FABRICATION OF HIGH-ASPECT-RATIO METALLIC MICRO-STRUCTURES BY REVERSE EXPOSURE METHOD

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Summary

High-aspect-ratio microstructures (HARMST) are commonly used in the integration of components to make functional microdevices and HARMST fabrication plays an important role in the micro-eletromechanical systems (MEMS) industry. Among the methods used to fabricate HARMST, LIGA is one of the best. Although the LIGA process is well developed, it is not used widely because it needs expensive X-ray sources for exposing the resist. Another way for fabricating HARMST is to use a thick photoresist and expose it by UV-lithography. SU-8 resist is the forerunner of commercial high-viscous photoresists in high-aspect-ratio applications. This is due to the low optical absorption of SU-8 near UV range which results in vertical sidewalls and uniform exposure. UV sensitive characteristics, high viscosity, and high functionality are some of the advantages of SU-8. In comparison to LIGA, it has provided the possibility to produce HARMST at lower cost.

This project looks into the use of SU-8 as an electroplating mold to fabricate high-aspect-ratio metallic microstructures. For the fabrication of SU-8 mold without cracks and delamination, key parameters affecting SU-8 photolithography process are first studied. These include pre-baking and post-exposure-baking time and temperature, exposure time, and relaxation time after pre-baking and before development. For UV exposure, a preliminary investigation is first conducted on two exposure methods: top-side and reverse-side. The reverse-side method is then chosen as it has several advantages in comparison to the top-side method, such as no UV light reflection as the light passes through the substrate, which is a drawback in typical UV lithography. Due to the hard contact without air gap between photomask and photoresist, the image resolution is high with no edge bead. Also in the reverse-side method, the UV light exposure window is wider and easier to control than the more commonly used top-side method.

After reverse-side exposure, the fabricated SU-8 mold is plated by nickel electroplating. Electroplating parameters have been studied and a pulse-plating method has been identified to have a good result for electroplating.

Finally, methods of fabrication micro-gear structures have been studied. The aim is to find a method to separate the metallic micro-gear from the SU-8 mold easily. Sacrificial photoresist, sacrificial photoresist and transparent resist, PDMS, and sacrificial copper methods have been investigated for the fabrication of the micro-gear structure. The conclusion is that using copper as a sacrificial material is more practical than the other methods. Using this method, a high-aspect-ratio metallic microstructure has been fabricated in an inexpensive way.

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1 Introduction

1.1 Background

Micromachining or microfabrication is a crucial process in the development of technologies to manufacture small three-dimensional structures with dimensions in the range of millimeters to nanometers, such as microdevices, microsystems, actuators and sensors. These include the use of a set of manufacturing methods that rely on thick and thin film batch fabrication methods for integrated electronic circuit. In general, the term micromachining usually refers to the use of precision technique such as lithography, for fabricating three-dimensional microstructures.

From the aforementioned, we can achieve miniaturization of devices with capabilities not possible to achieve by other conventional machining methods. Miniaturization has several advantages such as:

- Decrease weight
- Decrease volume
- Decrease costs
- Increase performance
- Increase reliability
- Increase speed

The demand for high-aspect-ratio microstructures (HARMS) has been increasing in the MEMS industry. HARMS are used in mechanical, biomedical, chemical, and electrical systems and devices including micro accelerator [1], micro-actuator [2, 3], polymerase chain reaction (PCR) system [4], micro mixer and reactor [5]. For example, a high-aspect-ratio metallic microstructure with vertical sidewalls can increase the output force of a micro-actuator [3], and it can hence be used as a mold for replica multichannel polymer chips [2]. Metallic high-aspect-ratio microstructures have several advantages including [6]:

- low driving voltage,
- larger displacement in actuator systems,
- increased structural rigidity,
- higher actuation force,
- large magnetic force due to the large volume,
- larger displacement in actuator systems,
- higher sensitivity in sensor application by virtue of large mass

Usual methods for fabricating HARMS include LIGA (Lithographie Galvanoformung Abformung), LIGA-like, and DRIE (Deep Reactive Ion Etching) processes. LIGA is a well-known method to make HARMS with a few millimeters in height and aspect ratios of up 100:1. One of the major problems of this method is its need for X-ray source. LIGA-like is a low-cost HARMS fabrication method using SU-8 as a resist but its aspect-ratio and resolution are lower than LIGA process. Another option to make HARMS is to use DRIE to make deep silicon trenches.

Electrodeposition through a mask is one of the main steps for the fabrication of electronic microstructures and three-dimensional devices in MEMS. Thick microstructures such as HARMS can be easily fabricated by this additive process, which selectively electroplates HARMS on conductive layers. By this method, thick microstructures can be easily fabricated in a simple, low-cost process at ambient temperature.

1.2 Objectives

To fabricate high-aspect-ratio metallic microstructure, three objectives are targeted. They are as follows:

1. For the fabrication of high-aspect-ratio metallic microstructures, the first need is the fabrication of a SU-8 micromold. When a thick photoresist is used as material for the mold fabrication, several problems must be solved, such as:

- Edge bead
- Resist cracking
- Resist delamination
- Resist residue

In this project we try to find a way to solve all these problems by optimizing the photolithography parameters and using a proper method for exposing UV light.

2. The second objective is proper nickel electroplating for filling the inside of the micro-mold. In this project, the parameters of electroplating are studied, and different electroplating methods are tried to overcome electroplating problems.
3. The last objective is to find a fabrication method which eases the process of separating the nickel microstructure from the SU-8 micro-mold. A good fabrication method should be fast and should separate the microstructures from the mold completely without any SU-8 residue. In this project, several fabrication methods are studied to choose the best among all.

1.3 Organization

The thesis is organized as follows:

- Chapter 2 introduces MEMS and discusses the major methods in MEMS fabrication and their limitations.
- Chapter 3 describes SU-8 as a negative epoxy resist and discusses its physical and chemical characteristics.
- Chapter 4 presents the UV exposure methods and the selection of the reverse method. It describes the preparation of exposure mask for SU-8 lithography and the details of photolithographic process of SU-8, and discusses micro-cracks and delamination, and means of their removal.
- Chapter 5 describes the electroplating process and the parameters affecting electroplating and the problems during electroplating.
- Chapter 6 presents the fabrication of SU-8 mold without cracks and delamination and means to optimize the electroplating of the mold.
- Chapter 7 discusses the fabrication process of a micro-gear structure that facilitates the separation of the nickel structure from SU-8 mold. This chapter demonstrates several methods for fabrication of micro-gears.
- Chapter 8 gives the conclusions and recommendations for future works.

2 Microfabrication techniques

2.1 MEMS

Mems (MicroElectroMechanical Systems) is the technology which integrates functional microsystems such as micro-electrical, mechanical, optical and other components to enable the whole system to sense, decide and react [7]. MEMS was termed around 1987 and referred to other related terms such as Micro Systems Technology (MST in Europe), Micromachines (in Japan), Micromechanics, MicroMachining Technology, Microdynamics, Micromechatronics, MicroEngineering Technology and MicroInstruments. Although "Micro" word in these terms means micro scale, it can be as large as a few centimeters.

MEMS is a vast and broad collection of microfabrication methods for building microstructures which can be integrated with electronic circuitry, resulting in new products and new product concepts. In fact, MEMS applications are more diverse than purely microelectronic integrated circuit (IC) applications. A map of MEMS applications is shown in Figure 2-1[8].

The first effort of MEMS application was back to the 1950's for silicon-based pressure sensors [9]. From that time until 1980's the pressure sensor technology changed to a low-cost manufacturing technology in batch size. During this period, many microfabrication processes were developed that were suitable for MEMS. About 1987, a series of workshops on MEMS and the MEMS term was announced as the start of a new field which integrates many fields of science and engineering [10]. The 1980's and 1990's were productive decades for MEMS industry. In 1982, the first 40,000 micromachined pressure sensors were produced for medical industry [11]. In 1994, this amount reached 20 million. Also, in 1982, 100,000 micromachined pressure sensors were produced for automotive industry but in 1994 this amount was over 25 million [12]. In the academic area, the number of conferences and journals in the MEMS area is increasing. Hence, government funding in this area is increasing too. But still there are many challenges in this technology and commercialization of this area which needs to be solved.

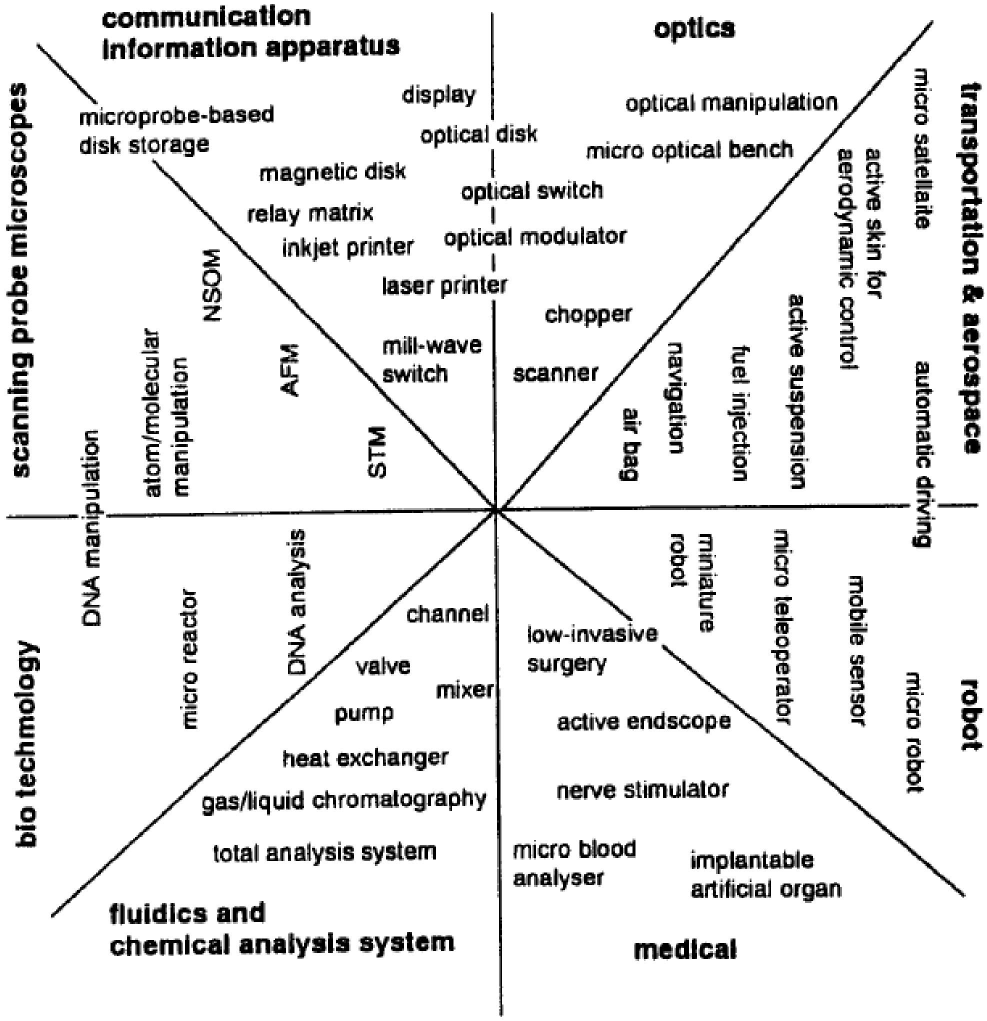


Figure 2-1 A map of MEMS applications [8]

There are several methods for fabrication of MEMS. This chapter will review microelectromechanical systems (MEMS). Then it discusses the major methods in MEMS fabrication and their limitation.

2.2 MEMS fabrication technologies

There are several microfabrication technologies which MEMS designers use in their microdevices. Bulk micromachining, surface micromachining and high-aspect-ratio machining are the three major ones for MEMS [13,14] in which photolithography, chemical and plasma etching, thin-film deposition and other manufacturing process originate from integrated circuit technology and microelectronic. Manufacturing processes such as surface micromachining and bulk micromachining refer to conventional techniques. The other methods such as LIGA developed for MEMS are referred to non-conventional techniques. In the following, the major MEMS fabrication methods will be discussed.

2.2.1 Conventional fabrication techniques

Bulk micromachining

In 1960's, this process was developed for precise silicon etching. During this process, a silicon wafer is covered by a mask and etched in desired orientation by etching solution. The solution removes unwanted parts and forms the microstructure. Figure 2-2 shows several constructions formed by this fabrication method such as beams, bridges, nozzle and membrane. [15]

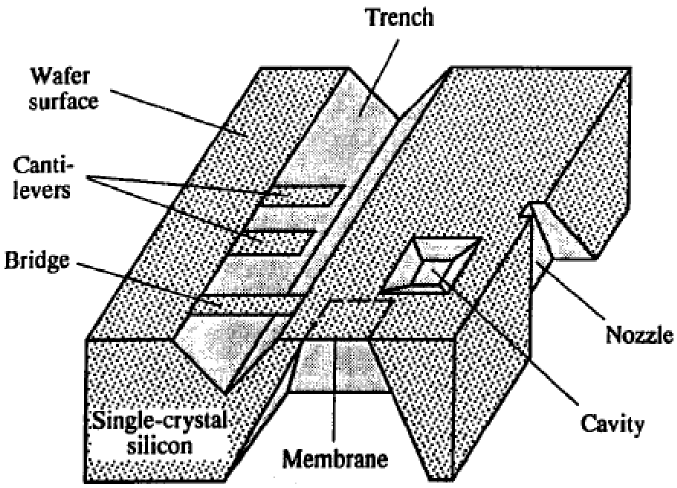


Figure 2-2 various bulk micromachining structures [16]

Surface micromachining

In this method, devices are formed by methods such as patterning, deposition, and etching of sacrificial and structural thin films on the silicon wafer. The fabrication of more complex structures than bulk micromachining is possible. Figure 2-3 shows a typical surface micromachining structure. [15]

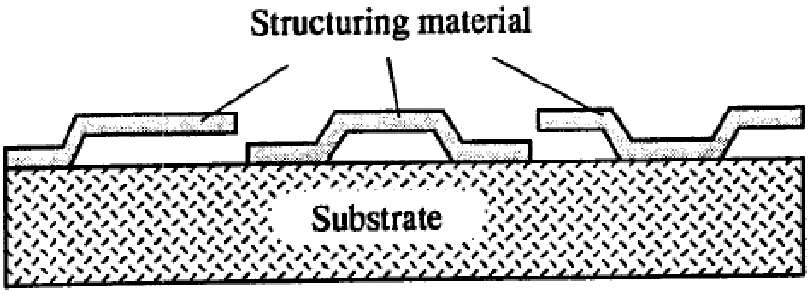


Figure 2-3 Typical surface micromachining structure [17]

2.2.2 Non-conventional micro-fabrication methods

In the following, we will discuss about the techniques known as high-aspect-ratio 3D microstructures.

LIGA

LIGA is a German acronym for Lithographie (lithography), Galvanoformung (Electroplating) and Abformung (Molding). This process was developed at the Institute for Nuclear Process Engineering in Karlsruhe of Germany in 1980s to make nozzles for uranium enrichment [18]. It can produce small precise structures with the heights of several hundred micrometers to 1 mm, or with the aspect ratio of more than 100. Figure 2-4 shows the LIGA process.

The limitation of LIGA is its need for X-ray synchrotron radiation source. The problem of X-ray source is not limited only to its cost, but also it is not adapted to the standards of cleanroom. So, the LIGA technique is not used widely except by a few research organizations [14]. This restriction encouraged the researchers to find other alternatives such as LIGA-like processes instead of LIGA technique.

LIGA-like processes

LIGA-like processes are the techniques similar to the LIGA process but at very low cost to make high-aspect-ratio structures.

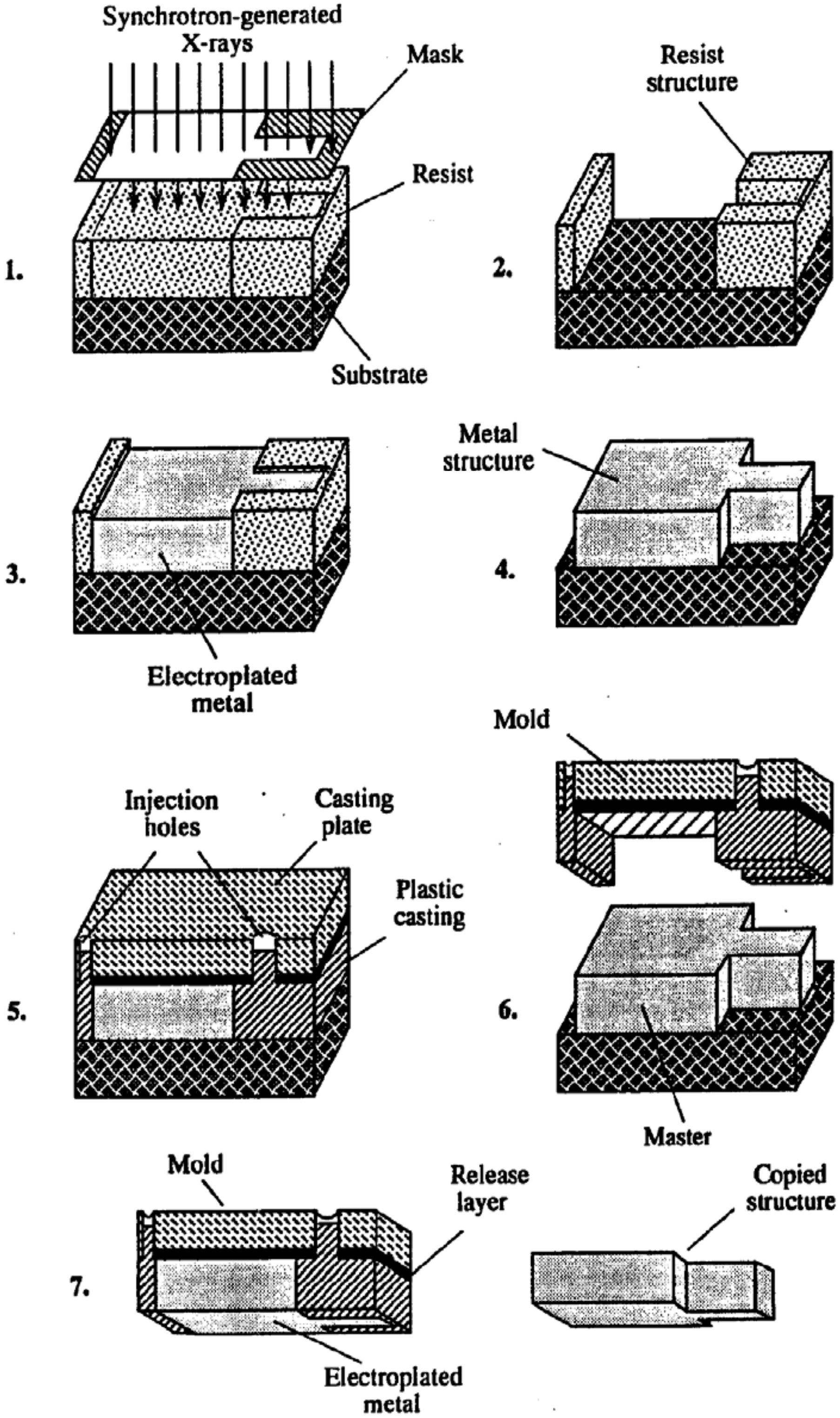


Figure 2-4 Steps in LIGA process [19]

In these processes, conventional UV is used instead of expensive synchrotron X-ray. Hence, the whole process can be done in a cleanroom. This process can be done in two ways: making molds from the thick photoresist photolithography, or dry etching of silicon wafers.

Thick photoresist:

Many efforts have been done for using thick photoresist in MEMS fabrication industry. Polyimide was used by several research groups as electroplating mold for fabrication of metallic structures [20]. It can be spun in the range of 10-50µm thickness just in a single coating.

A thick positive photoresist such as AZ4620 can reach to the thickness of 2-10µm in one single coating. Therefore, it is possible to reach a thickness of 35µm by triple coating and 22µm by double coating with good resolution [21].

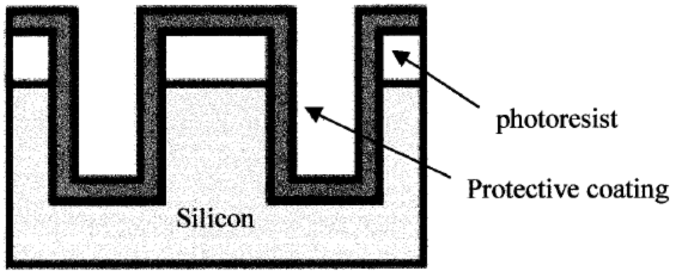
But all of these photo resists have two main problems: hard to coat thicker than 50µm and their lower resolution.

The advent of SU-8 made a revolution in the ultra-thick photoresist. The characteristics of this photoresist will be discussed in the next chapter. By using this photoresist, 650µm thickness can be achieved in a single coating. Hence it is possible to obtain more than 1 mm by using multiple spin coating. SU-8 is a low-cost process and has good mechanical properties and it can be used as a mold for subsequent process such as injection molding and electroplating.

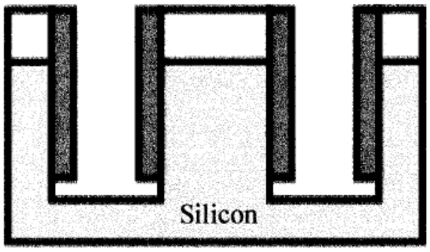
DRIE:

DRIE is an acronym for Deep Reactive Ion Etching. By this new dry etching method, aspect ratios of more than 50 can be obtained [22]. This is a two step process (Figure **2-5**).

In the first step, a passivating polymer is coated by the plasma deposition method on a patterned silicon wafer. In the second step, the desired parts will be etched. In this step, the fluorine radicals ionized of SF6 remove the protective coating from the area parallel to the substrate surface. Then, it starts to etch the exposed silicon area anisotropically in the normal RIE mode until it forms the desired vertical sidewall [23]. DRIE process made a revolution in bulk micromachining. It can be used to etch shallow and deep structure into the back side and front side of a wafer. It can also be used to etch through the wafer completely.



(a) Deposition



(b) Etching

Figure 2-5 Schematic of DRIE process

Multi-layer process

The previous methods can just make a 2D pattern which is extended in the third direction. So it can form just cylindrical and prismatic shapes. Therefore, the structures which are formed by those processes are not really true 3D structures but they are 2.5D structures

[24]. To solve this problem, many modified LIGA processes have been developed. These processes just only provide stepped structures, conical structures and sloped side wall structures. The multi-layer process is one of these processes. Firstly, this method was developed for a three-layer structure. Figure 2-6 shows the process involves photolithography; electroplating and planarization.

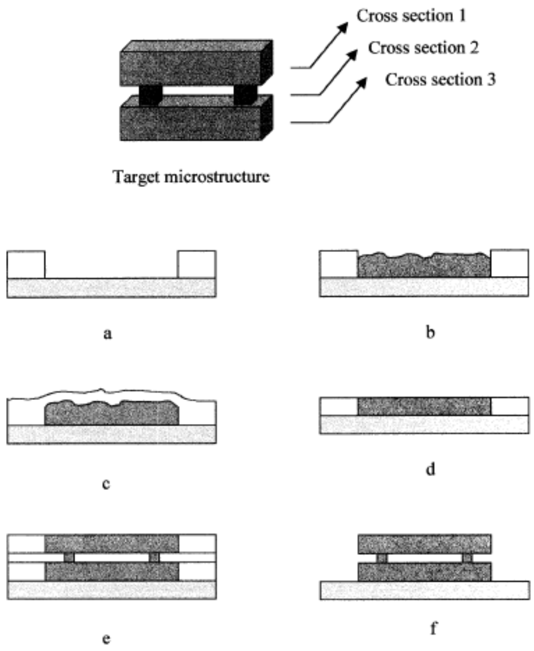


Figure 2-6 steps of multi-layer process [25]
a) Patterning of substrate b) Deposition of metal c) Stripping of photoresist and plating with sacrificial layer d) Planarization to reach to the desired thickness e) Repetition of the process f) Obtaining the 3D microstructure after stripping the sacrificial layer

Microstereolithography

This process is based on stereolithography which is used in rapid prototyping. This 3D microfabrication was developed in 1992 [26]. Figure 2-7 shows a schematic design of stereolithography machine used in the microstereolithography. The method of manufacturing is by stacking 2D layers and forms a 3D structure. UV curable polymer is used as material. In 1996, 2µm was reported as the minimum resolution of this process [27]. Microstructures manufactured by this method can be used directly or can be used as mold for plating metal structures. Figure 2-8 shows a fabricated chain by this method.

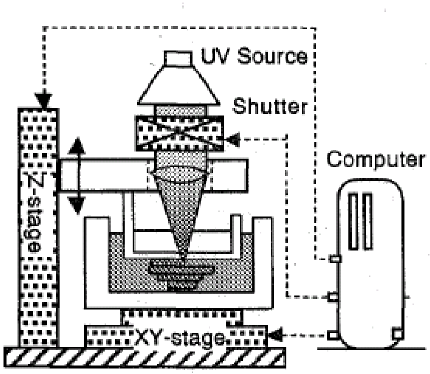


Figure 2-7 Schematic diagram of stereolithography desktop machine [28]

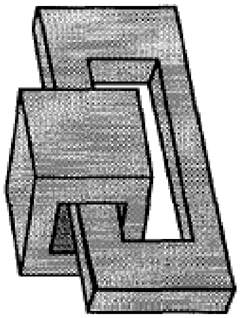
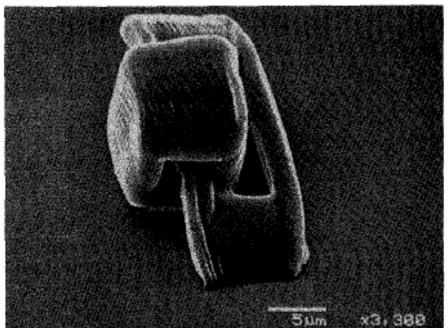
 (a) Schematic design of free connected chains [28]	 (b) SEM image of free connected chains made of solidified polymer [28]

Figure 2-8 fabricated chain by stereolithography method

3 Mold Fabrication

3.1 Photoresist

Photoresists are polymeric materials which make resist patterns on substrate by using photo-mask when they expose to ultra violet irradiation. Photoresists are classified into two groups: Negative and Positive resists. A positive resist is a resist with higher dissolution in exposed parts rather than in unexposed parts when exposed by UV while negative resist has the opposite effect. These resists can be divided into one-component or two-component systems [29]. One-component refers to sensitive homogeneous material. PMMA and COP are examples of positive and negative one-component resists, respectively. A two-component resist consists of a Photo-active component (PAC) in an inert matrix resin. A classical two-component resist is the novolac positive resist consisting of a novolac copolymer and a photo-active component called diazonaphthoquinone. Upon irradiation, the diazonaphthoquinone changes from a base soluble inhibitor to a base soluble photo-product so, the development of the resist results in direct copy of image (positive) from the mask on the substrate (

Figure **3-1**a).

A two-component negative resist is the cyclized polyisoprene synthetic rubber matrix with bisarylazide photo-active components, such as the Kodak KTFR. When the photoactive component releases acid due to irradiation, the matrix resin is polymerized to form inverse or negative patterns on the substrate (

Figure **3-1**b). Although this resist forms pinhole-free film, it has two problems. Firstly, oxygen in the resist radicals causes cross-linking. Hence, it is better that the resist is coated in nitrogen or vacuum environment. Secondly, swelling in the images of negative resist causes degradation of patterns, limiting the resolution (not greater than 2µm) [30]. These problems can be solved by using SU-8 insist of negative resist Kodak KTFR.

