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Fabrication of high aspect ratio vibrating cylinder microgyroscope structures by use of the LIGA process

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FABRICATION OF HIGH ASPECT RATIO
VIBRATING CYLINDER MICROGYROSCOPE
STRUCTURES BY USE OF THE LIGA PROCESS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Mechanical Engineering

By
Yohannes Mamo Desta
B.S., Embry Riddle Aeronautical University, 1991
December 2005
Dedication

To my late grandfathers,

Ato Desta Hailu

and

Gra-azmach Teklehaimanot Woldehiwot
Acknowledgements

The gentle guidance and patience of Dr. Michael Murphy was more than what I would have expected to find in an advisor; I will always be indebted to him. I cannot leave unmentioned the support of the remaining members of my committee, Drs. Jin Woo Choi, Wen Jin Meng, Warren Waggenspack, and Peter Wolenski; without their support, this journey would not have been completed.

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I was one of the first student members of the Microsystems Engineering Team (µSET), which was begun in 1993 by Dr. Michael C. Murphy to establish LIGA at LSU. Early faculty members of the group included Drs. Kevin W. Kelly, Wanjun Wang, En Ma, and Ben Q. Li while non-faculty members included Sandeep Akkaraju, Vikas Galhotra, and Venkat Sangeshetti, and Mr. Zhong Geng Ling. During the first two years, Dr. Marc Madou visited us in Baton Rouge on a regular basis and provided manuscript photocopies of his now famous book, *Fundamentals of Microfabrication*. Since 1993, several dozen students have gone through µSET. Since they are too numerous to list here, I would like to simply thank ALL the past and present members for providing a dynamic environment for learning and R&D.
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Abstract

Inertial grade microgyroscopes are of great importance to improve and augment inertial navigation systems based on GPS for industrial, automotive, and military applications. The efforts by various research groups worldwide to develop inertial grade microgyroscopes have not been successful to date. In 1994, the Department of Mechanical Engineering at Louisiana State University and SatCon Technology Corporation (Boston, Massachusetts) proposed a series of shock tolerant micromachined vibrating cylinder rate gyroscopes with aspect ratios of up to 250:1 to meet the needs of inertial navigation systems based on existing conventional vibrating cylinder gyroscopes. Each microgyroscope consisted of a tall thin shell metallic cylinder attached to a substrate at one end and surrounded by four drive- and four sense-electrodes. The proposed drive- and sense-mechanisms were capacitive-force and capacitance-change, respectively.

Since the high aspect ratio metallic microgyroscope structures could not be fabricated by using traditional silicon-based MEMS processes, a LIGA-based two layer fabrication process was developed. A wiring layer was constructed by using a combination of thick film photolithography and electroplating (nickel and gold) on a silicon substrate covered with silicon nitride and a tri-layer plating base; aligned X-ray lithography and nickel electroplating were used to build the high aspect ratio cylinders and electrodes.

Deficiencies in the LIGA process were also addressed in this research. Three types of X-ray mask fabrication processes for multi-level LIGA were developed on graphite, borosilicate glass and silicon nitride substrates. Stable and reliable gold electroplating methods for X-ray masks were also established. The plating rate and internal stress of deposits were thoroughly
characterized for two brands of commercially available sulfite-based gold electroplating solutions, Techni Gold 25E and NEUTRONEX 309.

The gaps between the cylinders and electrodes, which are defined by thin PMMA walls during electroplating, were found to be smaller than designed and deformed in many of the microgyroscope structures. The lateral dimensional loss (LDL) and deformation were identified to be related to the overall thickness and lateral aspect ratio (LAR) of the thin PMMA walls.
Chapter 1 Introduction

1.1 Microelectromechanical Systems (MEMS)

In 1959, Richard Feynman challenged the scientific community to begin the miniaturization of electronics, sensors, and actuators, with his famous speech titled *There is Plenty of Room at the Bottom* in which he spoke about “the problem of manipulating and controlling things on a small scale [1]. However, it was the invention of the first solid state amplifier by Walter Brattain and John Bardeen twelve years earlier that laid the foundation for the development of modern day solid state electronics and their miniaturization [2]. Today, a combination of lithography, etching, deposition, and doping technologies are used in integrated circuit (IC) manufacturing (microelectronics) to create a variety of electronic components, the simplest of which is the transistor.

Development in microelectronics has been rapid; the maximum number of transistors in an IC chip has increased from 1000 in 1970 to over 100 million by 2005–doubling every 18 months as Moore’s law predicts [2]. During the same period, the lithography technology, which is the primary factor that governs the number of transistors in an IC, has progressed from a mere 10 \( \mu \text{m} \) critical dimension (CD) down to 0.05 \( \mu \text{m} \).

During the last 30 years, the basic techniques used in microelectronics were also exploited to miniaturize electromechanical sensors and actuators, which came to be known as microelectromechanical systems (MEMS). In the 1990s, MEMS were extended to include optical, biological, and fluidic systems resulting in what are now known as microelectro-
optomechanical systems (MOEMS), bioMEMS, and microfluidics, respectively. Nowadays, MEMS have become ubiquitous to the extent that they are found in consumer products such as printer-heads in homes and offices and crash sensors for air-bag deployment in automobiles.

All MEMS devices have at least one length-scale that is on the order of 1 to 1000 µm and benefit from this length-scale in one or more of the following three aspects. First, miniaturized systems can easily be integrated with microelectronics resulting in compact systems [3-7]. Second, some physical phenomenon benefit tremendously from a reduction in linear length scale. For example, the increased surface area-to-volume ratio in MEMS improves the separation of fluids in capillary electrophoresis and gas chromatography [8]; heat transfer can be enhanced by the so called fin-effect [9-12]; and micro-electrodes and reactors can benefit from improved mass-transfer[13-15]. Third, since MEMS are often batch fabricated, reduction in cost can be attained for many microsystems.

1.2 MEMS Inertial Sensors

Inertial sensors are a class of sensors in which a structural element is perturbed because of inertial forces and the perturbation is sensed by taking advantage of one of the many transduction mechanisms such as capacitance, piezoelectricity, magnetism, optical (interferometric), acoustic, or tunneling. Two common types of inertial sensor are accelerometers (microaccelerometers) and gyroscopes (microgyroscopes) used to measure acceleration and rotation rate (change in orientation), respectively [7, 16, 17].

1.2.1 Microaccelerometers

When a proof-mass of an accelerometer is subjected to acceleration, the displacement of the proof mass or the force exerted by the proof-mass on the frame may be measured to determine acceleration. Alternatively, the proof-mass may be forced to remain in its unperturbed position using a feedback control system and the control force used to determine acceleration.
Microaccelerometers were among the first sensors to be micromachined, the first one being reported in 1979 by Roylance et al [18]. The first commercial microaccelerometer, the ADXL05, was introduced by Analog Devices (Norwood, Massachusetts) in 1991; the ADXL05 had a $0.5 \times 10^{-3} \text{g} / \sqrt{\text{Hz}}$ * noise floor with a $\pm 5\text{g}$ dynamic range [16]. Nowadays, microaccelerometers that satisfy the requirements of applications ranging from high-sensitivity low-g applications (e.g. hard drive protection in computers and inertial navigation) to low-sensitivity high-g applications (e.g. crash sensing for automotive air bag deployment systems) are commercially available. State-of-the-art microaccelerometers are mainly based on polysilicon capacitive comb-drives fabricated with surface-micromachining† [5, 19, 20].

1.2.2 Microgyroscopes

Microgyroscopes are mainly based on the coupling of an excited vibration mode into a secondary mode because of Coriolis acceleration as shown in Figure 1-1a [21-24]. The problems associated with friction and drive motors in conventional gyroscopes are avoided in microgyroscopes by replacing the spinning wheels of conventional gyroscopes with a variety of vibrating structures including inter-digitated capacitive comb-drives [6, 24-26] similar to those used in microaccelerometers or vibrating rings [6, 21, 24].

Vibrating ring gyroscopes use a circular ring or wineglass type of structure, which is driven in its 2nd mode of vibration; introduction of a rotation or change in orientation couples the vibration energy into another mode at $45^\circ$ as shown in Figure 1-1b [27-31]. Many vibratory

---

* When discussing inertial sensors, ‘g’ is commonly used to refer to the acceleration due to Earth’s Gravity, which is equal to 9.8 m/s².

† Surface-micromachining is an additive process whereby a series of deposition, masking, and etching techniques are used to produce microstructures on a substrate. The counter part to surface-micromachining is bulk-micromachining—a subtractive process in which a material such as silicon is etched by using either a wet or dry process to produce microstructures.
microgyroscopes are commercially available from manufacturers including Analog Devices, Robert Bosch GmbH (Germany), and Silicon Sensing Systems (Japan).

1.3 Inertial Navigation Systems

Although “civilian” global positioning system (GPS) provides relatively inexpensive positioning information for navigation purposes, its accuracy is limited to about 10 m. In addition, “civilian” GPS provides only a crude estimate of altitude, which is essential for many applications. GPS is also vulnerable to both intentional and unintentional jamming and a backup system is essential for safety. Inertial grade microaccelerometers and microgyroscopes are of particular importance to improve and augment inertial navigation systems based on GPS for industrial, automotive, and military applications [32]. High accuracy accelerometers and gyroscopes can be used to provide acceleration and orientation data that can be integrated to provide position in an inertial reference frame. The accelerometers and gyroscopes for use in inertial navigation systems are of the highest grade: accelerometers must have $\mu g$ resolution while gyroscopes need $1^\circ/h$ (0.00025 $^\circ/s$) or better. GPS, combined with inertial-grade microaccelerometers and microgyroscopes can be used to create an inertial navigation system capable of determining position to better than 1 m; such a system can be extremely useful for the next generation of autonomous motor vehicles as well as aerospace applications.

