KEY FACTORS FOR CONTROL OF MICRO STEREO LITHOGRAPHY SYSTEM

By

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To my family
ACKNOWLEDGMENTS

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<tr>
<td>CAD</td>
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<td>HDDA</td>
<td>Hexanediol Diacrylate</td>
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<tr>
<td>LIGA</td>
<td>German acronym for Lithography, Electroplating and Molding</td>
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<td>MEMS</td>
<td>Micro Electro Mechanical System</td>
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<td>μSL</td>
<td>Micro Stereo Lithography</td>
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<td>Ordinary Differential Equation</td>
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<td>3D</td>
<td>Three Dimensional</td>
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<td>Ec</td>
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KEY FACTORS FOR CONTROL OF MICRO STEREO LITHOGRAPHY SYSTEM

By
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Micro stereo lithography (µSL) process is gaining a lot of popularity due to its ability to fabricate complex and intricate 3D structure over a wide variety of materials. In order to build a µSL system several parameters need to be known. Some of the most important parameters are the curing depth and divergence of light produced by light source.

Curing depth is calculated as a function of initiator and absorber concentration. An extensive mathematical model is derived taking into account the initiator concentration, absorber concentration and temperature effects. Solutions with different absorber and initiator concentration are used to show the monotonic dependence of initiator and absorber on curing depth. The exponential dependence of temperature is also demonstrated.

Divergence study is performed to understand the effects of interference of light along the edges. As maintaining a closed gap between mask and monomer solution is a challenge, divergence study is used to derive the maximum allowed separation between mask and monomer solution.
CHAPTER 1
INTRODUCTION

History

A tremendous growth has been observed in the field of micro electro mechanical system (MEMS) during the past 20 years. Aside from laying planar 2D structure on the semiconductor substrate, MEMS technologies require micro fabrication of complex 3D structures. The most typical silicon micro machining technologies, anisotropic etching and surface micromachining are used in past to produce 3D structures. However, more complex structures cannot be fabricated using above mentioned techniques. Another limitation is due to the fact that these processes only apply to a handful of common semiconductors, metals and dielectrics [1].

In order to have complex 3D structures on a wide variety of materials, Becker et al. proposed LIGA process in 1986[2]. LIGA is a German word and it stands for Lithography, Electroplating and Molding. Primary template is formed using lithography and then its filled by metal using electro deposition. However, very complex structures cannot be formed using this technique.

3D Laser Chemical Vapor Deposition is presented by Williams and Maxwell [3]. They demonstrated this technology for manufacturing of helical microstructures. 3D LCVD uses a scanning laser beam to deposit solid materials. The shape of the fabricated part is controlled by focusing the scanning laser beam.

Another method is proposed by Cohen et al. [4]. They demonstrated electrochemical fabrication process as an extension of LIGA process to produce complex 3D structures. Metals are deposited in a layer by layer fashion which acts as electrode masks. The thickness of the layer is controlled by a planarizing procedure.
However, all of the above mentioned techniques suffer from high equipment cost and a very low throughput.

The shortcomings of the above mentioned techniques are addressed by a new technique termed stereo lithography. This technique was invented by Chuck Hull in 1986 [5]. This technique forms the basis of micro stereo lithography process. Micro stereo lithography process is same as stereo lithography process except for the fact that it is used to make much smaller parts.

**Working Principle**

The basic idea behind the micro stereo lithography process is the layer by layer formation of a UV curable resin. Exposing the resin to UV hardens a small layer. This layer is then moved down and fresh layer of resin covers the hardened surface. Exposing it again makes the second layer stacked on top of the first one. A schematic of such a process is shown in Figure 1-1.

Using such a technique, lateral resolution of as low as 600nm is achieved using a two photon polymerization process [6]. Another important benefit of using micro stereo lithography is freedom to fabricate on a vast variety of materials. It is not just limited to UV curable resins. Complex 3D shapes in ceramics and metals also are demonstrated by mixing fine powder with UV curable resin [7].

Micro stereo lithography can be subdivided into two main sub processes namely vector by vector micro stereo lithography and integral micro stereo lithography. In vector by vector approach a focused light beam is scanned on the surface of monomer [8]. It provides a very high level of resolution. It does not require any mask or any specific tool. A complex 3D structure with very high aspect ratio can be fabricated by slicing a
3D CAD file. However, the process takes a lot of time and thus not suitable for batch production of micro structures.