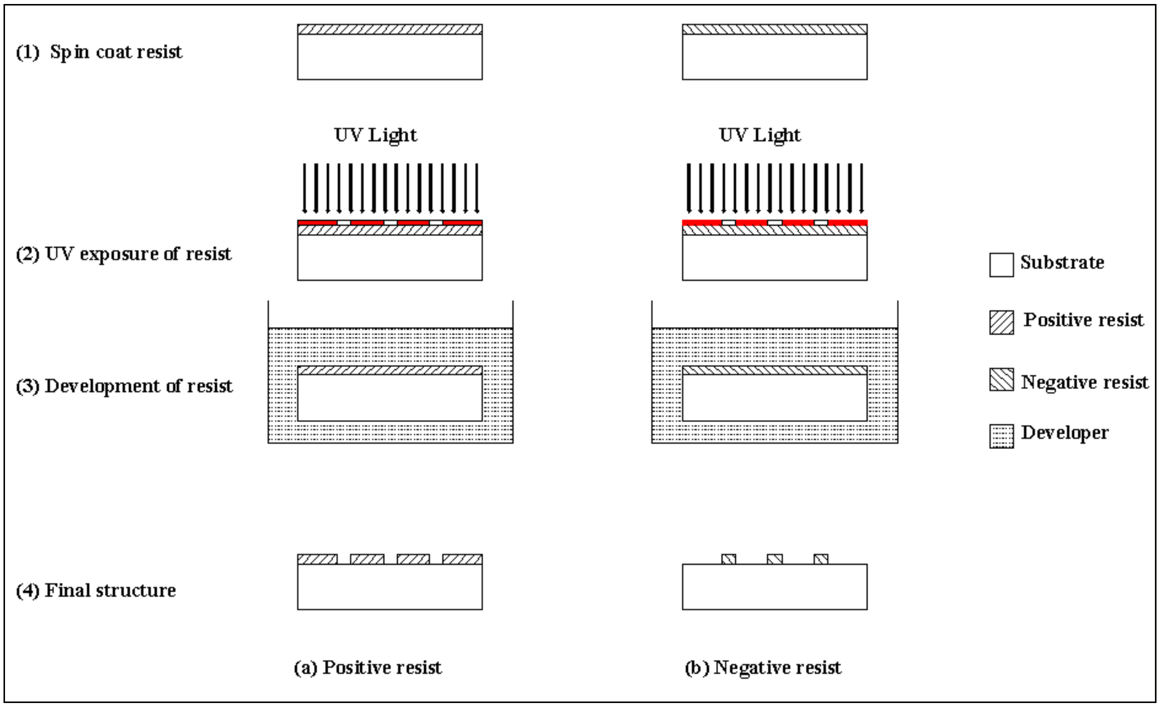


Figure 3-1 Process sequences for positive and negative resist

3.2 SU-8: Negative Epoxy Resist

SU-8 is a negative resist and its name is derived from EPON™ resin SU-8, which is the trademark of Shell Chemicals [31]. IBM developed a two-component negative photoresist which consists of EPON™resin SU-8 and a photo-initiator called triarylsulfonium salt dissolved in gamma butyrlactone (GBL) solvent. Chemically, SU-8 is known as glycidyl ether derivative of bisphenol-A novolac, which is a transparent solid epoxy resin. Photoresists such as SU-8 are based on epoxies. The prefix of epoxy refers to a bridge which consists of an oxygen atom linked to two other atoms, most often carbon, already combined in some way. This kind of structure is called 1,2-epoxide (Figure 3-2). A molecule which contains one or more 1,2-epoxy groups is defined as an epoxy resin. These molecules are able to convert to a thermoset form or three-dimensional network structures. This converting process is called crosslinking or curing [32].

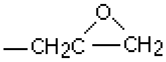


Figure 3-2 1,2-epoxy ring

3.2.1 Cross-Linking [32]

The process by which one or more types of reactants, i.e., a curing agent and an epoxide are changed from a low molecular weight to a highly crosslinked network, is called crosslinking or curing.

There are three categories for epoxy resin curing agents:

- Active hydrogen compound, which is cured by polyaddition reactions.
- Ionic initiators, which are subdivided into anionic and cationic.
- Crosslinkers, which couple through the hydroxyl functionality higher molecular-weight epoxy resins.

SU-8 has an average of eight functional epoxy groups (the highest functionality obtained commercially) to maximize resist sensitivity (Figure 3-3). Due to its low molecular weight (4000±1000 amu) dissolution of a wide range of solid SU-8 in solvent GBL is possible. Therefore, it produces resists of wide range of viscosity; so it can be possible to have film thickness from a few μm to a few hundred μm by spin-coating.

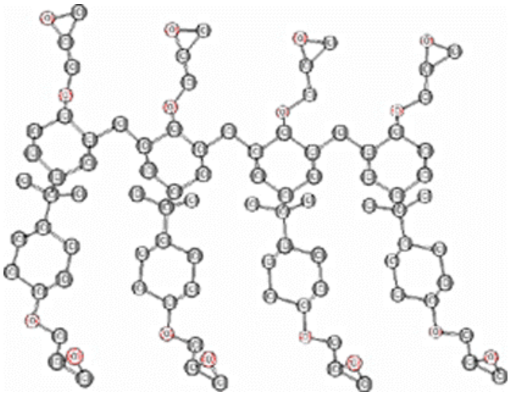


Figure 3-3 Basic SU8 molecule, note the 8 epoxy groups [32]

The melting point of solid SU-8 is 82°C but after curing and polymerization, the transition temperature (T_g) will reach 200°C. This high transition temperature causes the resist to have thermal stability and an excellent resistance to plasma etching. As Figure 3-4 shows, there is negligible absorption of UV radiation when the wavelength is greater than 360nm. Hence, it makes constant exposure of resist throughout the film, therefore vertical side walls with aspect ratio of 18:1 is possible. The photo-active component used in SU-8 resist is an onium salt called tri-aryl-sulfonium salt. This salt contains three aromatic compounds (aryl) covalently bonded to center sulphur atom, which is ionically bonded to a Lewis acid (e.g. BF_4^-, PF_6^-, AsF_6^- and etc.). One specific example of tri-aryl-sulfonium salt is triphenyl-sulfonium hexaflouroantimonate (Ph_3SSbF_6).

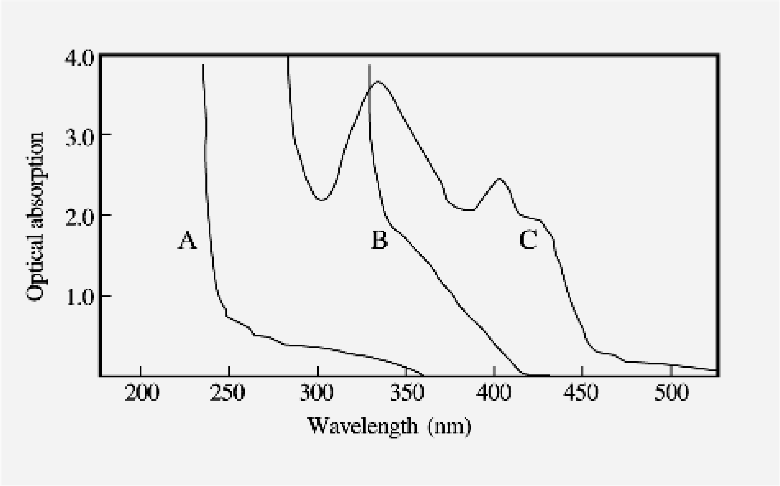


Figure 3-4 Optical absorption vs. wavelength for 25µm SU-8 resist (A=SU-8, B=Riston, C=novolac)[33]

3.2.2 The polymerization reactions of SU-8

A negative resist can become insoluble through free radical polymerization of bis-aryldiazide and can be polymerized by cationic polymerization. Unlike bis-aryldiazide, cationic polymerization of the resist films cross link SU-8. When UV irradiates, the tri-arylsulfonium salt is reduced to radicals (aryl and diarylsulfonium radicals) and then it reacts and forms strong acids which starts the cationic polymerization process [30].

There are three reaction steps for the cationic polymerization (Figure 3-5) of SU-8 [34]. They are photolysis, initiation and preparation steps. UV radiation breaks down the tri-arylsulfonium salt to generate Lewis acids. These acids react with the monometers to form the three-dimensional cross-linking polymers. The polymerization is done by the ring-opening of the 1,2-epoxy.

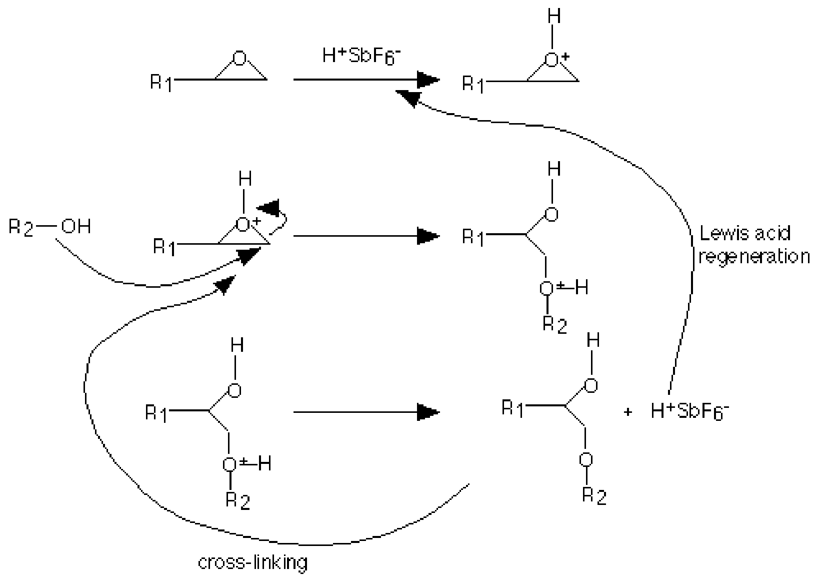


Figure 3-5 Cationic polymerization [32]

3.2.3 Photolysis of tri-arylsulfonium salts

Photolysis of tri-arylsulfonium salts can be divided into three steps. First step includes the separation of a carbon to sulfur bond by UV irradiation to form a diarylsulfonium cation radical, an aryl radical and anion. Secondary radicals will be resulted by further interactions between the monomer and radical species. Then hydrogen ions will be released to form strong acids (HPF_6, HBF_4 and etc) which are the initiators of the polymerization process.

In comparison with the other photo-initiators, using tri-arylsulfonium salts has different advantages. First of all, the presence of oxygen will not inhibit the photolysis process. Secondly, the photolytic rate and frequency response of the photo-initiators will be a function of the tri-arylsulfonium cations. By changing the cations, the rate and the frequency response of the photo-initiators can be changed. Thirdly, the easy photolysis of the tri-arylsulfonium salts does not relate to thermal decomposition. In the opposite direction, it can be seen that at higher temperature such as 150C, after several hours, only small thermal decomposition will occur. [30]

3.2.4 Initiation and propagation of polymerization

As described before, when UV irradiates, strong Lewis acids will form to make the initial protonation of monomer. One example is in multifunctional novolac-epoxy resin. The epoxy groups are attacked by Lewis acids and these acids open up the epoxide ring for next polymerization

At room temperature, photo-initiated cationic polymerization can occur but it is better to have post-baking after exposure for thick resist to increase the rate of cross- linking process. Oxygen does not inhibit the resist polymerization and long storage time is possible with mixture of photo-initiators and monometer. [30]

3.2.5 Chemical properties of SU-8

While the swelling of the resist and the existence of oxygen affect free radicals polymerization, cationic polymerization is not affected but it provides great chemical properties which is good for LIGA- like processes. These chemical properties are:

- Resist sensitivity (minimum dose that gives dimensional equality of clear and opaque feature): it is optimized because SU-8 has the largest number of epoxy groups per molecule.
- Excellent contrast (contrast:$1/\log(D_f/D_i)$, D_f: Extrapolated dose for full thickness, D_i : idealized minimum dose): excellent contrast is possible because of the low molecular weight of SU-8 where the unexposed resist in comparison with the polymerized resist dissolves at a faster rate, so it gives a good edge definition.

Therefore, the resist is stable at high temperature; therefore it prevents degradation of resist contrast which is good for electroplating of high-aspect-ratio structures in hot bath.

- Obtaining different thickness from 1μm to 650μm by single resist spin. Low molecular weight makes dissolution of resist in solvent easier, so it is possible to obtain different thickness.
- Due to Figure 3-4, during exposure, UV absorption is negligible, so it results into the relationship between thickness and exposure time.
- Excellent thermal resistance and stability during process and etch resistance to reactive ion etching (RIE) because of high glass transition for cross-linked resist.
- High adhesive strength, so it allows higher film stress without peeling due to wafer dishing or bowing [30].

3.2.6 Mechanical properties of SU-8

Compared to metals and ceramics, polymers are mechanically weaker in toughness and mechanical strength. But if densities are considered, they have equivalent specific strength and toughness [35]. Mechanical properties of SU-8 can be easily modified by energetic beam to shape cross-linked network which results into an increase in molecular weight but also film embitterment. Automotive industry has several efforts to develop ways to minimize such effect to increase the polymer’s life period, while, semiconductor industry has used this effect to make polymeric masks for next dry or wet etching of the under layer.

SU-8 can easily dissolve in solvent (GBL), so it allows the resist thickness to be from few microns to hundreds of microns by single spin-coating. When UV exposes, polymerization occurs to make highly cross-linked regions with high hardness but low toughness. Furthermore, the adhesive strength of epoxy bond allows highly stress SU-8 deposits on the substrate without any delamination.

Table 3-1 shows an overview of several mechanical and chemical properties of SU-8 photoepoxies:

Table 3-1 Mechanical and chemical properties of SU-8 [32]

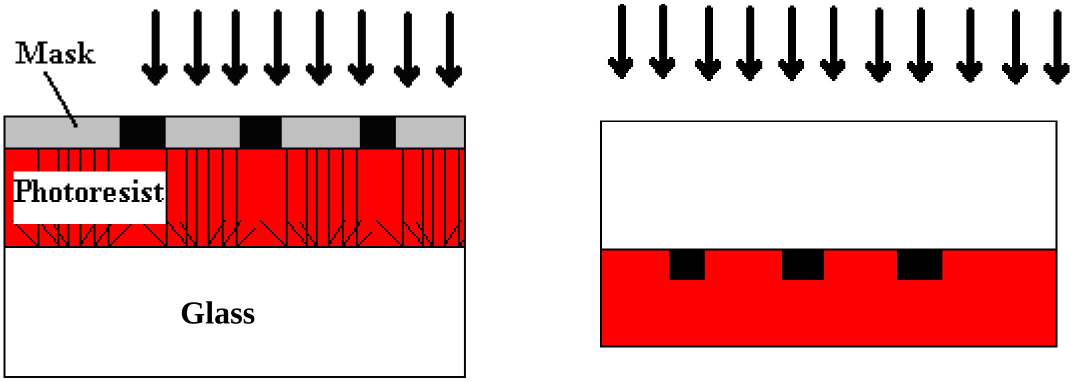
Young's modulus E	4.4 GPa
Poisson's coefficient	0.22
Viscosity	40% SU8-60% solvent : 0.06 Pa.s 60% SU8-40% solvent : 1.5 Pa.s 70% SU8-30% solvent : 15 Pa.s
Coefficient of thermal expansion CTE	50 ppm/K
Thermal conductivity	0.2 W/m K
Glass temperature	Tg: 200 °C
Degradation Temperature	~380 °C
Refractive index n	1.8 at 100 GHz 1.7 at 1.6 THz
Absorption coefficient	2 /cm at 100 GHz 40 /cm at 1.6 THZ
Relative dielectric constant	3 at 10 MHz

3.3 Comparison of reverse-side and top-side exposure

In this project we want to fabricate high-aspect-ratio metallic micro-structures using SU-8 mold. For the fabrication of SU-8 mold, we employ photolithography. If we use glass as substrate in photolithography, for exposing UV to SU-8 photoresist, there are two ways, top side and reverse side. In the following, we will discuss about the advantages and disadvantages of these two ways.

3.3.1 Light reflection from substrate

In the common top-side UV exposure method, UV light goes through the mask, then photoresist and at lastly reaches to the substrate (Figure 3-6.a). So, avoiding light reflection from the substrate is difficult and impossible. But in the reverse-side method, there is no UV light reflection in the photoresist layered during exposure. In this method, UV light goes through the substrate firstly (Figure 3-6.b) [36].

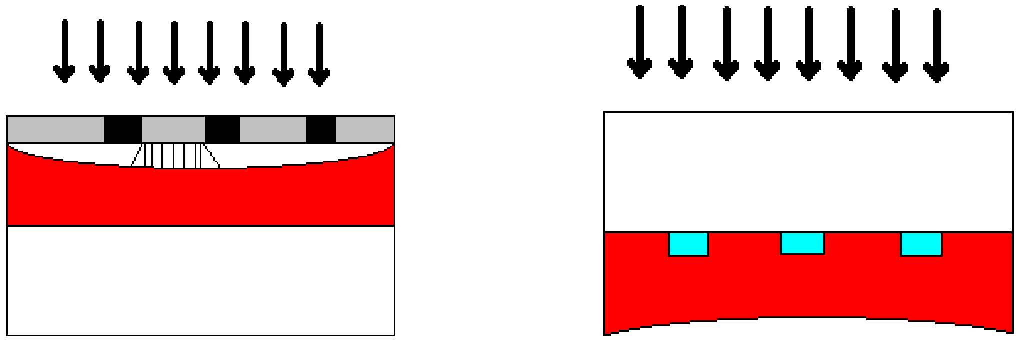


a)Top-side method b)Reverse-side method

Figure 3-6 light reflection in top-side and reverse-side method

3.3.2 Contact between exposure mask and SU-8

When thick SU-8 photoresist is coated on the substrate, edge bead happens. Edge bead in SU-8 is worse than the other photoresist because of its high viscosity. This is especially so when SU-8 is used for high thickness, requiring low spin-coat speed which causes the edge bead to be worse. Therefore, in the top-side method, there is usually an air gap between SU-8 and the exposure mask (Figure 3-7.a) which causes light scattering and decreases the image resolution. But in the reverse-side method, the contact is perfect and there is no air gap between photomask and photoresist (Figure 3-7.b), therefore the image resolution is high [36].



a)Top-side method b)Reverse-side method

Figure 3-7 Contact between exposure mask and SU-8 in top-side and reverse-side methods

3.3.3 Exposure window is wider and easier to control

In reverse-side method, the UV light exposure window is wider and easier to control than the common top-side exposure method [36].

3.3.4 No sticking of photomask to photoresist

In the reverse-side method, there is no direct contact between the photomask and SU-8 therefore the SU-8 photoresist does not stick to photomask and harm it.

Due to the advantages of reverse-side exposure, we decided to use this method in our project to fabricate high-aspect-ratio mold. In the following, we will discuss the methods to fabricate SU-8 molds.

3.4 Preparing exposure mask [37]

The first step for fabricating the SU-8 mold is preparing the exposure mask for SU-8 photolithography. For preparing of exposure mask, there are several photoresist options such as AZ 7220, AZ 4620, AZ 5214 and AZ 4330. All these photoresists can be used and there is not much difference in the results. In this project, AZ 7220 has been chosen.

***AZ 7220*:**

This photoresist is a high speed i-line resist. It is designed for non-critical layers where short development time or high photo-speed is necessary for high wafer throughput. This resist is used in the range of 1-2μm thickness. Excellent exposure and focus latitude are noted for this resist. 100mJ/cm^2 is the typical exposure requirement. For enhancing thermal stability, a post exposure bake cycle of up to 120°C is used. To use this photoresist its supplier's recommendation is given as Table 3-2:

Table 3-2 Process parameters of AZ 7220 [37]

Typical Process for 2.0 μm Film Thickness	
Softbake	110°C, 60 sec (range 90 to 120°C)
Exposure	110 mJ/cm^2, i-line stepper
Post Exposure Bake	110°C, 60 sec (range 110 to 120°C)
Development	AZ® 300 MIF Developer (Normality = 0.26), 5 sec spray, 55 sec puddle
Postbake (Hardbake)	115°C (range 115 to 125°C)

Depending on the conditions of the process and the substrate used, we need to optimize the parameters. To find the optimum value for the parameters, we need to do several trials and errors. Just following the values in Table 3-2, the results were not good, as can be seen in Figure 3-8.

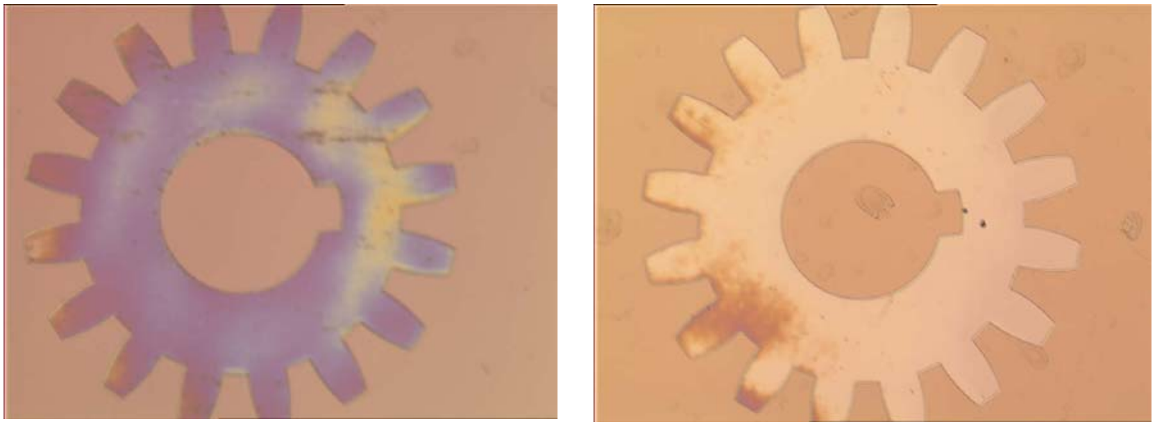


Figure 3-8 Patterned photoresist (photoresist residue is left inside the gear pattern)

Figure 3-8 shows that some amount of photoresist is left inside the gear pattern. Thus we can easily conclude that the exposure time is not enough. By several trials and errors, we found the value of 165mJ/cm^2 for energy, 1.5 times more than the recommended exposure time, to be best.

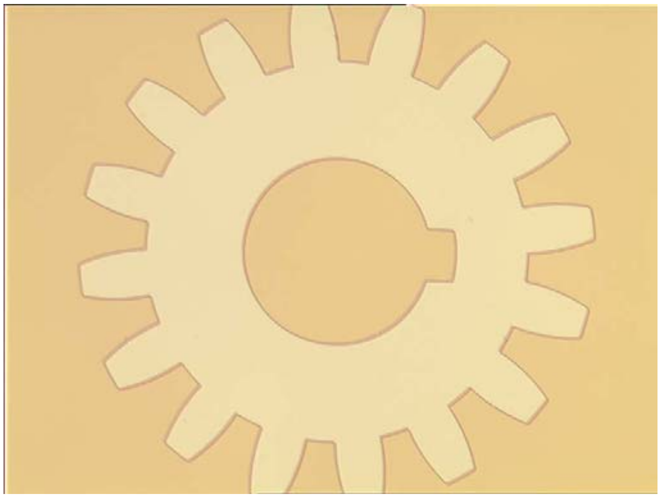


Figure 3-9 Patterned photoresist without photoresist residue inside the gear pattern

As it can be seen in Figure 3-9, there is no photoresist residue left inside the gear pattern and the sample is ready for the next step. If in any case we observe a little photoresist residue in the gears, we only need to do post exposure baking at 115°C for one minute and then keeping the samples in the AZ developer for a longer time. Due to the fact that the photo-lithography process of AZ 7220 in most of the parts is the same as the other photoresists, the details of each step will be discussed in section 4 of this chapter. Here the process of AZ 7220 will be discussed very briefly.

Steps of this process are as follows:

- ***Surface preparation***

Glass substrates are rinsed in ultrasonic acetone bath for 15 minutes, and then they are sprayed by IPA and DI water. After cleaning the samples, dehydration by hotplate at 120 °C for 10 minute is recommended.

- ***Spin-coating***

Two step spin-coating is used:

First step: Spin at 1000 rpm with acceleration of 200 for 5 seconds

Second step: Spin at 5000 rpm with acceleration of 600 for 30 seconds

- ***Relaxation time***

One minute is enough time for photoresist to stabilize itself

- ***Soft baking***

Soft baking is done on hotplate at 95 °C for one minute

- ***Exposure***

The exposure energy which is needed is 165mJ/cm^2

- ***Post exposure baking***

Post exposure baking is done on hot plate at 110 °C for one minute

- ***Development***

The samples are developed in AZ 400K developer and DI water (1: 1) for 30seconds then rinsing with DI water for another 30 seconds and finally dry with N_2 gas.

3.5 Nickel electroplating

After patterning of AZ 7220 on ITO glass, nickel electroplating must be done to make the exposure mask. We will discuss about the nickel electroplating and its parameters in detail in the next chapter. By nickel electroplating, a nickel membrane is deposited in the left open spots. Electroplating is carried out in a nickel sulfamate bath at 40-50C with a current density of 1-5 A dm^{-2} for 10-20 minutes. Figure 3-10 shows the results of electroplated sample (exposure mask). As can be seen in this figure, the two sides of ITO glass are opened in the AZ photolithography process until they can be electroplated. These two sides are used for having connection in both electroplating, first and last one.

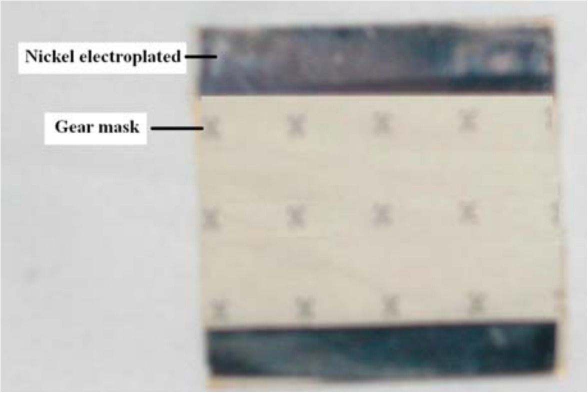


Figure 3-10 Exposure mask

3.6 Photo-Lithographic Process of SU-8

3.6.1 Introduction

The physical and chemical properties of SU-8 were discussed in the previous chapter. In this chapter, lithographic process of SU-8 will be discussed.