1.4 Applications and Specifications of Microgyroscopes

Microgyroscopes can be broadly divided into two categories based on applications: inertial grade and non-inertial grade. Inertial grade gyroscopes are used to maintain a fixed long-term heading in an inertial reference frame while non-inertial grade are typically used to measure relatively short term angular rates [31]. Non-inertial grade gyroscopes used in navigation are further divided into rate- and tactical-grade.
a) Principle of a vibrating gyroscope; b) A vibratory ring gyroscope in its 2nd mode of vibration [K = spring constant; v = velocity; $F_c$ = Coriolis force; $\Omega$ = rotation]
Table 1-1  Performance requirements for different grades of gyroscopes [14]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Rate Grade</th>
<th>Tactical Grade</th>
<th>Inertial Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angle Random Walk ($^\circ/\sqrt{h}$)</td>
<td>&gt;0.5</td>
<td>0.5-0.05</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Bias Drift ($^\circ/h$)</td>
<td>10-1000</td>
<td>0.1-10</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Scale Factor Accuracy ($^\circ/s$)</td>
<td>0.1-1</td>
<td>0.01-0.1</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Full Scale Range ($^\circ/s$)</td>
<td>50-1000</td>
<td>&gt;500</td>
<td>&gt;400</td>
</tr>
<tr>
<td>Max. Shock in 0.001 s (g)</td>
<td>$10^3$</td>
<td>$10^3$-$10^4$</td>
<td>$10^3$</td>
</tr>
</tbody>
</table>

The resolution of a gyroscope is limited by white noise and is expressed in terms of the standard deviation of the equivalent rotation rate per square root of bandwidth of detection ($^\circ/s/\sqrt{Hz}$) [17], which is also known as “angle random walk” and expressed in units of ($^\circ/\sqrt{h}$). The bias drift, commonly expressed in units of ($^\circ/h$), describes the long- or short-term cumulative error accrued in a measurement. The scale factor accuracy is the percentage change in the output signal per unit of angular rate. The performance requirements of gyroscopes used in navigation are summarized in Table 1-1.

Figure 1-2 summarizes the angular rate resolution and bandwidth requirements of microgyroscopes for various applications [16]. Low end applications such as automotive safety require rate resolutions of about 0.1 to 100 $^\circ$/s, while navigation applications may require as high as $1x10^{-5}$ $^\circ$/s.

The quality-factor (Q-factor) of a sensor is also an important parameter in evaluating microgyroscopes because it determines how well a system responds at its resonance frequency. Systems with high Q-factor resonate with greater amplitude. Since the coupling from the drive-mode to the sense-mode due to Coriolis force in vibratory gyroscopes is weak, microgyroscopes with high Q-factor are desired for improved sensitivity. In addition to the material, structural,
and operating conditions, thermoelastic- and electronics-damping also play significant roles in the overall Q-factor (thus sensitivity) of a microgyroscope [33].

![Figure 1-2: Angular rate and bandwidth requirements of gyroscopes for various classes of applications [16]](image-url)
1.5 LSU/SatCon Microgyroscope Overview

In 1994, SatCon Technology Corporation (Boston, Massachusetts) and the LSU Department of Mechanical Engineering proposed a series of tactical-grade shock tolerant micromachined cylindrical rate gyroscopes [21]. The proposed gyroscopes were essentially micromachined versions of existing conventional vibrating cylinder gyroscopes [29-31]. Figure 1-3 shows a solid model and a cross-sectional view of the proposed microgyroscope, which consists of a tall thin shell cylinder attached to a substrate at one end and surrounded by four drive- and four sense-electrodes. The cylinder and electrodes needed to be electrically isolated with a small gap between the cylinder and the electrodes. The high aspect ratio cylinders and electrodes needed to be fabricated on a layer of wiring pads on an insulating substrate.

In the original set of designs, the gaps between the cylinders and electrodes were four microns; the thickness of the cylinders ranged from 4 to 10 µm; and the overall height was 500 µm. The best of these designs was predicted to withstand up to 120x10³ g with a resonance frequency of 350 KHz. A microgyroscope was envisioned to be resonated in its 2nd mode as shown in Figure 1-1b by using electrostatic forces at a driving voltage of 200 V with amplitudes at the drive-electrodes of less than 1 µm. The predicted rate resolution of a typical device was computed to be 0.5 °/s at a Q-factor of 1000.

Over the course of the project, many designs were submitted by SatCon to LSU ME. The last set of microgyroscope designs is shown in Table 1-2. Designs 1-12 specify nickel as a construction material while 13-24 require copper to reduce magnetic striction. The aspect ratio of these devices based on the minimum gap between the electrodes and the cylinders ranged from

---

† The aspect ratio of a microstructure is defined as the ratio of the thickness (length perpendicular to the plane of the substrate) to the smallest lateral dimension.
125 to 200. Since the commencement of this research project in 1994, these microgyroscopes have remained the highest aspect ratio MEMS inertial sensors ever attempted by any research group.

Table 1-2  Finite element model prediction of vibrating ring microgyroscopes (SatCon Technologies Corporation): the drive- and sense- bias voltages for all designs are 200 V and the sense-resistances are 1 MΩ

| Design No. | Operating Environment | Radius (um) | Height (um) | Thickness (um) | Res. Freq. (KHz) | Drive Electrode Gap (um) | Sense Electrode Gap (um) | Drive Electrode Angle (deg.) | Sense Electrode Angle (deg.) | Max. Angular Velocity (deg./s) | Max. Stresses (kpsi) | Average Disp. (um) | Q-factor | Disp. to Gap Ratio | Average Operating Environment | Design No. |
|------------|----------------------|-------------|-------------|---------------|-----------------|-----------------------|-------------------------|-----------------------------|-----------------------------|------------------|-----------------|----------|----------------|-----------------------------|------------|
| 1          | Ni in air            | 133         | 500         | 6             | 341             | 4 4 9 16             | 25000                   | 2.657                       | 5.37                        | 0.2              | 152             | 0.049          | Ni in air 1     | 1                           |            |
| 2          | Ni in vac.           | 253         |             |               | 6 4 8 17         | 3150                  | 0.241                    | 6.16                        | 0.4                     | 778              | 0.050           | Cu in air 13    | Ni in vac. 2   | 2                           |            |
| 3          | Ni in air            | 191         | 750         | 8             | 202             | 6 5 10 15           | 11250                   | 0.984                       | 4.75                        | 0.27             | 233             | 0.045           | Ni in air 3     | 3                           |            |
| 4          | Ni in vac.           | 151         |             |               | 12 5 10 15       | 1280                  | 0.085                    | 6.09                        | 0.61                     | 1182             | 0.051           | Cu in air 14    | Ni in vac. 4   | 4                           |            |
| 5          | Ni in air            | 249         | 1000        | 10            | 148             | 7 6 9 16            | 6050                    | 0.430                       | 4.63                        | 0.36             | 314             | 0.051           | Ni in air 5     | 5                           |            |
| 6          | Ni in vac.           | 111         |             |               | 14 6 8 17        | 760                   | 0.038                    | 5.36                        | 0.73                      | 1621             | 0.052           | Cu in air 15    | Ni in vac. 6   | 6                           |            |
| 7          | Ni in air            | 307         | 1250        | 12            | 117             | 8 7 8 17            | 4070                    | 0.245                       | 4.22                        | 0.41             | 398             | 0.052           | Ni in air 7     | 7                           |            |
| 8          | Ni in vac.           | 88          |             |               | 17 7 8 17        | 515                   | 0.024                    | 4.83                        | 0.83                      | 2042             | 0.049           | Cu in air 18    | Ni in vac. 8   | 8                           |            |
| 9          | Ni in air            | 374         | 1500        | 15            | 99              | 9 8 8 17            | 3400                    | 0.180                       | 3.7                         | 0.43             | 467             | 0.048           | Ni in air 9     | 9                           |            |
| 10         | Ni in vac.           | 74          |             |               | 18 8 8 17        | 387                   | 0.016                    | 4.51                        | 0.92                      | 2380             | 0.051           | Cu in air 19    | Ni in vac. 10  | 10                          |            |
| 11         | Ni in air            | 1578*       | 6350        | 63            | 23              | 32 32 8 17          | 620                     | 104.39                      | 1.2                        | 0.59             | 1894            | 0.018           | Ni in air 11    | Ni in vac. 11  | 11                          |            |
| 12         | Ni in vac.           | 17          |             |               | 45 32 8 17       | 48                    | 6.02                     | 2.67                        | 2.31                      | 8273             | 0.051           | Cu in air 23    | Ni in vac. 12  | 12                          |            |
| 13         | Cu in air            | 51 32 9 16  | 32          | 17            | 51 32 9 16       | 32                    | 4.35                     | 3.03                        | 2.62                      | 10710            | 0.051           | Cu in air 24    | Ni in vac. 24  | 24                          |            |

* Hybrid design
Figure 1-3  LSU/SatCon microgyroscope structure: a) solid model showing the cylinder, four drive-electrodes, and four sense-electrodes; b) cross section of the proposed microgyroscope showing the gap between the cylinder and the electrodes
The aspect ratio of the LSU/SatCon microgyroscopes coupled with the metallic construction material posed challenges to the traditional silicon based MEMS processes. At the time, typical silicon surface micromachining techniques yielded structural heights of only a few-tens of micrometers whereas silicon bulk micromachining yielded a few-hundred micrometers.

The LIGA process, a specialized type of surface micromachining, combined deep-etch X-ray lithography (DXRL) with electroplating and molding to create high aspect ratio microstructure [34-36]. The use of X-ray lithography in LIGA enabled the maintenance of high precision over great structural heights. Compared to silicon-based surface and bulk micromachining, LIGA could be used to produce microstructure of several millimeters in height [37]. Furthermore, the reported sidewall slope of LIGA microstructures was better than 1% [38]. LIGA was proposed as a fabrication process because it was deemed most suitable to fabricate the proposed LSU/SatCon microgyroscopes.