On the other hand, in the integral micro stereo lithography a complete layer of monomer is exposed by projecting the image on it. In order to generate complex structure a digital micro mirror or an Liquid Crystal Display device can be used to project the image of cross section [9, 10]. To fabricate simple structure with high aspect ratio a fixed mask can also be used. The bitmap image is used to pattern light (typically UV) which is then focused onto the surface of a light curable resin to form a layer. Subsequent layers are built on top of previous layers to form a 3D structure. Because the light is focused, the realizable cross sectional is restricted. This limitation to mask projection micro stereo lithography can be overcome by "stitching" multiple segments of the total desired cross section together using a stage that can articulate in the X, Y axes. Multiple overlapping exposures are made at each level thus quilting together the total desired cross sectional area [11]. A comparison of different micro stereo lithography technique is shown in Table 1-1.

**Issues**

One of the main challenges in micro stereo lithography fabrication is to accurately quantify the curing depth. When a monomer solution is exposed to light, the extent of polymerization gradually decreases with an increase in depth from the surface. Curing depth is defined as the depth inside the monomer solution up to which a critical polymerization is occurred on UV exposure. It is usually a complex function of exposure dose, reactivity of monomer solution and temperature of the monomer solution. Curing depth dictates the thickness of layer to be formed. If a particular thickness is required, the amount of exposure dose needed is also governed by curing depth. Another
important issue is the viscosity of the UV curable resin. In layer by layer formation method after each step a fresh layer of monomer is required on top of polymerized surface. Also this small layer needs to be flat to ensure uniform polymerization across the entire cross section. After each step some time is required for fresh monomer layer to level across the surface. A more viscous liquid will require a longer leveling time and it may also happen that it will not level at all. In such a case platform should be dipped inside and then lifted back up [12].

Some other factors that limit the resolution of the micro stereo lithography process are bleaching and print through. At high exposure doses, stereo lithography monomers undergo bleaching as the polymerization reactions precede. As a consequence of bleaching, radiation penetrates the monomer more easily, thus causing polymerization at greater depths. Increased polymerization depths result in lower Z resolution. This phenomenon is known as bleaching effect [13]. Another challenge is the print through error [14]. When a layer is polymerized, the layer thickness is set to the depth where the exposure falls to the threshold exposure Ec. The monomer below this cured layer does not experience an exposure equal to Ec. However, it receives some exposure. As subsequent layers are polymerized, this point in the monomer receives incremental exposure until finally reaching Ec causing polymerization. The result is unwanted curing and the error introduced is called the print-through error.

This work deals with the issues mentioned above. An in depth study of curing depth is performed and presented in Chapter 2. The effect of absorber concentration, initiator concentration, light intensity and temperature is taken into account. The mathematical model is also supported by the experimental results.
The lateral resolution can also be limited by the divergence of collimated light source. A diverging light would set a maximum allowable separation between light source and monomer layer. Chapter 3 addresses the issue of divergence of collimated light source. Experimental results are shown to quantify the effect upon lateral resolution as a function of separation between a light source and monomer layer. Chapter 4 summarizes the results of curing depth study and divergence study.
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<td>3D Laser CVD</td>
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<td>Limited material process</td>
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<tr>
<td></td>
<td>Fast</td>
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<tr>
<td>EFab</td>
<td>True 3D geometry</td>
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<td>Vector by Vector μSL</td>
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<td>Complex free standing structure</td>
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<td></td>
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<td>Limited area of exposure</td>
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<td>Complex Structure</td>
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Figure 1-1. Micro Stereo Lithography system setup
CHAPTER 2
CURING DEPTH STUDY

Curing depth is defined as the depth up to which 3 dimensional gel networks is formed, when monomer solution is irradiated with light. The critical conversion point of gel network known as gelation decides the level of polymerization. This conversion point is a function of both reaction rate and amount of photons present. Active research has been going on to study the reaction kinetics of these systems [15, 16]. Numerous parameters influence the polymerization reaction rate. Some of the most influential parameters are temperature, concentration of absorber and initiator and light intensity. The effect of these parameters on overall bond conversion is well known however, an in depth study for the roles of these parameter on cure depth has not been done.