We can divide the whole lithographic process to eight steps as following (Figure 3-11):

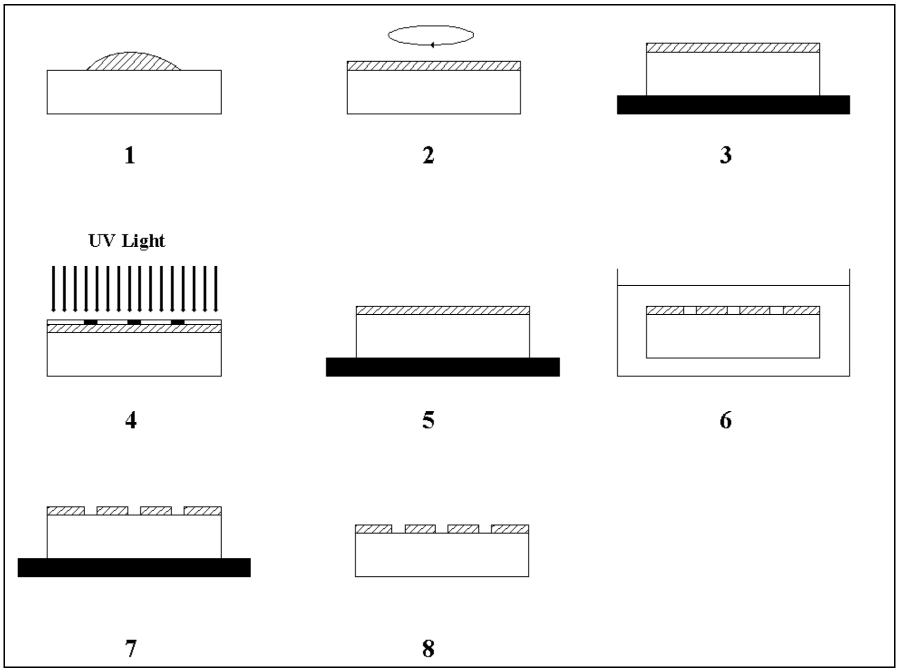


Figure 3-11 Photolithographic processing steps for SU-8:
1-Apply SU-8 resist, 2-Spin Coating, 3- Pre-baking, 4- UV-Exposure,
5-Post-baking, 6- Development, 7-Hard baking, 8-Final product

1- Surface preparation

2- Spin Coating

3- Soft baking

4- Exposure

5- Post Exposure Baking

6- Development

7- Hard baking

8- Stripping

Each of the above steps will affect resolution, measure of vertical side wall, defects density, planarization, control of thickness, adhesion to substrate and etch resistance. Hence, we must try to find the optimum value for the parameters in each step.

3.6.2 Photo-lithographic steps

Step 1: Surface Preparation

Surface cleaning

Surface cleaning of the substrate is one of the important parts of the photolithography process because all the structures will be built on the surface. To achieve maximum process reliability, the substrates should be cleaned and dried before SU-8 coating.

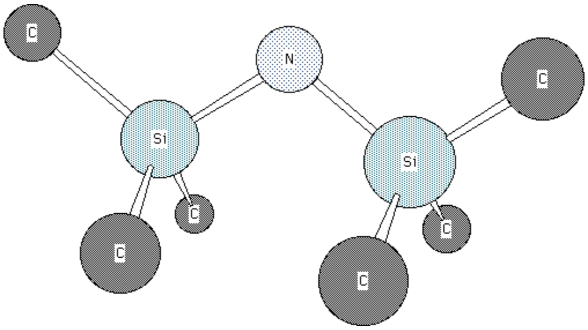
If the substrates are clean (virgin wafer or wafer with fresh thermal oxide), baking at 120°C- 140°C for three minutes is sufficient for the desorption of water. This baking process prevents any occasional resist lift-off (poor adhesion) due to moisture absorption at substrate and SU-8 interface.

If a substrate is contaminated with impurities, it should be cleaned with Piranha wet etch (H2SO4 and H2O2) followed by rinsing in DI water. There are other methods for substrate cleaning such as using reactive ion etching (RIE), barrel Asher supplied with oxygen or putting substrates in the acetone especially ultrasonic bath to remove organic impurities followed by rinsing in isopropyl alcohol to remove the acetone contaminated.

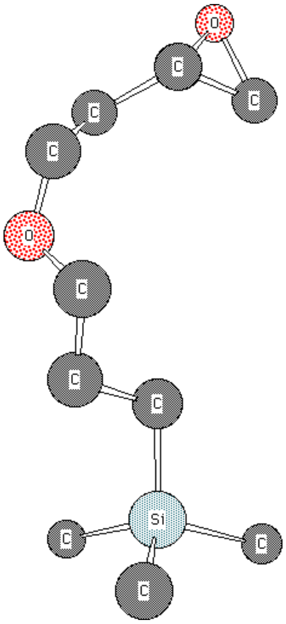
Adhesion promoting [38]

For increasing SU-8's adhesion on silicon or glass substrate, an adhesion promoter is used. There are several methods for improving the adhesion. One method is using classical promoter HDMS (Hexamethyldisilazane), which is used for thin film photoresists (Figure 3-12.a).

Epoxy molecule is the other choice for improving the adhesion (Figure 3-12.b). This molecule has two sides, on one side it has an epoxy group which reacts with SU-8 and on the other side it has methyl groups which stick on glass.



(a) HMDS



(b) Epoxy based promoter

Figure 3-12 Adhesion promoter for SU-8

Step 2: Spin Coating

The coating step should be preformed exactly after surface preparation to avoid re-adsorption of water or any particle. There are two methods to coat resist in semiconductor industries: Static and Dynamic dispensing method. Dynamic dispensing method is not suitable for SU-8 thick photoresist due to trapping of bubbles in the resist. So, the only choice will be static dispensing method. In this method wafer is placed on a suction chuck and the resist is poured manually on the substrate. Typically, it is enough to dispense 1 ml of resist for each inch of substrate. The wafer is initially rotated at a speed of 500 rpm for 5-10 seconds with acceleration of 100rpm/second. After that, according to the type of SU-8 to use and thickness to achieve, we choose our rotation speed by the data provided by the suppliers. Figure 3-13 shows some spin curves obtained for three different formulations. Also, Figure 3-14 shows the spin speed versus thickness for SU-8-2025, 2035, 2050 and 2075.

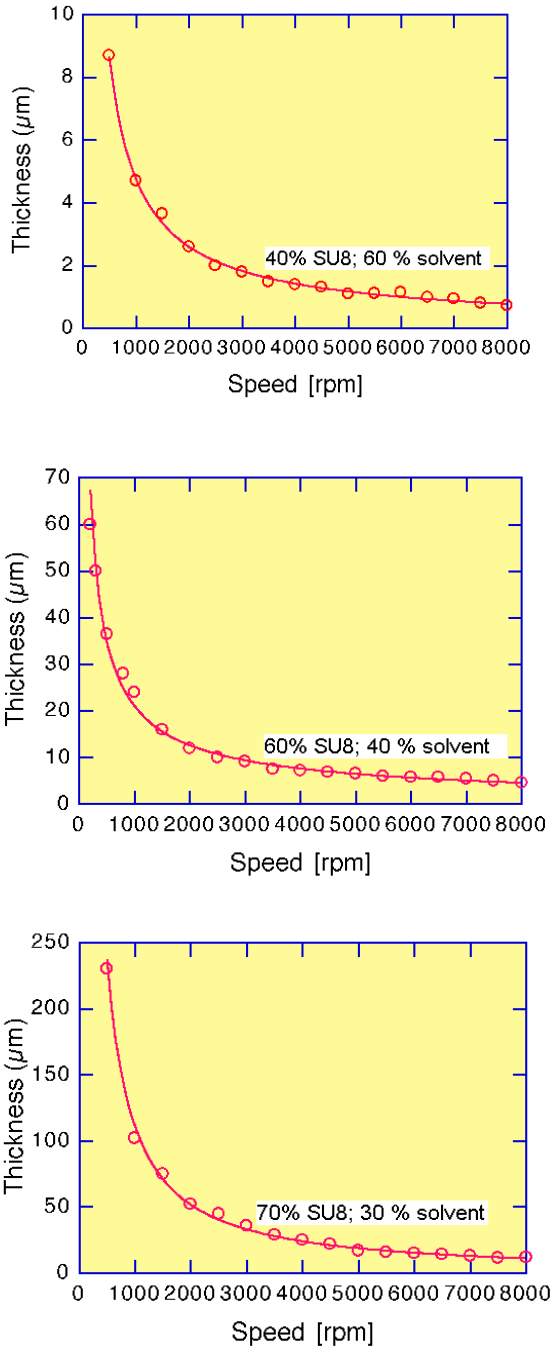


Figure 3-13 Spin curves for the three SU8 resist [32]

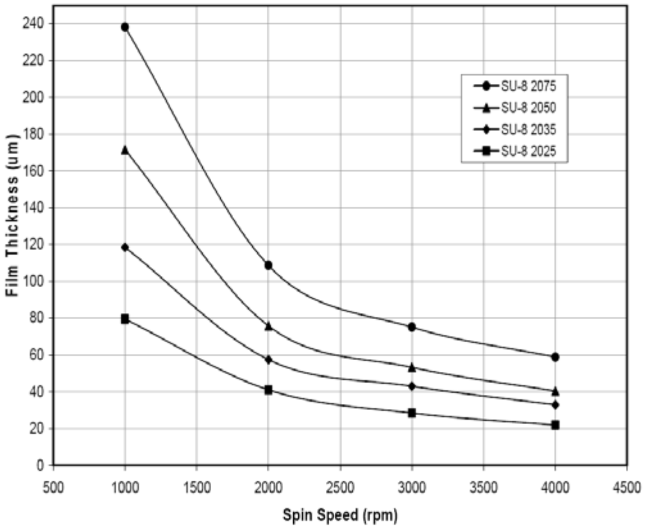


Figure 3-14 SU-8 2000 Spin speed versus thickness [39]

When the spin coater rotates in high speed, the resist is pushed to the wafer edge and the threads of resist will be spun off the wafer and deposited around the coater.

This two-step process makes an initial thick resist coating to be spread to the edge before it ramps up the speed to obtain a uniform film. This process hence decreases the edge bead of resist. For thin film resist, it works very well but for thick resist, it still has edge bead. One of the methods for removing edge beads is to leave the substrate one to two hours on a horizontal and flat surface at room temperature. The other method is using small stream of acetone or MicroChem’s EBR PG at the edge of the wafer either at the top or from the bottom. This method improves resist planarization but it leaves an edge ring around the substrate. The more recent automated spin coaters can be programmed automatically to perform this feature. If the edge bead is removed properly, the photo-mask can be placed into close contact with the wafer and thereby improves the aspect ratio and resolution.

3-Pre-Baking

Pre-baking step is another important part of the photo lithography process. This step influences: structure definition, mold’s aspect ratio, mold’s side wall, and development time and exposure energy. [40]

The spin coated film from the previous step has homogeneous dissolution EPON™ SU-8 monomers and tri-arylsulfonium photo-active components in a huge reservoir of solvent. The presence of solvent in resist is for facilitating of spin- coating process but it creates problem for UV absorption and causes the resist to stick to the photo-mask during UV exposure. Therefore, removing the solvent from the resist by pre baking step is necessary until it can be used for UV exposure.

For pre-baking, a level hot plate with good thermal control is used. It is not good to use convection oven for this step because it forms a layer on the resist which inhibits the evolution of solvent. If oven is used, increased baking time is needed or incomplete drying of film will result. But, by using hot plate, the heat flows to the substrate from the back side and this avoids formation of the crust at the resist surface. Therefore, ramped temperature is recommended. When substrate is put on the hotplate directly, it is observed that the thick resist flows to the center of the substrate but this phenomenon is reduced by using ramped temperature.

Pre-baking time is very important. If a proper time is not chosen, three problems will happen:

1- Problem in UV absorption

2- Sticking the resist to the photo-mask

3- Wrinkling in the resist (as it can be seen in Figure 3-15)

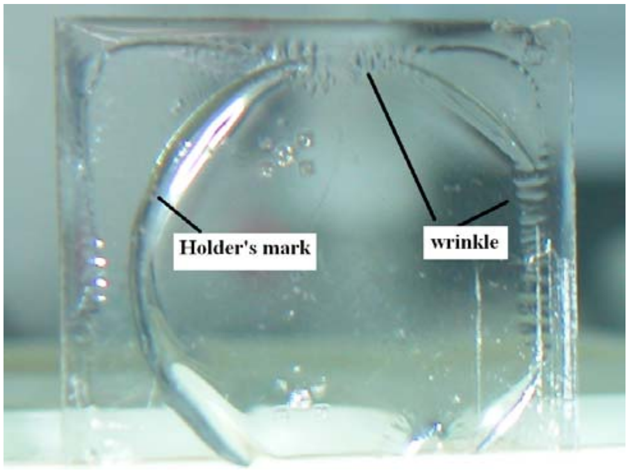


Figure 3-15 Wrinkling in the resist

Figure 3-16 Sample holder

To find the optimum time for pre-baking step at baking temperature (T=95C), the changes of SU-8-1050 on 1 inch wafer were measured by the help of a micro-balance after pre-baking in different periods of time (Figure 3-17) to measure amount of solvent vaporized.

From Figure 3-17, it can be seen that it is easy to estimate the minimum required pre-bake time. After 40 minutes, there is not any change in the weight of SU-8. So, to ensure that there is minimal solvent left in SU8, we can consider 50 minutes as the suitable time for pre-baking.

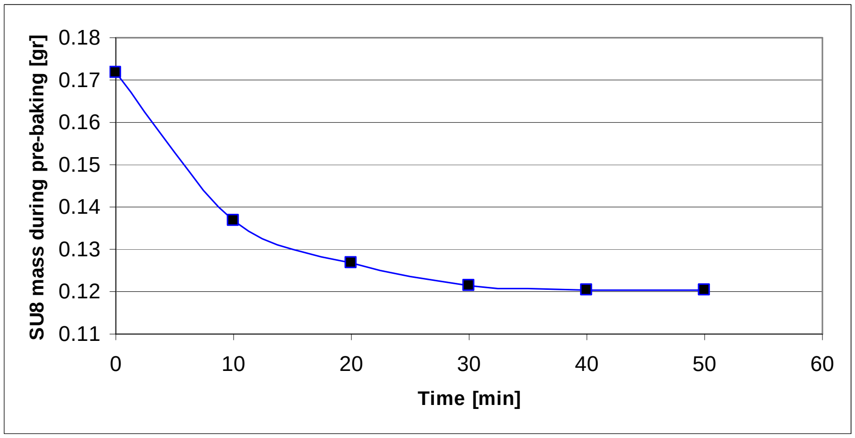


Figure 3-17 Mass of SU-8 2050 during bake [gr] vs. pre baking time [min]

There is another method for optimizing the baking time conditions. In this method, wafer will be removed from the hotplate after prescribed intervals and cool down in the clean room’s temperature. Then putting it on hotplate again, we must repeat this action until the wrinkles in the film leaves the film completely and or no longer seen in the film [39]. After this step, it is better to give a time to photoresist to rest and stabilize itself.

4-Exposure

The next step after pre-baking of SU-8 resist is UV exposure by using Karl Suss Mask Aligner (MA8). This machine uses a source of mercury light which has a beam source of between 300-450 nm which is near UV peak at 365nm. With reference to Figure 3-4, the optical absorption of SU-8 at 365 nm wavelength is negligible. So, we can conclude that exposure dose for SU-8 is directly proportional to the thickness of film. Upon irradiation, photolysis of tri-arylsulfonium salt occurs; it results in a strong acid which starts the cationic polymerization process. Cross linking (Polymerization) happens by nucleophilic interaction of epoxide oxygen with the carbocation produced by ring opening and protonation of an epoxide of another polymer chain. Figure 3-18 shows the Normalized film thickness remaining vs. exposure dose for 1µm thick film of resist. As it can be seen from this figure, 1.2mJ/cm^2 is the minimum dose which needs for 1 µm film thickness. Therefore for 200 µm film thickness which is used in this project, a minimum dose of 240mJ/cm^2 is needed. But in practice 240mJ/cm^2 dose is not enough, and higher dose must be used until it compensate the absorption and sufficient exposure to achieve sharp edge profile. Hence, for those substrates which are not reflective, a higher dosage is needed to compensate the absorption in the resist and substrate interface. The resists which are more viscous such as SU-8 1050+, they have less tri-arylsulfonium salts for improving the edge profile, therefore they require longer exposure time, too.

Due to the fact that we use reverse side exposure method in our project, so, light transmittance from the substrate (glass) also plays an important role in the calculation of exposure energy. In the next section we will discuss about it in details.

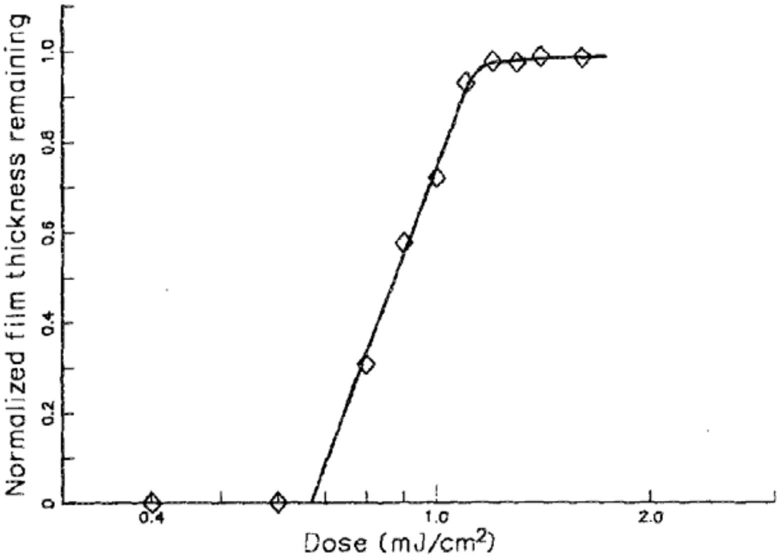


Figure 3-18 Normalized film thickness remaining vs. exposure dose (mJ/cm2) for 1µm thick film of resist [41]

Light transmittance

For calculating of exposure dose which is needed for exposure step, we need to know the following items:

1- UV transmission in ITO glass

2- UV transmission in different resist thickness

3- UV transmission after post exposure baking (If we want to have multi-layers)

The light intensity in all cases was measured by a UV intensity meter (Mode 1000, SUSS MicroTec).

Figure 3-19 shows that SU8 has a good UV transparency (70% transparency at 405nm for a 150µm film and 40% transparency at 365nm for a 150µm film). So, it makes SU8 as a good choice for fabrication of high structures.

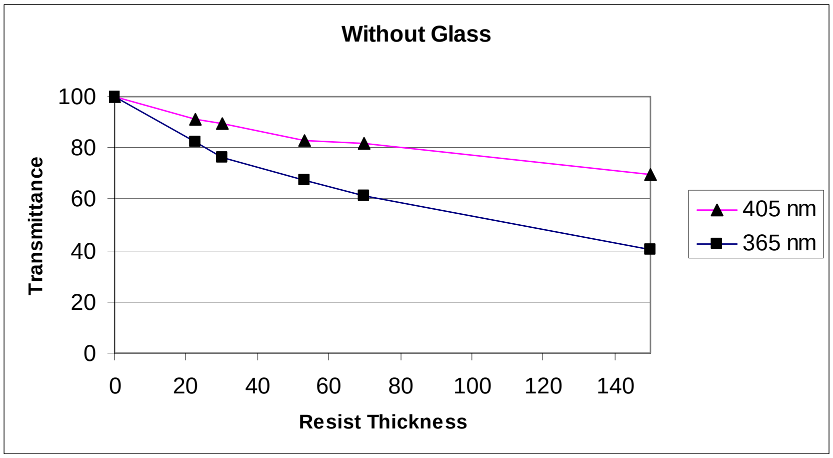


Figure 3-19 UV transmittance verses resist thickness (Without considering substrate)

As can be seen in Figure 3-19, Figure 3-20 and Figure 3-21, optical transmittance will decrease by increasing the resist thickness in ITO glass and common glass and without substrate. This decrease is more for 365 nm wavelengths rather than 405 nm wavelength.

If we want to use ITO glass, we must consider that UV energy will drop to 60 percent of its original value.

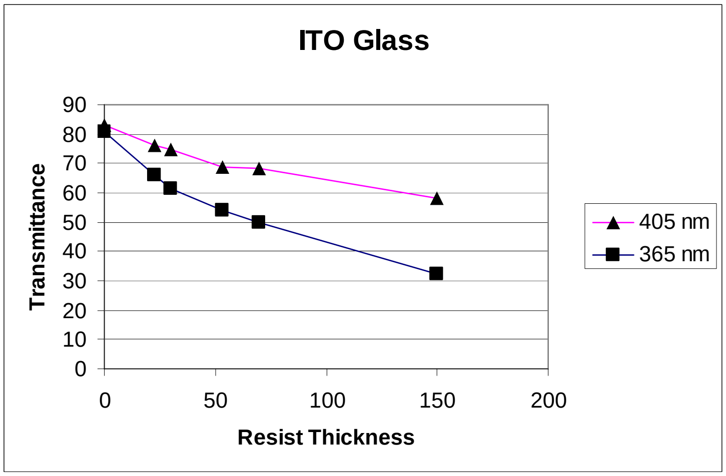


Figure 3-20 UV transmittance verses resist thickness (ITO glass)

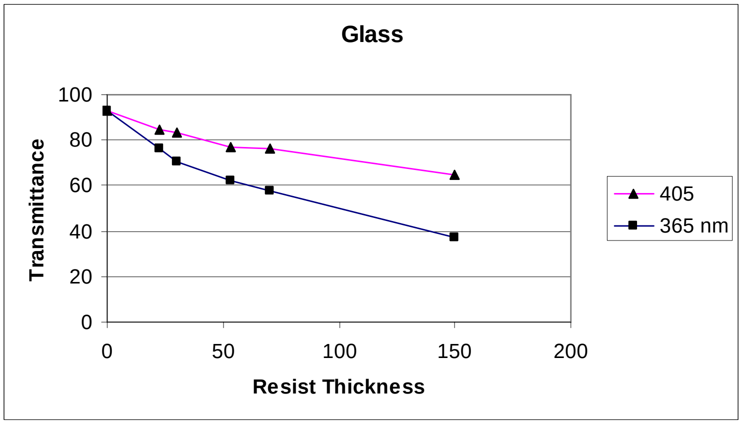


Figure 3-21 UV transmittance verses resist thickness (Common glass)

Figure 3-22 shows the UV transmittance for different wavelength. As can be seen in this figure for 405 nm wavelength, optical transmittance will increase.

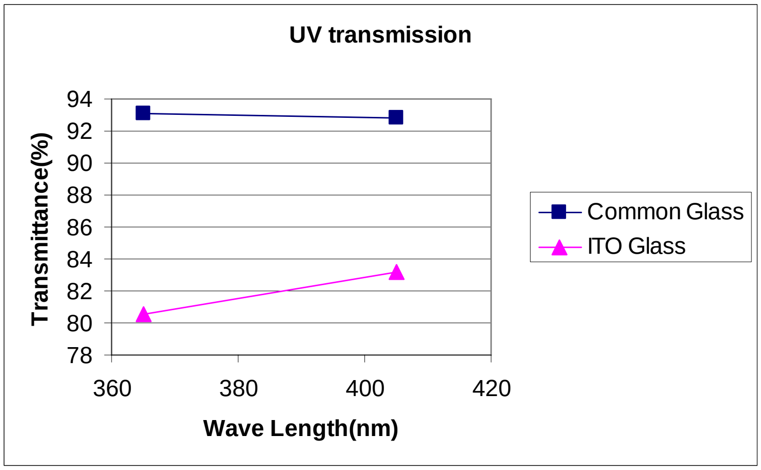


Figure 3-22 UV transmittance verses wave length

Figure 3-23 shows the optical transmittance after different steps (softbake, exposure, hardbake). As it can be seen, optical transmittance drops after doing each step but the amount of drop is not too much.

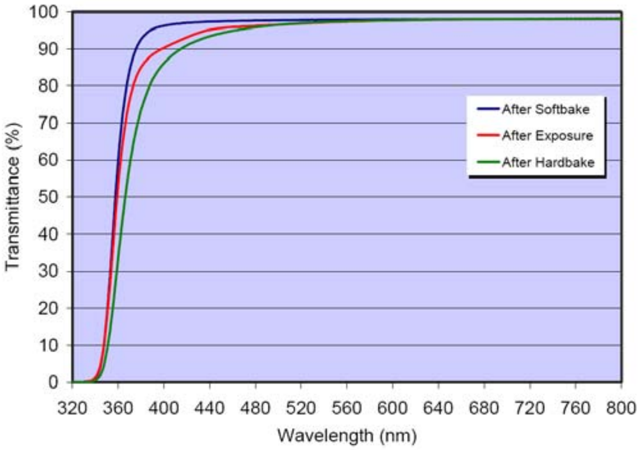
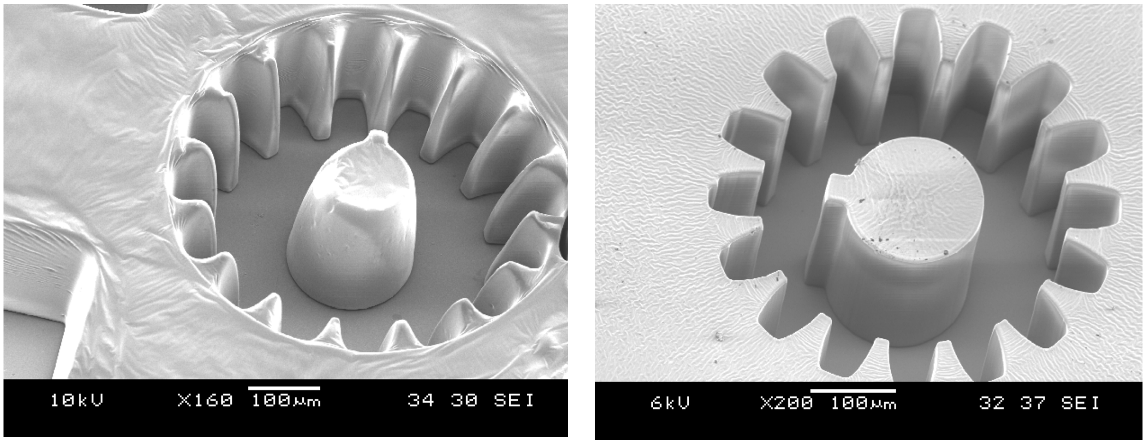


Figure 3-23 Optical transmittance

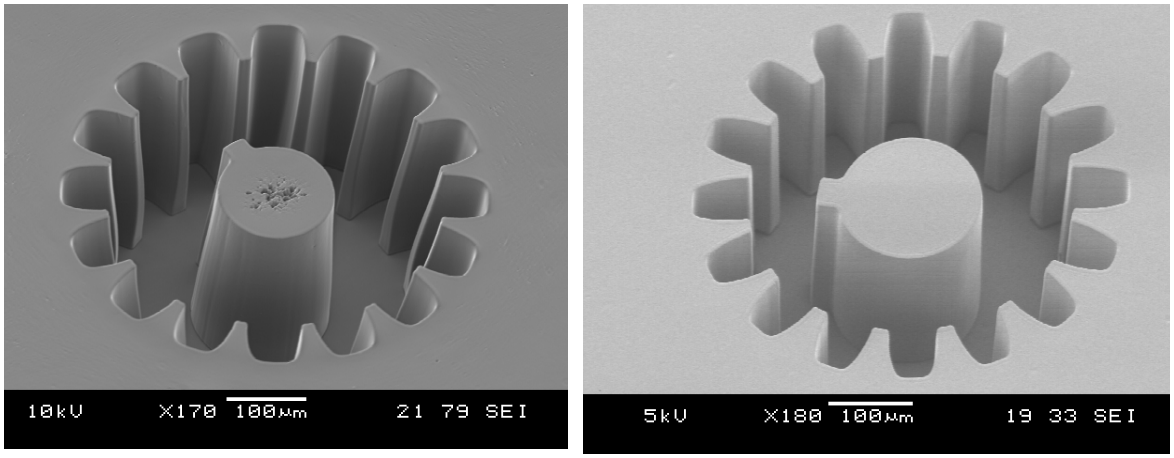
Different exposure energy was tried to find the optimum exposure energy required. Figure 3-24 shows the results of different experiments. As can be seen, when 240mJ/cm^2 is chosen for the exposure energy, it gives poor results and walls. When 480 mJ/cm^2 and

720mJ/cm^2 are chosen, the walls are not vertical. But when the exposure energy is more than 1440 mJ/cm^2 the walls are vertical with excellent shape. So, we chose 1440 mJ/cm^2 as the amount of exposure energy for all experiments.