1.6 Project Timeline and Funding

The work in this dissertation was primarily funded by a series of Small Business Initiative Research (SBIR) grants awarded to SatCon Technology Corporation and sub-contracted to the Department of Mechanical Engineering, Louisiana State University (LSU ME). The following briefly summarizes these grants and accomplishments.

The first SBIR Phase I grant for microgyroscopes was awarded to SatCon by the Department of the Army in 1994§. The research aimed to establish the optimum structure geometry, details of the fabrication process, and design of the sensing- and drive-electronics. The

design and testing of the gyroscopes and drive- and sensing-electronics was to be carried out by SatCon while the development of the fabrication process was sub-contracted to LSU ME.

The sub-contract from SatCon was used to launch a process development for multi-level high aspect ratio microstructures (HARM), specifically microgyroscopes, by using the facilities of the Microsystems Engineering Team (μSET) lab at LSU ME and the Center for Advanced Microstructures and Devices (CAMD). Since an X-ray mask, the primary tool for fabricating the proposed microgyroscopes, was not available at the time, a so called “transfer mask technique” was developed by Valadimirsky et al [39] at CAMD. The transfer mask process was attempted for the fabrication of high aspect ratio microgyroscopes but proved not to be feasible for high aspect ratio microstructures. Work on the transfer mask process also led to an in-depth study of gold electroplating for X-ray masks.

As part of this research project, nickel electroplating in high aspect ratio plastic molds by use of a nickel sulfamate-based bath and bonding of polymethylmethacrylate (PMMA), the primary X-ray resist material, to substrates was established in collaboration with other members of the μSET lab [10-12, 40-44].

The second SBIR Phase I grant** was funded by the US Air Force in 1995. This grant sought to continue the work begun in the previous SBIR award. At LSU, a sub-contract was used to further establish and develop the LIGA process. During this time, funding from the LSU Board of Regents was used to procure an X-ray mask containing the SatCon microgyroscope patterns as well as a variety of test structures from the Institute of Microstructure Technology (Karlsruhe, Germany). The X-ray mask, which was received from IMT over one year later, was used to

develop a single level LIGA process. However, lack of alignment markers on the X-ray mask prevented the development of a multi-level process.

A third SBIR Phase I grant†† was funded by the Ballistic Missile Defense Organization (BMDO) in 1997 to continue the R&D effort. Following the successful demonstration of single level microgyroscope structures, a Phase II grant was obtained from the same organization in 1998. This fund was used to procure an X-ray mask with alignment markers from IMT and develop a two-layer process.

A collaborative effort between the Institute for Micromanufacturing (IfM) (Ruston, Louisiana), CAMD, and µSET was also begun to develop a rapid and inexpensive method of fabricating X-ray masks by use of graphite substrates [45, 46]. The graphite mask technology was advanced further by this research project and was used to produce masks with alignment markers, which was subsequently used to produce sense- and drive-electrodes for a set of hybrid gyroscopes consisting of microfabricated electrodes and conventionally turned cylinders. The graphite mask technology also proved useful for other basic studies. Limitations of the LIGA process such as the lateral dimensional loss (LDL) and lateral aspect ratio (LAR) were also studied by using the graphite mask technology.

One of the main limiting factors in the rapid progress of the research on the fabrication of microgyroscopes was the lack of in-house X-ray mask technology. Although the graphite mask proved useful in some aspects, it did not address all of the needs of the microgyroscopes. After the last round of SBIR funding for microgyroscopes came to an end in 1999, the development of X-ray masks for high aspect ratio multi-level microstructures was continued at CAMD[47-55].

Subsequently, processes based on borosilicate glass and silicon nitride were developed and tested. An improved gold electroplating system was also established to address the needs of the new mask substrates.

1.7 Outline of Dissertation

Chapter 1 of this dissertation begins with an introduction to the field of MEMS and specifically, inertial sensors. Since the purpose of the research and development covered in this body of work was to develop a fabrication process for high aspect ratio vibrating cylinder microgyroscopes, their applications and specifications are also discussed followed by a synopsis of the proposals that funded this work. Overview of the LIGA process is presented in Chapter 2.

The remaining chapters in this dissertation follow the process sequences of the LIGA process. R&D in X-ray mask design and fabrication is presented in Chapter 3 followed by gold electroplating for X-ray masks in Chapter 4.

Many process sequences were developed as part of this research for the fabrication of the microgyroscope structures but only the ones that yielded promising results are presented in the main body of this thesis. Chapter 5 covers the most successful process sequences based on a titanium membrane X-ray mask purchased from the IMT (Karlsruhe, Germany) and a silicon nitride membrane X-ray mask fabricated in house. The process limitations that were encountered while developing these process sequences and the studies performed to understand and solve them are also presented in Chapter 5.

Chapter 6 provides a summary of the R&D effort, results, and conclusions as well as recommendations for future work.

Since the equations of motion of vibrating rings were considered helpful in the understanding of vibrating ring microgyroscopes, their derivation is presented in Appendix A. The transfer mask technique, a process which was shown to be non-suitable for high aspect ratio
microstructures but very useful for low aspect ratio prototyping and mold insert fabrication, is covered in Appendix B. The fabrication process for sense- and drive-electrodes for hybrid microgyroscopes is presented in Appendix C.
Chapter 2 LIGA – an Overview

2.1 Introduction

LIGA is a German acronym, which stands for Lithographie (lithography), Galvaniformung (electroplating), Abformung (molding). LIGA combines deep etch X-ray lithography (DXRL), electroplating, and molding for the batch fabrication of high aspect ratio microstructures [34, 56]. The LIGA process was developed during the 1980s under the direction of W. Ehrfeld at the Forschungszentrum Karlsruhe (FZK) (Karlsruhe, Germany), which was formerly known as Kernforschungszentrum (KfK), to fabricate separation nozzles for 235U for nuclear power [34, 56].

Figure 2-1 shows a schematic of the three main fabrication steps of the LIGA process. The first step consists of lithographic patterning of an X-ray sensitive resist. A resist layer bonded to a conductive substrate is exposed to synchrotron radiation through an X-ray mask, which is typically composed of X-ray absorbing patterns (e.g. gold) on a substrate that is relatively transparent to X-ray radiation (e.g. beryllium). Either the exposed or non-exposed resist material – depending on the tone of the resist material – is dissolved using an appropriate developer, which results in a plastic mold similar to the image on the X-ray mask. In a subsequent metallization step, the plastic mold is filled with metal by an electroplating process resulting in a monolithic metallic molding tool. Plastic or ceramic parts are fabricated cost-effectively in the final step of the standard LIGA process by molding.
Figure 2-1  Schematic of the LIGA process: a) X-ray exposure; b) wet etching with a developer solution; c) nickel electroforming; d) molding
2.2 X-Ray Lithography

In the 1950s and 1960s, synchrotron radiation (SR) was transformed from an undesirable byproduct of particle accelerators to a useful tool for basic scientific studies of the atomic structure of materials [57]. In 1972, Spears and Smith demonstrated that X-ray radiation can be used to produce high resolution patterns with proximity printing [58]. Much interest in X-ray lithography (XRL) remained until the late 1990s as XRL was touted to be the next-generation mode of lithography for integrated circuit manufacturing. In 1997, IBM demonstrated 400 MHz Power PC chips using XRL, while Mitsubishi produced 4 GHz chips in 2000.

Although, advances in ultraviolet (UV) photolithography coupled with copper-interconnect technology have helped Moore’s law (primarily driven by the lithographic technology) to still ring true without the need for XRL, it has found a niche in the fabrication of high aspect ratio microstructures commonly known as deep-etch X-ray lithography (DXRL). An appropriate X-ray source and exposure system, a suitable resist material, an X-ray mask, and a high contrast developer are the essential components of DXRL. The following sections will briefly discuss these fundamental components.

2.2.1 Radiation Source

Synchrotrons are electron storage rings in which beams of electrons with relativistic speeds are confined within a closed orbit by use of bending magnets in a high vacuum environment. As the trajectory of the electrons is changed by the bending magnets, they experience centripetal acceleration resulting in an emission of broadband photons ranging from far infrared to hard X-rays. The production of photons and radiative pattern is illustrated in Figure 2-2a. Derivation of the equations governing the production of light by synchrotrons shows that it is possible to present the spectral distribution by using a so called universal curve irrespective of the
The *universal curve* for the spectral flux of the radiation produced at a bending magnet is shown in Figure 2-2b [57, 59].

**Figure 2-2**  
a) Synchrotron radiative pattern \[ \beta = \frac{v}{c}; \ v = \text{the velocity of electrons, } c = \text{speed of light}; \]  
b) *Universal curve* for the spectral flux of a synchrotron \[ \lambda = \text{wavelength}; \ \lambda_c = \text{critical wavelength} \]
The low beam divergence and high energy (short wavelength) nature of synchrotron radiation makes it especially suitable as a light source for DXRL. Since the absorption length of materials generally increases with increasing photon energy (penetration depth increases), high energy photons are needed to pattern thick layers of X-ray resist materials with high precision. Effects of Fresnel diffraction also decrease with increasing photon energy making it possible to pattern submicron resolution patterns using proximity printing.

The spectral distribution of light produced by a bending magnet is only a function of the energy of the electrons and the radius of curvature of the bending magnet. For X-ray lithography, the raw spectrum from a bending magnet can be conditioned by using mirrors or filters. The spectrum can be ‘softened’ by inserting a mirror-system between the bending-magnet and the experimental station such that the mirrors reflect only the low energy photons forming a low band pass filter. Conversely, the spectrum can be ‘hardened’ by inserting filters between the bending magnet and the end station; the filters will absorb the low energy and transmit the high energy photons.

