ C \\
t &= 2.866s
\end{align*}
\]

\[
\begin{align*}
\sigma_{\text{max}} &= 77\text{MPa} \\
T &= 70^\circ C \\
t &= 2.516s
\end{align*}
\]

\[
\begin{align*}
\sigma_{\text{max}} &= 58\text{MPa} \\
T &= 85^\circ C \\
t &= 2.016s
\end{align*}
\]

\[
\begin{align*}
\sigma_{\text{max}} &= 53\text{MPa} \\
T &= 100^\circ C \\
t &= 1.866s
\end{align*}
\]

Figure 4.8 Von Mises stress distribution at the first maximum for different demolding temperature (maximum stress in PMMA resist marked)

However, we need to point out that the optimal demolding temperature is closely related to other process conditions. For example, thermal stress does not only depend on temperature drop, but also depends on the mismatch of thermal expansion coefficient of the resist, which can be influenced by material selection; friction coefficient between stamp and resist does not only depend on temperature, but also strongly relates with surface roughness and surface treatment like anti-adhesion coating; the mechanical strength does not only depend on temperature, but also depends on the material selected as well as strain rate. In conclusion, the analysis of optimal demolding temperature must include a comprehensive
consideration of selected material, process parameters and stamp geometries.

![Graph showing the highest local stress as a function of demolding time](image)

**Figure 4.9** The highest local stress as a function of demolding time (yield stress highlighted)

![Images showing normalized Von Mise stress distribution in PMMA domain](image)

**Figure 4.10** Normalized Von Mise stress distribution in PMMA domain at the first maximum for different demolding temperature

### 4.3.5 Influence of Stamp Aspect Ratio

Fabrication of high aspect ratio structures is a big technical challenge in thermal imprint lithography because structural damages occur more frequently for high aspect ratio
structure. We simulated the demolding process for the depth ratios of the single stamp structure from 0.1 to 0.5. The depth ratio is defined as the depth of the stamp structure over the total thickness of the Si stamp. The width of the feature structure on stamp and the thickness of the residual PMMA layer are kept constant. Thus, the depth ratio also represents the aspect ratio of the stamp structure. Figure 4.12 shows the highest local stress derived from the first maximum in the highest local stress versus demolding time curve for different depth ratios.

![Figure 4.11 Maximum normalized Von Mises stress vs. Demolding temperature](image_url)

As expected, a significant increase in the highest local stress is observed as the depth ratio increases, which indicates that for imprinting of high aspect ratio structures demolding becomes a significant challenge in addition to the difficulty in the cavity filling during molding. Furthermore, in the simulation, we assume the anti-adhesion coating to be perfect; however, zero adhesion is impossible even with anti adhesion coating. Thus, considering the
effect of adhesion force, high surface to volume ratio may bring additional difficulty in fabrication of high aspect ratio structures.

4.4 Conclusions

The demolding process in thermal imprint lithography was studied in detail by the FEM simulation based on the viscoelastic model of PMMA. We found two locations of stress concentration in the PMMA layer during demolding: the corner of transition zone between the replicated patterns to residual layer and the contact region between silicon stamp and replicated patterns. As demolding proceeds, the highest local stress shows two maximums, indicating that demolding failure can occur both at the beginning and the end of demolding. A systematic parametric study has been performed on the demolding rate, demolding angle, demolding temperature and the aspect ratio of the stamp structures. An accurate alignment in the stamp displacement direction is critical to the success of demolding and there exists a maximum allowed demolding angle leading to demolding without structural failure. Local

Figure 4.12 The highest local stress as a function of the depth ratio at the first maximum in the highest local stress versus demolding time curve for different depth ratios.

4.4 Conclusions
stress increases as demolding rate increases, particularly in non-normal demolding process. Both simulation and experiment results show that the optimal demolding temperature in given condition is around 70°C, with both excellent overall pattern quality and satisfactory local surface profile. Increase in the aspect ratio in the stamp structures leads to the increased local stress during demolding, indicating the difficulty in fabrication of high aspect ratio structures. In this paper, we only simulated simple structures such as a single symmetric structure. However, the results indicate that, the ability of the FEM simulation for complicated and actual structures will enable prediction of the demolding process as well as determination of a range of process parameters which will allow for successful demolding even at the stage of a process design in an economical and reliable way. This becomes more important with the increasing requirement of high aspect ratio and complex structures.
Chapter 5 Experimental Study of Demolding Process in Thermal NIL

5.1 Introduction

In chapter 4, we simulated the demolding process in thermal imprint lithography via finite element method and investigated the effects of several parameters, including demolding rate, demolding temperature, demolding angle, and stamp geometry. From the simulation results, rules of stress distribution and evolution were extracted and different parameters were evaluated. To verify the reliability of simulation results, in this chapter, we studied demolding in thermal imprint lithography via experimental approach. Since the only measurable parameter to quantitatively characterize the mechanical resistance during demolding is demolding force, which is defined as the force required releasing the stamp from the substrate. We measured the demolding force using a temperature and rate controllable demolding unit, which was modified from a standard mechanical tester. Particularly, we studied the effect of demolding temperature. Even though the Si stamp/PMMA resist/Si substrate assembly used in the experiments is not exactly identical to the 2D finite element model used for the simulation in terms of the shape and size of the patterns, the experimental results show satisfactory agreement with simulation result in general trends of stress evolution and temperature dependence study.

5.2 Experiment Procedure

In this section, we introduce the entire procedure of the experimental study of demolding force in sequence, including stamp fabrication, surface treatment, substrate preparation, thermal imprinting, and demolding. Several critical techniques, such as photolithography, silane coating and reactive ion etching are discussed in detail.
5.2.1 Stamp Fabrication

Stamp fabrication is the first step, and also one of the most important steps in thermal imprint lithography. The quality of replicated patterns is directly determined by the quality of stamp in terms of sidewall profile, aspect ratio, surface roughness and feature complexity. In this section, we describe stamp fabrication procedure in sequence: photomask design, pattern transfer by photolithography and reactive ion etching.

5.2.1.1 Photomask Design

A photomask is an opaque plate with holes or transparencies that allow light to shine through in a defined pattern, which is widely used for selective patterning on silicon substrate coated with photoresist in photolithography. Photomasks are typically transparent fused silica blanks covered with a pattern defined with a chrome metal absorbing film. The patterns of photomask used in the experiment consist of line gratings and dot array, which are shown in figure 5.1 and the detail information on the line width, dot size and period is given in table 5.1. The photomask design was then sent to a commercial company for the fabrication.

5.2.1.2 Photolithography

Photolithography, also known as optical lithography, is a widely used technique in microfabrication to selectively remove parts of a thin resist film (or the bulk of a substrate). It uses light to transfer a geometric pattern from a photomask to a light-sensitive chemical (photoresist) on the substrate. A series of chemical treatments then engraves the exposure pattern into the material underneath the photoresist.

Figure 5.2 presents schematics of the photolithography process. Test grade 4 inch silicon wafer from Silicon Quest (Santa Clara, CA) weas firstly spin-coated with an adhesion
promoter, hexa-di-methyl-silazane (HDMS) at 3000 rpm for 60 s in order to promote the adhesion between the photo-resist layer and the silicon substrate. After drying in air for 5 min at room temperature, the HDMS coated wafer was further spin-coated with S1813 positive photoresist from Shipley Company (Marlborough, MA) at 2000 rpm for 60 s and baked at 95°C for 90 s; hence, a 2 μm thick resist S1813 layer forms on the wafer as verified by profilometer measurements. Then, a UV exposure was performed on the coated silicon

Table 5.1 Detail Information on pattern layout of photomask

<table>
<thead>
<tr>
<th>Area Number</th>
<th>Pattern Type</th>
<th>Line width/Diameter (μm)</th>
<th>Period (μm)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Dots</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>Dots</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>Dots</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>Dots</td>
<td>9</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>Line Gratings</td>
<td>3</td>
<td>6, 8, 10, 12</td>
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<tr>
<td>6</td>
<td>Line Gratings</td>
<td>5</td>
<td>8, 10, 12, 14</td>
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<tr>
<td>7</td>
<td>Line Gratings</td>
<td>7</td>
<td>10, 12, 14, 16</td>
</tr>
<tr>
<td>8</td>
<td>Line Gratings</td>
<td>9</td>
<td>12, 14, 16, 18</td>
</tr>
</tbody>
</table>

Figure 5.1 AutoCAD pattern for the mask with line gratings and dot array
substrate using a Quintel UL 7000-OBS aligner and DUV exposure station from Quintel Corporation (Morgan Hill, CA), with the custom ordered photomask for a dosage of 70 mJ. The exposed wafer was developed in MF 319 developer solution for 120 s. Two developer trays were used to ensure better resist removal by reducing concentration changes of the developer solution due to resist removal from the photomask; the first tray was used to develop for about 40 s and the next tray was used for the remaining 80 s. The wafers were washed in a DI water bath for 2 min and blow-dried with N₂. Any residual resist layer in the recessed area of the resist patterns was removed by etching with O₂ plasma for about 10 s.