During the exposure time, it is better to use a long pass filter to eliminate UV radiation less than 350nm. If the exposure time is optimal, the latent image must be visible after 5-15 seconds of post exposure bake [39].



240 mJ/cm2 480 mJ/cm2



720 mJ/cm2 1440 mJ/cm2

Figure 3-24 Results of using different exposure energy

5- Post Exposure baking

Post exposure baking must be done after UV exposure. Cross-linking of SU-8 happens during this baking. This baking is very necessary because in the solid state when molecular motion is little, little reaction can occur. For having an effective baking, the temperature must be greater than 55 ° C (in this temperature the resist is solid). During the cross-linking formation, some shrinkage will happen due to densification and out-gassing of the solvent. Baking time is dependent on the baking temperature. Usually baking is done on hotplate at 95 ° C for 15 min. For stress reduction, it is better to heat the substrate slowly to the baking temperature and cooling it down slowly to 65 ° C.

6-Development

In order to remove the unexposed region from the left part selectively, the development step must be done. A good resist has a high resist selectivity and minimum swelling. Resist polymerization begins in exposure time and accelerates during the post exposure baking until it minimizes the diffusion of photo-active elements from the diffusion to the unexposed area therefore it keeps the dimensional accuracy of side walls. In the development step, the regions which are highly polymerized remain safe and the un-polymerized regions dissolves. MicroChem's SU-8 developer is used for SU-8 resist. Other solvents such as diacetone alcohol and ethyl lactate also can be used as an alternative. When high-aspect-ratio or thick film structures are developing, high agitation must be done. Therefore it is better to use ultrasonic or magnetic bath. The development time is dependent on the thickness of structures and can be found in the supplier's data sheet such as MicroChem [39].

7-Hard baking

The mechanical properties of SU-8 2000 are very good. However if the imaged resist is to be used as the final device, hard baking can be beneficial. Therefore this step is useful for those parts which are to be subject to thermal processing during their operation or for ensuring that the properties of SU-8 do not change during the application [39]. In this step the developed structure changes to a very hard material and cross-linking process will be completed. After this step, the stress due to the polymerization of resist is negligible but the stress due to the difference between thermal coefficients of the resist and the substrate during the baking process is significant. So this stress may lead to film delaminating or wafer bowing. The baking temperature is about 150 °C to 250 °C and the time of baking is between 5 to 30 minutes.

3.6.3 Resist Stripping

It is very difficult to strip SU-8 because it has been designed for a permanent and highly cross-linked epoxy material. So, it is a major problem to find a suitable stripper to remove this resist well. Some of the main problems of strippers are high temperature, long etching time, use of hazardous or non standard material and poor selectivity. Up to now, several methods have been used to remove this polymer. These methods can be classified into two groups; physical and chemical techniques.

Physical techniques are the techniques used to demolish or destroy the crosslinked SU-8 directly such as water jet and laser ablation. These methods are fairly selective to the SU-8 polymer over metal microstructure, but they are not able to remove all small areas of SU-8 from the high-aspect-ratio structures. Totally, these methods are good for some kinds of geometries [42].

In chemical methods, a chemical solution is used to remove the SU-8. Some of the methods for removing SU-8 are: NANO Remover PG, nitric acid (100%), piranha (H2O2:H2SO4), hot remover PG followed by wet etchant (H2SO4: H2O2: H2O=3:1:1)[43], hot NMP(methyl : pyrrolidone =1:2), oxygen/ fluorine plasma etching [44], KrF excimer laser [45] or water jet as a mechanical way but it is not good for fragile structures.

In the following, several mold removal methods will be discussed:

- *Hot NANO Remover PG*

This remover is recommended by MicroChem. It removes minimally the cross-linked SU-8. For removing the resist, it needs just to heat the remover bath to 50°C-80°C and immerse the substrate in it for 30-90 minutes [39]. But it has a problem that it may remove SU-8 from the substrate by lift-off mechanism instead of dissolution [46] so, the swelling resist generates internal stress at the interface and results in resist residues in the gaps between structures or destroying the structures [47].

- *Hot NANO Remover PG and etchant*

If the hot remover PG alone was not enough for removing the resist, we can use piranha after it. Piranha is sulfuric acid: hydrogen peroxide (H2SO4:H2O2=3:1). However it may damage nickel structure seriously and produce rough surface. So, it is recommended to use H2SO4:H2O2:H2O=3:1:1 instead of piranha and it is suggested to use it in the low temperature (60°C-80°C). The results of this etchant in low temperature are better than piranha due to decreasing the etchant concentration and operational temperature [47].

- *Embedded structure in substrate and hot NANO Remover PG*

In this method, the electroplated structure embedded in the substrate is at least 1μm. Hence, it is better that the thickness of the electroplated structure is less than two-third of the resist mold. This method provides a stronger structure which can withstand internal stress. So, when hot Remover PG is used, the structure will be remained in place [47].

- *Reactive ion etching (RIE)*

RIE can etch SU8 at the rate of 1-4 μm/min. However, RIE has several drawbacks. Firstly the metal mold's temperature is not controlled. Secondly, the etch rate may drop significantly when the metal is present in the mold; so the etching rate of pure resin is not a good way to measure etching rate of metal structures surrounded by resin. Thirdly, low pressure and lack of coupled plasma in the chamber of RIE leaves etch species compared to the other oxidative methods. This method is good and useful for thin films but for films of several hundred-micron thick has not been proven [48].

- *Molten salt bath*

In this method, an oxidizing salt like sodium nitrate is mixed with a hydroxide salt and the other additives. This is used in the range of 300°C-400°C, until it does not damage the Ni structure [48]. Generally, nickel and nickel alloys are resistant to the nitrate bath [49]. One of the advantages of this method in comparison with the other oxidative process is that the salt is a good heat transfer medium; so it does not heat the nickel structure above the temperature of the bath. One of the drawbacks of this method is that the surface appearance of the metal structures seems to be dull after the process [48].

- *Burning*

The simplest way for removing SU-8 is to burn it off in a simple furnace at 450°C-600°C. This method is completely cheap and simple but it can damage the resultant metal structure [49]. SU-8 is a hydrocarbon polymer. So, at high temperature it reacts with oxygen and produce water and carbon dioxide. The degree which shows the amount of remaining SU-8 after burning is related to the temperature used (Figure 3-25). At temperatures higher than 600 °C, SU-8 removal is complete. Note that at high temperatures, the metal microstructure will be oxidized which decreases the structure lifetime. To prevent the oxidation of microstructure's surface, it is better that the burning process happens in an inert atmosphere like nitrogen [50].

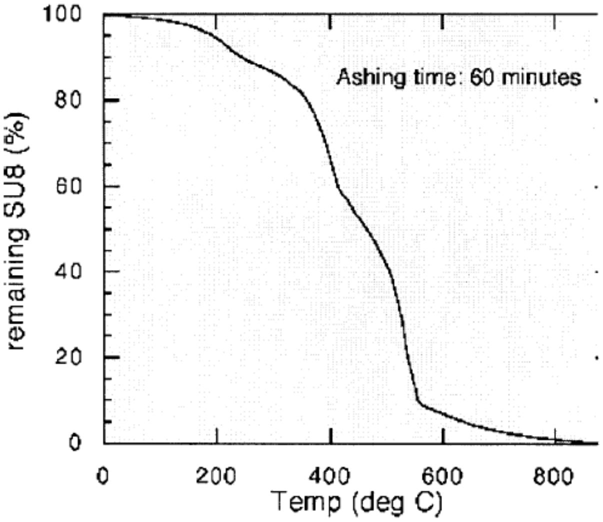


Figure 3-25 Burning of SU-8 in air [51]

- *Sacrificial layer*

One of the methods used to release microstructure from SU-8 is the use of a sacrificial layer. A number of materials can be used as a sacrificial layer such as: porous silicon, silicon dioxide, phosphosilicate glass, titanium, polyimide, or photoresist.

- *Magnastrip and MS-111*

Two kinds of solvent mixtures, MS-111 and Magnastrip, have been developed by Sandia National Libraries which can strip and remove SU-8[51]. Their method for removing SU-8 is by peeling and crazing rather than dissolution. This technique is a good method for stripping SU-8 but not be used for high-aspect-ratio microstructures [50].

- *Excimer laser micromachining*

Scanning of a laser beam can remove SU-8 completely. Studies shows that by increasing the fluence, the etch rate will increase. Figure 3-26 shows that pre baking temperature does not affect etch rate and also there is an ablation threshold (0.05J/cm^2) for fluence which below it, there no etching [50].

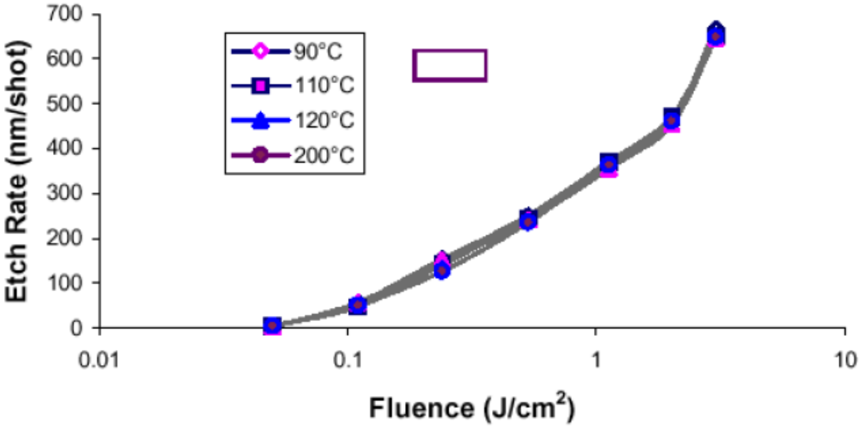


Figure 3-26 Variation of etch rate of SU-8 with laser fluence [50]

- SMST stripper[52]

SOTEC MICROSYSTEMS produced the SMST stripper which can strip SU-8 without delamination and without attacking nickel. The etchant is used at 100°C degree.

3.6.4 Micro cracks and delamination

In some cases, micro cracks and delamination can be observed on the structure's surface (Figure 3-27 and Figure 3-28). Micro cracks and delamination appear due to the internal stress in the structure and this stress release in the form of cracks and delamination. There are different possibilities for internal stress. The possibilities are as follow:

- Difference in thermal expansion coefficient between substrate[silicon(2.6*10E-6/°C), quartz(0.55*10E-6/°C),etc] and SU-8 films(~ 50*10E-6/°C[53])
- Polymerization shrinkage during the soft baking process [54]
- Lack of relaxation time for rehydration of resist between prebake and exposure steps. This relaxation time not only can avoid micro cracks but also can reduce the exposure energy, development time and dissolution of the unexposed resist parts by developer.[40]
- Thickness of the SU-8 film [55]

With the increase of thickness, internal stress increases in the resist. Therefore it increases the deformation of SU-8 surface. The deformation results in a large gap between resist and photo mask, which may cause failure of exposure. [55]

- Thermal stress during the process
- Internal stress in the resist due to high exposure dose and soft-baking time[56]
- Post exposure temperature

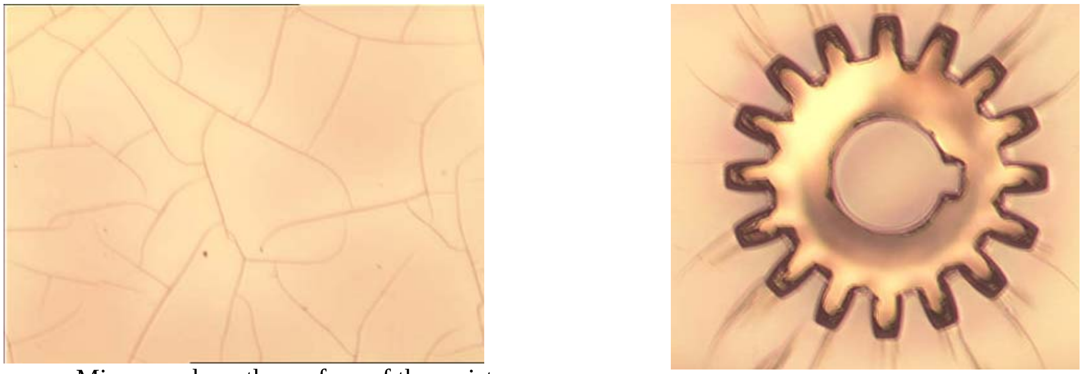
Studies show that decreasing temperature of the post exposure bake to 55°C can decrease the internal stress up to 70% [55]

- Substrate size

Substrate size has very little effect on the internal stress but smaller substrate is preferred [55]

For avoiding the micro cracks, we must:

- Optimize the processing parameters, Soft baking time and temperature, post exposure baking temperature and time and exposure time
- Change the design. Avoid sharp concave corners which can act as nucleation points for cracks[54]
- Slow down cooling rate, because cooling rate has an important effect, as cracks will decrease with slower cooling [57]
- Hard bake step can be useful for annealing and removing the surface cracks. The temperature for hard baking is 150°C for two minutes. [39]



Micro crack on the surface of the resist

Micro crack on the pattern

Figure 3-27 Micro cracks

Figure 3-28 Sever delamination

3.6.5 SU-8-Residual

Before the electroplating step, the gear pattern must be free from SU-8 residue. One of the drawbacks in using SU-8 is that it leaves resist residues near the developed areas and exposed patterns. This residue is difficult to remove and makes problem for electroplating of the desired pattern. Figure 3-29 shows the SU-8 residue left after SU-8 development. There are several methods for overcoming this problem such as:

- Using RIE (Reactive Ion Etching) which is commonly used for removal of residue [58, 59]. Using RIE has some disadvantage such as increasing cost and process complexity.
- Using an OmniCoat layer. Although it can help but it needs RIE to remove residue completely
- Using laser to remove the residue [60]. This process is useful but there are many parameters which must be optimized.
- Selecting proper process parameters such as soft baking and post baking temperature and time, exposure and development time. After that, rinsing the patterns in acetone in a controlled way [61]. Figure 3-30 shows the developed pattern is completely clean without any SU-8 residue.

This project presents a simple and inexpensive method for not having residue inside the SU-8 mold structures by using following strategies:

Selecting proper process parameters

In this strategy, low temperatures have been used in the whole SU-8 photolithography process by choosing low soft baking and post exposure-baking temperature. Choosing low temperature in photolithography process makes unexposed SU-8 does not become hard and difficult to remove from structure after development. Therefore, after development all the residue will separate from the structure very easily.

Relaxation time

Relaxation time after soft baking helps to dissolve the unexposed resist parts by developer sooner. Hence, in this project we used enough time for relaxation part.

Using reverse side method

By using reverse-side exposure method, light does not reflect from the substrate to the unexposed area. Therefore, it does not expose undesired SU-8 inside the structure. Hence, there is no SU-8 residue inside the walls.

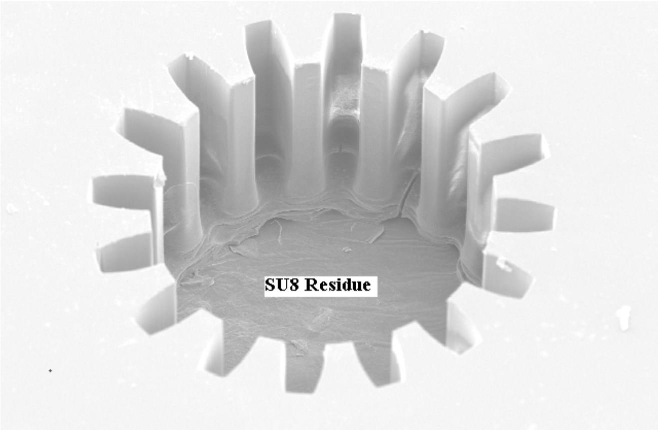


Figure 3-29 SU-8 residue on ITO glass

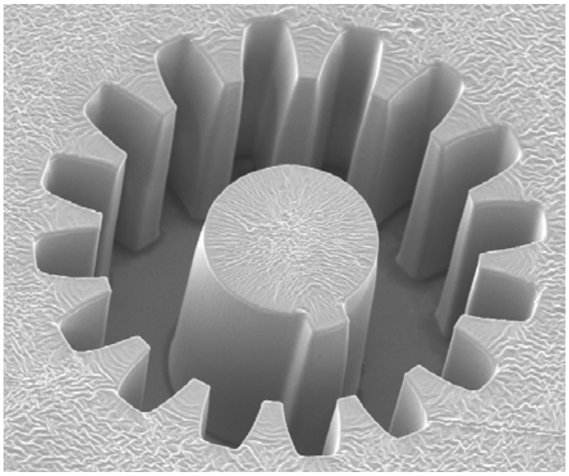


Figure 3-30 SU-8 pattern without any residue

As was discussed in this chapter we chose reverse-side exposure method to fabricate SU-8 mold. In this section, we discuss the selection of parameters to fabricate SU-8 mold without cracks and delamination.

3.7 Experiment 1- Mold fabrication

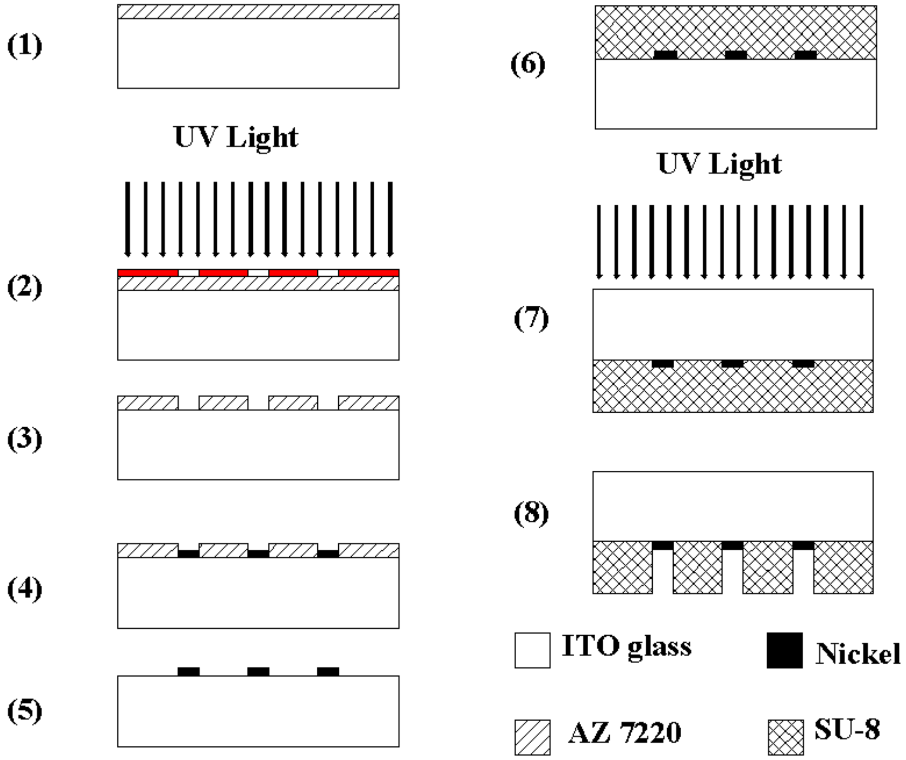


Figure 3-31 SU-8 mold fabrication steps
1- Coating a thin layer AZ7220 positive photoresist (2µm) on ITO glass 2-Patterning of AZ7220 photoresist 3-Development the photoresist 4-Electroplating nickel 5-Removing the AZ7220 photoresist by acetone 6-Coating a thick SU-8 photoresist by spin coater 7-Patterning SU-8 photoresist 8-Development of the SU-8

Figure 3-31 shows the whole SU-8 mold fabrication steps. The whole process was started with coating a thin layer AZ 7220 on ITO glass and patterning it with the help of routine UV lithography. Then AZ 7220 was developed, to lift up the exposed area. By the help of nickel electroplating, nickel was plated in the open spot areas. Then AZ 7220 was rinsed away by acetone to form the nickel mask. After it, a thick SU-8 2050 was spin-coated and patterned on the nickel mask. Then SU-8 mold was developed to make the mold ready for the next steps.

For mold fabrication, the challenging part is to find the photolithography parameters of SU-8 and to control them to have a good-accuracy mold.

Table 3-3 shows the photolithography parameters of SU-8 for the first experiment.

Table 3-3 Photolithography parameters of SU-8 for the first experiment

Parameter	Setting
Cleaning method	Ultrasonic acetone bath (15 min) + IPA spray+ DI water+ Dehydration by hotplate at 120°C (10 min)
Relaxation time	5 min
Spin-coating:	Spin at 250 rpm (5s), acceleration 50 + Spin at 1000 rpm (45s), acceleration 150
Relaxation time	1 min
Soft baking	65°C(7min) + 95°C (60min)
Relaxation time	30 min
Exposure energy	1440 mJ/cm2
Post exposure baking	65°C (5 min) + 95°C (15min)
Relaxation time	30 min
Development	SU-8 developer (15 min) + Acetone (50s) +IPA (spray) +DI water (spray) + Pressurized nitrogen

3.7.1 Results and discussion

After the first experiment two phenomena were observed:

- Appearance of cracks on the pattern (Figure 3-32)
- Separating of SU-8 resist from the glass substrate (Figure 3-33)

Cracks can be seen on the surface of resist easily. Therefore, it can be seen that the hole of gear is not exactly in the center of gear so it means there is a gap between resist and substrate (ITO glass) and delamination has happened. In sever cases, complete delaminating happens as it can be seen in Figure 3-33.

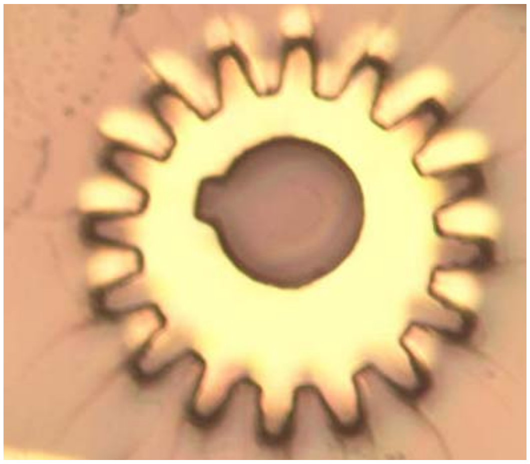


Figure 3-32 Crack on the pattern

Figure 3-33 Complete delamination

3.7.2 Solution

The separation of SU-8 from substrate and cracks on the pattern depends on the internal stress. The internal stress in the resist depends on many parameters, such as exposure dose and soft baking time, so for overcoming these problems, we decreased these two parameters in the following experiment.

3.8 Experiment 2- Mold fabrication (soft baking and exposure energy)

For overcoming crack and delamination problems, in this experiment, soft-baking and exposure time were decreased.

3.8.1 Soft-baking time

To find the sufficient time in thick resist of SU-8 for pre-baking (T=95°C), the changes of SU-8 2050 on 1 inch wafer were measured by the help of a micro-balance after pre-baking in different period of times as was mentioned in chapter 3. As it can be seen in Figure 3-17, the minimum required pre-baking time is 50 minutes. After passing this period of time, the majority of surface solvent had vaporized and the resist was sufficiently rigid for contact exposure without damaging the photomask.

3.8.2 Exposure time

Exposure time was decreased to 480 mJ/cm^2. This amount is about 1.5 times more than the amount of energy used for silicon substrate. 1.5 was chosen because the substrate is glass [39].

Table 3-4 shows the photolithography parameters of SU-8 for the second experiment.

Table 3-4 Photolithography parameters of SU-8 for the first experiment

Parameter	Setting
Cleaning method	Ultrasonic acetone bath (15 min) + IPA spray+ DI water+ Dehydration by hotplate at 120°C (10 min)
Relaxation time	5 min
Spin-coating	Spin at 250 rpm (5s), acceleration 50 + Spin at 1000 rpm (45s), acceleration 150
Relaxation time	1 min
Soft baking	65°C (7min) + 95°C (40min)
Relaxation time	30 min
Exposure energy	480 mJ/cm2
Post exposure baking	65°C (5 min) + 95°C (15min)
Relaxation time	30 min
Development	SU-8 developer (15 min) +IPA (spray) +DI water (spray) + Pressurized nitrogen

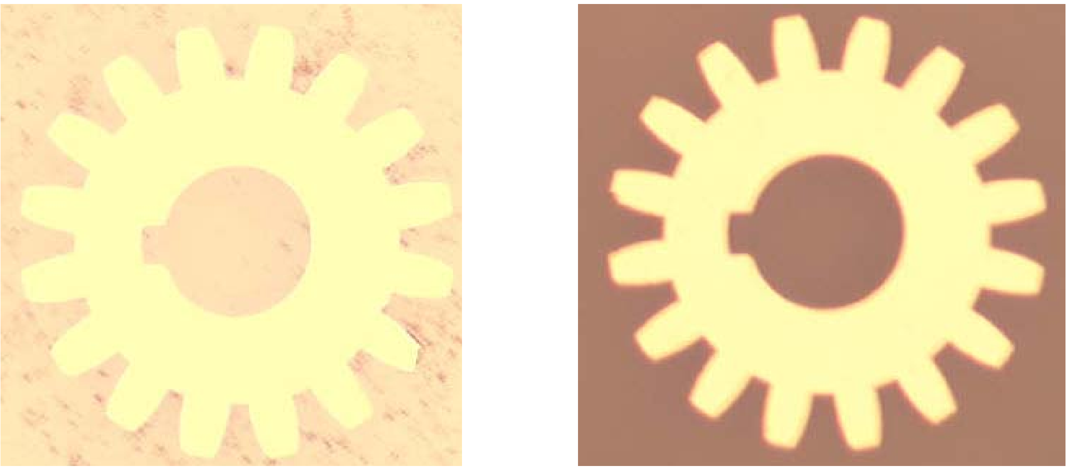
3.8.3 Results and discussion

There was not any more change in the results as cracks and delamination were still observed. Due to the fact that for having sharp edge, the exposure energy must be high, hence, we did not change the exposure energy for the next experiments but look for other parameters.

3.8.4 Solution

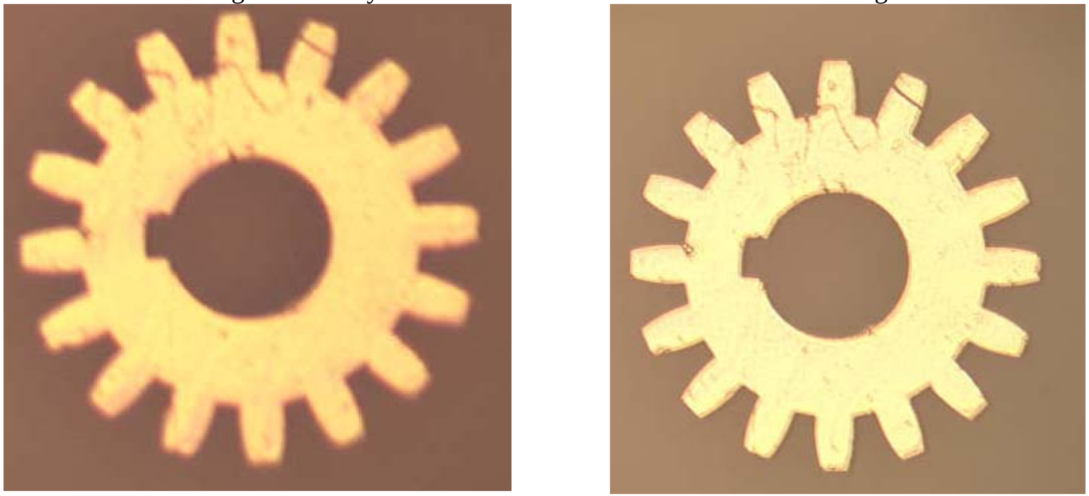
If we review the images of each step (Figure 3-34) again, it can be easily observed that cracks and delamination happen exactly after development. So, it was decided that it was better to increase the relaxation time between post exposure baking and development to decrease the internal stress.