2.2.2 Beamline and X-Ray Scanner

Figure 2-3a shows a schematic of one of the X-ray lithography beamlines at CAMD. The X-ray radiation moves from the source point within the bending magnet and passes through the beryllium end-window and filters until it reaches the X-ray scanner. Inside the scanner, X-ray resist material on a substrate is exposed to radiation through an X-ray mask as shown in Figure 2-1a. Since the X-ray beam at the exposure point has a rectangular format with a Gaussian distribution in the vertical direction, a scanner is used to expose large areas; Figure 2-3b shows a DEX02 X-ray scanner (Jenoptik GmbH, Jena, Germany), which was extensively used in this research.
Figure 2-3  A typical X-ray exposure system at CAMD: a) XRLM1 beamline schematic; b) DEX02 X-ray scanner (Jenoptik GmbH, Jena, Germany)
2.2.3 X-Ray Resists and Developers

In the first step of the LIGA process, a polymeric X-ray resist material is used to create an electroplating mold by using a combination of X-ray exposure and development. Depending on the tone of the resist, either the exposed or un-exposed regions are dissolved by using an appropriate developer solution. The choice of resist material and developer solution for deep X-ray lithography is based on resolution, absorption characteristic, sensitivity, contrast, and mechanical stability. The ideal resist material would have submicron resolution, low absorption coefficient, high sensitivity, and good mechanical stability. In most cases, since the resist material needs to be removed at the end of the fabrication process, it must also be easily removable by either a wet- or dry-etching process. The ideal developer would have high dissolution selectivity between exposed and un-exposed resists.

2.2.3.1 Polymethylmethacrylate (PMMA)

The most common X-ray resist material is high molecular weight PMMA, which has the common trade names of Plexiglas® and Perspex® among others. The typical PMMA resist for MEMS applications contains molecules with molecular weights between 1,000 and 1,000,000 g/mole with an average of 600,000 g/mole [60]. When PMMA is exposed to ionizing radiation such as X-rays, scission of the long polymer molecules and cross-linking begin to occur simultaneously [59]. Since PMMA is used as a positive resist, the exposure dose must be chosen such that scission is predominant.

XRL substrates with relatively thin layers of PMMA (< 15 µm) are prepared by multiple-spin coating of a solution made of high molecular weight PMMA in a solvent and subsequent baking to remove the solvent [40, 61]. Intermediate thickness PMMA (15 µm – 100 µm) substrates are best prepared by polymerizing methylmethacrylate (MMA) on the surface of the substrates [62]. DXRL substrates are prepared by bonding a thick sheet (1 - 3 mm) of high
molecular weight PMMA to a substrate by use of a solvent or a PMMA resin and machined to the desired thickness [63, 64].

PMMA meets nearly all of the requirements of the ideal X-ray resist but its sensitivity is low; a bottom dose of at least 2000 J/cm³ is needed to develop PMMA cleanly. At CAMD, a 100 mm-diameter sample with a PMMA thickness of 500 µm would require a total exposure time of at least 5 hr at one of the bending magnet beamline, which increases the cost but most importantly reduces throughput.

Several developing solutions exist for PMMA but the GG developer is the most commonly used solution for DXRL. The developer contains diethyleneglycol mono-butyl ether, morpholine, 2-aminoethanol and water while the GG rinse contains only diethylene glycol mono-butyl ether and DI water [35]. Megasonic development systems significantly increase the rate of development for aspect ratios of up to 10 but are found less effective for recesses with aspect ratios of greater than 10 [65, 66]. Figure 2-4 shows PMMA microstructures produced at CAMD by use of X-ray lithography.

2.2.3.2 SU-8 Photoresist

The search for a high sensitivity resist material for DXRL has lead researchers to try UV photoresists as well as formulate new materials for X-ray lithography [67-70]. The most successful of these attempts has been the use of SU-8, which is a highly sensitive, epoxy-based, chemically amplified, negative tone UV photoresist developed at IBM during the late 80s [71]. Various formulations of SU-8 are manufactured and distributed by MicroChem Corp. (MCC) (Newton, Massachusetts).

SU-8 photoresist is composed of SU-8 epoxy molecules dissolved in either gamma-butyrolacton (GBL) or cyclopentanone (CP) mixed with a photo-acid generator (PAG) made of a combination of triaryl sulfonium salt and sulfonium hexflorate [72]. When exposed to
Figure 2-4 PMMA resist patterned by use of X-ray lithography: a) 2 µm-thick resist pattern with submicron resolution; b) 2000 µm-thick PMMA gear
radiation, the PAG produces a weak Lewis acid that initiates cross-linking of the epoxy molecules. A post exposure bake is used to supply additional thermal energy to complete the reaction quickly. Cross-linked SU-8 is highly resistant to chemical attack and may even be used as a structural material. Although unexposed SU-8 can be dissolved by using a variety of solvents, only propylene glycol monoether acetate (PGMEA) is sold as a commercial developer by MicroChem Corp.

The sensitivity of SU-8 to X-ray radiation is dependent on the concentration of PAG present in its formulation. The sensitivity of the standard MCC formulation of SU-8 (5 % PAG) to X-ray radiation is 10 J/cm³, making it two orders of magnitude more sensitive than PMMA [73-76]. Thus, the exposure time of an SU-8 sample can be as much as two orders of magnitude less than that of PMMA. SU-8 solves the exposure throughput issue associated with the use of PMMA but introduces a new challenge; cross-linked SU-8 is highly resistant to chemical attack. At present, there are no known chemicals that can dissolve cross-linked SU-8. Successful removal of SU-8 is dependent on dry-etching [77, 78], oxidation in molten salt bath [79], or electrochemical etching in a mixture of strong acids.

The use of a negative tone photoresist such as SU-8 also expands the geometrical capabilities of the LIGA process. Multilevel resist molds and microstructures with well controlled sidewall slopes can be fabricated using SU-8. Figure 2-5 shows a series of SU-8 microstructures produced at CAMD. A comparison of the characteristics of PMMA and SU-8 resist is presented in Table 2-1. The microstructure quality (sidewall slope and surface roughness) of PMMA and SU-8 are comparable [80]. At present, PMMA is used in LIGA for applications, where the clean and selective removal of the photoresist mold is crucial, while SU-8 is primarily used for applications where the metallic parts can be extracted from the resist mold by mechanical means [81, 82].
Table 2-1  Comparison of the characteristics of the two commonly used X-ray resists

<table>
<thead>
<tr>
<th></th>
<th>PMMA</th>
<th>SU-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical structure</td>
<td>Acrylic polymer</td>
<td>Epoxy-like</td>
</tr>
<tr>
<td>Tone</td>
<td>Positive</td>
<td>Negative</td>
</tr>
<tr>
<td>Exposure mechanism</td>
<td>Scission</td>
<td>Cross-linking</td>
</tr>
<tr>
<td>Density</td>
<td>1.18 g/cm³</td>
<td>1.16 g/cm³</td>
</tr>
<tr>
<td>Dose threshold</td>
<td>2000 J/cm³</td>
<td>10 J/cm³</td>
</tr>
<tr>
<td>Removal</td>
<td>Wet-etch (easy)</td>
<td>Dry-etch (difficult)</td>
</tr>
</tbody>
</table>

2.3  X-Ray Masks

During X-ray lithography, the pattern on an X-ray mask is transferred to the resist layer on a substrate. A high atomic weight (Z) material deposited on a low Z membrane is used as an X-ray mask in LIGA. Boron nitride, diamond, silicon, silicon nitride, titanium, Kapton® and beryllium can all be used as mask membrane materials while gold is the most commonly used X-ray absorber material. The design, material selection, and fabrication of X-ray masks are covered in Chapter 3.

2.4  Electrodeposition

Due to its good mechanical properties and relative ease of electroforming, nickel has been the material of choice for LIGA structures. Nickel can be electrodeposited from sulfamate- [83] or sulfate-based baths [43]. The typical sulfamate-based bath contains nickel sulfamate (Ni(NH₂SO₃)) as a source of nickel ions and boric acid as a buffer. Sulfate based baths contain nickel sulfate (NiSO₄) and nickel chloride as sources of nickel ions and boric acid as a buffer. In addition, cumarin and saccharin are used for their grain refining and leveling effects. Electroforming high aspect ratio micro-structures poses a great challenge in terms of the
transport of ions to deep trenches. The addition of a surfactant reduces the surface tension there by enhancing the electroforming process.

Although Ni-P, Ni-Co, Ni-Fe, Ni-Mo, and Ni-Mg can all be electroplated, the most widely used alloy in LIGA is the Ni-Fe alloy. At a concentration of 20 % Fe, Ni-Fe exhibits a soft magnetic property making it suitable for use in magnetic cores [84]. The properties of alloys such as Young’s modulus, internal stress, surface roughness, electrical conductivity, permeability, and coercivity can be controlled by varying the current density, pulse plating, and annealing parameters [85].

2.5 Sacrificial Layer

The standard LIGA process produces microstructures that are fixed to a substrate at their base. Sacrificial layers are used to partially or completely release microstructures from a substrate by using a selective etchant. Copper and titanium are two materials that are especially suited for use with nickel microstructures [86]. Ni-Fe alloy has also been demonstrated to be useful as a sacrificial layer [87].