5.2.1.3 Reactive Ion Etching

Reactive ion etching (RIE) is an anisotropic etching technique widely used in microfabrication. Chemically reactive plasma is used to remove materials deposited on wafers or bulk silicon self. The plasma is generated under low vacuum by an electromagnetic

Figure 5.2 Schematic of photolithography
field and high-energy ions from the plasma attack the wafer surface.

A typical reactive ion etching (RIE) system consists of a cylindrical vacuum chamber, with a wafer platter situated in the bottom portion of the chamber. The grounded wafer platter is electrically isolated from the rest of the chamber. Gas enters through tiny inlets in the top of the chamber, and exits to the vacuum pump system through the bottom. The types and amount of gas used vary depending on the etching process; for instance, sulfur hexafluoride is commonly used for etching silicon; oxygen is usually used to remove residual polymer. Gas pressure is typically maintained in a range between a few millitorr and a few hundred millitorr by adjusting gas flow rates and/or adjusting an exhaust orifice.

Plasma is initiated in the system by applying a strong RF (radio frequency) electromagnetic field to the wafer platter. The field is typically set to a frequency of 13.56 megahertz, applied at a few hundred watts. The oscillating electric field ionizes the gas molecules by stripping them of electrons, creating the plasma. In each cycle of the field, the electrons are electrically accelerated up and down in the chamber, sometimes striking both the upper wall of the chamber and the wafer platter. At the same time, the much more massive ions move relatively little in response to the RF electric field. When electrons are absorbed into the chamber walls they are simply fed out to ground and do not alter the electronic state of the system. However, electrons absorbed into the wafer platter cause the platter to build up charge due to its DC isolation. This charge build up develops a large negative voltage on the platter, typically around a few hundred volts. The plasma itself develops a slightly positive charge due to the higher concentration of positive ions compared to free electrons. Because of the large voltage difference, positive ions tend to drift toward the
wafer platter, where they collide with the samples to be etched. The ions react chemically with the materials on the surface of the samples, but can also knock off (sputter) some material by transferring some of their kinetic energy. Due to the mostly vertical delivery of reactive ions, reactive ion etching can produce very anisotropic etch profiles, which contrast with the typically isotropic profiles of wet chemical etching.

For etching low aspect ratio structures in Si and for etching of PMMA for window opening, a TECHNICS series 800 RIE machine located at the CBM² facility on South Campus of LSU was used. Two different gases, CF₄ and SF₆ are available for silicon etching. SF₆ etching is of high etching rate and usually creates an undercut for the etching profile, which will lead to interlocking of resist material and thus demolding failures. The etching rate of CF₄ etching is much slower and produces sidewalls of highly tapered shape. Thus, we combined these two gases together and tried to find an optimal condition for silicon etching, which may give a preferred sidewall profile for NIL which is slightly tapered sidewalls.

Considering the much faster etching rate of SF₆, we etched the silicon substrate by the combination of the two gases with three different recipes: (CF₄ 90s + SF₆ 25s)×3, (CF₄ 150s + SF₆ 25s)×3 and (CF₄ 240s + SF₆ 25s)×3. The working power is 100 watts and the working pressure is 250 millitorr. Figure 5.3 shows SEM images for the silicon etching profile for different recipes. The recipe of (CF₄ 240s + SF₆ 25s)×3 gives the best result with slightly tapered sidewall that is preferred etching profile to be used as stamps for imprinting. The depth of the structures for the stamp used for the demolding force experiments was 500 ~ 1000 nm.
5.2.2 Surface Treatment – Anti Adhesion Coating

Despite significant advances in surface micromachining technology, strong adhesion remains a key challenge, which limits the life time and reliability of MEMS devices. Local defects, even structural collapse may occur during demolding as a result of strong adhesion, particularly for the high aspect ratio structures with high surface to volume ratio. Strong adhesion is generally caused by capillary, electrostatic and van der Waals forces, and in some cases by “chemical” forces such as hydrogen bonding and solid bridging.

Self-assembled monolayer (SAM) coating has been demonstrated as an efficient way in eliminating release stiction through minimization of the surface tension of stamp. In this experiment, the SAM molecule used here is a fluorinated silane molecule 1H,1H,2H,2H-Perfluorodecyltrichlorosilane (C_{10}H_{4}Cl_{3}F_{17}Si). This molecule consists of a head group with three chlorosilanes and a fluorinated, long carbon chain (C10).

Upon deposition, the chlorinated silane groups in the molecule formed bonds with the hydroxylated silicon surface with the presence of H₂O on the surface, leaving volatile HCl gas (Fig 5.4). In addition, cross-linking between silane groups in the neighboring molecules also occurs, leading to a coating layer with high density. Those reactions between the head group and the hydroxylated Si surface leave the fluorinated tail group at the surface side, which renders the surface hydrophobic. As a result, the presence of a silane layer on Si lowers the adhesion force between the polymer and the stamp with respect to an untreated stamp. This helps ease demolding and produce better surface finish for the imprinted polymer. As mentioned earlier, hydroxylation of the Si surface is a prerequisite for such reactions to occur, which was achieved by treating Si surfaces with O₂ plasma shortly before the silane coating
Prior to silane coating, silicon stamps were cleaned sequentially with acetone, isopropanol, and distilled water and then exposed to O$_2$ plasma at 150 watts and 250 millitorr for about 10 s in order to produce the hydroxylated Si surface. The stamp is blow-cleaned by

Figure 5.3 Silicon etching profile for different recipes (a) (CF$_4$ 90s + SF$_6$ 25s)$\times$3; (b) (CF$_4$ 150s + SF$_6$ 25s)$\times$3; (c) (CF$_4$ 240s + SF$_6$ 25s)$\times$3
compressed N₂, then loaded into the CVD chamber. The chamber is evacuated to the base pressure of 6×10⁻² torr. After shutting down the valve to the pump, the valve to the ampule filled with the fluorinated silane is opened and the sample is exposed to the evaporated silane molecules, which diffuses from the ampule to the chamber, for 10 min. After silane deposition, the valve to the ampule is closed and the chamber is again evacuated to the base pressure before venting the chamber with Argon gas. After removing the sample, the chamber is subsequently cleaned with acetone and pumped again to the base pressure so that the system is kept under vacuum until the next use.

The quality of anti-adhesion coating was evaluated by contact angle measurements because the surface energy of a surface is related to the contact angle by Young’s Equation. Figure 5.5 shows the variation of water contact angles of a silicon wafer surface before and after silane coating. It can be seen that the water contact angle significantly increases from

![A schematic of silane coating on silicon surface](image)
39° to 107°, indicating an increased hydrophobicity of the silicon surface.

Since only a monolayer of silane molecules needs to be formed on the silicon surface,

excessive coating time will not enhance the coating quality and even make it worse. Figure 5.6 shows the contact angle as a function of coating time. Usually, 5 - 10min is a proper deposition time for silane coating.