The typical reactants in photo polymerization reaction are initiator, and monomer molecule. The reaction mainly consists of three steps. The first step is initiation of free radical by photo radiation. The reaction involved is as follow

\[ I_2 + h\nu \rightarrow i + \dot{i} \]  \hspace{1cm} [2-1]

The initiator molecule is split to generate free radicals when UV light shines upon it and is denoted by \( \dot{i} \). These free radicals combine with monomer molecules to generate longer chain radicals or oligomers. This process step is known as propagation and the reactions involved are as follows

\[ M + \dot{i} \rightarrow M \] \hspace{1cm} [2-2]

\[ M + M_n \rightarrow M_{n+1} \] \hspace{1cm} [2-3]

The last step is the termination. Free radicals can combine with it or can combine with a chain to terminate the reaction. The reactions involved are as follows
\[ \dot{I} + I \xrightarrow{k_t} I_2 \quad [2-4] \]

\[ \dot{M}_n + \dot{I} \xrightarrow{k_t} M_{n+1} \quad [2-5] \]

\[ \dot{M}_n + \dot{M}_m \xrightarrow{k_t} M_{n+m} \quad [2-6] \]

**Mathematical Model**

A model for curing depth is derived using the kinetic equation for photoinitiated polymerization [17].

\[ - \frac{d[M]}{dt} = R_i + R_p \approx R_p \quad [2-7] \]

where \( R_p \) is given by

\[ R_p = k_p [M][\dot{I}] \quad [2-8] \]

\( R_p \) is the rate of polymerization and \( R_i \) is the rate of initiation of free radical by UV light exposure. \([M]\) is the concentration of monomer and \([\dot{I}]\) is the concentration of radical chain. \( k_p \) is the reaction rate constant of propagation. During steady state, initiation of radicals due to light impingement is balanced by termination. Hence using the steady state approximation, \([\dot{I}]\) can be expressed [17].

\[ R_p = k_p [M]\sqrt{\frac{R_i}{2k_t}} \quad [2-9] \]

where \( R_i \) is the rate of initiation of polymer and \( k_t \) is the reaction rate constant of termination. The initiation rate \( R_i \) is a function of intensity of incident light. Its value is given by

\[ R_i = 2\theta e[Init]I_z \quad [2-10] \]

\( I_z \) is the intensity of light at a depth \( z \) in the monomer solution. \([Init]\) is the concentration of initiator, \( \theta \) is the quantum yield of photo initiator and \( e \) is the molar
extinction coefficient. Intensity of incident light at depth $z$ can be given by Beer Lambert law. As the monomer solution is homogenous and scattering of light is negligible, Beer Lambert law can be applied. According to this, intensity of light in a medium at a depth $z$ is given by [18, 19]

$$I_z = I_0 10^{-ε[Init]z} \quad [2-11]$$

where $I_0$ is the intensity of light at the surface. Hence Equation 2-10 can be written as

$$R_i = 20ε[Init]I_0 10^{-ε[Init]z} \quad [2-12]$$

Substituting the value of $R_i$ in the Equation 2-12

$$-\frac{d[M]}{dt} = R_p = k_p[M]\sqrt{\frac{20ε[Init]I_0 10^{-ε[Init]z}}{2k_t}} \quad [2-13]$$

Assuming the terms on right hand side are time independent, separation of variable can be used to obtain a closed form solution of the differential equation. However, if the temperature dependence of reaction rate constant $k_p$ and $k_t$ are taken into account, no closed form solution can be obtained. Thus the temperature dependence is handled later in this chapter and numerical solutions are generated using MATLAB®.

Bringing $[M]$ on the left hand side and integrating with respect to time yields

$$\log\left(\frac{[M]_0}{[M]}\right) = \left(k_p\sqrt{\frac{20ε[Init]I_0 10^{-ε[Init]z}}{2k_t}}\right) t \quad [2-14]$$

The degree of polymerization $x_n$ is defined as

$$x_n = \frac{[M]_0}{[M]} \quad [2-15]$$
The relationship between degree of polymerization $x_n$ and extent of polymerization $p$ can be given as

$$x_n = \frac{1}{1 - p}$$  \[2-16]\n
Substituting this and squaring both sides yield

$$\left(\log(1 - p)\right)^2 = \frac{k_p^2 2 \phi e [Init] I_0 t^2}{2k_t} 10^{-e[Init]z}$$  \[2-17]\n
Curing depth is defined as the depth at which the extent of polymerization reaches a threshold $p_c$ known as gel point [20, 21]. At this threshold transition from polymer to monomer takes place and it limits the curing depth. Substituting this and taking natural log on both sides