If partial release of the microstructures is desired, a multi-layer plating base, e.g. chrome/copper/titanium, is first deposited on a substrate and the titanium layer is patterned using a combination of photolithography and wet-etch to expose the underlying copper layer to form anchors. An X-ray resist layer is applied over the patterned substrate. The X-ray mask is aligned to the titanium pattern on the wafer and exposed with X-rays. After development, exposure, planarization, and resist removal have been completed, the titanium sacrificial layer is selectively etched resulting in cantilever like structures. The sacrificial layer technique combined with LIGA is sometimes referred to as SLIGA [88].
Figure 2-5  SU-8 microstructures produced by use of X-ray lithography: a) controlled sidewall slopes made with multiple tilt-and-rotate exposure; d) multi-level microstructures
2.6 Molding

Molding is the primary method of mass production of microstructures in LIGA. Hot-embossing, reaction-injection-molding, or injection-molding can produce polymeric microstructures with high resolution [89]. Embossing involves the pressing of a polymer layer, which has been heated above its glass transition temperature, over a heated metal mold insert. To obtain structures with minimal defects, hot embossing is carried out in vacuum. Injection molding involves the injection of a polymer at high temperature into an evacuated mold insert at high pressure. Separation of the mold from the mold-insert is done after the temperature of the system has been reduced below the glass transition temperature. In reaction-injection-molding, an actively reacting polymer resin with a mold release agent is injected into the mold insert. Separation is done after the polymerization process is completed.

2.7 Applications

Since its inception in Germany over two decades ago, a variety of LIGA based MEMS microstructures and devices have been fabricated by many researchers throughout the world. These devices have found applications in optics, micro-fluidics, mechanics, and thermal applications.

The sidewall roughness of microstructures produced by the LIGA process heavily depends on the type of X-ray mask used for lithography. In the best case, the average surface roughness of LIGA components is 10-15 nm; this relatively low surface roughness makes LIGA suitable for making a variety of refractive and reflective optical elements. Some of the optical devices fabricated by use of the LIGA process include Fresnel zone plates by Munchmeyer et al [38] and lenses made by using a re-flow process presented by Ruther et al [90].

A microspectrometer was also successfully developed and commercialized at FzK in the early 1990s [91]. A LIGA-based embossing tool was used to pattern a three layer PMMA
waveguide creating grating step heights as small as 0.2 mm. The core material was made of PMMA with a refractive index of 1.49 at 589 nm, while the cladding is a copolymer containing 78% methylmethacrylate and 22% tetrafluoropropylmethacrylate with a refractive index of 1.476 at 589 nm [92]. The device was found to be well suited for spectroscopic analysis in the visible and near infrared region, where it can be used for detection and analysis of heavy metal ions in water, detection of toxic agents in smoke, and detection of oxygen content in blood. The FzK microspectrometer is now commercialized by STEAG microParts GmbH (Germany) and has found its way into medical devices such as the BiliCheck™ (SpectRx, Inc.), an instrument used to measure the levels of bilirubin in infants.

Numerous electrostatic devices including capacitive microaccelerometers have also been made by the LIGA process [86, 93, 94]. The accelerometer presented by Both et al [94] distinctly stands out from other electrostatic devices because the sensor elements were movable molded structures fabricated by aligned-embossing on a CMOS chip covered with a sacrificial layer. The microaccelerometer presented by Both et al demonstrated that it was possible to integrate CMOS circuitry with LIGA to produce devices inexpensively.

Mohr et al presented a micromotor with an electrostatic wobble drive with tooth shaped rotor and stators [92]. The turning angle of a rolling cycle of the rotor was matched with the angle of the switch cycle therefore minimizing the friction between the rotor and the axle [95, 96]. This design resulted in micromotors that were capable of operating at high speeds with little frictional wear.

Other devices fabricated by use of LIGA include a self-priming in-line gear pump [97], microelectrodes [13], a gimbal-type microgyroscope [98], tips for atomic force microscopy [40], multi-level microfluidic systems [99], microtiter plates [100], and micro-harmonic drive gear systems [101].
2.8 Concluding Remarks

LIGA has found a niche in applications, where high aspect ratio or nearly vertical sidewall in microstructures is vital. LIGA also expands the realm of surface micromachining from that of 2-D to a truly 3-D fabrication process by using multi-level lithography and electroplating processes. Unlike silicon micromachining, a wider choice of materials is available in LIGA. However, the high cost and low throughput of synchrotron radiation has impeded the commercial success of LIGA. The use of the high sensitivity photoresist, SU-8, along with advances in mold insert fabrication and molding are expected to make LIGA commercially viable in the near future.
Chapter 3 X-Ray Masks for Multi-Level LIGA

3.1 Introduction

In the first step of the LIGA process, the pattern on an X-ray mask is transferred to a resist material by use of X-ray lithography. The X-ray mask is essentially composed of microstructures made of an X-ray absorbing material on a highly X-ray transparent substrate. In a typical X-ray mask, a variety of high resolution patterns with critical dimensions ranging from sub-micrometer [102-104] to several millimeters [49, 105] can be present.

As the starting point for any LIGA process, an X-ray mask is perhaps the most critical piece of the LIGA “puzzle.” The quality of microstructures including the sidewall surface roughness is mainly determined by the mask substrate material and the fabrication process. In addition, since most defects on a mask propagate through the lithography, electroplating, and molding processes, yield is significantly affected by the quality of the mask. Therefore, an X-ray mask must be properly designed: materials for the substrate and X-ray absorber need to be properly selected and their thicknesses sized by taking into account the requirements of the microstructures for which the mask is intended.

The LSU/SatCon microgyroscope structures had aspect ratios from 125 to 200 with overall structural heights of up to 1500 µm. Furthermore, the relatively thin wiring layers and the high aspect ratio cylinders/electrodes needed to be aligned with better than 10 µm accuracy during X-ray lithography. Since the smallest critical dimension of the microgyrosopes was 4 µm, the X-ray mask must produce peak-to-peak roughness of no more than 1 µm (¼ CD).
The following sections present detailed discussions of the material selection, design, fabrication process, and performance of four types of masks used to fabricate multi-level high-aspect ratio microstructures. The graphite, borosilicate, and silicon nitride mask fabrication processes were developed at CAMD, while the titanium mask was purchased from IMT (Karlsruhe, Germany). The titanium mask fabrication process is included as a comparison to the other methods developed at CAMD.

### 3.2 Mask-Blank and Absorber Material Selection

The primary role of an X-ray mask-blank is to provide structural support for the absorber pattern needed to form an image during X-ray lithography while the absorber material should block the incoming X-ray radiation with high efficiency. The mask-blank and absorber materials also play major roles in dissipating the heat generated by the absorption of radiation by both the mask-blank and absorber materials. Since X-ray masks are subjected to high levels of radiation over long periods, the construction materials must have high radiation resistance and show little change in X-ray and optical transmission as well as mechanical properties. The following sections discuss the mask-blank and absorber material selection process in depth.

#### 3.2.1 X-Ray Transmission Characteristics

The X-ray attenuation properties of materials are mathematically described by the Beer-Lambert law as

$$ P(x) = P_0 e^{-x/L}, \quad \text{3-1} $$

where $P_0$ is the incident X-ray power per unit area, $x$ is the thickness, and $L$ is the attenuation length [106]. The attenuation length is simply the inverse of the mass attenuation coefficient, $\mu$, and depends on the photon energy as well as the type of material. Equation 3-1 can be expanded further and presented as a function of the wavelength, $\lambda$, such that
\[ P(x) = \int_0^\infty \frac{\partial P_0(\lambda)}{\partial \lambda} e^{-\mu(x)\lambda} d\lambda. \]

At a thickness equal to the attenuation length \( x = L \), the radiation retains \( 1/e \) of the original intensity while the remainder is absorbed by the material. The attenuation lengths of candidate mask-blank materials were computed using a web-based tool hosted by the Center for X-ray Optics (CXRO) (Berkeley, California) [107] and are shown in Figure 3-1; the attenuation lengths generally increase with increasing photon energy so the materials act as high band pass filters.

Synchrotrons produce a continuous spectrum of radiation ranging from infrared to hard X-rays, which is often referred to as white light. An effective transparency, \( T_{\text{eff}} \), can be defined for a set of exposure conditions as the ratio of the dose deposited at the bottom of a resist with a mask-blank in place to the dose deposited without a mask-blank and written mathematically as

\[
T_{\text{eff}} = \frac{\int G\left(\frac{\lambda}{\lambda_c}\right) \mu_R e^{-\mu_R \lambda} e^{-\mu_M d_M} d\lambda}{\int G\left(\frac{\lambda}{\lambda_c}\right) \mu_R e^{-\mu_R \lambda} d\lambda},
\]

where \( G \) is the spectral distribution function of the radiation incident upon the X-ray mask, \( \lambda_c \) is the critical wavelength, \( \mu_R \) and \( \mu_M \) are the attenuation coefficients of the resist and mask respectively, and \( d_M \) is the thickness of the mask-blank [108]. Figure 3-2 shows the raw spectral distribution of photons, \( G \), produced at the bending-magnet beamlines at CAMD. The effective transparencies of some commonly used mask-blanks are shown in Figure 3-3 for 100 eV to 30,000 KeV photon energy range.

### 3.2.2 X-Ray Attenuation Characteristics of Absorber Materials

An effective absorption, \( A_{\text{eff}} \), can be defined for an X-ray absorber material such that \( A_{\text{eff}} = 1 - T_{\text{eff}} \), where \( T_{\text{eff}} \) is the effective transmission given by Equation 3.3.
Figure 3-1  X-ray attenuation lengths of various mask-blank materials
Figure 3-2  Spectral distribution of photons generated at the XRLM3 bending magnet beamlines at CAMD: 1.3 GeV ring energy; 2.928 m bending magnet radius; 10 m distance from the source point; 1.66 KeV critical energy
Figure 3-3  Effective transparency of selected mask-blank materials at the bending magnet beamlines at CAMD (1.3 GeV)
The spectral distribution, $G$, used in determining $A_{\text{eff}}$ is the radiation that is incident upon the absorber material after passing through the front-end window, filter, and mask-blank materials. Eight metals ranging in density from 7.31 g/cm$^3$ to 21.45 g/cm$^3$ are considered for use as absorber materials (Table 3-1).