5.2.3 Thermal Imprint Lithography

The procedure of thermal imprint lithography consists of three steps in sequence: molding (including preheating), cooling and demolding, which altogether determine the replication fidelity and the mechanical stability of the patterns. During the molding step, a silicon stamp with desired structures is pressed into a substrate coated with a thin polymer resist. After conformal molding, the stamp/substrate assembly is cooled down to below the glass transition temperature (T_g) of the resist while pressure is held constant. Finally, the pressure is released and the stamp is separated from the substrate during demolding. The schematic of thermal imprint lithography has already been shown in figure 2.1
5.2.3.1 Spin Coating

Prior to spin coating, a silicon wafer was preheated at 95°C for 5 min to dehydrate the Si surface. An excess amount of a PMMA solution was placed on the substrate by syringe through a filter in order to remove any dust particles and air bubbles. Then, the substrate was rotated at a certain angular velocity to homogeneously coat the PMMA over the silicon surface. The angular velocity of rotation is determined by several factors, including the required film thickness, the concentration of PMMA solution and the molecule weight of solute PMMA. For example, to deposit PMMA film of 10 μm, we spin coated 25% weight percentage, 25,000 molecule weight PMMA solution on silicon wafer at 1000 rpm for 60s. After spin coating, the sample was soft baked for another 5 min at 95°C.

5.2.3.2 Thermal Imprinting

Commercial Obducat nanoimprint system was employed in imprinting experiments, which is shown in figure 5.7. Imprinting pressure, temperature and time were set to be 40 bar, 175°C and 30min, respectively. A piece of a rubber sheet was placed on top of the silicon stamp to ensure homogenous distribution of pressure. As shown in figure 5.8, imprinted

![Figure 5.6 Water contact angle on silicon wafer as a function of coating time](image.png)
PMMA patterns exhibited satisfactory overall pattern quality and local contrast. All the operations were performed in a 1000× modulus cleanroom (Figure 5.9).

5.2.4 Demolding Experiment

Demolding is a process to overcome all level chemical and mechanical interactions between silicon stamp and PMMA resist, formed by the history of molding and cooling. For the laboratory scale imprinting of micro- and nanostructures, demolding is performed
manually using a sharp razor blade. There are several inherent disadvantages for this manually demolding method. First, it is difficult to control the demolding rate and structural damages may occur as a result of the impact load. Second, the stamp is not normally separated from the substrate and non-zero demolding angle would increase concentrated local stress. Third, since the demolding is performed manually, high temperature demolding (~100°C) is a challenge and accurate temperature control is also difficult to be realized. In order to overcome all the difficulties mentioned above, an automatic demolding unit is built based on a standard mechanical tester from MTS Company.

### 5.2.4.1 Standard Mechanical Tester

Figure 5.10 shows the main frame of standard mechanical tester MTS Insight 5, which is used to acquire the force-displacement relationship during demolding. Demolding rate was controlled by accompanied software Testwork 4. The minimum test speed is 0.001 mm/min and the speed accuracy is ±0.05% of the full speed. The position resolution is 0.001mm. Demolding force is detected by the load cell of 5 kN capacity and the accuracy of
force measurement is ±0.03%.

5.2.4.2 Fabrication of Vacuum Chuck

The fixture to hold the imprinted silicon stamp/PMMA resist/silicon substrate assembly during demolding is another important component in the system. There are several requirements that need to be considered in the design and building of the fixture. First, the low toughness silicon stamp/substrate should not be broken in test. Since silicon is only ~500 μm thick, it is difficult to fix the thin wafer with metallic clamps. In addition, Si is a very brittle material and thus, metallic clamps could be the point of stress concentration. Second, the position of Si stamp and substrate must be fixed to ensure the normal demolding. Since the thickness of silicon wafer is very thin (~500μm), it is extremely difficult to fix the silicon stamp and substrate firmly from sides. Third, to ensure accurate force measurement, no soft
material which may serve as a damping layer should be added in. Fourth, the force should be applied uniformly on the whole area of stamp. Fifth, it should be easy to separate the sample from adapter, without any contamination, both for sample and fixtures. As a result, glue cannot be used to sample to the main frame of material tester.

In order to satisfy all the requirements mentioned above, a brass vacuum chuck was built to hold the Si stamp/PMMA resist/Si substrate assembly. Figure 5.11(a) shows the side view of vacuum chuck and figure 5.11(b) is the top view of AutoCAD design of the vacuum chuck.

Figure 5.11 (a) Side view of the brass vacuum chuck and (b) Top view of AutoCAD design of vacuum chuck

The theoretical maximum holding force can be calculated based on the groove area:

\[
F_{\text{max}} = (P_0 - P_V) \times S = (1e5 - P_V) \times \pi \times \sum_{n=1}^{5} (r_{2n}^2 - r_{2n-1}^2)
\]

\[
= (1e5 - P_V) \times \pi d \times \sum_{n=1}^{10} r_n \approx 282.6 - 0.002826 \times P_V (N)
\]  
(Equation 5.1)

where \(P_0\) refers to one atmosphere; \(P_V\) refers to the vacuum pressure inside the chuck; \(r_n\) refers to the radius of the \(n^{th}\) groove.
If we assume that the vacuum chuck can be evacuated to the absolute vacuum \((P_V=0)\),
\(F_{\text{max}}\) can reach up to 282.6N. In real case, the base pressure of the vacuum chuck achieved
using a mechanical rotary pump was \(~ 10^{-1}\) mTorr, which corresponds to the holding force of
280 N. Thus, this value is the maximum demolding force which can be measured using the
vacuum chucks as fixtures to hold the stamp and substrate.

5.2.4.3 Temperature Control System

Temperature control is an important function in the demolding unit. The temperature
control system consists of thermal controller, thermocouple, heater and solid state relay.

Figure 5.12 shows devices and cable connections inside the temperature control box.

![Cable connection inside the temperature control box](image)

Figure 5.12 Cable connection inside the temperature control box

Thermal controller is the core device in the temperature control system. In principle,
the thermal controller utilizes a closed control loop. It constantly measures the current from a
thermocouple and controls the switch for the power to the heater depending on the difference
between the set point and the actual temperature. In order to minimize the
undershoot/overshoot, a proportional-integral-derivative (PID) controller is used in the
experiment. A PID controller attempts to correct the error between a measured process variable and a desired setpoint by calculating and then outputting a corrective action that can adjust the process accordingly, based upon three parameters, the proportional, the integral and derivative values. The proportional value determines the reaction to the current error, the integral determines the reaction based on recent errors and the derivative determines the reaction based on the rate by which the error has been changing. By "tuning" the three constants in the PID controller algorithm the PID can provide individualized control of the process requirements including error responsiveness, overshoot of setpoint and system oscillation. Figure 5.13 shows a block diagram of a PID controller.

![PID Controller Diagram](image)

**Figure 5.13 A block diagram of a PID controller**

Thermocouple is a widely used type of temperature sensor and can measure a wide range of temperatures, offering excellent compromise of cost, accuracy and reliability. In our experiment, K type thermocouple is used to be compatible with the thermal controller. K type thermocouple is made of Chromel (Nickel-Chromium Alloy) / Alumel (Nickel-Aluminum Alloy) and available from -200°C to 1200°C with accuracy of ±2.2°C.

Solid state relay (SSR) is an electronic switch. Unlike an electromechanical relay,
SSR contains no moving parts. The types of SSR include photo-coupled SSR, transformer-coupled SSR, and hybrid SSR. A photo-coupled solid state relay is controlled by a low voltage signal which is isolated optically from the load. The control signal in a photo-coupled SSR typically energizes an LED which activates a photo-sensitive diode. The diode turns on a back-to-back thyristor, silicon controlled rectifier, or MOSFET transistor to switch the load.

Heater is the output element in the system. A group of electric-thermal resistances are embedded in a brass block with excellent thermal conductivity. The heater is activated by DC power voltage and cooled off by air convection. The system can be heated up at 5°C/min.

The working mechanism of the temperature control system is simple. The thermocouple is placed into a hole built in a vacuum chuck to detect the surface temperature. The temperature reading is then sent to the temperature controller as an input signal. If the detected temperature is lower than the set point, output signal will active the heater to heat up. As soon as the detected temperature reaches the set point, the solid state relay becomes active and the temperature is maintained at the setpoint.

5.3 Results and Discussion

In this section, we present results from demolding force measurements performed with the modified mechanical tester and scanning electron microscope (SEM) images of the imprinted PMMA patterns. After reproducibility testing, systematic measurements were done to investigate influence of demolding temperatures. Finally, we discuss the experimental results and compare with pervious simulation results.