$$z_c = \frac{2}{2.303 e [Init]} \log \left( \frac{k_p t}{\log(1-p_c)} \sqrt{\frac{2 \phi e [Init] I_0}{2k_t}} \right)$$  \[2-18]\n
Equation 2-18 reveals the dependence of curing depth $z_c$ on exposure time $t$ and initiator concentration $[Init]$. As initiator concentration is increased, the rate of reaction increases, however, the increase in initiator concentration decreases the amount of photon reached at depth $z$. These two conflicting behaviors give rise to an optimal value of initiator concentration beyond which curing depth starts to decrease. Differentiating $z_c$ with respect to $[Init]$ yields

$$\frac{\partial z_c}{\partial [Init]} = \frac{2}{2.303 e [Init]^2} \left( \frac{1}{2} - \log \left( \frac{k_p t}{\log(1-p_c)} \sqrt{\frac{2 \phi e [Init] I_0}{2k_t}} \right) \right)$$  \[2-19]\n
Equating it to zero yields the optimal value of $[Init]_0$ as

$$[Init]_0 = \frac{e k_t}{\phi e I_0} \left( \frac{\log(1-p_c)}{k_p t} \right)^2$$  \[2-20]\n
Putting the value of $[Init]_0$ in the Equation 2-18 yields
Figure 2-1 shows a plot of curing depth as a function of both initiator concentration and energy dose. Curing depth increases with an increase in energy dose. However, for increasing initiator concentration it first increases, attains a maximum value and then rolls off. As predicted by Equation 2-20 the optimum value of initiator is a function of energy dose also. Due to this, the maximum value of curing depth in Figure 2-1 is obtained at different values of [Init] for different values of energy dose.

**Effect of Absorber Addition**

Sometimes it is required to have a small curing depth. For instance in micro stereo lithography, if curing depth is too high then the step size needs to be high too which in turn reduces the lateral resolution [22].

In order to reduce the curing depth certain absorbers may be added to the monomer solution. The role of the absorber is to absorb the incoming photon thereby decreasing the reaction rate. Since absorber only affects the incoming photon and does not have any influence on generation of radical, in presence of absorber the rate of initiation of polymerization process can be written as

\[ R_l = 2\theta \varepsilon [Init] I_z = 2\theta \varepsilon [Init] I_0 10^{-(\varepsilon_{Init}[Init] + \varepsilon_{Abs}[Abs])z} \]

where [Abs] is the concentration of absorber in the monomer solution. Substitution of Equation 2-22 in to Equation 2-9 yields

\[ Z_c = \frac{2}{2.303(\varepsilon_{Init}[Init] + \varepsilon_{Abs}[Abs])} \log \left( \frac{k_p t}{\log(1-p_c) \sqrt{2\theta \varepsilon [Init] I_0}} \right) \]

Assuming absorber absorbs bulk of the light and contribution of initiator in light absorption is negligible as compared to absorber Equation 2-23 can be simplified to
Looking at Equation 2.24 it can be observed that curing depth is now a monotonically increasing function of initiator concentration. Hence by using an absorber curing depth can be controlled more accurately.

Differentiating Equation 2.24 with respect to \([\text{Init}]\) yields the maximum value of \([\text{Init}]\) up to which monotonicity is insured. The maximum value of \([\text{Init}]\) is thus given by

\[
[\text{Init}]_{\text{max}} = \frac{k_t}{\phi \epsilon I_0} \left( \log \left( \frac{k_p t}{\epsilon} \right) \right) \left( \frac{\epsilon_{\text{Init}}[\text{Init}] + \epsilon_{\text{Abs}}[\text{Abs}]}{\epsilon_{\text{Init}}[\text{Init}]} \right)^2 \approx [\text{Init}]_0 \left( \frac{\epsilon_{\text{Abs}}[\text{Abs}]}{\epsilon_{\text{Init}}[\text{Init}]} \right)^2
\]

Equation 2.25 predicts that by addition of absorber, the optimum value of \([\text{Init}]\) can be increased substantially and thus curing depth can be controlled more precisely by changing the initiator concentration.