**Table 3-1  Densities and absorption characteristics of candidate X-ray absorber materials**

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm$^3$)</th>
<th>Thickness for 80% Absorption</th>
<th>Patterning Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>8.908</td>
<td>12.7</td>
<td>Electroplate</td>
</tr>
<tr>
<td>Copper</td>
<td>8.920</td>
<td>12.5</td>
<td>Electroplate</td>
</tr>
<tr>
<td>Tin</td>
<td>7.310</td>
<td>5.5</td>
<td>Electroplate</td>
</tr>
<tr>
<td>Lead</td>
<td>11.34</td>
<td>3.7</td>
<td>Electroplate</td>
</tr>
<tr>
<td>Tantalum</td>
<td>16.65</td>
<td>3.1</td>
<td>Dry-etch</td>
</tr>
<tr>
<td>Tungsten</td>
<td>19.30</td>
<td>2.8</td>
<td>Dry-etch</td>
</tr>
<tr>
<td>Gold</td>
<td>19.32</td>
<td>2.2</td>
<td>Electroplate</td>
</tr>
<tr>
<td>Platinum</td>
<td>21.45</td>
<td>2.1</td>
<td>Electroplate</td>
</tr>
</tbody>
</table>

Tin, lead, tantalum, tungsten, and gold have been used previously as absorbers either as alloys or elemental form. Nickel and copper are considered because they are commonly used as structural materials in LIGA, while platinum has high density and can be electroplated. The absorption characteristics and effective absorption curves of the candidate metals are shown in Figure 3-4 and Figure 3-5.

In addition to the absorption characteristics, the ease of formation and the processing conditions of the absorber material need to be considered. Electroplating and reactive ion etching (RIE) are two methods that are commonly used to form absorber layers for X-ray masks. All of the candidate absorber materials listed in Table 3-1 with the exception of tantalum and tungsten can be electroplated with varying levels of difficulty from aqueous solutions with plating rates of 1 to 300 µm/hr at bath temperatures ranging from 20 to 100 °C.
Figure 3-4  X-ray attenuation lengths of candidate X-ray absorber materials
Figure 3-5  Effective absorption of various X-ray absorber materials for the XRLM1 beamline at CAMD (1.3 GeV)
A lead-tin alloy (90:10) formed by electroplating was reported by Fischer et al. as an inexpensive absorber material [106]. However, Fischer reports that for an average photon spectrum of 20 KeV, a 40 µm-thick layer of lead-tin alloy provides a contrast ratio of only 20 for a 1 mm-thick layer of X-ray resist, which is insufficient for both PMMA and SU-8 lithography. Copper, nickel, and tin can also be easily electroplated; but similar to the lead-tin alloy reported by Fischer et al., they all have relatively long attenuation lengths as shown in Figure 3-4. The use of materials with long attenuation lengths increases the necessary thickness of the photoresist mold on the mask-blank adding another level of complexity to the mask fabrication process.

Tantalum and tungsten are both refractory metals with relatively high densities but with the exception of chromium, refractory metals can only be electroplated from molten-salt baths at temperatures as high as 850 °C [109], which makes them incompatible with mask-blank and photoresist materials. However, tantalum [103], tungsten [110], and lead [111] can be deposited with physical vapor deposition (PVD) and patterned with reactive ion etching (RIE) to form absorber patterns for X-ray masks. High-aspect ratio absorber patterns with sub-micrometer critical dimensions that are usually susceptible to structural collapse can be produced by using all dry processes such as PVD and RIE; but both of these processes are very slow, making it difficult to form absorber layers greater than 3 µm in thickness.

Gold and platinum have the highest effective absorption among the candidate absorber materials. Therefore, a relatively thin layer of one of these materials can be used as an absorber; for example, only 2.2 µm thick gold or platinum is needed to provide an effective absorption of 80% as opposed to 12.6 µm of nickel or 3.7 µm lead. Gold can be electroformed easily out of cyanide or sulfite based baths [112-116] into patterned photoresist layers ranging in thickness from sub-micrometer [52, 112] to over one-hundred micrometer [117] with temperature ranging from 25 to 80 °C. Platinum can be electroplated out of aqueous solutions based on ammine or
acid chloride from 30 to 90 °C [109]. However, since gold electroplating is extensively used in jewelry, a myriad of well-established processes are commercially available; therefore, gold was selected as the material-of-choice for X-ray masks.

### 3.2.3 Thermoelastic Properties of Mask-Blanks

The absorption of photon energy by an X-ray mask during lithography leads to an overall increase in temperature of the mask, which may be a significant source of pattern distortion. Mask-blanks are also exposed to temperatures as high as 150 °C during the soft bake and post exposure bake cycles of the mask fabrication process and must be able to withstand these large temperature variations without damage or in case of membranes, loss of the tensile stress.

Vladimirsky et al used an X-ray mask with built-in thermal resistors to measure the temperature rise during exposure at a soft X-ray beamline at the Synchrotron Radiation Center (University of Wisconsin-Madison) and showed that for highly transparent masks with low absorber coverage, the maximum change in temperature, $\Delta T_{\text{max}}$, could be limited to less than 10 °C [118]. Zetter et al. reported $\Delta T_{\text{max}}$ as high as 70 °C in titanium membrane masks [119]. The temperature rise in X-ray masks was also studied at CAMD using thermocouples mounted directly on the mask surface shielded by an absorber material. Figure 3-6 shows the temperature history during exposure of a beryllium mask with an approximately 75% absorber coverage at the XRLM1 and XRLM4 beamlines. The lowest $\Delta T_{\text{max}}$ of 2 °C was measured at XRLM1 beamline at 120 mA ring current and the largest $\Delta T_{\text{max}}$ of 30 °C was measured at the XRLM4 beamline at 137 mA ring current. XRLM1 is a bending magnet beamline with a power flux at the mask of $2.98 \times 10^{-3}$ W/cm$^2$/mA, while XRLM4 is a wiggler beamline with a power flux of $2.70 \times 10^{-2}$ W/cm$^2$/mA.
Figure 3-6  Temperature rise in an X-ray mask with 35 μm-thick gold absorber on a 500 μm-thick beryllium substrate with 75% absorber coverage
As the temperature of a mask increases, the membrane expands, decreasing the tension in the membrane. Since most modern X-ray scanners have water cooled mask holders, the expansion of the mask frame can be neglected. To minimize pattern distortion, the expansion of the mask per unit length due to $\Delta T_{\text{max}}$ must be less than the pre-existing strain in the mask-membrane; this condition sets a lower limit for the pre-stress of a membrane, $\sigma_{\text{membrane}}$. On the other hand, the yield strength of the membrane, $\sigma_{\text{yield}}$, must be greater than the pre-stress in the membrane to avoid plastic deformation. These two conditions can be summarized as

$$\frac{\Delta T_{\text{max}} \alpha E}{1 - \nu} < \sigma_{\text{membrane}} \leq \frac{\sigma_{\text{yield}}}{n}, \quad 3-4$$

where $n$ is a factor of safety and $\alpha$, $E$, and $\nu$ are the coefficient of thermal expansion, modulus of elasticity, and Poisson’s ratio of the membrane material respectively. In practice, absorber patterns contain structures of various asymmetric shapes and sizes and since the thickness of the absorber layer is usually much larger than the thickness of the membrane, the thermoelastic behavior of the absorber material dominates.

Unlike membranes, thick substrates do not need to be pre-stressed for stability. Thick substrates expand and contract in response to the temperature changes during use – only constrained by the strength of the bond to the mask frame. Therefore, minimizing mask distortion by selecting a material with high thermal conductivity as well as a low coefficient of thermal expansion is imperative. The maximum temperature rise also depends on exposure conditions such as scan-speed, acceleration, dwell-time, scan length, and beam current; all of these parameters must be optimized to minimize $\Delta T_{\text{max}}$.

### 3.2.4 Surface Suitability of Mask-Blank Materials

Absorber patterns are typically produced by using a combination of lithography and electroplating or dry-etching. Low surface roughness, low porosity, and good adhesion to metals
and photoresists are some of the desirable surface characteristics for mask-blanks [120]. An electrically conductive surface that is also suitable for electroplating can simplify the fabrication process by eliminating the need to deposit an electroplating base.

Beryllium can be formed into a membrane for mask-blanks [104, 108] or obtained as a thick substrate (> 250 µm) from Brush Wellman Corp. (San Jose, California), the largest beryllium product manufacturer in the world, with various surface finishes ranging from a ‘super best-buff’ to a polished ‘mirror-finish’ with average roughness of 1.4 µm and 0.1 µm, respectively. The high roughness ‘super best buff’ finish is suitable for masks fabricated with X-ray lithography as the roughness enhances the adhesion to PMMA resist [121], whereas the ‘mirror finish’ beryllium is best for photolithography. Although beryllium has low resistivity, the native oxide prevents successful electroplating. Therefore it is necessary to activate the beryllium surface by either a chemical pickle with concentrated nitric acid or an anodic pickle in phosphoric acid [109], which are both incompatible with photoresists. A suitable electroplating base, such as gold, needs to be deposited by physical vapor deposition (PVD) to make the surface suitable for electroplating.