5.3.1 General Force-Displacement Response during Demolding

Demolding failures are determined by the value of local stress in resist with respect to
the yield stress of the resist. Plastic deformation occurs after yielding and in ultimate cases, the structure will collapse. However, it is difficult to measure the local stress on a micro/nano scale domain. Thus, in order to quantify the mechanical resistance in demolding, we measured demolding force, which is the force required to release the stamp from replicated resist normally. Demolding force is mathematically defined as the difference between the maximum tensile force during demolding and the reference force after the stamp is completely released from resist (zero force). The demolding force represents the cumulative effect of the thermal stress, adhesion and friction force. Higher demolding force indicates higher mechanical resistance in demolding and correspondingly, higher probability of structural damages.

Figure 5.14(a) shows a typical force vs. time curve during normal demolding process at 70°C. We magnified the curve after the transition zone from compressive to tensile force (Figure 5.14(b))

Figure 5.14 (a) force vs. time curve during demolding and (b) the determination of demolding force

After placing the stamp/resist/substrate assembly on the lower vacuum chuck, top vacuum chuck was moved down slightly toward the stamp and the force was set to zero when it is approaching. Then, a compressive force of 3500 N was first applied in order to ensure
that the top vacuum chuck is in hard contact with the backside of silicon stamp so that no leakage occurs at the interface. Note that the negative sign of force corresponds to a compressive force. After that, the top vacuum chuck was moved up at a velocity of 0.03 μm/s. As demolding proceeds, the compressive force was released and the slope of the curve in compressive region was the global stiffness of the assembled parts along the displacement direction. The nonlinearity of the measured force-time curve was due to some flexible parts (most probably the composite plates for thermal insulation) and slight misalignment between the two vacuum chucks. When the compressive force reached approximately -150 N, the force-time curve entered a flat regime in which the contact force is constant while demolding proceeds. We believed that it was the transition zone from compressive to tensile state. Interestingly, the compressive to tensile transition did not occur at zero force, but -150 N. The difference was considered to be an additional force required to overcome the bending of substrate. After compressive to tensile transition, the tensile force kept increasing and the stamp/resist/substrate assembly was pulled from both sides. Then, the force value reached a maximum and finally dropped back to zero force after the stamp was completely released from the resist. The demolding force is defined as the difference between the peak value of tensile force and the force after the stamp is totally demolded, as shown in the plot.

For each demolding condition, at least four effective measurements were performed. For the case that significant defects are observed in the molded structure after demolding, the measured data were discarded because the measured force then cannot account for the actual demolding force. Figure 5.15 shows force-time curves for a sequence of identical measurements for demolding at room temperature. The average demolding force is 77.1 N
and the standard deviation amounts to 15 N.

5.3.2 Influence of Demolding Temperature

Temperature is one of the most important parameters for demolding in thermal imprint lithography not only because the flow of polymer resist in molding process depends on temperature, but also because the thermal stress, friction, adhesion and mechanical strength of resist are temperature-dependent. In principle, the thermal stress generated during cooling for elastic materials is linearly proportional to the temperature difference between the molding and demolding, assuming thermal expansion coefficient to be constant; the adhesion is stronger and friction coefficient is also higher at lower temperature, because the chemical interactions are more stable [Hammerschmidt et al., 1999]; the mechanical strength of PMMA is monotonously decrease function of temperature. As a result, an optimal demolding temperature may be determined by consideration of all aspects of material properties and process conditions.

In this experiment, we measured the contact force during demolding with identical
stamp and substrate at three different temperatures (25°C, 70°C and 100°C) and repeated at least four times at each temperature.

Figure 5.16 (a) shows the force-time curve at three different temperatures. The general trends of the force-time curve are similar at different temperatures, which consists of four regions: compressive force (F < 150 N); compressive to tensile transition (F = 150N); tensile force (F > 150N) and zero force status after releasing. However, the demolding force values show great variation. Figure 5.16(b) plots the demolding force obtained from the force-time curves at three different demolding temperatures, which clearly indicates that there the best demolding temperature among three tested temperatures, is 70°C.

5.3.3 Inspection of Imprinted PMMA Patterns

To understand the temperature effect, we also observed the replicated PMMA patterns demolded at different temperatures by scanning electronic microscope (SEM). Figure 5.17 shows the replicated PMMA patterns of 5 μm line width, 10 μm period and 10 μm depth. It should be noted that the stamp used for the demolding force measurements was 4 inch wafer and has low aspect ratio patterns with ~ 50 nm thickness because the maximum demolding

![Figure 5.16](image_url)
force that can be measured using the designed vacuum chucks was 282.6 N. For SEM inspection, high aspect ratio patterns were used for a better observation of demolding failure that might occur at different demolding conditions.

At a demolding temperature of 25°C, large portion of imprinted PMMA patterns were ripped off due to high thermal stress and adhesion, even though the survived structures show excellent surface roughness and sharp sidewall; at 100°C, most of the transferred patterns survived after demolding, however, large local plastic deformation occurred at top surface, the sidewalls as well as the bottom trenches of imprinted patterns due to low mechanical strength of PMMA at elevated temperature. When the demolding was performed at 70°C, the local plastic deformation in the imprinted PMMA patterns is significantly reduced and the global pattern quality is satisfactory, furthermore, the inspection corroborates the demolding force measurement results in which the optimal demolding temperature was found to be 70°C.

5.3.4 Comparison with Demolding Simulation

Both the inspection of the imprinted PMMA patterns and the measurement of demolding force showed that 70°C is the optimal demolding temperature with the stamp design, resist and process conditions used in the experiment. Demolding at high temperature will not result in large area damages in patterns such as ripping, however, local distortion and warpage occur, thus reduce the accuracy of pattern transformation; on the other hand, low demolding temperature shows excellent profile of replicated PMMA patterns, but, large portion of patterns are ripped off due to extremely high residual stress. The demolding force measurement also shows lower demolding force at 70°C, which implies that the demolding is
easiest at 70°C, within three tested temperatures.

![Figure 5.17 Imprinted PMMA patterns (line gratings) at different demolding temperature of (a) 25°C, (b) 70°C and (c) 100°C](image)

There were several differences between simulation and experiment as follows. First, the size and geometry of the stamp used in the experiment were not exactly identical to the 2 dimensional finite element model used in simulation. In the simulation, we analyzed only one segment of the stamp based on axis-symmetric assumption, while in the experiment, a 4-inch diameter stamp with line gratings and dots array at different locations was used. Second, the process conditions in experiment were not exactly same as in simulation, for example, the demolding rate in experiment is even lower than in simulation in order to acquire enough data point and a high preload (3500 N) is applied before demolding starts in experiment to ensure high vacuum. Third, the methods to evaluate the structural damages are also different. In simulation, we focused on the value and the area of local high stress; while in the experiment, we evaluated the demolding temperatures by inspecting the imprinted patterns and a macroscopic quantity – demolding force.

Despite all the aspects mentioned above, the simulation results show satisfactory
agreement with the experiment inspection and measurements with regard to demolding
temperature. Both confirmed that an optimal demolding temperature lies between the high
and low temperature, which implies a balance between the absolute value of residual stress
and mechanical strength of the material.
Chapter 6 FEM Simulation for UV Imprinting

6.1 Introduction

UV nanoimprint lithography (UV-NIL), also known as step and flash imprint lithography, is an important variant of nanoimprint lithography developed by Wilson’s group in 1997. Figure 6.1 shows schematic of the UV-NIL process. First, an organic transfer layer is spin coated on a silicon substrate; then, a transparent stamp with desired micro/nanostructures is closely aligned over the coated substrate; once in proximity, a low viscous solution of photopolymerizable resin is dispensed into the gap between the substrate and the stamp; the microcavities on the stamp is filled by the resin as a result of capillary action; once the stamp cavities are fully filled by the resin, the whole assembly is exposed to UV light and the resin is solidified by the cross-linking of resin; finally, the stamp is separated from the substrate and usually, the process is followed by transfer layer etching by O₂ plasma and barrier striping.