### Effect of Temperature

Temperature plays a major role in the polymerization reaction rate. Reaction rate can be increased exponentially by increasing the temperature. Since polymerization reactions are usually exothermic, the temperature of monomer solution increases as reaction proceeds further. This increased temperature can drastically change the curing depth. Thus it is necessary to model the effect of temperature on curing depth model derived in previous section. While deriving the curing depth equation, it was assumed that except for \([M]\) every other parameter is temperature independent. However, this is not quite the case. Both initiation rate and termination rate of radicals are altered by changing the temperature of the monomer solution. The reaction rate constants of radical initiation \(k_p\) and termination \(k_t\) are strong function of temperature. Their value can be given by Arrhenius relationship
If the temperature of system changes with time, value of $k_p$ and $k_t$ also changes with time. As the reaction proceeds, the temperature of the system increases due to heat released by enthalpy of reaction. As the temperature increases, the reaction rate increases and polymerization goes on deeper and deeper. By including the temperature effect it is expected to have a larger value of curing depth as compared to the case without temperature consideration.

The rate of increase of temperature can be computed by the total heat generated by the polymerization reaction. If $\Delta H$ be the amount of heat generated per mole of the polymer then

\[
\frac{nC_p}{\partial t} = A_{exposure}\Delta H \frac{d[M]}{dt} = \left(\Delta Hk_p[M]\frac{20\varepsilon[Init]I_010^{-e[Init]z}}{2k_t0}\right)\left(e^{-\frac{Eap}{2kT}+\frac{Eal}{2kT}}\right)
\]

\[
-\frac{d[M]}{dt} = k_p0[M]\frac{20\varepsilon[Init]I_010^{-e[Init]z}}{2k_t0}\left(e^{-\frac{Eap}{2kT}+\frac{Eal}{2kT}}\right)
\]

Inclusion of temperature dependence prohibits the derivation of a closed form equation for curing depth. In order to compute curing depth as a function of time, Equations 2-28 and 2-29 needs to be solved numerically. However, the curing depth $z_c$ is not an independent variable, routine methods of solving ODE does not work here.

In order to obtain curing depth as function of time, curing depth is set to a particular fixed value and then Equations 2-28 and 2-29 are iterated to obtain the time required to reach the gel point. This method is then iterated for different values of curing
depth to plot curing depth as a function of time. The differential equations are solved in MATLAB® using ode45 solver.

Figure 2-2 shows the curing depth as a function of time for different areas of exposure. As the area of exposure is increased, curing depth increases drastically. As the curing depth is a strong function of temperature, if a smaller area is exposed the rise in temperature is insignificant. For smaller area the curing depth is similar to as predicted by Equation 2-8. For large area of exposure curing depth increases significantly initially and then rolls off. The same behavior can be observed in temperature profile also as shown in Figure 2-3.

Figure 2-3 shows the change in temperature as a function of time, it is interesting to note that temperature starts to increase rapidly but then rolls off. The primary reason behind such a behavior is the fact that as time passes by, more and more reaction goes to completion and thus the heat generated rolls off as time passes by.

The strong temperature dependence can be observed by looking at $T = 200$ sec. Even for a temperature difference of $15^\circ C$ the change in curing depth is more than 40%. Also the % change in curing depth is at its maximum at start and then it keeps a constant value. Both of these factors points to the fact that temperature plays a major role in curing depth.

**Experiment Setup**

In order to verify the validity of curing depth model proposed, experimental study of curing depth is performed. The monomer used for the curing depth study is HDDA (Hexanediol Diacrylate). HDDA’s chemical structure is shown in Figure 2-4. The photo initiator used is 2-hydroxy-2-methylpropiophenone and photo absorber used is 2-hydroxy-4-(octyloxy)benzophenone. The chemical structure of photo initiator and
absorber is shown in Figure 2-4 A and 2-4 B. The concentration of photo initiator is taken as 2% and 4% and concentration of absorber is taken as 1% and 3%. Mercury lamp is used to produce illumination. The UV lamp produces monochromatic light of wavelength 365nm with divergence less than $2.5^0$.

The experimental setup for curing depth study is shown in Figure 2-5. A clear glass plate is used as mask and is kept in contact with the monomer solution. The top surface of the glass mask is covered with a UV blocking layer. A small square opening of $1\text{mm}^2$ is cut at the center. The reason behind exposing a small area is to minimize the temperature effects.

The UV light intensity is kept at its maximum value of $13.1\text{mW/cm}^2$. Exposure dose is varied by opening the shutter for a variable time. Shutter is opened from 10s to 200s in the step of 10s. The resulting structure formed is then rinsed with methanol and dried off by blowing nitrogen to remove any un-polymerized monomer. After rinsing the thickness of polymer is measured using a screw gauge. The curing depth is then plotted as a function of time and is shown in Figure 2-6 to Figure 2-9.