Graphite is one of the allotropes of carbon and has a hexagonal sheet-like structure. Graphite can be found in various forms including pyrolytic graphite and rigid graphite. The sheet-like structure is maintained in pyrolytic-graphite with a very weak bond between the sheets. As a result, pyrolytic-graphite cleaves very easily along the weak bond parallel to the hexagonal plane; this property which is sometimes referred to as ‘flaky,’ makes pyrolytic graphite unsuitable for use as an X-ray mask-blank. On the other hand, rigid-graphite is composed of graphite particles with typical grain sizes ranging from 1 µm to 20 µm compressed to form a bulk material. Rigid-graphite possesses low resistivity and can readily be electroplated with good adhesion. Rigid graphite is also highly porous and exhibits high surface roughness [122].
Regardless of the undesirable high surface roughness (for photolithography) and high porosity, X-ray masks have been successfully produced on graphite [105], [46], [49].

Vitreous carbon, also called glassy carbon, is an amorphous form of carbon produced by the thermal decomposition of cross-linked polymers. Vitreous carbon has low density (1.4 g/cm$^3$), no porosity, and possesses excellent X-ray transmission characteristics but it poses one serious challenge – its surface provides poor adhesion to metal layers deposited by either physical vapor deposition (PVD) or electroplating. Since vitreous carbon is non-toxic it is even more desirable than beryllium as a mask-blank material. However, the poor adhesion of metals deposited on the surface has prevented its use as a mask-blank.

Silicon nitride and borosilicate glass have low surface roughness and show no porosity and are most suitable for photolithography. These materials are not electrically conductive and a metallic plating base must be deposited to make them suitable for electroplating.

Titanium membranes are formed by sputter deposition and to improve the adhesion of photoresists and electroplated metals to titanium, the surfaces are treated with an alkaline-peroxide (AP) solution resulting in approximately 500 nm-thick layer of titanium dioxide (TiO$_2$). Although the roughness of the titanium increases as a result of the AP treatment, high quality sub-micrometer resolution patterns have been produced with electron beam, X-ray, and photolithography [104].

3.2.5 Optical Transmission

Mask-blanks with high optical transmission simplify the fabrication of an X-ray mask with alignment markers. Depending on thickness, glass, silicon nitride, silicon carbide, and polyimide membranes can provide acceptable levels of optical transmission, while beryllium, graphite, vitreous carbon, and titanium are all opaque.
Methods have been devised by various researchers to create optically transparent alignment markers even on opaque mask-blanks. In one approach developed for titanium and beryllium membrane masks at the IMT (Karlsruhe, Germany), the membrane material under the alignment markers is selectively etched to create stencil alignment markers [108]. An alternative method was developed at CAMD for opaque mask-blanks by mounting the mask-blank on an optically transparent glass ring and patterning the alignment markers on the glass ring at the same time that the high-aspect ratio microstructures are formed on the mask-blank [49].

### 3.3 Selected Mask-Blank and Absorber Materials

The X-ray and optical transmission, thermoelastic properties, and radiation stability of some candidate mask-blank materials are summarized in Table 3-2. Apart from the high coefficient of thermal expansion of beryllium and opacity to visible light, it is one of the best materials for mask-blanks. Nevertheless, the toxicity of beryllium [123] limits its ubiquitous use and beryllium-based masks were not pursued as part of this research.

<table>
<thead>
<tr>
<th>Table 3-2</th>
<th>Qualitative comparison of the relevant properties of selected X-ray mask-blank including an hypothetical “ideal” mask-blank material</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>X-ray Transmission</strong></td>
<td><strong>Optical Transmission</strong></td>
</tr>
<tr>
<td>Beryllium</td>
<td>High</td>
</tr>
<tr>
<td>Graphite</td>
<td>High</td>
</tr>
<tr>
<td>Vitreous Carbon</td>
<td>High</td>
</tr>
<tr>
<td>Borosilicate Glass membrane</td>
<td>Medium</td>
</tr>
<tr>
<td>Silicon Nitride Membrane</td>
<td>Medium</td>
</tr>
<tr>
<td>Titanium Membrane</td>
<td>Low</td>
</tr>
<tr>
<td>Ideal Mask-Blank Material</td>
<td>High</td>
</tr>
</tbody>
</table>
An acceptable level of X-ray transparency may be achieved using thin membranes made of titanium; but formation of thin, stress-controlled, and defect free titanium membranes is an arduous process mastered only by the lead practitioners of LIGA in Karlsruhe, Germany – the birth place of LIGA. Two titanium masks were commercially procured from IMT (Karlsruhe, Germany) in the course of this research and their fabrication process is presented in Section 3.5.1.

The high X-ray transmission, low resistivity, and high thermal conductivity of rigid-graphite and vitreous carbon make them attractive for use as mask-blanks. Since these materials are fairly inexpensive and readily available, they were evaluated as possible mask-blanks. A mask fabrication process for rigid-graphite is presented in Section 3.5.2. The non-porosity and amorphous nature of vitreous carbon is expected to be advantageous for X-ray masks and an attempt was made to solve the problem associated with the adhesion of metals and preliminary results are presented.

Figure 3-3 shows that it is necessary to use approximately 6 µm-thick glass to obtain 75% effective transparency. Kupka et al. demonstrated that D 263 (Schott GmbH), a commercially available borosilicate glass, can be etched from an initial thickness of 80 µm down to a final thickness of 30 µm [124] and used to make an X-ray mask. In this research, glass films 30 µm-thick, commonly used in liquid crystal displays, were commercially procured and a process was developed for making masks on these glass films. The fabrication process is presented in Section 3.5.3 of this dissertation.

The deposition of stress controlled silicon nitride is well understood and its use both in microelectronics and micromachining is widespread. Furthermore, the high strength of silicon nitride allows it to be formed into thin, large area membranes. 1 µm-thick silicon nitride membranes with internal stress from 10 MPa to 80 MPa have been used to make masks with
areas as large as 5 cm x 7 cm. Section 3.5.4 describes the X-ray mask fabrication process for on silicon nitride membranes.

### 3.4 Mask-Blank and Absorber Thickness Sizing

The most important factor in determining the thicknesses of a mask-blank material is the effective transparency of the material, $T_{\text{eff}}$, which is a measure of how well the mask-blank is able to transmit X-ray radiation of a given spectrum. The absorber thickness is determined based on the absorption contrast, $C_{\text{absorption}}$, provided by an absorber of a given thickness. The following sections discuss the sizing of the thickness of different mask-blank and absorber materials.

#### 3.4.1 Mask-Blank Thickness

X-ray mask-blanks can be classified into two categories: thick-substrates and membranes. Thick-substrates have sufficient structural stiffness to be handled and processed without additional support and range in thickness from 100 µm to 1000 µm. Conversely, membrane type substrates lack structural stiffness and must be mounted on a frame or formed in situ with built-in tensile stress during processing and use.

In Section 3.2.1, the transmission characteristics of mask-blank materials were discussed and the $T_{\text{eff}}$ of these materials are shown in Figure 3-3. An acceptable level of $T_{\text{eff}}$ can be selected and used to determine the maximum thickness needed to achieve this level of transparency. The choice of an acceptable $T_{\text{eff}}$ is based on a few practical considerations, which can best be illustrated by use of an example. If the raw-spectrum of radiation from a bending magnet beamline at CAMD is used to irradiate a 500 µm-thick PMMA layer without an X-ray mask, the top-to-bottom dose ratio, $R$, will be equal to 261 with a $T_{\text{eff}}$ of 100%. As shown in Table 3-3, the $R$ decreases from the initial level of 261 to 9 by inserting a 220 µm Be front-end window and a 400 µm Be mask-blank yielding a $T_{\text{eff}}$ of 75%. To achieve a dose ratio of 5, an additional 10 µm-thick aluminum filter needs to be inserted yielding a $T_{\text{eff}}$ of 51%.
Table 3-3  Effective transparencies at the XRLM1 beamline with various beamline elements for a 500 µm-thick layer of PMMA

<table>
<thead>
<tr>
<th>Beamline and exposure elements</th>
<th>Effective Transparency ((T_{\text{eff}}))</th>
<th>Dose Ratio of 500 µm PMMA ((R))</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (raw-spectrum)</td>
<td>N/A</td>
<td>261</td>
</tr>
<tr>
<td>220 µm Be (front-end window)</td>
<td>100%</td>
<td>23</td>
</tr>
<tr>
<td>400 µm Be mask-blank</td>
<td>75%</td>
<td>9</td>
</tr>
<tr>
<td>10 µm Al</td>
<td>51%</td>
<td>5</td>
</tr>
</tbody>
</table>

The same level of transparency of 51% can also be achieved by using a 700 µm-thick Be substrate and no Al filters instead of the 400 µm Be mask-blank combined with a 10 µm-thick Al filter. However, inserting an Al filter in-front of the mask removes low energy photons, which would have otherwise increased the maximum temperature of the mask during use as discussed in Section 3.2.3.

The 75% transparency level shown on Figure 3-3 also differentiates the materials that need to be formed into membranes from those that are rigid enough to be self-supporting. The thicknesses for 75% \(T_{\text{eff}}\) for the various mask-blank materials considered are listed in Table 3-4.