Also, due to the fact that the difference in thermal expansion coefficient between substrate glass (0.55×10E-6/°C) and SU-8 film (~ 50×10E-6/°C) is high, it is better to decrease the soft-baking temperature until the thermal stress is decreased.



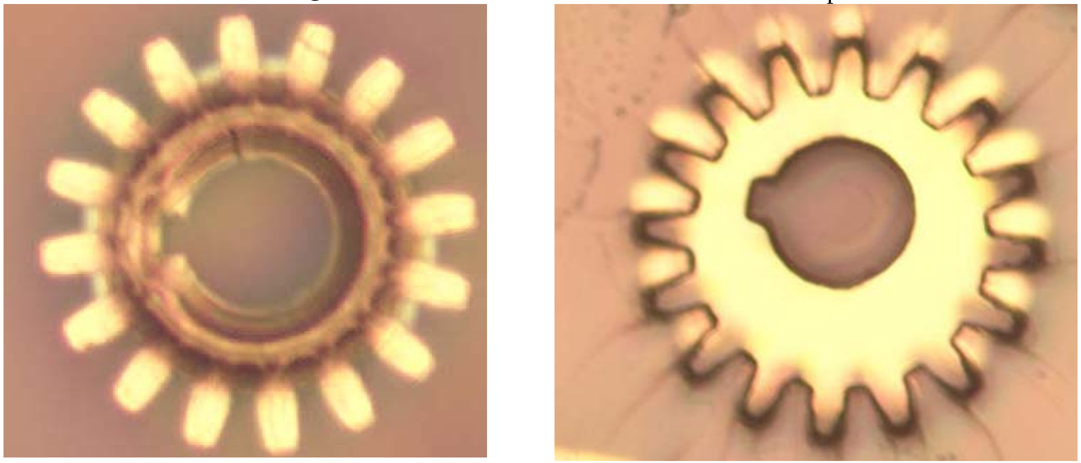
1- Before cleaning AZ 7220 by acetone

2- After cleaning AZ 7220



3- After soft-baking

4-After exposure



5-After post exposure baking

6- After development

Figure 3-34 steps of photolithography process

3.9 Experiment3 - Mold fabrication (soft baking temperature and relaxation time)

For overcoming crack and delamination problems, in this experiment, soft-baking temperature was decreased and relaxation time was increased.

3.9.1 Soft baking temperature

To decrease the thermal stress, soft baking temperature was decreased from 95°C to 65°C. Therefore, another experiment was conducted to be the same as previous one for measuring soft-baking time. The condition of experiment was same as the previous one. As can be seen from Figure 3-35, the minimum required pre-baking time is 60 minutes. After passing this period of time, the majority of surface solvent has vaporized and the resist is sufficiently rigid for contact exposure.

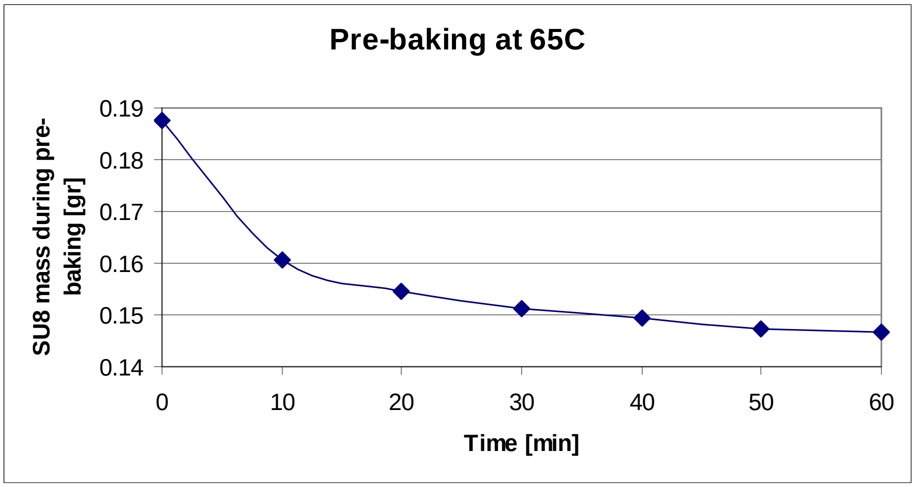


Figure 3-35 Mass changes of SU-8 2050 with the time at 65C

3.9.2 Relaxation time

As mentioned earlier, give more time to the resist for releasing the stress, the relaxation time was increased to 24 hours between post exposure baking and development.

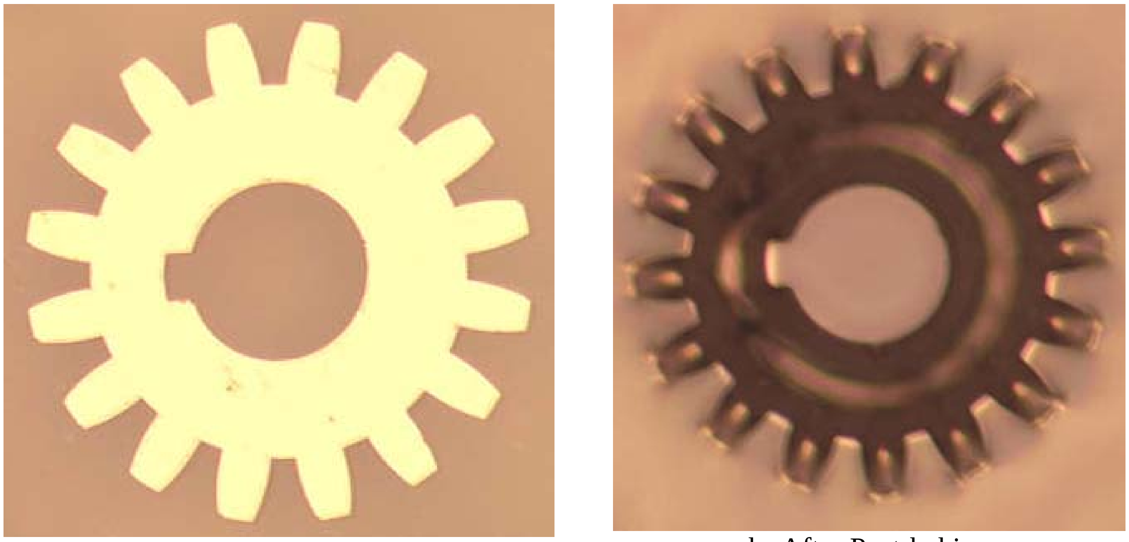
Table 3-5 shows the photolithography parameters of SU-8 for the third experiment.

Table 3-5 Photolithography parameters of SU-8 for the third experiment

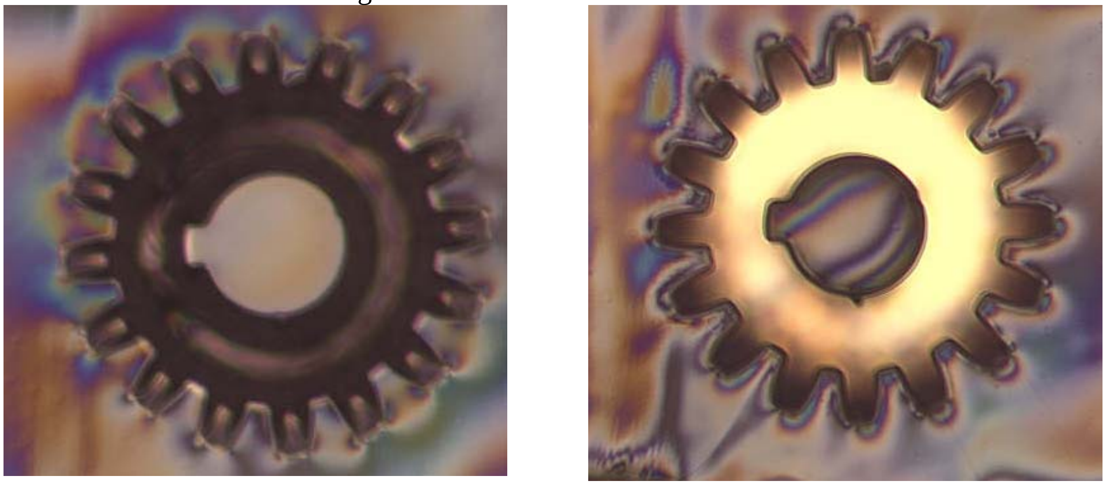
Parameter	Setting
Cleaning method	Ultrasonic acetone bath (15 min) + IPA spray+ DI water+ Dehydration by hotplate 120 ° C (10 min)
Relaxation time	5 min
Spin-coating	Spin at 250 rpm (5s), acceleration 50 + Spin at 1000 rpm (45s), acceleration 150
Relaxation time	1 min
Soft baking	65°C (60min)
Relaxation time	30 min
Exposure energy	1440 mJ/cm2
Post exposure baking	65°C (5 min) + 95°C (15min)
Relaxation time	One night
Development	SU-8 developer (15 min) + Acetone (50s) +IPA (spray) +DI water (spray) + Pressurized nitrogen

3.9.3 Results and discussion

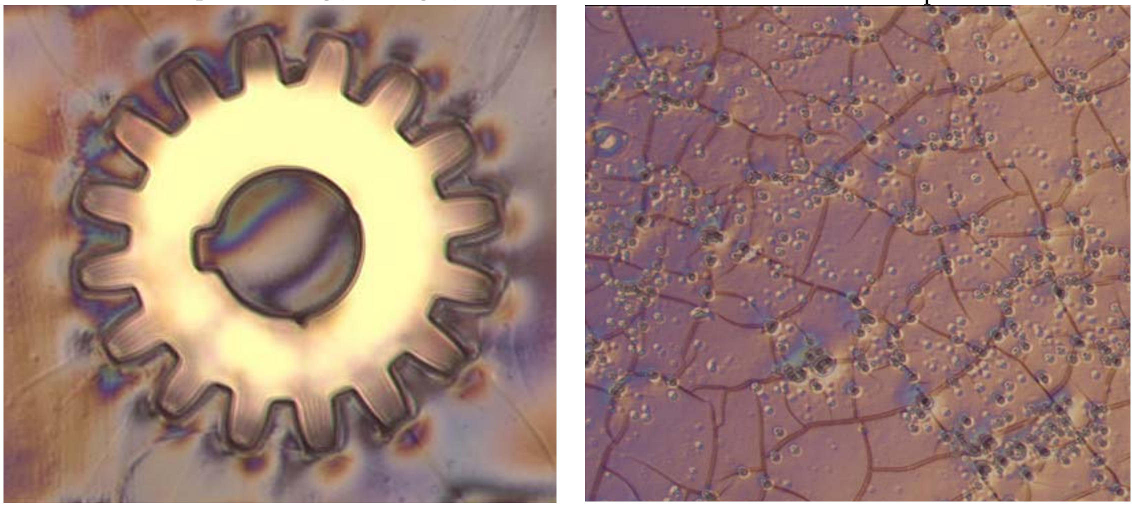
As can be seen in Figure 3-36, there is a good improvement in the results. Soft baking at low temperature reduces the stress induced due to the thermal mismatch between glass and SU-8, so, preventing cracking. Hence, one-night relaxation time helps the internal stress inside the SU-8 to release. Furthermore, we found that although using acetone could remove SU-8 residue [62], it caused cracks on the SU-8 surface. Therefore, it is better to optimize the process parameters instead of using acetone for removing SU-8 residue.



a- After soft-baking b- After Post-baking



c- After post-baking(one night) d- After development



e- After Rinsing with Acetone[50seconds] f- Cracks on the SU8's surface

Figure 3-36 Steps of photolithography process

3.9.4 Solution

The results show that still there was some stress inside the resist which must be decreased. One other parameter left for decreasing internal stress was post exposure baking temperature. As for soft baking temperature, the post exposure baking temperature caused thermal stress inside the resist. So, it is better to use low temperature for post exposure baking.

3.10 Experiment 4- Mold fabrication (post exposure baking temperature)

For overcoming crack and delamination problems, in this experiment, the post exposure baking temperature was decreased.

3.10.1 Post exposure baking temperature

As has been reported by other researchers, it is possible to decrease post exposure baking temperature to 55°C [63].

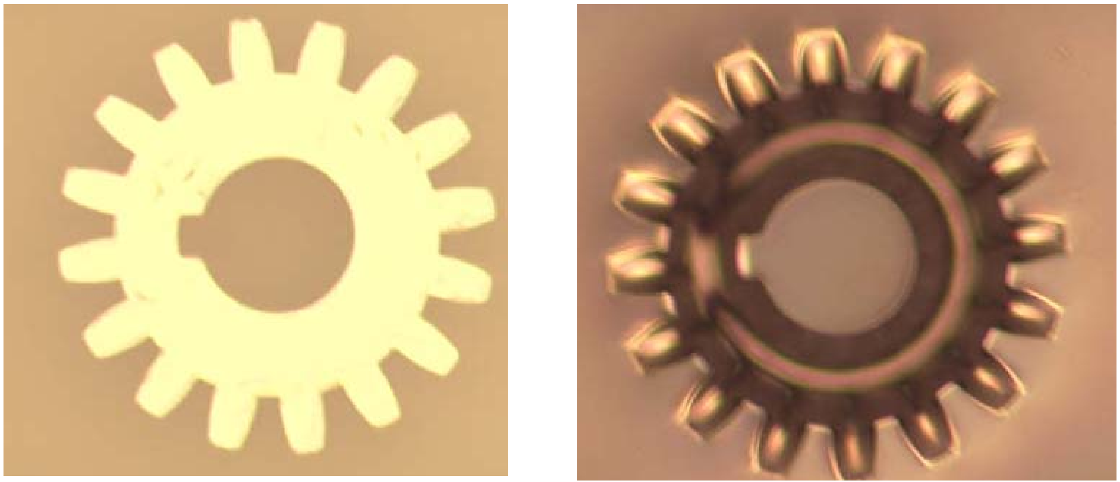
Table 3-6 shows the photolithography parameters of SU-8 for the fourth experiment.

Table 3-6 Photolithography parameters of SU-8 for the fourth experiment

Parameter	Setting
Cleaning method	Ultrasonic acetone bath (15 min) + IPA spray+ DI water+ Dehydration by hotplate 120°C (10 min)
Relaxation time	5 min
Spin-coating	Spin at 250 rpm (5s), acceleration 50 + Spin at 1000 rpm (45s), acceleration 150
Relaxation time	1 min
Soft baking	65°C (60min)
Relaxation time	One night
Exposure energy	1440 mJ/cm2
Post exposure baking	55°C (40 min),
Relaxation time	One night
Development	SU-8 developer (15 min) +DI water (spray) + Pressurized nitrogen

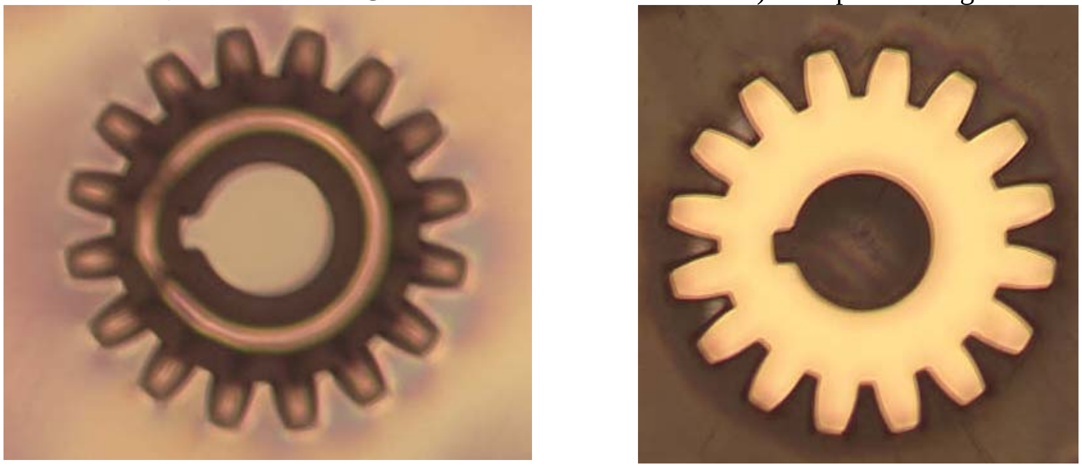
3.10.2 Results and discussion

As can be seen in Figure 3-37, with the help of all modification, there was no crack on the resist surface and no delamination happened. So, with the help of Table 3-6 we can make the molds for the next step (nickel electroplating) without any problem. Figure 3-38 shows the SEM image of gear mold.



a)After soft-baking

b)After post-baking



c)After post-baking (one night)

d)After development

Figure 3-37 Steps of photolithography process

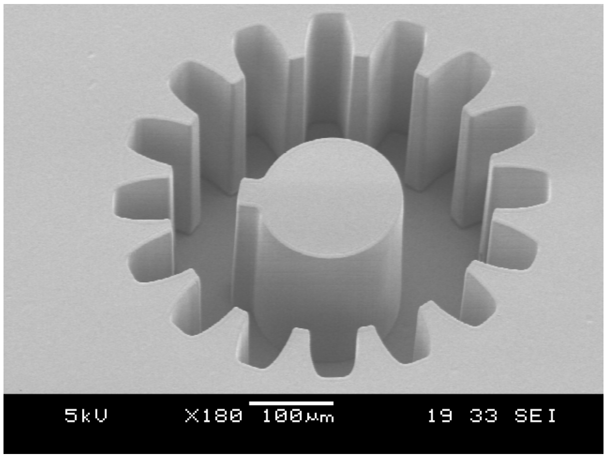


Figure 3-38 SEM image of gear mold

3.11 Experiment 5- Mold fabrication (two layers)

In this experiment, for increasing the height of the structure, instead of one SU-8 layer, two SU-8 layers were coated on the ITO glass. Hence, at first, one SU-8 layer was coated and soft-baked, and then the second SU-8 layer was coated and soft-baked.

Table 3-7 shows the photolithography parameters of SU-8 for two layer mold fabrication.

Table 3-7 Photolithography parameters of SU-8 for the fifth experiment

Parameter	Setting
Cleaning method	Ultrasonic acetone bath (15 min) + IPA spray+ DI water+ Dehydration by hotplate 120 °C (10 min)
Relaxation time	5 min
Spin-coating	Spin at 250 rpm (5s), acceleration 50 + Spin at 1000 rpm (45s), acceleration 150
Relaxation time	1 min
Soft baking	65 °C (60min)
Relaxation time	1 hrs
Spin-coating	Spin at 250 rpm (5s), acceleration 50 + Spin at 1000 rpm (45s), acceleration 150
Soft baking	65 °C (4hrs)
Exposure energy	1440 mJ/cm2
Post exposure baking	65 °C(5 min), 95 °C(25 min)
Relaxation time	4hrs
Development	SU-8 developer (22 min) +DI water (spray) + Pressurized nitrogen

3.11.1 Results and discussion

As can be seen in Figure 3-39, delamination happened and the walls of the structure were not straight. So, this method did not seem a good way for increasing the height of structure. Therefore other methods were tried. It was decided to increase the height of the structure after electroplating, as shown in Figure 3-40. This is left for future work.

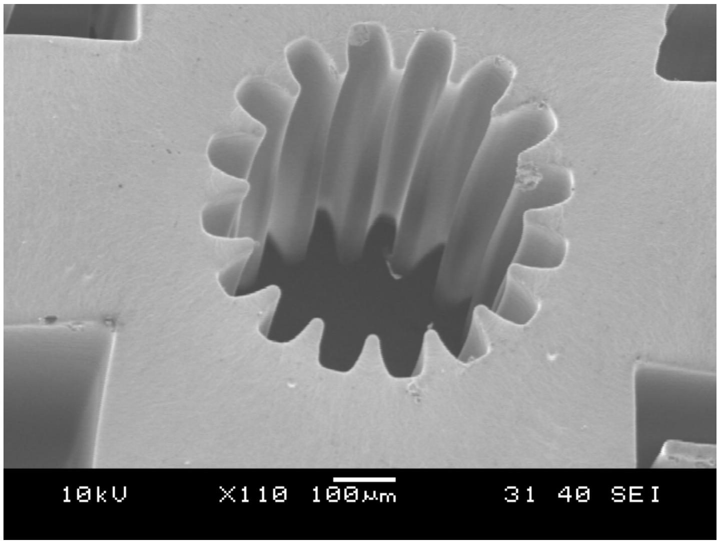


Figure 3-39 SEM image of gear mold for two layers

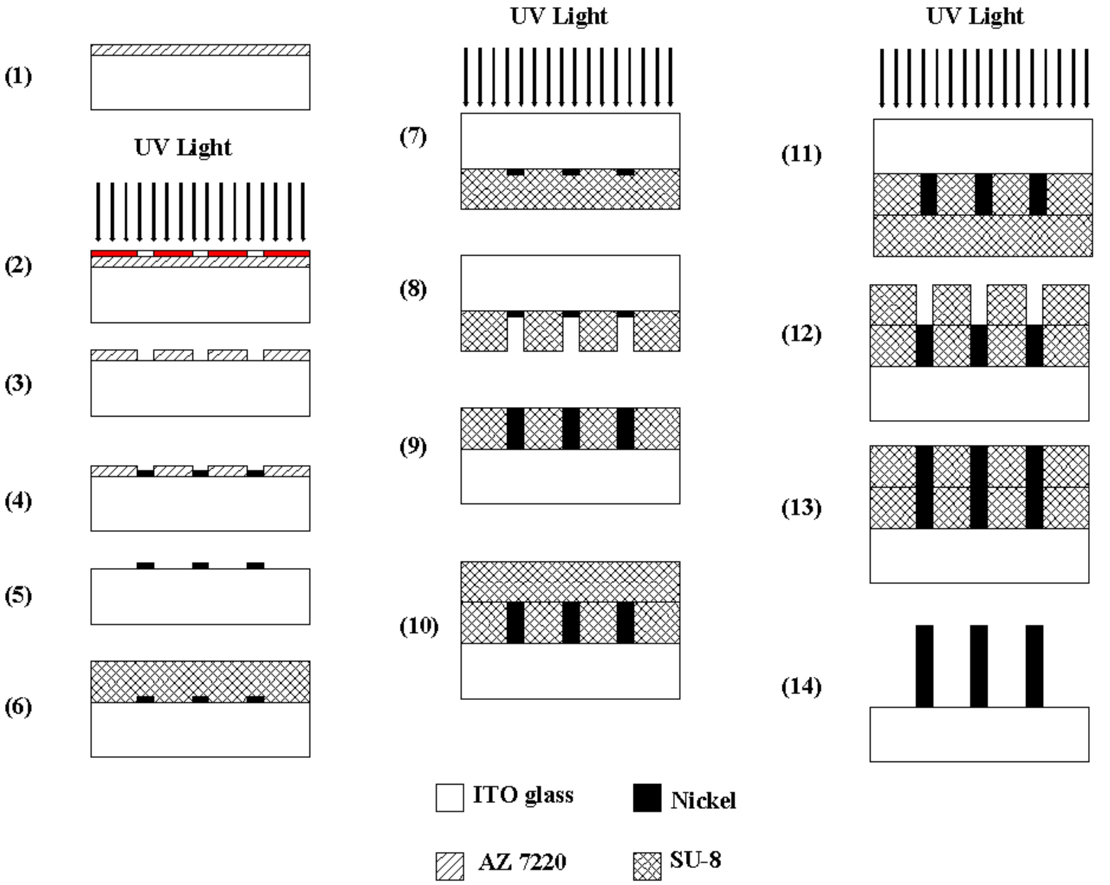


Figure 3-40 SU-8 mold fabrication steps for two layers
1- Coating a thin layer AZ7220 positive photoresist (2µm) on ITO glass, 2- Patterning of AZ7220 photoresist, 3- Development of the photoresist, 4- Electroplating nickel, 5- Removing the AZ7220 photoresist, 6- Coating of a thick SU-8 photoresist, 7- Patterning SU-8 photoresist, 8- Development of the SU-8, 9- Electroplating nickel, 10- Coating of a thick SU-8 photoresist, 11- Patterning SU-8 photoresist, 12-Development of the SU-8, 13-Electroplating nickel, 14- Removing SU-8

4 Electroplating

4.1 Electroplating

Electroplating is a process by which a metallic cation transports through an electrolyte and deposits on a substrate by an electric current. Nowadays, there are many applications for electroplating and this process has a good potential to be used in high-aspect-ratio structures such as LIGA process. This additive technology has several advantages such as:

- Cheap capital equipment
- Low operating cost
- Reliability
- Precise control
- Quick process
- Very low temperature process(50C), so it is IC-compatible processing
- Magnetic structural material available
- High conductivity structural material available
- No clean room needed
- Few process variable
- High-aspect-ratio devices can be achieved

The entire of electroplating process involves:

1- Preparation of substrate

2- Preparation of electrolyte

3- Electroplating process

The characteristics of the resultant electroplated structure, such as uniformity, thickness and mechanical properties can be controlled by plating parameters, such as electrolyte composition, plating temperature, current and pH of electrolyte, discussed below.

Electroplating can be applied to a wide range of materials, including conductive polymers, metals, metal alloys and some semiconductors. Almost 17 metals can be used in this process, namely as: Ni, Co, Fe, Cr, Pb, Ir, Sn, Pd, Zn, Rh, Ru, Cu, Ag, Cd, In, Pt and Au. But only a few of them can be used for electro-deposition of microstructures.

Among all the metals which can be electroplated, nickel is commonly used in MEMS industry. It has good mechanical properties, such as hardness, yield strength and Young's modulus and good resistance against corrosion; so it has been chosen as the structural material in this project.

4.2 Electrochemical deposition

Electrochemical deposition or electroplating can be divided into two groups:

- electrodeposition
- electroless deposition

Electrodeposition refers to the decrease of metal ions from electrolyte solution to the solid metal by an external current. LIGA and LIGA-like process are examples of this process by which metal and metal alloys are plated onto the mold structure to make microstructures.

In electroless deposition, metal ions at the catalytic surface are reduced by a chemical agent inside the solution, and thus external current is not needed. This process gives more uniform plating rather than electrodeposition because it depends on the chemical reaction without current distribution problem [64].