Figure 2-6 and Figure 2-7 shows the curing depth as a function of time for different initiator and absorber concentrations. It is readily visible that with an increase in initiator concentration curing depth increases.

The dependence of initiator concentration on curing depth can be computed as follows. Equation 2-6 can be simplified as follows.

$$Z_c = \frac{2}{2.303 \epsilon_{Abs}[Abs]} \log \left( \frac{k_p t}{\log(1-p_c)} \sqrt{\frac{20 \epsilon_{Init} t_0}{2k_t}} \right) = A \log(t) - B$$  \[2-30\]

$$A = \frac{2}{2.303 \epsilon_{Abs}[Abs]}; \quad B = A \times \log \left( \frac{\log(1-p_c)}{k_p} \sqrt{\frac{2k_t}{0 \epsilon_{Init} t_0}} \right)$$  \[2-31\]
For absorber = 1%, \((B_1/A_1) - (B_2/A_2)\) yields 0.53 whereas \(\log(\sqrt{2})\) has a value equals 0.35.

For absorber = 3%, \((B_1/A_1) - (B_2/A_2)\) yields 0.45 whereas \(\log(\sqrt{2})\) has a value equals 0.35. The slight discrepancy is due to the fact that curing depth is computed using steady state assumption which gives rise to square root dependence. When steady state is not obtained initiator will have dependence which is greater than square root as rate of initiation is higher than rate of termination.

Figure 2-9 shows the curing depth as a function of time for different absorber concentration. It is readily visible that with an increase in absorber concentration curing depth decreases.

In order to understand the significance of curing depth, another experiment for constant curing depth is performed. If two different solutions have same curing depth then the resulting polymerized structure would be the same. The overall process does not depend on the individual absorber and initiator concentration but depends upon the curing depth. In order to validate this hypothesis Two monomer solutions, one having 1% initiator and 2% initiator and other having 3% absorber and 2% initiator are taken. Their curing depth curve is shown in Figure 2-10.

These two solutions are irradiated to the UV light of intensity 13.1 mW/cm\(^2\) with an area of exposure of 1 mm\(^2\). The mask contains two types of pattern which results in holes of 82 µm and 164 µm diameter with 100 µm and 200 µm of pitch and posts of the same dimensions as holes.
The two monomer solutions were irradiated for the same amount of time = 100s. Solution of low absorber has a very high curing depth and thus results in loss of features. The results are shown in Figure 2-11. Also, the loss of feature is more pronounced in the structure with lower feature size.

Solution having 3% absorber and 4% initiator is abbreviated as Solution 1 and Solution having 1% absorber and 2% initiator is abbreviated as Solution 2.

The case for constant curing depth is shown in Figure 2-12. The solution with lower absorber concentration is irradiated for a smaller period of time. Looking at the Figure 2-9 for a constant curing depth of 100µm, Solution 1 is exposed for 20sec and solution 2 is exposed for 100 sec. The resulting structure is shown in Figure 2-12.

By observing Figure 2-12 it can be said that both the solutions resulted in similar looking structures. However, the exposure time is greatly reduced for solution with low absorber concentration. It is evident from Figure 2-11 and Figure 2-12 that curing depth is among the most important parameter for polymerization process. If two monomer solutions have same curing depth then they will result in similar looking structures despite having entirely different absorber and Initiator concentrations.

Curing depth can be tuned by varying initiator and absorber concentrations, however, addition of absorber makes the tuning easy. An increase in absorber concentration will decrease the curing depth and increase in initiator concentration will increase the curing depth. Their dependence is derived analytically in Equation 2-24.

Another important parameter is the temperature of monomer solution. It has exponential dependence on rate of reaction and thus it can change the curing depth substantially. The situation is exacerbated by the fact that temperature provides a
positive feedback and thus a large increase in curing depth is observed at the start of the reaction. This behavior result in print through error if a large area is exposed and temperature consideration is not taken into account.
Figure 2-1. Curing Depth as a function of both initiator and energy dose. The parameters used to generate this image are taken from. [12]
Figure 2-2. Curing Depth as a function of time and area of exposure. The red curve shows the curing depth for an exposed area of 1mm$^2$, the blue curve shows the curing depth for an exposed area of 10mm$^2$ and the green line shows the curing depth for an exposed area of 1cm$^2$. 
Figure 2-3. Temperature as a function of time and area of exposure. The red curve shows the curing depth for an exposed area of 1\text{mm}^2, the blue curve shows the curing depth for an exposed area of 10\text{mm}^2 and the green line shows the curing depth for an exposed area of 1\text{cm}^2.
Figure 2-4. Chemical structure of A) cis-7,cis-11-Hexadecadienyl acetate B) 2-hydroxy-2-methylpropiophenone and C) 2-hydroxy-4-(octyloxy) benzophenone [23].