Compare with thermal NIL, UV-NIL has several critical advantages: First, in thermal NIL, the polymer resist is heated above its glass transition temperature in molding, as a result, high thermal stress is formed in the polymer resist as cooling down to demolding temperature. Furthermore, the heating and cooling processes cost longer time other than molding self; however, in UV-NIL, the photopolymerizable resin is solidified by UV irradiation, the intrinsic stress due to the crosslinking of photopolymerizable resin is much lower than the thermal stress in thermal NIL and also, cycle time is greatly shorten since no heating and cooling processes are needed. Second, in thermal NIL, the polymer flow is driven by high external pressure, thus, for stamps with large depressed area and high aspect ratio structures, incomplete filling
of the cavities may occur; by the way, the stamp may be bended or even damaged during imprinting; however, in UV-NIL, the flow behavior of photopolymerizable resin is driven by the capillary force, thus, it is more suitable for large area and high aspect ratio imprinting because the filling process in UV-NIL is much easier than thermal NIL; moreover, since no high pressure is applied, the lifetime of stamp is prolonged and flow stress is lower. Third, due to high pressure and adhesion force between the stamp and polymer resist, high demolding force is required to release the stamp from imprinted patterns in thermal NIL; however, in UV-NIL, no high demolding force is required.

In this chapter, we simulated the solidification process in UV-NIL using commercial FEM software, ANSYS 10.0. The distribution of Von Mises stress was studied and compared with thermal NIL. It was found that for the identical model the solidification process in UN-
NIL induces much lower stress than the residual thermal stress in thermal NIL.

6.2 Volumetric and Mechanical Properties

The solidification of the photopolymerizable resin with UV exposure occurs via cross-linking between the photopolymer precursors and is accompanied by volumetric shrinkage. During the cross-linking reaction, interaction potential between photopolymer precursors changes from Van der Waals force to covalent bonding. The average distance between the molecules decreases and leads to volumetric contraction. Volumetric shrinkage usually depends on the composition of the precursor resin, time and intensity of UV irradiation. We simulated the solidification process with different volumetric shrinkage from (0.3% to 3%) which occurs during UV NIL and found that the local high stress is linearly proportional to volumetric shrinkage.

Mechanical properties including Young’s modulus and Poisson’s ratio also depend on exposure conditions and material composition. Even though many UV-curable resins are commercially available, there is no representative resin like PMMA or PC used in thermal NIL. Thus, we took in our simulation the UV-curable resin used in the work of Mary B. Chan-Park et al. and used the materials properties thereof. The Young’s modulus is 4 MPa and the Poisson’s ratio is 0.3 [Park et al., 2005].

6.3 Finite Element Method Model and Preliminary Theoretical Analysis

Since ANSYS software is not able to simulate the UV irradiation and solidification process directly, isotropic equivalent thermal strain is applied on the resin based on the volumetric shrinkage. 4-nodal linear structural element PLANE42 is applied for all the components including stamp, photoresist and substrate, and a contact pair TARGET169-
CONTACT172 is created at the interface between stamp and UV-curable resin.

2D FEM model (Figure 6.2) was created based on the plane stress assumption. The bottom surface of substrate is confined and symmetric boundary condition is applied on the centerline. A glued interface is defined between Si substrate and the UV-curable resin, and a slip allowed interface is defined between stamp and the resin. The top surface of stamp was confined.

To calculate the equivalent thermal strain, we assume that the volumetric shrinkage is homogeneous and isotropic in the layer of the UV-resin, as shown in figure 6.3. The linear contraction can be related to the volumetric shrinkage by the following equation:

\[
\frac{\Delta X}{X} = \frac{\Delta Y}{Y} = \frac{\Delta V}{3V} \tag{Equation 6.1}
\]

Thus, the thermal stress on X and Y direction can be simply expressed as:

\[
\sigma_x = \frac{E \Delta X}{X} = \frac{E \Delta V}{3V} \; ; \; \sigma_y = \frac{E \Delta Y}{Y} = \frac{E \Delta V}{3V} \tag{Equation 6.2}
\]

Due to the plane stress assumption, we have:

\[
\sigma_z = 0 \tag{Equation 6.3}
\]
Thus, Von Mises stress can be calculated:

\[
\sqrt{\frac{(\sigma_x - \sigma_y)^2 + (\sigma_x - \sigma_z)^2 + (\sigma_y - \sigma_z)^2}{2}} = \sigma_x = \sigma_y = \frac{E \Delta V}{3V}
\]  

(Equation 6.5)

From equation 6.5, the local stress is proportional to the volumetric shrinkage. Thus, a proper combination of process parameters, thus, it is crucial to minimize the volumetric shrinkage of the resin in solidification.

6.4 Simulation Results of Solidification in UV Imprint

To study the local stress distribution in UV-curable resist after solidification, we simulated the solidification process with different shrinkage ratio, from 0.3% to 3%. Figure 6.4 shows the distribution of Von Mises stress in resist domain after solidification. The highest local stress increases linearly as volumetric shrinkage increases. At the lowest volumetric shrinkage of 0.4%, the stress distribution is low and almost uniform over the whole area; while at the highest volumetric shrinkage of 3%, the highest local stress is
concentrated at the corner of transition zone between replicated patterns and residual layer, similar to the stress distribution in the thermal NIL.

Figure 6.4 Von Mises stress distribution in UV resist after solidification for different volumetric shrinkage (mark the highest local stress in each figure)

Figure 6.5 the highest local stress as a function of volumetric shrinkage.
Figure 6.5 shows the linear dependence between the highest local stress and volumetric shrinkage. When the volumetric shrinkage is 3.0%, the highest local stress amounts to ~ 22MPa, which is almost one third of the residual thermal stress generated during the cooling process in the thermal NIL.

Furthermore, the simulation is based on the assumption that the adhesion between stamp and UV resist is strong enough to hold the shrinkage of the UV resist, and thus no separation was allowed. That’s also why local stress increases as volumetric shrinkage ratio increases; however, if high quality anti-sticking coating is applied to stamp surface, solidified resin material may be separated from stamp and local stress can be even lower.
Chapter 7 Demolding Simulation for Injection Molding

7.1 Introduction

With the rapid advance of micro and nanotechnologies, high quality, low cost and high throughput fabrication methods of MEMS devices are of crucial importance. Injection molding, a well established technique in macroscopic production of polymer parts in industry for decades, has been accommodated as a microfabrication technique by minimizing the structure size on mold insert to micro scale [Su et al., 2004].

![Injection molding machine](image)

Figure 7.1 Schematic and equipment of injection molding [Courtesy of B. You et al]

Similar to the thermal imprint lithography, the injection molding process consists of three steps in sequence: injection (molding), cooling and ejection (demolding). First, a melted polymer is fed by a screw into the mold block through a nozzle; then it fills into microcavities of the mold insert at an injection molding temperature which is well above the glass transition temperature of the polymer. For many injection molding processes, additional compression is
applied to the mold block in addition to the pressure applied by the screw. The system is then cooled down to an ejection temperature and the polymer filled into the microcavities is solidified. Finally, the molded polymer part is separated from the mold insert at the ejection temperature. There are significant differences in terms of physical process between injection molding and thermal imprint lithography – for injection molding, the polymer melt at the sprue is frozen first during cooling and after the polymer at the sprue is frozen, pressure on molded part is released, thus, molded part can shrink freely.

Compared with other molding techniques such as thermal imprint lithography (hot embossing), thermal forming and casting, injection molding has much shorter cycle time. Thus, it is the preferred process for the cost-effective mass production of polymeric products at the industrial level.