4.3 Electroplating Mechanism

Figure 4-1 shows a simple electroplating set up used in this project. Both the sample and nickel are immersed in the electroplating solution. The sample and nickel are connected to the negative and positive terminals respectively. So, the sample is cathode and nickel is anode. When there is enough bias between cathode and anode, electrons will move from the anode to the cathode. At the cathode, a reaction occurs and results in the deposition of nickel on the sample. This reaction is as follows:

$$Ni^{2+} + 2e^{-} \Rightarrow Ni \qquad (4\text{-}1)$$

At the other side, which is the anode, another reaction occurs whereby the nickel dissolves into the electrolyte.

$$Ni \Rightarrow 2e^{-} + Ni^{2+} \qquad (4\text{-}2)$$

This reaction helps the electrons to flow to the power supply and nickel ions flow inside the solution. Therefore, a hydrogen reaction occurs near the cathode, resulting in formation of hydrogen bubbles:

$$2H^{+} + 2e^{-} \Rightarrow H_2 \qquad (4\text{-}3)$$

This process must be avoided because the hydrogen bubbles decrease the electroplating quality.

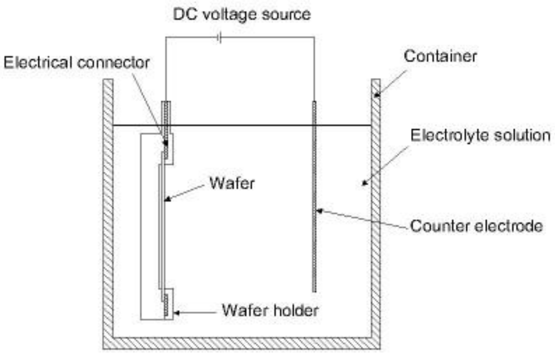


Figure 4-1 Typical setup for electroplating [65]

4.4 Electroplating Calculation

For calculating the required current density needed for obtaining a certain thickness in a definite time, Faraday's law is used. Faraday's law saying that when there is 96485 coulombs of electrical charge through the solution of electrolytic, one gram equivalent weight of anode substance is electroplated on the cathode. One gram equivalent weight refers to equivalent weight in grams. Nickel ion (Ni^{2+}) which is in the plating bath needs 2 electrons to change to Ni atom until it can be deposited. The gram equivalent weight gives the value of the material being plated out according to the number of required electrons to neutralize the atomic weight in grams from the ions of the material [66]. This value can be calculated by dividing the molecular or atomic mass of the substance to the moles number of electrons achieved or lost.

By considering the Faraday's law:

$$W = \frac{I \times t \times GEW}{F} \qquad (4\text{-}4)$$

Where:

W: Deposited weight (grams)

I: Current (Amperes)

t: Period time of electroplating;

GEW: Gram Equivalent Weight (grams/equivalent)

F: Faraday's constant (96485 C/mol)

By definition:

$$GEW = \frac{Mol.Wt.}{n_e} \qquad (4\text{-}5)$$

$$W = \rho_{Ni} \times Vol. \qquad (4\text{-}6)$$

$$Vol. = A \times T \qquad (4\text{-}7)$$

Where:

Mol.Wt : Molecular Weight of Nickel=58.71 gr/mol

n_e: Valance of material (which is 2 for nickel);A: Electroplated area (cm^2).

ρ_{Ni}: Nickel's density (8.9gr/cm^3)

Vol.: Volume (cm^3)

T: Total thickness of deposited material (cm);

So:

$$GEW = 29.355 \qquad (4\text{-}8)$$

$$W = 8.9 \times A \times T \qquad (4\text{-}9)$$

With substituting equation (4-8) and (4-9) in equation (4-4):

$$8.9 \times A \times T = \frac{I \times t \times 29.355}{96488} \qquad (4\text{-}10)$$

$$T = \frac{I \times t \times 29.355}{96488 \times 8.9 \times A} \qquad (4\text{-}11)$$

$$T = (3.413 \times 10^{-5}) \frac{It}{A} \qquad (4\text{-}12)$$

So the rate of electro-deposition of nickel will be:

$$R = (0.3413)\frac{I}{A} \qquad (4\text{-}13)$$

Which R is the rate of plating in thickness (μm/s). But it must be considered that in practice, efficiency is not 100% and some current is consumed for the evolution of hydrogen around the cathode.

4.5 Electroplating parameters:

There are several parameters which affect electroplating that we will discuss about them in the following:

1-Current density:

Current density can be calculated by dividing the plating current to the plating area. Due to the Faraday's law, increasing in the current density results into the increased in the rate of plating. Furthermore, studies have shown that the deposited films with high current density are smoother than the films plated with lower current density [67]. Also, it must not be increased from a certain value obtained by trials and errors.

2- pH:

pH depends on the chemical composition of the electrolyte but totally it must be kept in a range of 1.5 to 5 to have a good electroplating [68]. During electroplating, pH must always be controlled. If pH is greater than desired value, drops of dilute hydrochloric acid are used to decrease the pH. If pH is less than desired value, potassium hydroxide is used to increase the pH. [69]

3- Temperature

Temperature plays an important role in electroplating. It has been observed that at high bath temperature, the surface finish is poor and grain size is large [70]. The recommended temperature for nickel electroplating is 45 ° C to 60 ° C.

4-Agitation:

When electroplating occurs, the concentration of ions near the cathode will decrease. For minimizing the regions with low concentration, agitation is useful. Hence, agitation can remove hydrogen bubbles from cathode’s surface when they are evolving during the process, so it prevents pitting inside the platting structure. It was reported that with increase in agitation, surface roughness will decrease [71]. Therefore, agitation must be in a proper value which prevents pitting and poor surface finishing.

5- Bath Composition

Electrolyte bath for nickel electroplating is made from sulphate salts of Ni and chloride. Sulphate bath decrease the cathode efficiency but gives good surface finish on the other hand, chloride bath increase cathode efficiency but gives poor surface. So, for having a good result, sulphate salts and chloride are mixed together to create Watts Bath. [72]

Therefore, it must be noticed that some additives are usually added to the Watts bath, organic sugar and boric acid. They are called additives. Boric acid plays the role of pH buffer and organic sugar (saccharin) is added to improve the surface finish and reduce the stress. Table 4-1 shows the chemical concentration for electroplating solution. Between all these chemicals, nickel sulfamate ($NiSO_4$) plays the role of nickel carrier during plating.

Table 4-1 Composition of technical nickel "S" sulfamate electroplating solution [73]

	Chemicals	Quantity(in 1 liter)
1	Nickel Sulfamate Concentrate(20 oz/gal)	500 ml(75 g nickel)
2	Nickel Bromide Concentrate(28.3 oz/gl)	57 ml (12 g nickel)
3	Boric Acid	38g
4	NP-M2 Anti-pit	1.6 ml
5	JB-100 Stress Reducr	10 ml

4.6 Pulse electroplating [74]:

Pulse plating is a new technique for deposition of metals and alloys. In the conventional DC electroplating, there is just one parameter, current, which can be changed. But in pulse plating there are three parameters:

1- Peak current density (i_p)

2- The cathodic duration (on time)

3- The presence of reversed current (off time)

The sum of "on" and "off" time make one pulse cycle. The important equations in pulse plating are as follows:

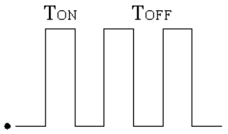
$$\text{Duty cycle} = \frac{Ontime}{Ontime + Offtime} \times 100$$

I_a (average current density) = i_p* duty cycle

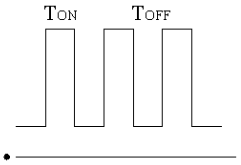
The average current is similar to what used in DC electroplating. The value of duty cycles may vary from 1 to 100% and "on" and "off" times can vary from microseconds to milliseconds. So, for obtaining a desired average current density, we need an unlimited number of combinations of different current pulses. In electroplating, simple square wave pulses are usually used for electroplating, though a variety of combination of wave pulses could also be used as it can be seen in Figure 4-2.

Studies have shown that pulse plating has good effect on the properties of electroplated parts [75, 76]. Pulse plating gives a finer deposit because current density in pulse plating is higher than the corresponding DC density. It results into an increased nucleation rate and leads to finer grains. Depends on the nature of the electrochemical reactions, current efficiency may decrease or increase. Other beneficial effects of pulse plating include improvements in mechanical and physical properties, higher rate of deposition, low inclusion level and reduction in porosity [77, 78, 79, and 80].

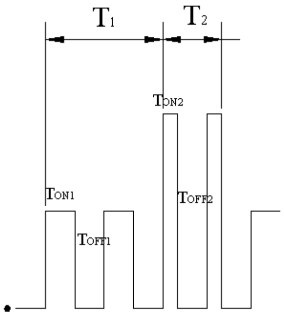
For nickel electroplating, Sutter [81] reported improvement and progress in hardness, microthrowning power and reduction in porosity of nickel deposits. Hence, by using pulse reverse current method an improvement in ductile deposits, crack free coatings and brightness were obtained by using amide bath for nickel deposits [82, 83].



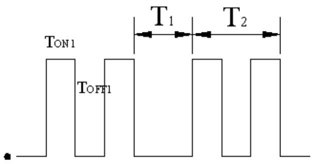
PULSE



SUPER IMPOSED PULSE



DUPLEX PULSE



PULSED PULSE

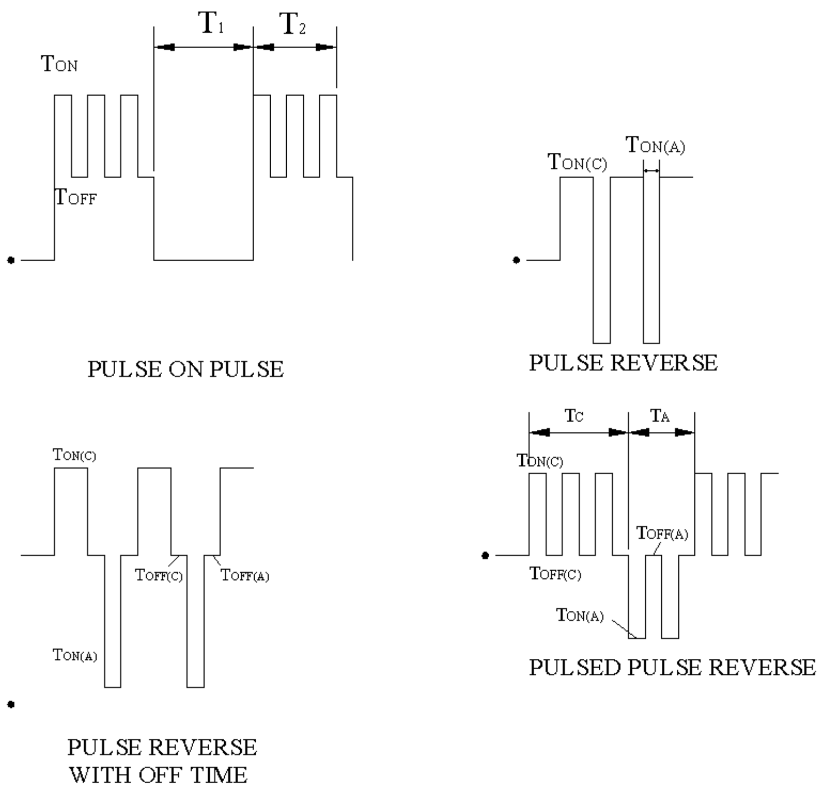


Figure 4-2 variety of combination of wave pulses used in pulse plating

4.7 Poor coating

In some cases, it was found that the features were not coated efficiently. This is due to two reasons [84]:

- Poor wet-ability
- Hydrogen bubble

Poor wet-ability:

One of the factors which affect electroplating is wet-ability of the molds. For increasing the wet ability, there are two ways. One way is immersing the molds in DI water for 8-10 minutes and then used pressurized nitrogen to dry them. This immersing process helps to remove the air entrapped in the molds especially when the molds have small openings. So this process ensures the contact between seed layer and electrolyte. It is better to use ultrasonic for this immersion [85].

Second method is adding Kodak Photoflo to the electrolyte solution to decrease the surface tension of the seed layer. This wetting agent ensures that the solution gets into the structures especially high-aspect-ratio structures and all the structures for electroplating. It is suggested to add 10ml surfactant per liter of the bath for features with opening less than 2µm [86]. After adding the Kodak Photoflo, it is needed to stir it for about 45 minutes. This additive makes a great difference in the electroplating of the molds.

Hydrogen bubble:

The released hydrogen gas near the cathode during the electroplating process decreases plating efficiency and results into poor electroplating. When hydrogen bubbles form during electroplating, they get entrenched and get accumulated in the small structures. So, pits are formed in the structure as the bubbles prevent electroplating. Stirring helps to remove the stagnant bubbles from the surface of feature and improves the plating.

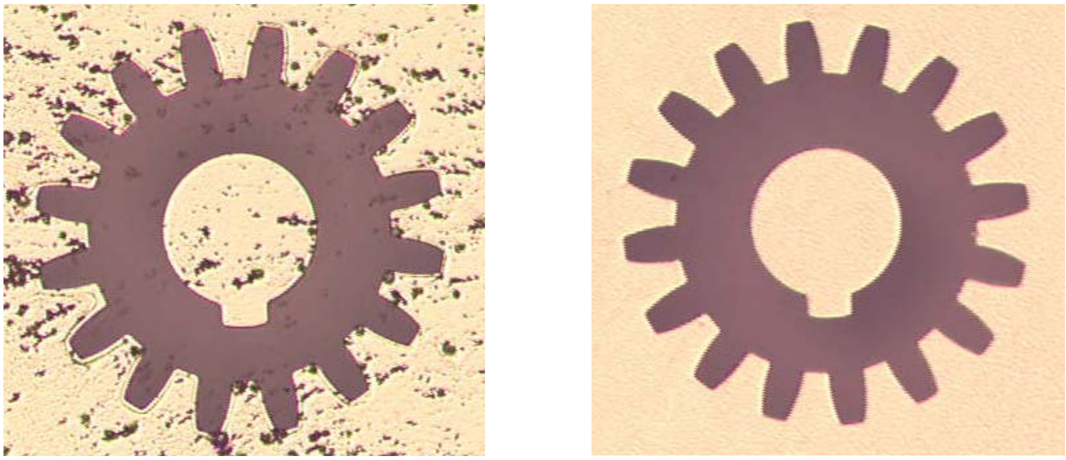
4.8 Problems during electroplating

There are other problems that can happen during electroplating. Table 4-2 shows some examples [87].

Table 4-2 Nickel electroplating's trouble shooting [87]

Pitting	Roughness	Poor coverage
1-Very low anti-pit concentration	1- Airborne dirt	1- poor cleaning
2- Organic/ oil/ grease contamination	2- Boric acid precipitating	2- contamination
3- Colloidal suspended material	3- Insufficient filtering or contamination	3- None-uniform current density
4- None uniform or no agitation	4- _______	4-Insufficient stirring

After a period time of electroplating, the solution does not work properly. Figure 4-3 shows an electroplated mask with several pits. To overcome this problem, it is enough just to add 2-3 anti-pitting drops to the electroplating solution. Figure 4-3 shows the results of electroplated mask after adding anti-pitting to the solution.



a) Before using anti-pitting b) After using anti-pitting

Figure 4-3 Electroplated mask before and after using anti-pitting

4.9 pH dropping

After a period time of electroplating, the pH may drop. It can be checked easily by a pH meter. If pH is below 3, we need to increase it. There are different methods to increase pH as following:

1- Adding 1 cc. chemically pure sulfuric acid to increase the pH up to 3. After adding sulfuric acid, there is need to stir the solution and wait for 5 minutes. If the pH is still under 3, add another 1 cc. sulfuric acid again and repeat till pH 3 is released [88].

2- The easiest way is plating dummy parts for one day. After one day the pH will increase automatically [89].

4.10 Micro-electroplating

Micro electroplating can be divided into two categories:

1- Through-mask plating

2- Maskless plating

4.10.1 Through-mask plating

In this kind of electroplating, a mask plays the role of an insulator to cover parts of substrate where plating is not required. In this plating, the shape of structure is controlled by the mask. Through-mask plating can be divided into three groups (Figure 4-4):

1.1- Plating

1.2- Over plating

1.3- Back plating

Usually electroplating is continued until the whole height of the resist is coated. But if plating continues after filling the structure, over-plating occurs and mushroom structures are formed. Back plating is done when a micro-mold is needed and we do not need free-standing structures.

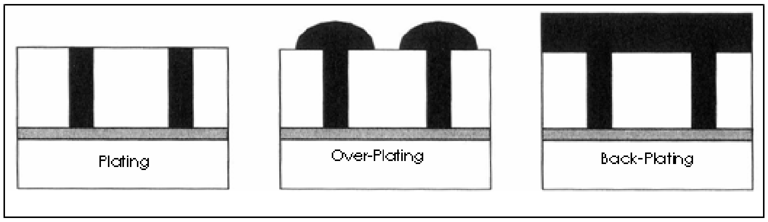


Figure 4-4 Types of through-mask plating [90]

4.10.2 Mask-less plating [91]

In this kind of plating, no mask is used and the entire surface will be plated simultaneously.

4.11 Equipment

Here is the list of equipment used in the electroplating process:

Digital weighting scale (XT 220A Precisa): Used after each electroplating to measure the changes in the bath weight.

DC Power Supply (Hewlett Packard E3631A): Used to provide DC power and has constant current (CC) and constant voltage (CV). Its resolution is ± 1mA when it is set in constant current mode.

pH meter (Radiometer analytical, Ion check 65): Used to measure the pH of the solution

Thermometer (ETS-4 fuzzy): Used to measure the temperature of the solution and fixed it at the desired value.

Hotplate magnetic stirrer: Used to raise the temperature of the solution to the desired value which is needed for electroplating. A stirrer is used during the electroplating.

Multi-meter: Used to measure current output

SEM, JSM-5600: Used to determine the thickness of micro-mold to calculate electroplating time.

Gold sputtering coater (JFC-1200): Before measuring the resist’s thickness, the surface of the mold must be conductive so gold sputtering coater is used.

4.12 Electroplating experiments

4.12.1 Experiment 1

In this experiment, the fabricated mold in chapter 3 was electroplated. In all experiments, before electroplating, all the molds were sputtered until they became conductive. The condition of electroplating is listed in Table 4-3.

Table 4-3 Electroplating parameters

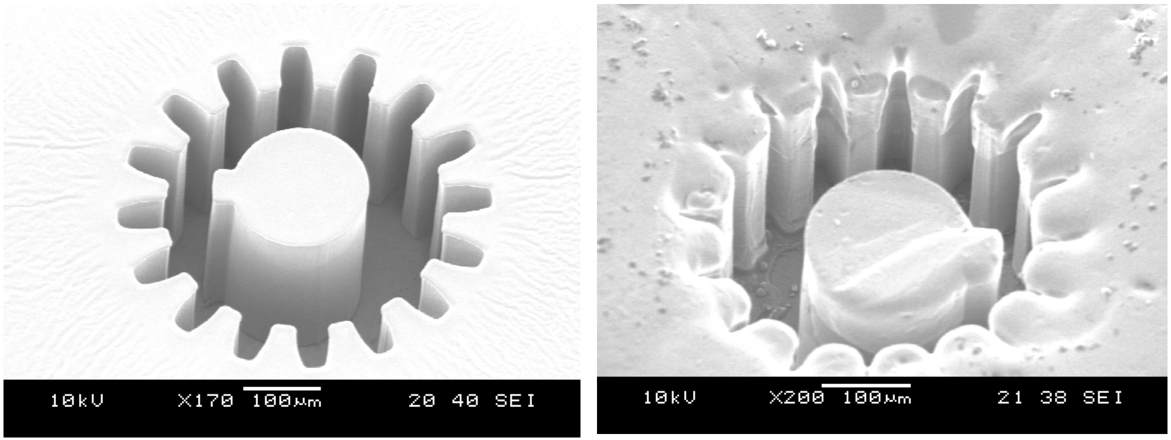
pH	4.5
Temperature	45 °C
Current	50mA
Duration	24 (hrs)
Remark	No pulse plating

Results and discussion

As can be seen in Figure 4-5, after a period of electroplating, the mold surface will be covered and it is not possible for plating to continue and fill the mold. The reason for this phenomenon is that when the current is high, the plating rate is high. So the surfaces which are nearer to the anode get plated sooner than the other places. As a result, it does not allow time for other places to be plated, especially the gaps. This issue is one of the main issues of high-aspect-ratio plating.

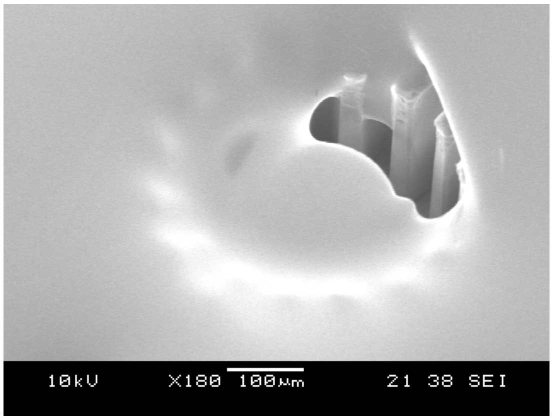
Solution

The first and the simplest way to overcome this problem is using low current to decrease the rate of electroplating.



a) Mold before electroplating

b) Mold after 5hrs electroplating



c) Mold after 24 hrs electroplating

Figure 4-5 Mold's electroplating

4.12.2 Experiment 2- Electroplating (low current)

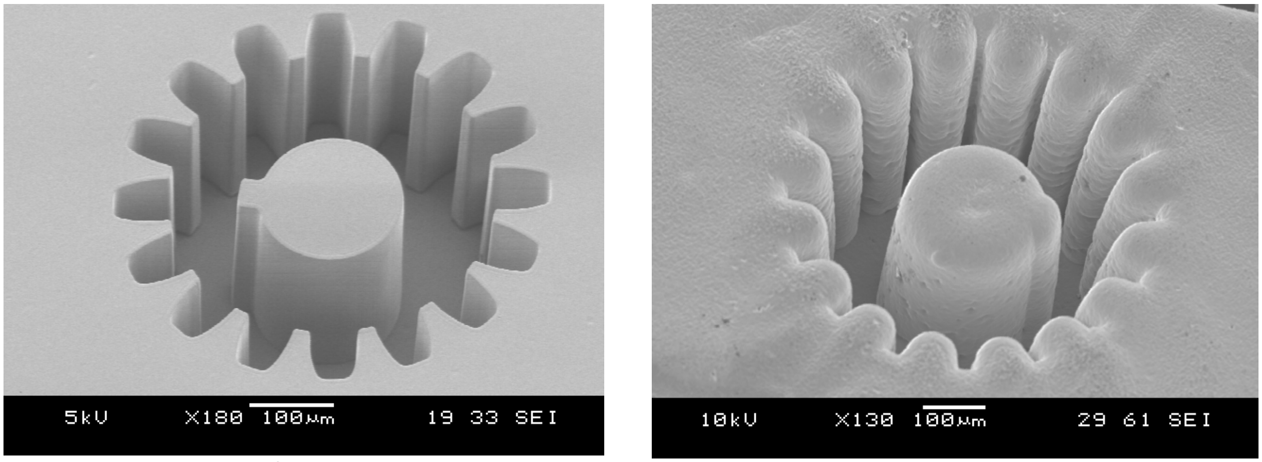
In this experiment, for overcoming the problem of incomplete filling of the mold, low current was used. The condition of electroplating is in the Table 4-4. As Table 4-4 shows, two different currents were used. The first one (10mA) was used for filling the mold. The second one (50mA) was used for back electroplating of the structure.

Table 4-4 Electroplating parameters

pH	4.5
Temperature	45°C
Current 1	10mA
Duration 1	72 (hrs)
Current 2	50mA
Duration 2	24 (hrs)
Remark	No pulse plating

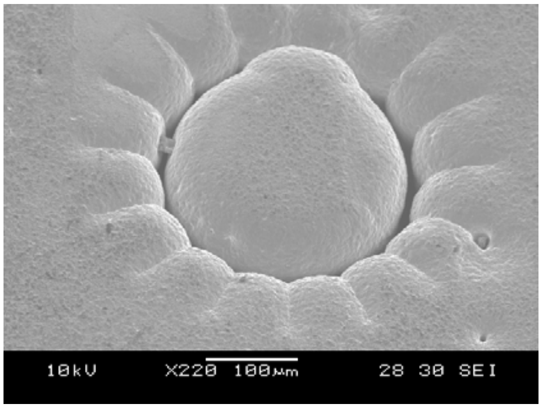
Results and discussion

As can be seen in Figure 4-6, the electroplating was improved, but still needed to be improved further to decrease the pores inside the micro-structures.



a) Mold before electroplating

b) Mold after 24hrs electroplating



c) Mold after 24hrs electroplating

Figure 4-6 Mold’s electroplating

4.12.3 Experiment 3- Electroplating (Pulse plating)

In this experiment, for overcoming the problem of pores inside the micro-gear, pulse plating was used. The condition of electroplating is in Table 4-5. As in previous experiment, two different currents were used. The first one (10mA) was used for filling the mold. The second one (50mA) was used for back electroplating of the structure. In this electroplating reverse current was also used to overcome the problem of pores inside the micro-structures. Reverse current used in this experiment was twice that of forward current but for a short time (2 seconds). As the results of this step will be discussed in the next chapter, we will not show the results here.

Table 4-5 Electroplating parameters

pH	4.5
Temperature	45 °C
Current 1	10mA(30seconds)
Current 1(reverse)	20mA(2seconds)
Duration 1	48 (hrs)
Current 2	50mA(30seconds)
Current 2(reverse)	100ma(2 seconds)
Duration 2	24 (hrs)
Remark	Pulse plating

5 Fabrication of micro-gear structure

One of the challenges in the fabrication of microstructures by SU-8 mold is the separation of the nickel structure from SU-8 mold. In this chapter, we discuss the method of fabrication micro-gear structure such that we can separate the nickel structure from the SU-8 mold easily. Several methods are studied, but only one of these methods is used in this project; others are left for future work.

5.1 Sacrificial photoresist

In this method, a thick photoresist layer is used which plays the role of sacrificial material to ease the process of separating the nickel structure from SU-8 mold. The whole fabrication process is as follows (Figure 5-1):

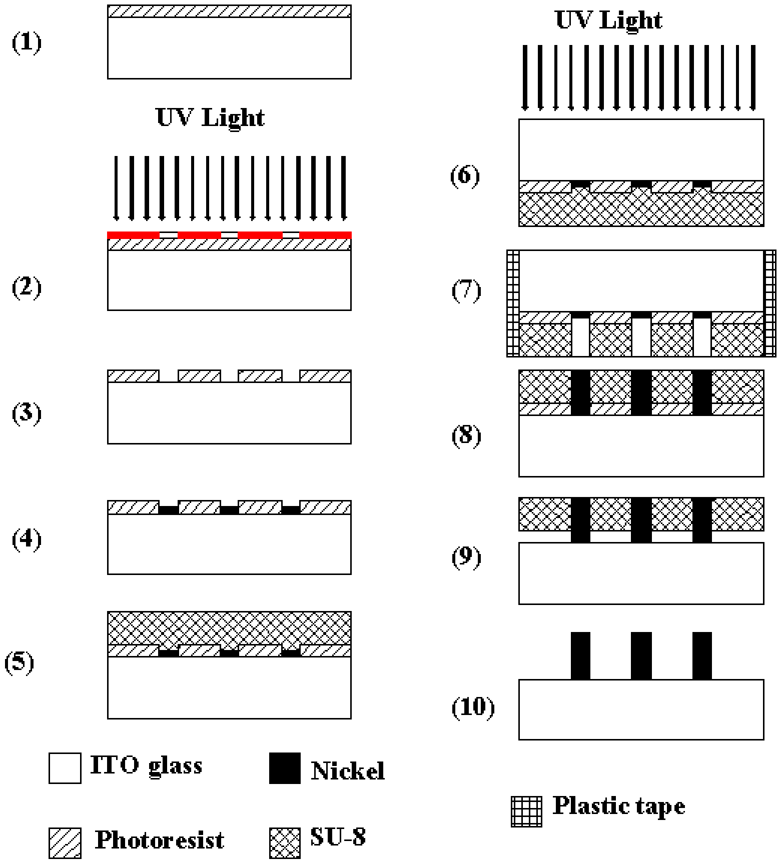


Figure 5-1 Mold fabrication process (Sacrificial layer)
1-Coating a thick layer photoresist (10-20µm) which plays the role of sacrificial material and mold for the first electroplating 2-Patterning of the thick photoresist 3-Development of the photoresist 4-Electroplating of nickel to make the mask 5-Coating of a thick SU-8 photoresist 6-Patterning of SU-8 photoresist 7-Development of the SU-8 8-Electroplating of nickel 9-Removing photoresist by acetone 10-Separating nickel structure from SU-8

5.1.1 Sacrificial photoresist

AZ 4000, NR7-6000P, SPR 220, Polysilicon, silicon compound, phosphosilicate glass all can be used as a thick sacrificial photoresist. Here, just we will discuss about SPR 220 and AZ 4000.