Figure 2-5. Experimental setup used for curing depth study.
Figure 2-6. Curing depth as a function of time for constant intensity exposure and absorber concentration of 1%. The black line shows the logarithmic fit and its Equation is shown next to the curve.
Figure 2-7. Curing depth as a function of time for constant intensity exposure and absorber concentration of 3%. The black line shows the logarithmic fit and its Equation is shown next to the curve.
Figure 2-8. Curing depth as a function of time for constant intensity exposure and initiator concentration of 2%. The black line shows the logarithmic fit and its Equation is shown next to the curve.
Figure 2-9. Curing depth as a function of time for constant intensity exposure and initiator concentration of 4%. The black line shows the logarithmic fit and its Equation is shown next to the curve.

\[ y = 85.712 \ln(x) - 109.57 \]

\[ y = 34.896 \ln(x) - 59.415 \]
Figure 2-10. Curing depth as a function of time for constant intensity exposure. The two solutions have both different initiator and absorber concentration.

\[ y = 77.047 \ln(x) - 139.08 \]

\[ y = 34.896 \ln(x) - 59.415 \]

CHAPTER 3
DIVERGENCE STUDY

In proximity micro stereo lithography it is required to maintain the monomer top layer and mask in close proximity (~50-100 µm) to overcome the divergence of collimated light source. However, maintaining such a small gap during a polymerization run is troublesome. A number of factors can disturb the top layer of monomer and cause the monomer and mask surface to be in contact. Some of the factors are vibration due to stepper motor and curling due to stress in the polymer structure. These factors further reduce the gap as the polymerization reaction proceeds making it more susceptible to unwanted contact.

The value of divergence angle of light source sets up a maximum value of the separation between mask and monomer layer. If monomer is beyond that limit, spatial resolution of resulting structure will be distorted or in a worst scenario everything will be exposed uniformly. To understand it more clearly consider the case shown in Figure 3-2. The mask consists of UV blocking holes as shown in Figure 3-1. The UV light is convergent with an angle of $\theta$. The diameter of resulting holes is shown as a function of depth. It is interesting to note that diameter of holes first increases and then starts decreasing. Also when it obtains its maximum value the light can also start making diffraction patterns which will result in distorted shape.

**Experimental Setup**

In order to quantify the result, a divergence study is performed. Si wafers are coated with SU-8 photoresist. It is a negative photoresist, used to make high aspect ratio structures. SU-8 has a maximum absorption at 365 nm which coincides with the
UV lamp used in this study. When exposed to light, it becomes insoluble to the photoresist developers. The chemical structure of SU-8 is shown in Figure 3-3.

The mask used to illuminate the wafer has a pattern as shown in Figure 3-1. The diameter of the hole is 41µm and the pitch is 50µm. The SU-8 coated Si wafer is put at a certain distance below the mask and then irradiated for 30 sec. The exposed wafer is then developed. The resulting pattern for different separation distance $d_{sep}$ is shown in Figure 3-4 A to Figure 3-4 E.

The diameters of the resulting holes on the Si wafer are tabulated in the table 3-1. The angle of divergence of light is calculated using the formula