When injection molding is used for producing micro- and nanoscale patterns, the increased surface-to-volume ratio significantly affects the flow behavior of the polymers. Significant researches have been done in the study of mechanical and thermal behavior of the melted polymer during injection [Hung et al., 2001; Yu et al., 2002; Ruprecht et al., 2002; Despa et al., 1999]. Both numerical simulation and experimental measurement showed that proper combinations of injection parameters, like the mold cavity temperature and injection speed and injection pressure ensure the perfect dimension accuracy of pattern replication. However, the study of cooling and ejection (demolding) process in injection molding is still lacking, even though most of structural failures of molded polymer parts occur during these steps. High local stress is generated in both the mold insert and molded polymer parts mainly due to three factors: the first is the thermal stress formed during cooling as a result of the
mismatch of thermal expansion coefficients between the mold insert and the molded polymer part; the second is the adhesion between the mold insert surface and molded part, from chemical bonding, electrostatic interaction or mechanical interlock and it becomes significant when the structure scales down or anti-sticking coating of the mold insert surface is not perfect; the third is friction force between mold insert and molded part when relative sliding occurs, which is simply assumed to be linearly proportional to the normal force due to the thermal stress and the adhesion force. The proportionality constant is known as friction coefficient. In order to minimize the thermal and adhesion induced stress, thus to ensure the success of pattern replication, in-depth understanding of the mechanical response of molded polymer part during cooling and demolding is imperative.

Recently, several groups have focused on the study of polymer mechanical behavior during cooling and demolding [Fu et al., 2006; Worgull et al., 2006]. Fu et al. analyzed the stress evolution during the ejection process of injection molding and concluded that the microstructures at the edge of mold insert is exposed to the highest stress while inside structures are protected [Fu et al., 2006]. Based on isotropic shrinkage assumption, they predicted that a critical temperature exists, below which there is no surface contact between mold insert and resist and thus demolding force is zero. However, the isotropic shrinkage assumption used in their study is questionable, since only the thermal shrinkage towards the local center of a certain micropost is considered while the global thermal shrinkage towards the centerline of the whole mold insert/molded part was not taken into account. This will lead to a significant error in predicting the stress and deformation behavior during demolding, particularly for those structures far from the global centerline. Worgull et al. simulated the
cooling process in hot embossing and studied the location dependence of local stress [Worgull et al., 2006]. Based on simulation results, they proposed a method of building additional structures around the active pattern area to protect the active patterns from the high stress concentration. However, the demolding process during hot embossing is different from that for injection molding as described above. In this chapter, we extend the finite element method (FEM) simulation to the demolding process for injection molding in order to achieve a better understanding of the stress distribution and evolution, and deformation behavior of molded polymer parts. Simulation results show that the microstructures at the edge of mold insert is exposed to the highest shear stress resulting in a visible distortion in the molded part. The microstructures inside are protected from high stress and no visible deformation was observed. We also study the influence of the friction coefficient and geometries of the microstructures in the mold insert. We find that the local maximum stress in the molded part can be reduced up to 25% by modifying sharp corners of the microstructures in the mold insert to have a draft angle.

7.2 Simulation Methodology and Results

7.2.1 2 Dimensional FEM Model

Figure 7.2 shows the 2-D finite element method (FEM) model and the boundary conditions used in the simulation. The materials for the mold insert and the substrate were brass and polycarbonate (PC) sheet, respectively. The brass mold insert contains three identical recessed structures located at 100, 200 and 300 mm from the centerline (symmetric boundary). The width and depth of the recessed structure are both 400 μm. The plane stress assumption was made to simplify the simulation. This can be justified because there is little
deformation of the molded part in the vertical direction during the whole processes of cooling and demolding. Vertical displacement was confined at both the top surface of the brass mold insert and the bottom surface of the molded PC part. A symmetric boundary condition was applied on the centerline. 4-nodal linear structural element PLANE42 was applied on both brass mold insert and molded PC pattern, with gradually decreased element size from 50 μm for areas of low and uniform stress distribution to 12.5 μm for sharp corners and interfaces where high stress is concentrated. A standard contact pair of TARGET169-CONTACT172 was created on the interface between the mold insert and the molded PC part. Sliding and separation were allowed at the interface.

7.2.2 Mesh Sensitivity

To ensure the reliability of simulation results, it is necessary to verify the convergence of the simulation; in other word, the results are independent on the mesh size. To prove that, we meshed the model with elements of different sizes while the element size ratio between different region kept identical. Simulation was repeated under identical conditions (material properties, contact algorithm, load step). As shown in Figure 7.3, after cooling, shear stress at

![Figure 7.2 2 dimensional FEM model for cooling and demolding simulation](image)

**7.2.2 Mesh Sensitivity**

To ensure the reliability of simulation results, it is necessary to verify the convergence of the simulation; in other word, the results are independent on the mesh size. To prove that, we meshed the model with elements of different sizes while the element size ratio between different region kept identical. Simulation was repeated under identical conditions (material properties, contact algorithm, load step). As shown in Figure 7.3, after cooling, shear stress at
the interface near the corner area converges to a certain value while the mesh density increases. This indicates that the finite element analysis is mathematically reliable.

7.2.3 Process Assumptions

To simplify the finite element analysis without losing rationality and generality, several assumptions were introduced.

First, the mechanical response of both brass mold insert and PC substrate at simulated scale (microscale) is governed by equations of the continuum mechanics.

Second, microcavities in the brass mold insert are completely filled with the PC melt at the molding temperature of 300 °C. Su et al. showed by simulation as well as experiment, that at 300 °C and 50MPa injection pressure, the depth to opening ratio approaches 0.707, which means the optimal filling [Su et al., 2004]

Third, the stress in the PC melt during the injection process is neglected. This assumption can be justified by results of the temperature-dependent residual stress.
measurement at the polymer-metal interface [Wang et al., 2001]. Since the injection temperature is well above the glass transition temperature of given polymer, the flow stress is much less than the thermal stress generated during cooling and the shear stress at the interface due to friction during demolding.

Fourth, there is no heat transfer between different components during cooling and the whole system is cooled down at an identical cooling rate.

Fifth, no adhesion is taken into account in the simulation. We assume that the anti-sticking coating on the surface of mold insert is perfect, thus the adhesion can also be ignored, comparing with the thermal stress.

Finally, all the material properties are assumed to be time/temperature independent and isotropic.

7.2.4 Material Properties

Both brass mold insert and molded PC parts are assumed to be linear elastic materials with constant Young’s modulus, Poisson’s ratio and coefficient of thermal expansion listed in table 7.1.

Table 7.1 Material properties of brass and polycarbonate used in simulation [Makrolon GP data sheet]

<table>
<thead>
<tr>
<th></th>
<th>Young’s Modulus (Gpa)</th>
<th>Poisson’s ratio</th>
<th>Thermal Expansion Coefficient (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brass</td>
<td>97</td>
<td>0.31</td>
<td>2.05e-5</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>2.4</td>
<td>0.37</td>
<td>7e-5</td>
</tr>
</tbody>
</table>

7.2.5 Simulation

The simulation consists of two load steps: cooling and demolding. During cooling process, the mold insert and molded polymer part are cooled down from a temperature of
150°C to the ejection temperature (100°C). Even though the actual temperature of the PC melts during injection amounts to ~ 300 °C, the stress generated in the molded part during molding is still low before the temperature drops down to the T_g of PC (T_g = 150 °C). Considering the assumption made for the simulation that the flow stress in melting polymer can be ignored when temperature is well above glass transition temperature, the cooling process starting from 150 °C will lead to the very similar, but much simplified results to actual case. During the demolding process, normal displacement of 500 μm is applied on the top surface of mold insert, while the bottom surface of molded PC is still fixed. Different from the cooling process in thermal imprint, since the viscoelasticity of polymer is not included here, the demolding process is considered to be temperature and rate-independent.

The Navier-Stokes equation, energy conservation equation, geometry equation and constitutive equation are simultaneously solved using commercial finite element analysis software ANSYS 10.0. Since the material properties of both brass and polycarbonate are assumed to be rate-independent, analysis time only serves as a tracking parameter, not as actual, chronological time. In order to study the stress evolution during demolding, we divided the demolding step into 20 sub-steps and save the results after calculation of each sub-step.

### 7.2.6 Stress Distribution in Polycarbonate after Cooling

In the first load step, the brass mold insert/molded PC was cooled from 150°C to the ejection temperature of 100°C. Figure 7.4 shows the shear stress distribution in molded polycarbonate after cooling. Since the coefficient of thermal expansion of polycarbonate is much higher than that of brass, thermal shrinkage of molded polycarbonate towards the
centerline is limited by the brass mold insert. As a result, within a microcavity, high shear stress concentrates at the inner corner of the transition zone between molded polycarbonate and residual layer closer to the centerline where the molded PC and the brass mold insert are in hard contact. On the other side, since we assume there is no adhesion between mold insert and molded polymer, polycarbonate shrinks freely towards the centerline and a narrow gap is formed between mold insert and molded part for the outer corner.