SPR 220[92]

SPR 220 is an i-line (365 nm wavelength) photoresist used for a wide range of film thickness (1-10µm) in a single coating. This photoresist has excellent plating and adhesion characteristics, so it is a good option for using in thick film application.

Characteristics

- g line(436 nm wavelength) and i line capable
- Thickness more than 10 µm with good uniformity in a single coat
- Fast photo-speed 210mJ/cm^2 for 1.1µm lines/spaces@4.0µm film thickness(i-line)
- Excellent dry and wet adhesion
- Ni/Fe, Cu and Au plating without cracks
- MIF and MIB developer compatible
- Compatible with a wide range of substrates

Coating

Figure 5-2 shows the relation between resist thickness and spin speed for 4” substrates. As can be seen, at the speed of 1500 for SPR220-7, we can achieve 10µm thickness.

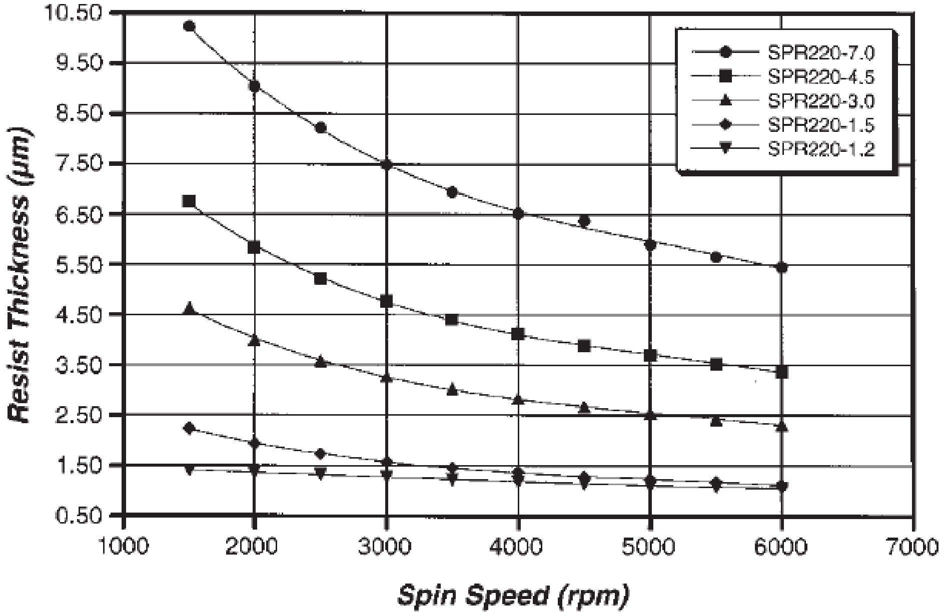


Figure 5-2 Relation between resist thickness and spin speed [92]

Transparency

From the point of transparency, SPR 220 is also a good choice. As can be seen in Figure 5-3 , the transparency of this photoresist improves after UV exposing.

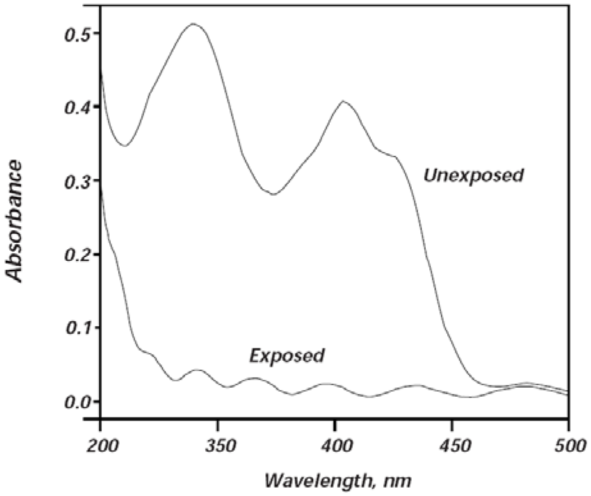


Figure 5-3 Relation between absorbance and wavelength for SPR 220 [92]

AZ 4000 Photoresists [93]

From the point of thickness, AZ 4000 Photoresists are good options. As Figure 5-4 shows, AZ 4000 photoresists can give thickness up to 30μm which is good enough for the sacrificial process. Hence this kind of photoresist can be easily removed by acetone. The only problem of AZ 4000 photoresists is their transparency. They are not transparent photoresist.

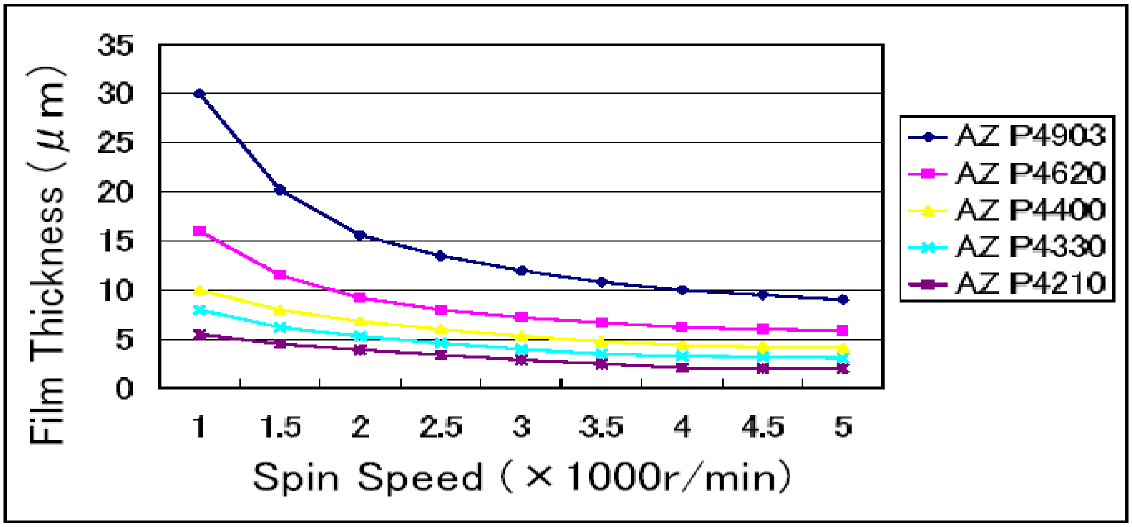


Figure 5-4 Relation between film thickness and spin speed in different AZ resists [93]

Using photoresist as sacrificial layer has several advantages and disadvantages as follows:

5.1.2 Advantages

1- Coating can be done on substrate easily

2- Sacrificial photoresist layer can be removed easily

3- Thickness of sacrificial layer can be controlled

4- It can be removed easily by a benign solution which does not effect microstructure

5.1.3 Disadvantages

1- Sacrificial photoresist can be attacked and dissolved by SU-8

2- Sacrificial photoresist can be attacked by SU-8 developer

This technique is left for future work.

5.2 Sacrificial photoresist and transparent resist

One problem which may happen in the pervious method is the thick photoresist is opaque. So, it does not let the UV light pass through the resist properly. To overcome this problem, there is another method. In this method, we use both thick photoresist and transparent resist and we change the place of thick photoresist with transparent resist after making the mask.

The whole fabrication process is as following (Figure 5-5):

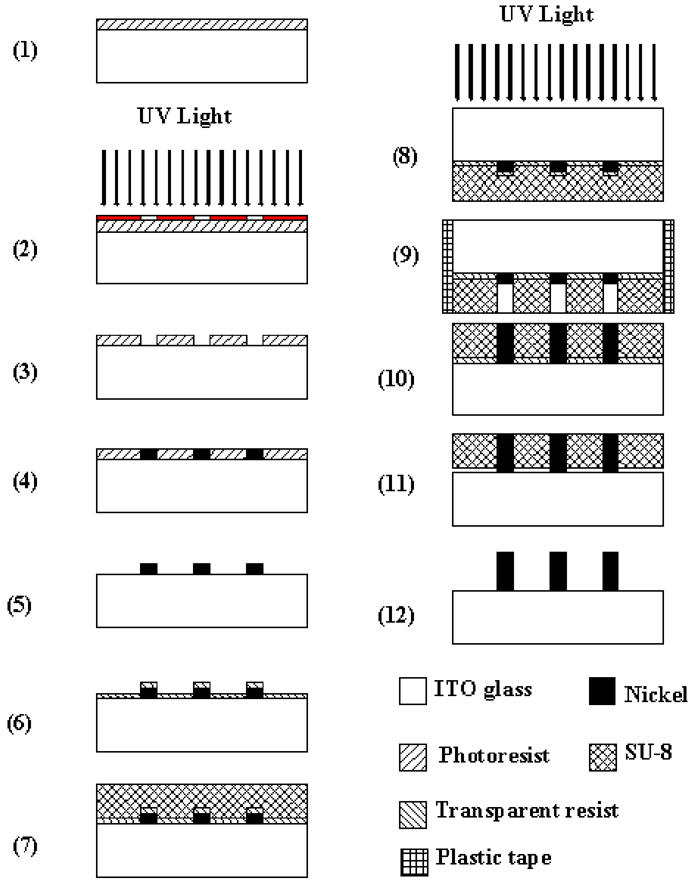


Figure 5-5 Mold fabrication process (Sacrificial layer and transparent resist)
1-Coating a thick layer photoresist (10-20µm) 2-Patterning of photoresist 3-Development of the photoresist 4-Electroplating nickel to make the mask 5-Removing photoresist by acetone 6-Coating transparent resist 7-Coating of a thick SU-8 photoresist 8-Patterning SU-8 photoresist 9-Development of the SU-8 10-Electroplating nickel 11-Removing transparent resist 12-Removing SU-8

This technique is left for future work.

5.3 Using PDMS technique

This is an indirect method for removing SU-8. In this method instead of using SU-8 as a mold for microstructure, PDMS (Polydimethysiloxane) is used. The whole fabrication process is as follows:

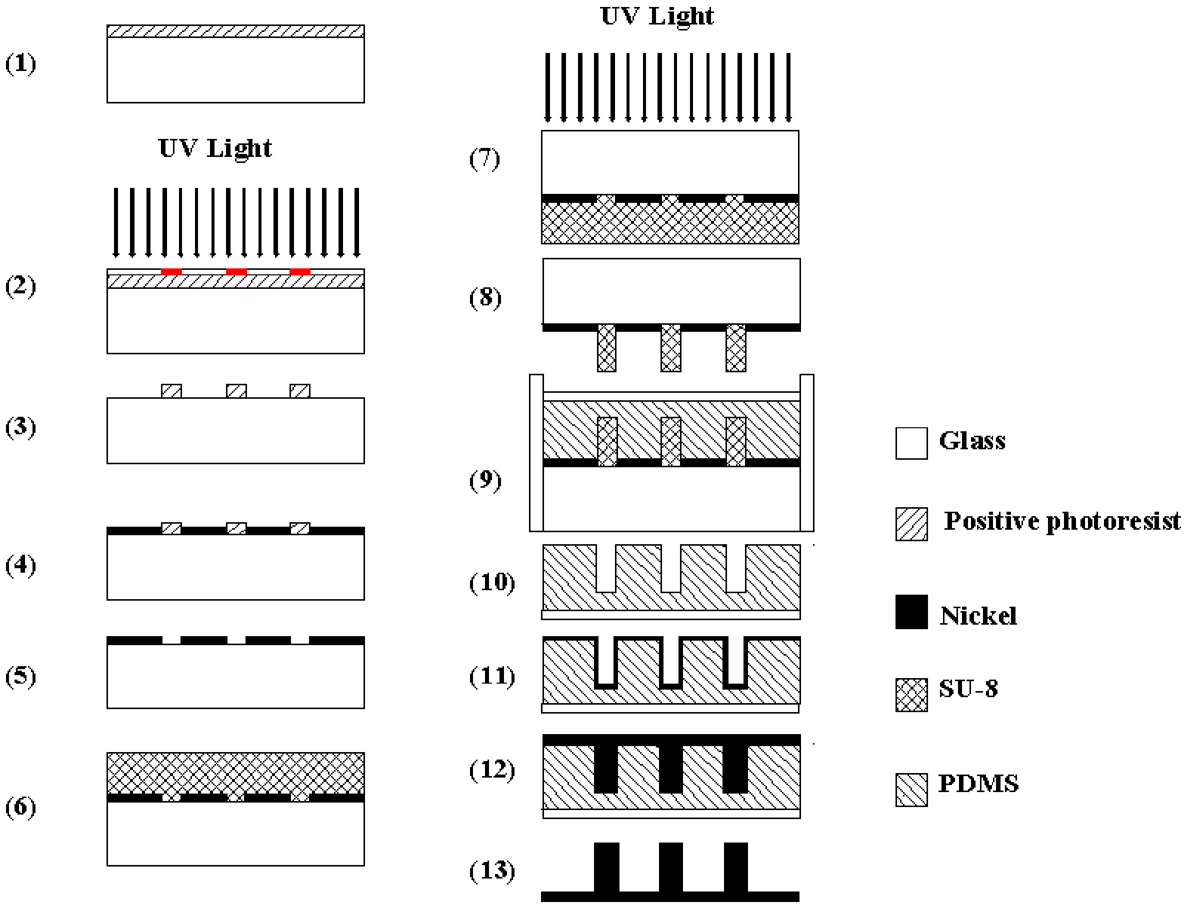


Figure 5-6 Mold fabrication process (PDMS technique)
1-Coating a thin layer photoresist on ITO glass (2µm) 2-Patterning of photoresist 3-Development of the photoresist 4-Electroplating nickel to make the mask 5-Removing photoresist by acetone 6-Coating of a thick SU-8 photoresist 7-Patterning SU-8 photoresist 8-Development of the SU-8 9-Casting PDMS 10-Curing and peeling off PDMS mold 11-Coating a seed layer by electron beam evaporation 12-Electroplating inside the PDMS mold 13-Separating PDMS from nickel structure

PDMS elastomer is used most widely in the fabrication of nano-lithography, rapid prototyping and various microfluidic devices. PDMS has several advantages including: [94, 95]:

- optically transparent
- chemically inert
- non-toxic

- longer life and resistance to chemicals and decomposition
- light
- non flammable
- durable and compatible to microelectronics
- can be used in a wide range of temperature from -100°C-100°C,
- high flexibility(the shear modulus is between 100kPa-3MPa)
- very low loss tangent (tan δ<<0.001)
- high dielectric strength (~14V/µm)
- low glass transition temperature (T_g ~ -125°C)
- can be made fast

Due to PDMS's properties, it has been used as inverse mold for high-aspect-ratio microstructures [96, 97].

5.3.1 Advantages of using PDMS technique

Surface

This technique has a good smooth surface result. Metallic microstructure can be released from PDMS simply, without using any chemical material which means no damage happens for the surface of microstructure. This is a good advantage for this method in comparison with the other methods of removing SU-8.

Cost

This method is a cheap and very simple method and the price of PDMS is also cheap. By a SU-8 master mold, easily we can fabricate a lot of PDMS replica in a short time.

Rapid

This is a rapid method for making high-aspect-ratio structures because this method omits most part of the fabrication process.

Simple removing

Removing PDMS from microstructure is simpler and easier than removing SU-8 from microstructure.

Non-clean-room process

Using PDMS does not need any cleanroom environment which decreases the need for special equipment.

5.3.2 PDMS problem

Although PDMS has several advantages but it has its own disadvantage which limits its wide application. The surface of PDMS is hydrophobic, so it is difficult to spread and transfer aqueous solutions [98].

Several methods have been used to improve the PDMS surface and hydrophilize it. These methods include chemical, physical or a combination of physical and chemical [98]. Between all the methods, oxygen plasma is used most widely to hydrophilize PDMS surface. Nevertheless, this method suffers from a problem. This problem is its short lifetime before hydrophobic recovery [99]. To overcome this problem, a two step modifications has been suggested [100] by using some gases.

Other surface modification methods can be used such as: silanization, adsorption of polymer or protein and lipid coating [101], accumulation or depletion of surfactant in PDMS [99].

Crack

When copper sputtering is used to make the PDMS surface conductive, PDMS surface is attacked by high power plasma. So, micro cracks appear on its surface as it can be seen in Figure 5-7 and Figure 5-8. In order to avoid this crack formation, it is recommended to use electron beam evaporation instead of sputtering. But the deposition profile used in electron beam evaporation of copper is directional and anisotropic. Therefore, the PDMS surface is needed to be rotated and tilted during the evaporation to deposit the copper seed layer on the PDMS surface conformally.

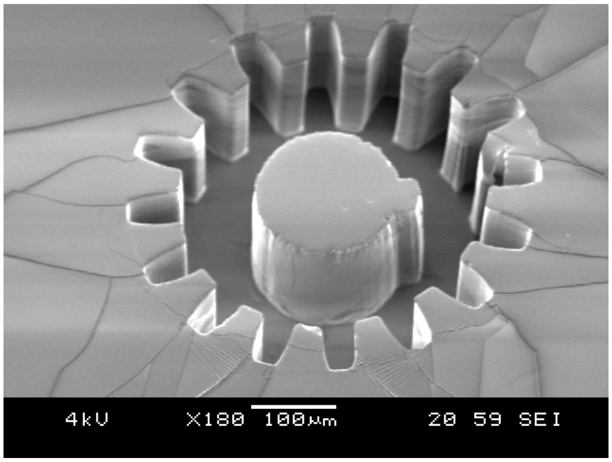


Figure 5-7 Micro cracks on the gear surface

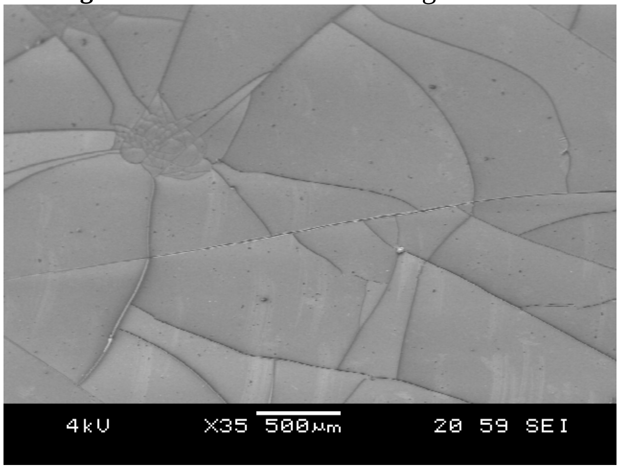


Figure 5-8 Micro cracks on the PDMS surface

5.3.3 Micro mold fabrication parameters

To achieve excellent dimensional accuracy and surface roughness in micro mold fabrication, some parameters such as mixing time, degassing time, curing temperature and curing time must be optimized. These parameters and their adjustment will be discussed in the next sections.

Dosage of curing agent and pre-polymer

For mold making, the most common silicone compound used is RTV (Room Temperature Vulcanizing) silicone. This silicone is mixed in two parts, base and catalyst. RTV silicones have two main classes:

1- *Tin catalyzed or condensation cure silicones*

These silicones are easier to use and less expensive. They are not inhibited by many materials and they have low viscosity; so they can be poured easily. They tend to become brittle after several years and begin to split and tear. These kinds of silicones are used for field work.

2- *Platinum catalyzed or addition cure silicones*

They are often called elastomer with greatest chemical and temperature resistance, are inhibited by many naturally occurring compound and can remain flexible for many years. These kinds of silicones are used for important laboratory work.

RTV 615 has been chosen for the experiments. In RTV 615, the recommended dosage for RTV 615A (pre-polymer PDMS) and RTV 615B (curing agent) is 10:1. Experiments have shown that a slightly more dosage of curing agent of up to fifteen percent is still acceptable and the quality of mold is sufficiently enough. Therefore, the excessive use of curing agent will decrease the mold life and make it possible to tear [102]. On the other hand, insufficient dosage of curing agent will cause the PDMS to cure partially. Figure 5-9 shows the softness and stickiness of the catalyst-deficient regions on the mold surface. This figure shows that the vicinity of mold cavity is not cured completely.

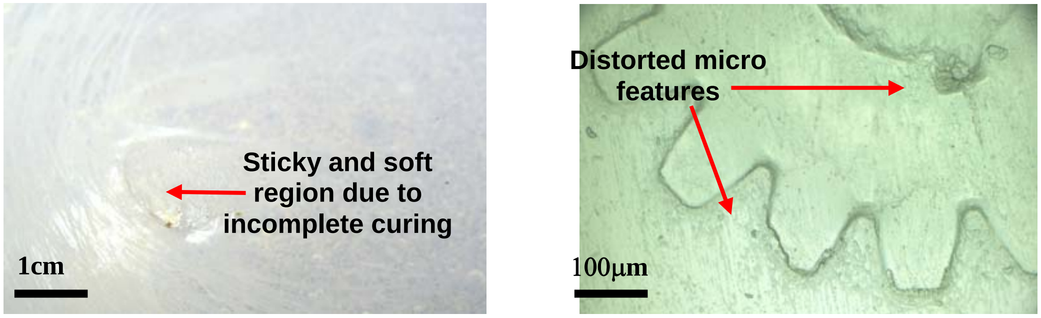


Figure 5-9 Partial curing at mold surface (left) and micro gear cavity (right) [103]

Mixing and degassing time

Mixing and degassing time must be controlled carefully to ensure that the processing time of mixing and degassing does not exceed the PDMS pot, during which the PDMS is still fluid [104]. If degassing or mixing time exceeds pot life, it results in void formation in the micro mold. Figure 5-10 shows void formation in mold due to degassing beyond silicone pot life. When the pot life passes, the PDMS mixture starts to harden and cross-link. So, if there are still bubbles inside the mixture, the hardening mixture will trap the air bubbles and cure them and form permanent voids inside the micro mold. If these voids form near the cavity, they will distort the micro gear feature.

To have a void-free micro mold with a smooth surface, mixing and degassing must be done well. The total time of mixing and degassing process must not be more than the PDMS pot life. With the help of a high speed mixer, 2-5 minutes of mixing time are recommended to ensure complete mixing. Hence 10-15 minutes degassing time are recommended for the process [103].

For removing bubbles without the use of a vacuum pump, other methods can be used. One of them is using ultrasonic agitation. It is enough to put the mixing PDMS inside the ultrasonic machine for 5-10 minutes. After this time most bubbles will disappear from the mixing solution.

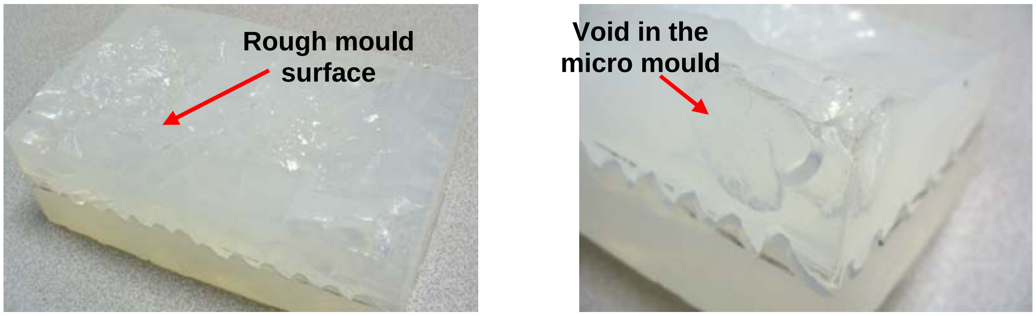


Figure 5-10 Void formation in mold due to degassing beyond silicone pot life [103]

Curing Time and temperature

Curing time and curing temperature are two parameters which affect each other. When PDMS cures at higher temperature, it needs less curing time [102,104]. Table 5-1 shows the cure temperature and curing time for RTV 615. Curing time can be greatly decreased by using fast-acting curing agent.

Table 5-1 Cure times/temperatures for RTV 615[96]

Cure Temperature (^{0}C)	25	40	65	70	100
Approximate Cure Time (hours)	18-24	10-12	4	2-3	1

To achieve excellent dimensional accuracy, it is recommended to cure PDMS at 40 °C [105].

5.3.4 Experiment

RTV 615A (pre-polymer PDMS) and RTV 615B (curing agent) were mixed together with a weight ratio of 10:1 and poured on the SU-8 microstructure. Then it was cured and peeled off from SU-8 to make reverse image. The PDMS used in this experiment was from Sylgard 184, Dow Corning, USA. All experiments have been done in a class-100 clean room. Table 5-2 shows the parameters and setting for the experiment. In order to avoid entrapped air bubbles, ultrasonic machine was used. Then PDMS was coated by a thin layer of copper by sputtering method for electroplating.

Table 5-2 Effective parameter settings for mold fabrication

Parameter	Setting
Amount of curing agent added to pre-polymer	10-15% by weight of silicone rubber
Mixing time for silicone rubber with catalyst	10 min(by hand)
Time for removing bubble	10-15 min
Method of removing bubbles	Ultrasonic machine
Curing time for PDMS	24 hours
Curing temperature for PDMS	25^{o}C

PDMS is a very flexible material and may deform during electroplating. Also using a thick PDMS increase the stiffness and may can not solve the problem. Therefore, it is recommended to use a glass and bond it to the PDMS replica before electroplating [106]. This indirect removal method has three steps:

- Preparing a SU-8 microstructure mold (Figure 5-11)
- Making PDMS replica by casting of SU-8 mold (Figure 5-12)
- Electroplating inside PDMS

As mentioned before, this technique has several advantages but it still needs to work in two parts:

- *Making PDMS replica*: PDMS casting results were not good enough and we need to optimize the parameters of PDMS casting to achieve better results.
- *Separation*: after electroplating inside the PDMS, it was a little difficult to separate the microstructure from PDMS. Hence, there is need to understand and solve the problem.