$$\theta = 2 \tan^{-1} \frac{d_{hole} - 41}{2d_{sep}}$$

As noted from the table the angle of divergence of collimated light source is in the order of $1.3^\circ$. Using this value the maximum value of $d_{sep}$ can be computed by substituting $d_{hole} = 50 \, \mu m$. Substituting this, yields a maximum value of 400µm on separation between mask surface and monomer layer. At separation of 400 µm between mask and monomer, all lateral features will be lost. This case is shown in Figure 3-4 D. At 400 µm separation the definition of holes is completely lost and a strong interference pattern is observed. This interference pattern increases as separation between mask and monomer solution increases. Even at 200 µm the edges of holes are not perfectly round and presence of interference pattern can be observed along the edges. When the separation is higher than maximum allowed value the entire substrate is exposed. This can be seen in Figure 3-4 E where the separation is kept twice the maximum allowed value. In this case the entire SU-8 is exposed.
Divergence study becomes extremely useful to set the gap between mask and monomer layer. Since this gap is constrained by divergence of light source and also since the effect of interference increases with an increase in separation, a smaller value of gap is preferred. For typical cases the gap desired is usually tens to hundreds of micron. However, maintaining such a small gap during the polymerization process is a big challenge. Numerous factors can change the gap between mask and monomer and may result in unintentional contact between the two. The surface roughness of substrate itself is usually few tens of microns. It results in a big challenge to obtain a gap which is of the same order. Meniscus effect on edges also poses a challenge to obtain such a small gap. Apart from these factors the gap between mask and monomer layer changes during the polymerization process also. A very small vibration can cause a contact between mask and monomer layer. Also as polymerization process happens a new monomer layer comes on top of polymerized structure which further reduces the gap. Also if during the polymerization process if polymerized part is not fully cured and is under stress, it may bend and cause the monomer solution to contact the mask surface.

Taking these factors into consideration, the gap between monomer and mask can not be fixed to an arbitrary small value. As seen from the results, the lateral feature size does not degrade if the gap is kept less than half the maximum allowed gap. The divergence study not only provides an upper bound on the gap between mask and monomer but also provides the range on which the lateral resolution is preserved.
Table 3-1. Experimentally computed angle of convergence at different depth

<table>
<thead>
<tr>
<th>Separation in um</th>
<th>Diameter of hole in um</th>
<th>Angle of Divergence in °</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>42</td>
<td>1.16°</td>
</tr>
<tr>
<td>100</td>
<td>43.2</td>
<td>1.26°</td>
</tr>
<tr>
<td>200</td>
<td>45.4</td>
<td>1.26°</td>
</tr>
</tbody>
</table>

Figure 3-1. Profile of mask having walls between holes as opaque to UV.

Figure 3-2. Diameter of Hole as a function of Depth.

Figure 3-3. Chemical Structure of SU-8 Photoresist [24].
Figure 3-4. Structure developed on SU-8 coated wafer as a function of distance. A: $d_{\text{sep}} = 50\mu$m, B: $d_{\text{sep}} = 100\mu$m, C: $d_{\text{sep}} = 200\mu$m, D: $d_{\text{sep}} = 400\mu$m, E: $d_{\text{sep}} = 800\mu$m,
CHAPTER 4
CONCLUSION

Among the various parameters to characterize and control a polymerization process, curing depth is one of the most important parameter. It is directly responsible for the minimum lateral feature size. Hence to obtain a particular cross section, curing depth needs to be controlled very precisely. Also to avoid excess polymerization via punch through error, per step displacement and exposure dose is determined by curing depth and thus it has to be controlled accurately. An extensive mathematical model of curing depth is presented in this work. The effect of initiator and energy dose is derived and optimal curing depth is computed. As initiator has a complex dependence on curing depth, controlling the curing depth by just varying initiator is difficult. The optimal curing depth is not only a function of initiator but also of energy dose. In order to tune the curing depth more accurately, absorber is added so that effect of initiator is simplified. With the addition of absorber curing depth can be increased or decreased more accurately by increasing or decreasing the concentration of initiator or absorber. The mathematical model incorporating all of these factors is derived and verified using experimental results. The strong dependence of curing depth on lateral resolution also suggests that two solutions with similar curing depths will produce similar structure. This property of curing depth is verified using experimental results. These results suggest that monomer solution behaves according to curing depth which is a combination of both initiator and absorber concentration rather than their individual concentrations.

Another important parameter in characterizing micro stereo lithography is the divergence of collimated light source. This divergence sets the maximum allowable limit on the mask – monomer separation without loss of lateral feature size. The effect of
increasing separation on lateral feature size is demonstrated. This study not only provides an upper limit on allowable gap but also the safe region of operation to ensure lateral resolution is not distorted.

These two parameters are two of the most parameters in a micro stereo lithography process. These parameters can be used to obtain the value of different variables such as initiator and absorber concentration, exposure dose, step size and gap between mask and monomer. These are the main parameters in a lithography process. By performing a curing depth and divergence study, these parameters can be set accurately which will result in more accurate polymerization process.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Abhinav Pandey is a graduate student at University of Florida in Electrical and Computer Engineering. He received his Master of Science degree from University of Florida in spring 2011. He received his Bachelor of Technology degree from Indian Institute of Technology, Kanpur in Electrical Engineering in 2009.