The maximum value for the local stress concentrated at each microstructure is also highlighted in figure 7.4. The simulation results clearly reveal that the maximum shear stress located at the micropost farthest from the centerline is much higher (59.8MPa) than the other two microposts (17 and 5.5 MPa) located closer to the centerline. In order to evaluate the deformation behavior of PC, the maximum shear stress criterion was employed, which is widely used to predict the yielding of ductile materials. The maximum shear stress at the outmost microcavity is above the yield stress of PC 41.3MPa [Makrolon GP data sheet], indicating that plastic deformation will occurs locally. The maximum shear stress values at the two inner microcavities are much lower than the yield stress and thus the material is still undergoing elastic region. The simulation results show good agreement with previous finite element analysis results in terms of the stress distribution versus the location of structures from the centerline [Fu et al., 2006]. Moreover, the molded polycarbonate pillar shows visible distortion at the corner of the transition zone between the mold insert and the molded polycarbonate for the outmost microcavity, which has not been reported by previous research groups. We believe this is the location where local defects are initiated. More fundamental study needs to be done for a better understanding of the crack initiation and crack propagation.
in molded PC parts.

7.2.7 Stress Evolution during Demolding

The success of demolding is determined by properties of the materials used, geometries and scales of the microstructures on the mold insert, and process parameters. Since the maximum shear stress at the outmost microcavity is much higher than the other two inner microcavities, we focused on the shear stress evolution during demolding at the outmost microcavity. We assumed that anti-adhesion coating on the brass mold insert surface is perfect and thus the friction coefficient is zero. As a result, only the residual thermal stress accounts for the local stress. Figure 7.5 shows how the shear stress at the outmost microcavity evolves as demolding proceeds. Because the yield stress of brass is much higher than the shear stress produced during cooling and demolding, we can exclude the possibility of any deformation in the brass mold insert. The simulation results reveal that there are two locations of stress concentration in the molded PC part. The first location is at the corner of the transition zone between the molded PC and the residual layer and the second location is the contact region between the molded PC and the mold insert which moves up as demolding proceeds. And the highest local stress experiences its maximum at the onset of demolding, indicating that structural damages are most probable to occur at the very beginning of demolding.

7.3 Effect of Friction Coefficient

As we discussed in introduction, structural damages of the molded polycarbonate may result from the thermal stress, adhesion and friction. The friction force is determined by the adhesion, normal projection of the thermal stress to the mold insert surface and friction
coefficient, as expressed by Equation (1)

$$f = \int_{s} \mu \cdot (\sigma + \sigma') ds$$

(Equation 7.1)

where $\sigma$ is surface adhesion, $\sigma'$ is normal projection of the thermal stress to the mold insert surface, and $\mu$ is the friction coefficient.

Figure 7.4 Shear stress distribution in Polycarbonate after cooling

As we assumed that there is no adhesion on the interface between brass mold insert and molded polycarbonate, the friction force is only determined by the normal projection of the thermal stress, the friction coefficient and contact area. Since the thermal stress is
determined by the mismatch of thermal expansion coefficients between the brass mold insert and the molded PC, and the temperature difference from the $T_g$ of PC to the ejection temperature, for selected materials and given process, residual thermal stress is constant; the contact area is also constant for given mold insert. Thus, minimization of the friction coefficient becomes the major approach to reduce the friction force.

![Figure 7.5 Shear stress evolution during demolding process (without friction)](image)

The influence of the friction coefficient on the local stress for injection molding was determined by repeating the simulation with different friction coefficients from 0 to 0.3. Figure 7.6 shows the evolution of the shear stress for the outmost post of the molded PC during demolding with friction coefficient of 0.3. Compared with the stress evolution during demolding without any friction, shown in figure 7.5, the maximum local stress increases up to 20%. This indicates higher probability of structural damages during demolding. Furthermore, the high stress area also expands, thus, the effect of friction at the interface is
not only limited to the regions near the interface, but also significantly contributes to the region far away from the interface.

Figure 7.7 plots the highest local stress as a function of demolding time for the three microcavities located differently from the edge to the symmetric center. The yield point of shear strength for PC is highlighted in the first curve which stands for the evolution of the highest local stress of the micropost at the edge from the structural center. A highest increase in the highest local shear stress was observed for the micropost farthest from the centerline.

7.4 Stress Evolution with Modified Mold Insert

Even though the anti-adhesion coating of the mold insert surface is an efficient way to reduce the friction at the interface between mold insert and molded polymer, it cannot prevent stress concentration at edges of the structures. In addition, the lifetime of the surface coating
is still an issue because part of the surface coating is removed after a few cycles. In this section, we investigated the influence of mold insert geometries on the local stress in the molded PC part. The draft angle structure of 100μm width and 45º tilt angle was built at the corner of protrusion on mold insert structure, as shown in figure 7.8. Since the stress concentration factor depends on the geometrical singularity of a structure, we expect that the

Figure 7.7 The highest local stress versus demolding time for the three microposts located (a) 300 mm, (b) 200 mm, and (c) 100 mm from the symmetric center
draft angle structure will release the stress concentration at a sharp corner to some extent. To identify the effect of modification of mold insert geometry quantitively, we simulated the cooling and demolding process with modified mold insert.

Figure 7.8 2-D FEM model for modified mold insert with a draft angle

In order to ensure the comparability with the previous simulation results without the draft angle structure, all the simulation conditions, including mesh density and gradient, material properties, boundary conditions, load setting, solver selection, were kept identical with the previous simulation. Basically, the shear stress distribution after cooling and its evolution during demolding shows similar behavior to the simulation results without the draft angle structure. Figure 7.9 shows the shear stress distribution in PC after cooling. The microstructure at the edge of the mold insert is exposed to the highest shear stress. Within the same microcavity, the stress is concentrated at the corner of the transition zone between molded PC and residual layer which is close to the centerline. A narrow gap was generated on the other side of the structural corner.

Figure 7.10 shows the shear stress evolution in PC during the demolding process. Despite the similar stress distribution and evolution, the shear stress values of the modified
mold insert were reduced significantly with respect to those for the original mold insert without the modification. Figure 7.11 plots the highest local stress in molded PC as a function of demolding time for both original mold insert and modified mold insert. For both cases, the highest shear stress shows the maximum at the beginning of demolding, then decreases to a constant level rapidly. At the beginning of demolding where the local stress experiences its maximum, the shear stress value can be reduced up to 25% while near the end of demolding the reduction in the shear stress amounts to approximately 15%.

Figure 7.9 Shear stress distribution after cooling (modified mold insert)
Comparing with the simulation results of original and modified mold inserts, we can conclude that the shear stress in molded PC during demolding can be minimized by applying a draft angle structure in the mold insert. Since the high stress always concentrates at sharp corners with high geometry singularity, it is critical to avoid the sharp corner in mold insert design or introduce certain modification like draft angle or round corner in the fabrication.

### 7.5 Dependence on Size and Shape of Modified Structure

Figure 7.12 shows the shear stress distribution in PC for mold inserts with different draft angle structures. The width of the draft angle structure was varied from 0 (unmodified
mold insert) to 200 μm while keeping the 45° draft angle (Figure 11(a)-(d)). In addition, the mold insert structure with round corner of 50 μm radius was also simulated (Figure 12(e)). The highest stress value is also shown for each structure. The maximum stress is reduced as the width of the draft angle structure increase. If we compare the structure with the round corner of 50 μm radius with the draft angle structure of 50 μm width, the rounded structure shows less shear stress by 16%.