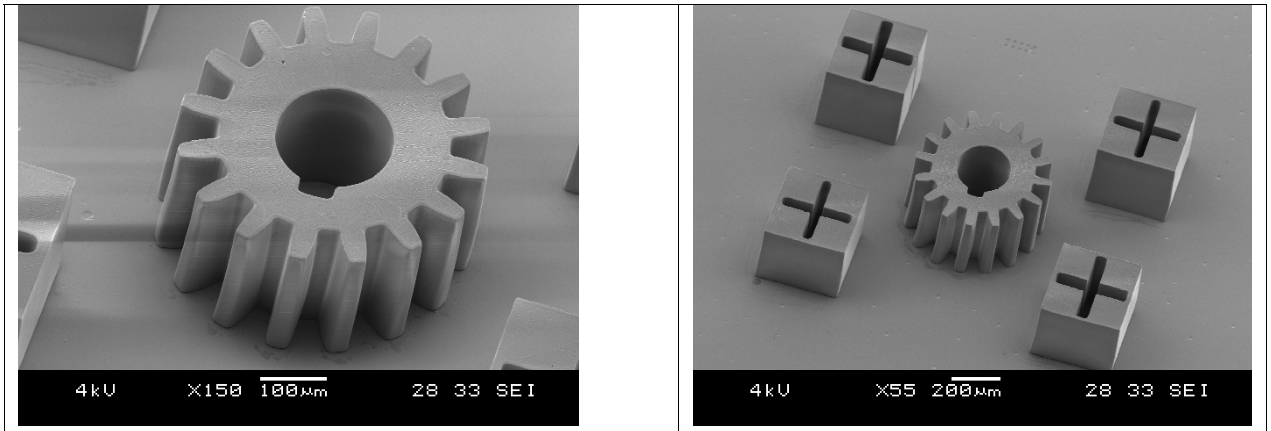


Figure 5-11 SU-8 microstructure mold

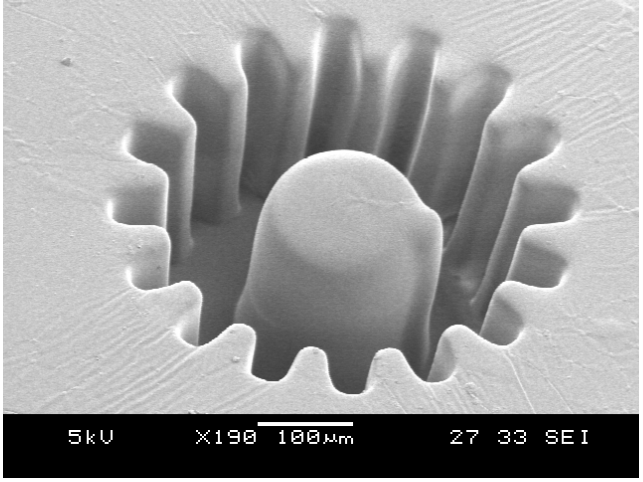


Figure 5-12 PDMS replica by casting of SU-8 mold

5.4 Sacrificial copper

In this method, a thin copper layer is used which plays the role of sacrificial material to ease the process of separating the nickel structure from SU-8 mold. The whole fabrication process is as follows (Figure 5-13):

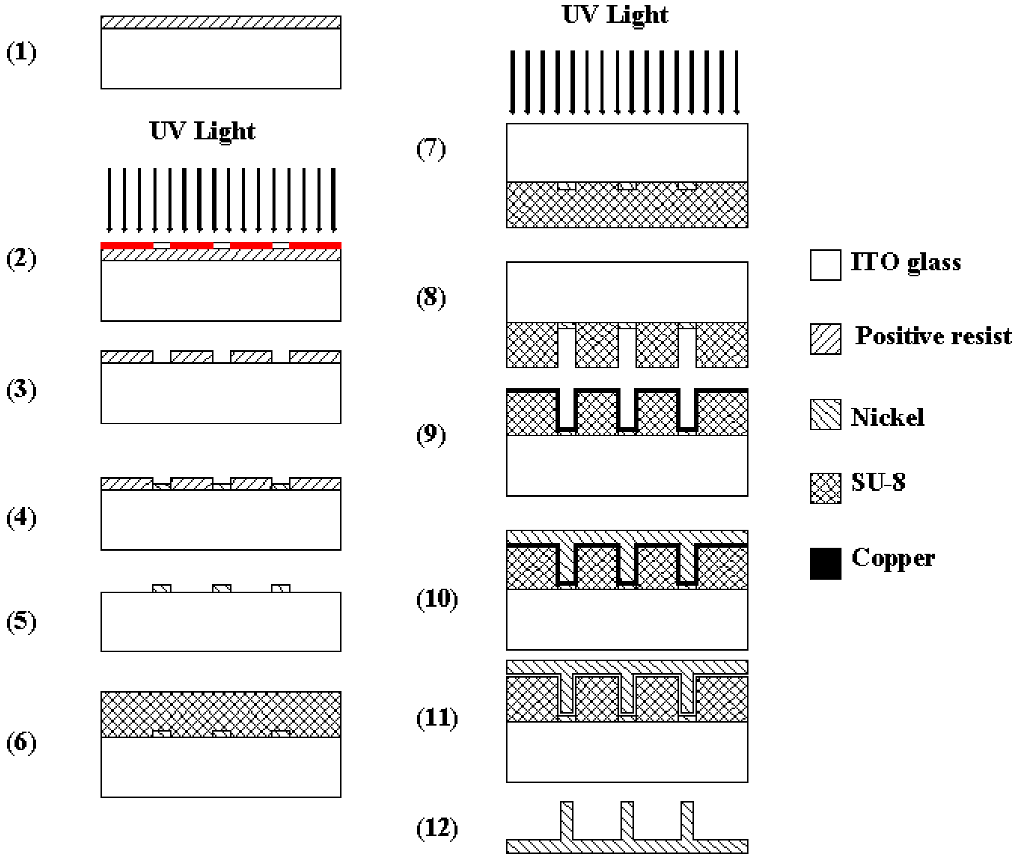


Figure 5-13 Mold fabrication process (Sacrificial copper)
1-Coating a thin layer AZ7220 positive photoresist (2µm) 2-Patterning of AZ7220 photoresist 3-Development of the photoresist 4-Electroplating nickel 5-Removing the AZ7220 photoresist 6-Coating of a thick SU-8 photoresist 7-Patterning SU-8 photoresist 8-Development of the SU-8 9-Sputtering a thin layer of copper 10-Electroplating nickel 11-Etching copper 12-Completed structure

In this method, after fabrication of SU-8 mold, the SU-8 mold is coated by a thin layer of copper. Then, the nickel microstructures are electroplated within the patterned SU-8 template on the ITO glass base in the solution of nickel sulfamate bath. Finally, the high-aspect-ratio nickel microstructure is obtained after etching the thin copper layer by copper etchant. In the following, we will discuss about each steps in detail.

5.4.1 Copper as a sacrificial material

Using sacrificial layer is a basic technique in MEMS fabrication. To cite an example, in surface micromachining, some material is deposited and some removed. Without sacrificial method, MEMS fabrication would be impossible. In most of the cases, photoresists are used as sacrificial layers to define a feature or plate molds or protect a desirable area during etching. Polysilicon, phosphosilicate glass silicon compound are other sacrificial materials used in MEMS fabrication.

In this method, a thin sputter or evaporated metal (copper) deposition is used. This thin metal layer plays two roles:

- seed layer
- releasing the electroplated microstructure from SU-8 by etching it

5.4.2 Copper sputtering

For deposition of a thin copper layer, Denton DC/RF sputtering system was used. The setting parameters are in the Table 5-3.

Table 5-3 Sputtering parameters

Parameters	Value
Base pressure	10^{-6}mtorr
Time taken to base pressure	45 min
Process pressure	4.92mtorr
DC power	200 W
Deposition time	5min
Voltage	419 V
Current	0.48A

5.4.3 Removal of sacrificial layer

For removing sacrificial material, two ways can be used: dry etching or wet etching. No matter which way is used, the rules on etching are as follows:

1) Speed: it must be tried to decrease etching time
2) Selectivity: etchant must not have any effect or have less effect on main structure and material; so it must just etch the sacrificial material
3) Completion: sacrificial material must be removed completely
4) Integration: During the process of etching, delicate microstructures should not be damaged

Wet etching is a cheap and fast process. This process can etch blind geometries which dry etching can not do. Wet etching of copper has been studied and used widely in printed circuit board (PCB) [107, 108] and surface finishing industries [109]. Usually for removing a metal, the metal must be oxidized from the metallic state to ionic. So, it is needed to use an oxidizing agent in the etchant. Electrochemical anodic etching can be used as a choice to oxidize by passing the current to a work piece. Therefore, it is possible to add acid or alkaline to increase the etching rate. The common oxidizing agent used for etching copper includes cupric chloride, chlorite, ferric chloride, organic nitro compounds, peroxide and chlorite. Copper etchants can be in the alkaline acidic range.

In this process, a reliable and fast copper etching process is needed which does not have a negative effect on nickel (target material and main microstructure). Figure 5-14 shows the micro gear structure when APS copper etchant 100 was used which is not compatible with nickel. As can be seen, there are several pores on the structure’s surface.

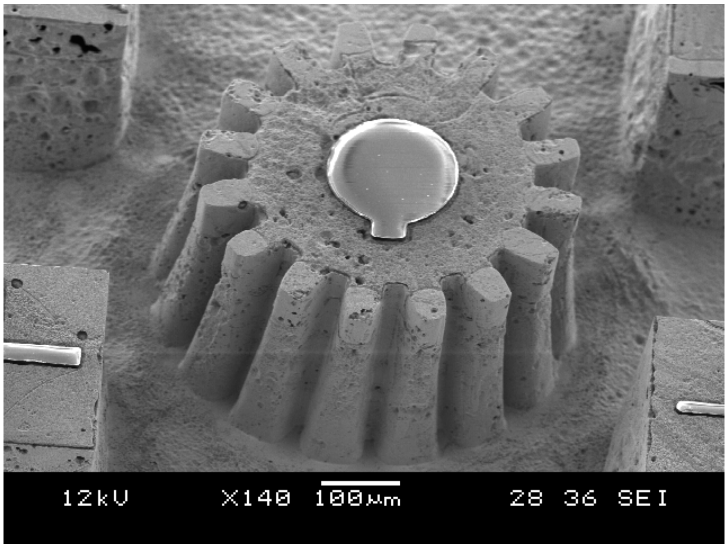


Figure 5-14 Not good nickel compatibility (APS copper etchant 100)

Table 5-4 shows several copper etchants used in electroplating and used in MEMS and printed circuit board industries. Although the etchants in this table are nickel compatible, the etchants with slow etching rate and having bubble formation during etching process are not considered as copper etchant for our process. Slow etching rate needs more time and it is not good. Hence, bubble formation induces stress and force to free standing structures such as cantilevers and beams and break the delicate and fine microstructures.

Table 5-4 Common copper etchants

	NaClO2 System		Cu Salt System		
	C-38 NaClO2 NH4OH	NaClO2 16g/l NH4HCO3 32g/l	CuSO4 15g/l NH4OH 400ml/l	CuCl2 NH4Cl NH4OH	Cu(NO3)2 6g NH4OH 36ml H2o 500ml
		Ref. [110]	Ref.[110]	Ref. [110]	Ref.[111]
Ni compatibility	Yes	Yes	Yes	Yes	Yes
Etching Rate µm/hr	460	Very slow	18	Vigorous	Very slow
Bubbles from reaction	No	No	No	No	No

	H2O2 System						other
	H2O2: NH4OH:H2O(v/v)			H2O2:HAC			HNO3 0.5% vol H3PO4 50% vol HAC 49.5% vol
	1:1:12	1:1:1:6	1:1:10	H2O2 15ml/l HAC 10%(v/v)	H2O2 50ml/l HAC 2%(v/v)	H2O2 100ml/l HAC 1%(v/v)	
	Ref.[112, 113]			Ref. [110]			Ref.[114]
Ni compatibility	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Etching rate µm/hr	0.3	7	Vigorous	2.3	15.4	7.8	3.6-7.2
Bubbles from reaction	Yes	Yes	Yes	No	No	No	No

5.4.4 ENSTRIP C-38 stripper

ENSTRIP C-38 is designed to remove copper from steel and stainless steel substrate quickly and it is a two-component, ammoniacal immersion stripper [115].

This etchant can be operated in a pH range of 9.3-10.5 and from room temperature to 38°C [116]. The mechanism of its reaction is as follows:

On the surface of etching:

$CLO_2^- + H_2O + 2e \rightarrow CLO^- + 2OH^-$

$2Cu - 2e \rightarrow 2Cu^+$

$Cu^+ + 2NH_3 \rightarrow [Cu\,(NH_3)_2]^+$

In the bulk solution:

$CLO_2^- + H_2O + 2e \rightarrow ClO^- + 2OH^-$

$2[Cu\,(NH_3)_2]^+ + 4NH_3 - 2e \rightarrow 2\,[Cu\,(NH_3)_4]^{2+}$

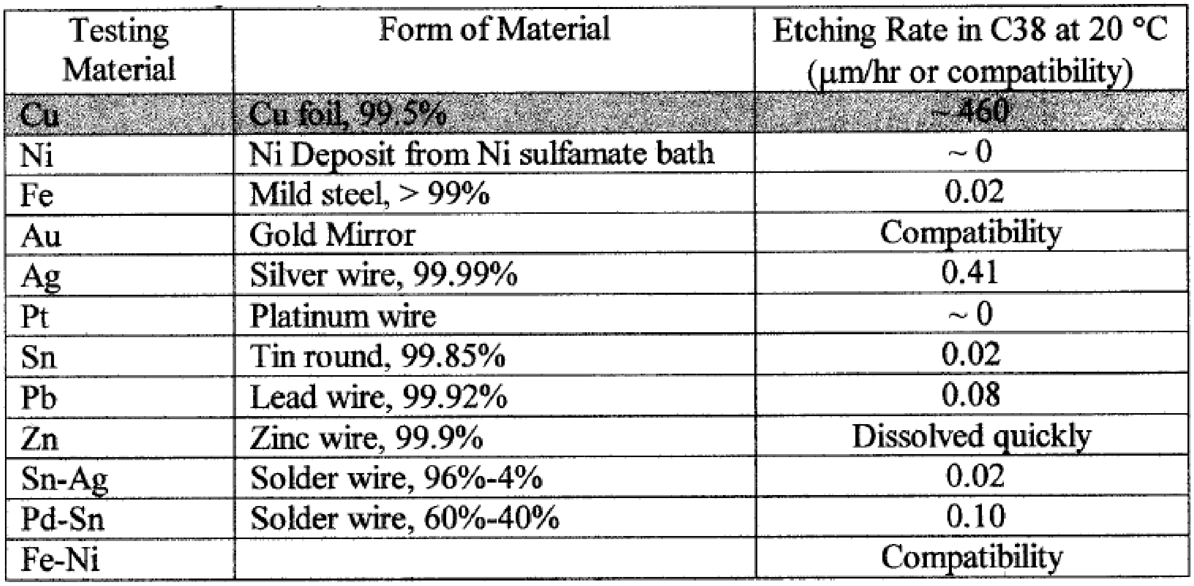
Experiments show that C-38 does not attack nickel significantly and the corrosion rate is about 72µm/yr. So, for a short time of etching, the total amount of etched nickel is negligible. Table 5-5 shows the compatibility of some metals and alloys in C-38. It can be seen that all metals and alloys compared to the etching rate of copper are compatible with C-38.

The etching rate of copper at room temperature by C-38 is around 460 µm/hr. This rate of etching can be adjusted by diluting the C-38. Figure 5-15 shows the etching rates in diluted C-38. These etching rates for actual geometry can be even lower and depends on the complexity of the geometry. Etching rate is determined by two parameters:

1- Delivery of the fresh etchant to the etching surface

2- Delivery of reaction products to the bulk solution

Table 5-5 Compatibility test of some materials in C-38 [112]



Testing Material	Form of Material	Etching Rate in C38 at 20 °C (µm/hr or compatibility)
Cu	Cu foil, 99.5%	~460
Ni	Ni Deposit from Ni sulfamate bath	~ 0
Fe	Mild steel, > 99%	0.02
Au	Gold Mirror	Compatibility
Ag	Silver wire, 99.99%	0.41
Pt	Platinum wire	~ 0
Sn	Tin round, 99.85%	0.02
Pb	Lead wire, 99.92%	0.08
Zn	Zinc wire, 99.9%	Dissolved quickly
Sn-Ag	Solder wire, 96%-4%	0.02
Pd-Sn	Solder wire, 60%-40%	0.10
Fe-Ni		Compatibility

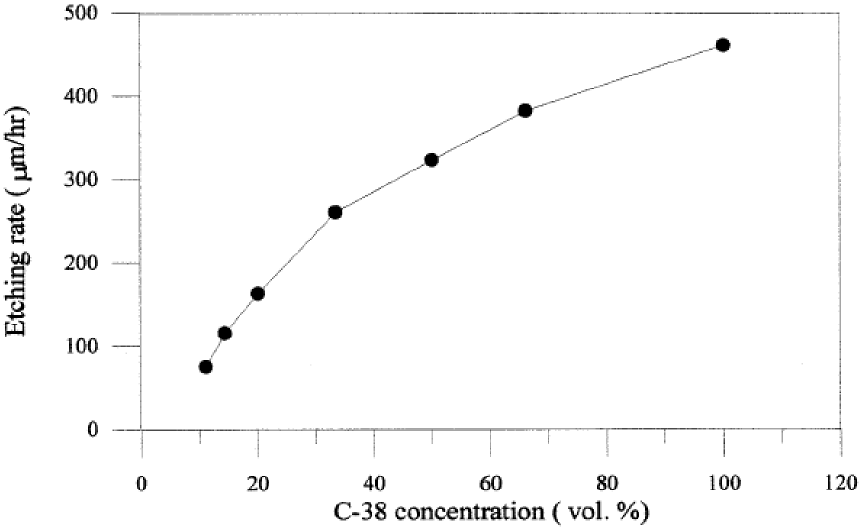


Figure 5-15 C-38 concentration vs. etching rate [112]

Some other parameters such as stirring the solution can improve the etching rate. Studies have shown that the etching rate of copper by C-38 at 36°C while stripped by ultrasonic is about 2.7 times as large as one with magnetic stirring [112]. Too violent stirring can damage the microstructure such as using ultrasonic agitation.

It is better a drying process is applied after the wet etching process until it removes the liquid inside the microstructure. A simple method is that after rinsing the part, it is immediately put into an alcohol solution until alcohol replaces the water inside the microstructure. Then the part is immediately transferred to an oven at 60°C for 5-10 minutes to evaporate the alcohol and dry the microstructure.

So, the whole procedure for stripping copper from nickel is as follows. At first, copper is etched in diluted C-38 (C-38: H_2O = 1:4-5) without striping. After that, the microstructure is dipped into an IPA (Isopropanol alcohol) beaker and it is slowly moved until IPA is displaced with etchant. Then, the microstructure is dried as it is described before.

5.4.5 Results

Figure 5-16 shows the micro gear structure after separating from SU-8 mold. Figure 5-17 shows six micro gears on a sample, Figure 5-18 shows SU-8 mold and Figure 5-19 shows the nickel sample and SU-8 mold. As can be seen from all these figures, we can conclude that by this method we can separate nickel micro-structure from SU-8 without damaging the SU-8 mold except the inner part.

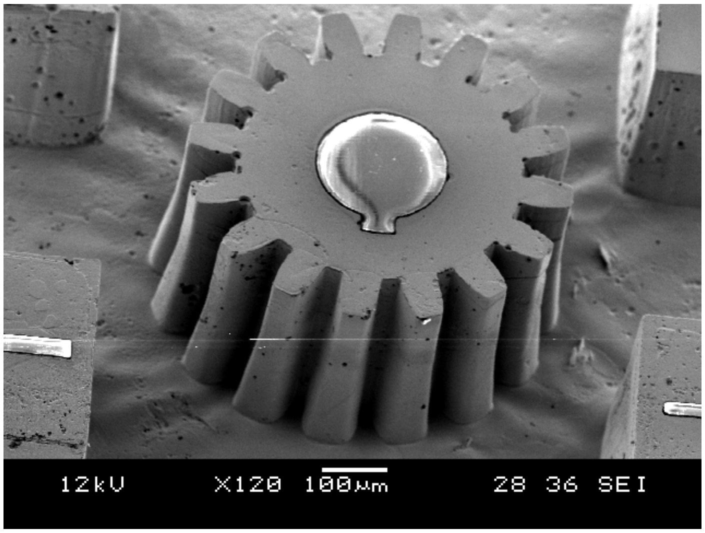


Figure 5-16 Micro gear structure

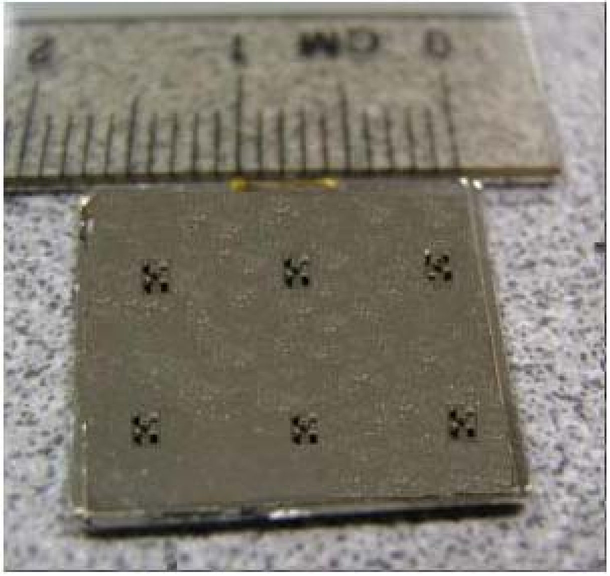


Figure 5-17 Micro-gear structures on the sample

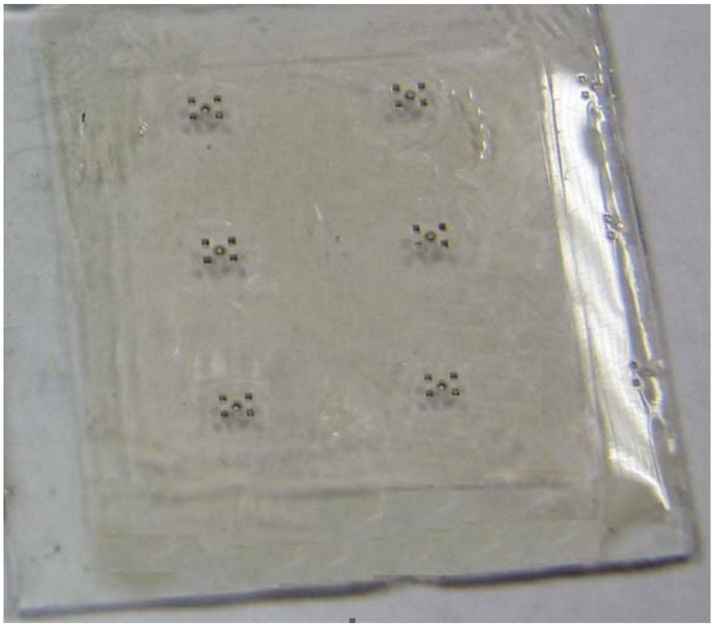


Figure 5-18 SU-8 mold

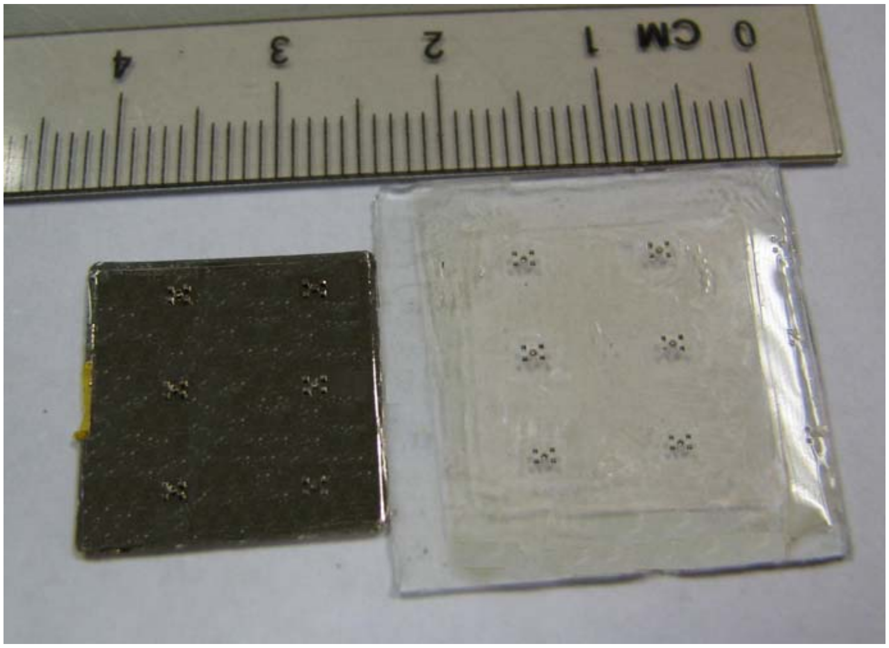


Figure 5-19 Nickel sample and SU-8 mold

6 Conclusions and future work

6.1 Conclusions

In this project, using a suitably developed SU-8 mold by the reverse exposure method, followed by an electroplating process, and a sacrificial method, high-aspect-ratio metallic microstructures have been fabricated.

In the first step for overcoming the problems of top-side UV exposure, such as light reflection from substrate; contact between exposure mask and SU-8; and sticking of photomask to photoresist, a reverse side method is chosen.

Then parameters of mold fabrication are studied by which a set of optimized parameters are identified to produce a SU-8 mold without any cracks, delamination and SU-8 residue. We need to decrease soft-baking time and temperature, post exposure baking time and temperature and to have relaxation time after soft-baking and before development.

The next step after mold fabrication is to suitably electroplate it. It is found that the only way to electroplate SU-8 mold completely without any pores inside the structure is to use pulse-electroplating in low current by controlling electroplating parameters such as pH, temperature, agitation and bath composition.

Lastly, for separating nickel microstructure from SU-8 mold easily, there is the need to choose a proper method for fabricating the microstructure. Several methods have been studied such as sacrificial photoresist; sacrificial photoresist and transparent resist; using PDMS technique; and sacrificial copper. Each of these processes has several advantages and disadvantages as follows:

Sacrificial photoresist: This method has been used by some researchers but still needs to work on it. It has several advantages such as: sacrificial photoresist can be removed easily by a benign solution without any effect on microstructure; and thickness of sacrificial layer can be controlled. One problem of the method is that the sacrificial photoresist can be attacked and dissolved by SU-8 and SU-8 developer.

Sacrificial photoresist and transparent resist: This method is very similar to sacrificial photoresist method. The only difference is that the photoresist will be replaced by transparent resist after making the mask. The reason for this change is that the photoresist is opaque and does not let UV light pass through the photoresist properly.

PDMS technique: This is an indirect method for removing SU-8. This method has several advantages, such as smooth surface result, low cost, rapid method, simple removing and non-clean room process. This technique can be a good solution for fabricating high-aspect-ratio microstructures.

Sacrificial copper: In this project, we focus on sacrificial copper method and can fabricate high-aspect-ratio metallic microstructure by this method. In comparison with other methods, this method is very simple and fast. Therefore, this method does not damage SU-8 mold so we can use it for several times, which can be another advantages in comparison to the other methods.

6.2 Recommendations for future work

There are several aspects in this project that can be investigated in the future:

- In mold fabrication, we just spin-coat one layer of SU-8 and able to achieve 200µm thickness SU-8 mold. But there is potential to have thicker mold, the suggestion for a method to have a thicker mold by spin coating SU-8 after each electroplating is given in section 6.5.1.

- In the part of fabricating micro-gear structure by sacrificial photoresist, several possible works can be looked into to study more about the options for photoresist and means to overcome the problems of attacking SU-8 and SU-8 developer to sacrificial photoresist.
- The sacrificial photoresist and transparent resist method needs several works to study more about the options for transparent resist and how to overcome the problems of attacking SU-8 and SU-8 developer to transparent resist.
- In the part of fabricating micro-gear structure by PDMS technique, the electroplating part has not been done and there is possible further work to optimize the PDMS casting parameters.

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