Figure 7.13 plots the highest shear stress in molded polycarbonate after cooling as a function of the draft angle width. Upon application of a draft angle with a small width, the shear stress decreases first significantly. However, the slope decreases as the draft angle width becomes larger than 100 μm. This indicates that there exists a critical draft angle size around 100 μm, above which the shear stress does not strongly depend on the draft angle size. Thus, it is not necessary to build a large draft angle structure, which is sometimes not acceptable in the design of mold insert structures for specific applications. There exists an appropriate draft angle size for each geometries where the shear stress in molded part can be
reduced and the overall shape of the molded part is not much deviated from the desired mold insert design, which can be determined by the FEM simulation. Even though the round corner

Figure 7.12 Shear stress distribution after cooling for PC molded with (a) original mold insert, modified with 50 μm width draft angle (c) 100 μm width draft angle (d) 200 μm width draft angle, and (e) 50 μm radius round corner

Figure 7.13 The highest local stress as a function of draft angle size

reduced and the overall shape of the molded part is not much deviated from the desired mold insert design, which can be determined by the FEM simulation. Even though the round corner
structure is more effective in minimizing the local stress, it will be much more difficult in micromachining.

7.6 Conclusions

The cooling and demolding process of injection molding was studied by FEM simulation. Similar to results for NIL, we found two locations of stress concentration: the corner of transition zone between molded polycarbonate and residual layer, and the contact region between molded polycarbonate and mold insert, which moves up as demolding proceeds. However, the local shear stress does not drop dramatically at onset of demolding, which was observed in the simulation of NIL. We believe that the difference originated from different material models: In the simulation of thermal imprint lithography, PMMA resist was assumed to be viscoelastic model and stress relaxation may account for the stress drop as time goes while in the simulation of injection molding, molded polycarbonate is simply defined as linear elastic model, thus the stress only depends on the deformation. The microstructure at the edge of mold insert, which is the farthest from centerline, is always exposed to the highest shear stress, while inside structures are protected, which achieve good agreement with previous research from several groups.

To understand the contribution of friction force to the level of local shear stress, we simulated the cooling and demolding process with different interface friction coefficients of 0 and 0.3, with all the other conditions identical. Comparison results showed that the local shear stress is 20 % lower in case of zero friction. This indicates that surface coating could be an efficient way to facilitate the injection molding.
The influence of mold insert geometry was also studied and it was found that the local stress can be reduced up to 25% by modifying the protrusions on mold insert with a draft angle. Some preliminary work on the size and shape dependence of draft angle was done and we expect that there exists a certain critical size, above which the local stress is independent on the size of draft angle structure.

In this chapter, we only simulated simple structures based on the linear elastic model, which does not perfectly describe the behavior of PC. However, the results indicate that, the ability of the FEM simulation for complicated and actual structures will enable prediction of the stress and deformation behavior for the demolding process of injection molding and that it is a powerful tool in determination of a range of process parameters which will allow for success in injection molding even at the stage of a process design in an economical and reliable way.
Chapter 8 Conclusions and Future Work

8.1 Summary

In this thesis, we studied the stress behavior in resist layer and the likelihood of structural damages during demolding process, for thermal imprinting lithography, step and flash imprint lithography and injection molding, via commercial finite element method (FEM) software ANSYS 10.0. All the simulation details, such as stamp geometry, element and mesh, material properties, contact algorithm, boundary conditions, load step setting and process assumptions were discussed. Stress distribution and evolution in resist layer were obtained from simulation. Rules of stress/deformation behaviors were extracted from simulation results and underlying physics was discussed. Parametric study was performed systematically to understand the effects of various process and geometric parameters.

In order to verify the simulation results, we studied the demolding process of thermal imprint lithography experimentally. Experiment procedures from stamp fabrication, substrate preparation, to molding and demolding were introduced in sequence and critical techniques such as silane coating, reactive ion etching were specifically discussed. Imprinted PMMA patterns were inspected by scanning electronic microscope (SEM), which provided us the intuitionistic evidence to evaluate the effect of different temperature; furthermore, to quantify the mechanical resistance during demolding, a standard material tester was modified to measure the demolding force at different demolding temperatures repeatedly.

8.2 Conclusions

In the demolding process of thermal imprint lithography, we found two locations of stress concentration in the PMMA layer during demolding: the corner of transition zone
between the replicated patterns to residual layer and the contact region between silicon stamp and replicated patterns. As demolding proceeds, the highest local stress shows two maximums, indicating that demolding failure can occur both at the beginning and the end of demolding. A systematic parametric study has been performed on friction coefficient, demolding rate, demolding angle, demolding temperature and the aspect ratio of the stamp structures. Simulation results indicated that high friction coefficient leads to high stress in demolding and structural damages may be avoided by anti-adhesion coating; an accurate alignment in the stamp displacement direction is critical to the success of demolding and there exists a maximum allowed demolding angle leading to demolding without structural failure; local stress increases as demolding rate increases, particularly in non-normal demolding process; both simulation and experiment results show that the optimal demolding temperature in given condition is around 70°C, with both low demolding force, excellent overall pattern quality and satisfactory local surface profile; increase in the aspect ratio in the stamp structures leads to the increased local stress during demolding, indicating the difficulty in fabrication of high aspect ratio structures.

Similar to simulation results of thermal imprint lithography, we found two locations of stress concentration during demolding step of injection molding: the corner of transition zone between molded polycarbonate and residual layer, and the contact region between molded polycarbonate and mold insert, which moves up as demolding proceeds. It was also indicated that the microstructure at the edge of mold insert is always exposed to the highest shear stress. As we expected, local shear stress decreases as friction coefficient on the interface decreases. The influence of mold insert geometry was also studied and it was found that the
local stress can be reduced up to 25% by modifying the protrusions on mold insert with a draft angle. This is quite significant because, for most cases in injection molding, there are no strict requirements on the geometry of molded pattern at the base. Thus, we can greatly reduce the likelihood of structural damages via this method. Some preliminary work on the size and shape dependence of draft angle was done and we expect that there exists a certain critical size, above which the local stress is independent on the size of draft angle structure.

Based on the assumption of isotropic thermal shrinkage and strong adhesion, we found the linear relationship between volumetric shrinkage and local high stress in demolding process of step and flash imprint lithography. The simulation results also indicated that the residual stress in demolding of step and flash imprint lithography was much lower than that of thermal imprint lithography.

In this thesis, we only simulated imprint with stamp of very simple structures, such as a single symmetric structure or multiple symmetric structures. However, the results indicate that, the ability of the FEM simulation for complicated and actual structures will enable prediction of the demolding process as well as determination of a range of process parameters which will allow for successful demolding even at the stage of a process design in an economical and reliable way. This becomes more important with the increasing requirement of high aspect ratio and complex structures. In addition, the new designed demolding unit, which enables the normal demolding with controlled temperature and speed, is significant in reducing the structural damages from declining demolding and offers an excellent tool for parametric study of demolding process.
8.3 Future Work

The present study focused on the stress analysis in polymer resist layer with stamp of very simple and ideal structures and revealed basic rules of stress concentration and evolution during demolding. Some preliminary results were extracted from parametric study. However, as we addressed in the introduction chapter, the research on demolding is still quite lacking. Both the simulation and the experiments are far from perfect.

The present simulation can be improved by several considerations. First, the quasi-static structural analysis in present simulation can be extended to a thermal-structural coupled analysis based on the consideration of heat transfer between stamp and resist. Second, taking the surface roughness into account, the interface between the stamp and resist should be represented by fractal geometry, not the flat surface used in present simulation. More detailed local modeling is imperative. Third, as we mentioned previously, the interface between stamp and resist is neither “standard”, which means there are no interactions between each other, nor “no separation”, which prevents any normal separation; but an intermediate state of the two. In present simulation, we employed “no separation” boundary condition, which is more close to physical reality; however, we may expect more accurate results by defining an intermediate boundary condition properly. One possible solution is to define “dead/birth” spring element on the interface. Fourth, the simulation can also be extended to three dimensional, which is more realistic.

Experimental study can also be extended by scaling down the feature size and increasing the aspect ratio of stamp. Surface treatment by chemical vapor deposition of different chemicals, plasma deposition of different target can be performed to prepare the
stamp. Not only the demolding force, but also the dissipated thermal energy during demolding can be used to characterize the mechanical resistance during demolding. By the way, in evaluation of the mechanical behavior, we did not consider the difference on material properties between thin film and bulk materials. By measuring the elastic modulus by nanoindentation, we can expect to get more accurate results.
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Vita

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