Table 3-4  Comparison of selected mask-blank materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
<th>Thickness for 75% (T_{\text{eff}}) (µm)</th>
<th>Availability (µm)</th>
<th>Type of Substrate</th>
<th>Commercial Source</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryllium</td>
<td>1.8</td>
<td>400</td>
<td>&gt; 250 µm</td>
<td>Self-supportive</td>
<td>Brushwellman Corp. (San Jose, CA)</td>
<td>$500-$2000</td>
</tr>
<tr>
<td>Vitreous Carbon</td>
<td>1.4</td>
<td>105</td>
<td>&gt; 100 µm</td>
<td>Self-supportive</td>
<td>Goodfellow Corp. (United Kingdom)</td>
<td>~$120</td>
</tr>
<tr>
<td>Graphite</td>
<td>1.7</td>
<td>100</td>
<td>&gt; 150 µm</td>
<td>Self-supportive</td>
<td>POCO, Inc. (Decateur, TX)</td>
<td>~$15</td>
</tr>
<tr>
<td>Glass</td>
<td>2.3</td>
<td>10</td>
<td>30µm, 80µm</td>
<td>Membrane</td>
<td>Schott GmbH (Germany)</td>
<td>~$100</td>
</tr>
<tr>
<td>Silicon Nitride</td>
<td>2.4</td>
<td>6</td>
<td>1 µm</td>
<td>Membrane</td>
<td>DIMES (Netherlands)</td>
<td>~$200</td>
</tr>
<tr>
<td>Titanium</td>
<td>4.5</td>
<td>2</td>
<td>2.8 µm</td>
<td>Membrane</td>
<td>IMT (Karlsruhe, Germany)</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Other factors such as the availability of a material in a given thickness and cost were also taken into consideration when determining the thickness of a mask-blank material. All of the materials except titanium membranes are commercially available from different vendors. Although X-ray masks made on Ti membranes can be commercially procured, the mask-blanks are not available. Beryllium is the most expensive material out of the six, while graphite is the lowest cost.

3.4.2 Absorber Thickness Sizing

In Section 3.2.2, the X-ray attenuation characteristics of gold, tantalum, lead, nickel, copper, and tin were discussed; and by virtue of its short absorption length and ease of formation, gold was chosen as the most suitable absorber material. In this section, the minimum thickness of gold for an X-ray mask is determined.

The relative efficiency of an X-ray mask in transmission and the absorption of radiation during lithography is measured by a dimensionless parameter called contrast. Two types of contrasts are generally defined in relation to X-ray masks: the transmission-contrast, \( C_{\text{trans}} \), is the ratio of the total power transmitted through the mask-blank \( (P_M) \) to the total power transmitted through both the absorber and the mask-blank \( (P_A) \), whereas the absorption-contrast, \( C_{\text{absorp}} \), is defined as the dose absorbed at the bottom of the resist in the exposure area \( (D_{BR}) \) to the dose absorbed at the top of the resist in the shielded region \( (D_{TA}) \) [64].

The definition of the powers and doses used in the calculation of the absorption and transmission contrasts are shown in Figure 3-7 and Figure 3-8. The transmission-contrast depends on the properties of the mask and the spectrum of radiation used for lithography, but the absorption-contrast also depends on the absorption length and thickness of the resist. Thus, absorption contrast is a better indicator of a mask’s suitability for a particular lithographic task.
Figure 3-7  Definition of doses used in the calculation of the absorption contrast of a mask
In this dissertation, the absorption contrast will simply be referred to as the “contrast” and denoted by $C$ such that

$$C = \frac{D_{BR}}{D_{TA}}.$$

The raw-spectrum of radiation emitted at a bending magnet beamline is a function of only the electron energy and the bending magnet radius and contains photons from the far infrared to hard X-rays. The dependence of the attenuation length of a material on the photon energy coupled with a continuous spectrum of radiation results in a higher dose being absorbed at the top of an X-ray resist than the bottom as shown in Figure 3-8. The top-to-bottom dose ratio $R$, is defined as $R = D_{TR} / D_{BR}$, where $D_{TR}$ and $D_{BR}$ are the doses at the top and bottom of the resist respectively. $R$ is an important parameter that needs to be considered carefully in deep X-ray lithography. A high dose ratio (>7) results in resist foaming and dimensional instability, while a low dose ratio (<3) requires a thick absorber layer and longer exposure time. The dose ratio can be varied by changing the thicknesses of the beryllium window, the mask-blank, and additional filters placed anywhere in front of the resist layer.

An absorption contrast curve, which is independent of the type of mask-blank used, can be generated for a given beamline, resist thicknesses, and dose ratio, $R$. The absorption contrast curve can be defined as a ‘characteristic contrast curve’ (CC curve) and it relates the thickness of the absorber to the contrast at a constant dose ratio. The CC curves for resist thicknesses from 250 µm to 1000 µm and a dose ratio of 5 for CAMD’s bending magnet beamlines are shown in Figure 3-9; this figure serves as a useful reference to determine the minimum thickness of the absorber for an X-ray mask or estimating the contrast provided by a mask for a particular lithographic job. Figure 3-9 shows that a 13 µm-thick layer of gold is sufficient to provide a contrast of 50 for resist thicknesses of up to 1000 µm with a top-to-bottom resist dose ratio of 5.
Figure 3-8  Attenuation of X-ray power by the beamline filter, mask-blank, absorber, and X-ray resist
Figure 3-9  Contrast characteristic (CC) curves for the bending magnet beamlines at CAMD at a top-to-bottom dose ratio of 5 (since the density and absorption characteristics of PMMA and SU-8 are similar, this plot can be used for both PMMA and SU-8 resists)
3.5 Fabrication Methods

X-ray masks can be classified into three categories based on the smallest lateral dimension present on a mask, commonly referred to as critical dimension (CD), as high-, medium-, or low-resolution. The choice of fabrication process depends on the type of mask to be fabricated as summarized in Figure 3-10. High-resolution X-ray masks for high-aspect ratio microstructures possess CDs as small as 0.2 µm and can only be fabricated using a two step process. In the first step, an intermediate mask is made by using a combination of electron-beam (e-beam) writing and gold electroplating. Soft X-ray lithography is then used to transfer the pattern from the intermediate mask into a thicker layer of PMMA followed by gold electroplating to make the final X-ray mask, commonly referred to as a working mask, which is suitable for DXRL.

Typically, the intermediate mask would have an absorber thickness from 2 µm to 3 µm, while the working mask would have 15 µm to 25 µm -thick resist. The best example of a high-resolution working mask is used to make a hot-embossing tool for a microspectrometer and has a focusing diffraction grating of 0.2 µm by 2 µm steps [91, 125]. Recently, van Kan et al. at the National University of Singapore have produced high-resolution patterns similar to those found on working masks by proton-beam lithography raising the possibility of making high-resolution working masks with a single step process [126, 127].

Medium-resolution X-ray masks are fabricated using a two step process but the intermediate masks are made with either laser-writing or UV lithography of photoresist layers ranging from 3 µm to 10 µm in thickness in lieu of e-beam lithography. The working masks are made by a process similar to high-resolution working masks, i.e. soft X-ray lithography followed by gold electroplating. Due to the limitations imposed by the laser-writing and UV lithography, the CD of medium-resolution X-ray masks is limited to approximately 3 µm.
Figure 3-10  Summary of X-ray mask fabrication methods
The demands of MEMS technologies during the last two decades have catalyzed the development of a multitude of thick (>10 µm) photoresists. One of these photoresists is SU-8, an epoxy-based negative tone resist developed at IBM in the early 1990s [71], [128]. Patterns as small as 5 µm CD with thickness of over 50 µm can be patterned using SU-8 photolithography and used to fabricate low-resolution X-ray masks in a single step process.

3.5.1 Titanium Membrane Mask Fabrication

The fabrication process of titanium membrane X-ray masks has been well-established for over two decades; titanium masks are commercially available from IMT (Karlsruhe, Germany) – the ‘birth place’ of LIGA. Two X-ray masks with a variety of microstructures including microgyroscopes were purchased from the IMT. These masks were fabricated by using the two-step high-resolution mask fabrication method outlined in the following section; the process sequence is shown in Figure 3-11.

3.5.1.1 Intermediate Mask

A 100 nm layer of carbon followed by a 2.8 µm layer of titanium were sputter deposited on a silicon substrate; during the sputtering process, the deposition conditions were monitored and controlled such that the resulting titanium film possess tensile stress. The titanium layer was wet-oxidized by use of an alkaline-peroxide (AP) treatment and a 2.5 µm-thick layer of PMMA was spincoated and baked on the oxidized titanium. The mask pattern was written by use of a 100 KeV e-beam writer and developed. The resulting resist pattern was electroplated with 2.2 µm-thick gold. The remaining PMMA resist was exposed with X-ray radiation and removed using a developer. Finally, an Invar frame was bonded to the titanium membrane and the membrane was released from the carrier silicon substrate.
Figure 3-11  Fabrication process of titanium membrane masks: a) 100 Å layer of carbon followed by 2.5 μm titanium was sputter deposited on a silicon wafer; b) The titanium layer was wet oxidized, coated with 2.5 μm layer of PMMA, and patterned by e-beam lithography; c) The PMMA pattern was electroplated with gold, the PMMA stripped, and an invar frame bonded to the titanium and removed from the silicon carrier wafer to yield the intermediate mask; d) 35 μm layer of PMMA was applied on a similarly prepared wafer as shown in a) and patterned by soft X-ray lithography; e) The PMMA pattern was electroplated with gold, the PMMA stripped and bonded to an invar frame is bonded; and the titanium was removed from the carrier wafer to yield the working mask.
The underlying carbon layer provided poor adhesion between the sputter deposited titanium and the silicon substrate thereby aiding the membrane release process.

Figure 3-12 shows a series of high resolution gold patterns similar to those found on high resolution intermediate mask.

3.5.1.2 Working Mask

The fabrication of the working mask began with a 2.8 µm-thick wet-oxidized titanium layer similar to the one used for intermediate masks. Approximately 35 µm-thick PMMA resist was formed by polymerizing a mixture of high molecular weight polymethylmethacrylate (PMMA) powder in methylmethacrylate (MMA) with the aid of benzoylperoxide (BPO), N,N-dimethylaniline (DMA), and γ-methacryloxypropyltrimethoxysilane (MEMO). BPO and DMA served as initiator and hardener, respectively. The addition of MEMO caused the PMMA to cross-link, which lowered the sensitivity of the PMMA but increased the resist contrast. MEMO also helped in the formation of chemical bonds to the titanium dioxide layer formed by the AP treatment. The PMMA layer was annealed at 115 °C with slow ramp-up and cool-down cycles to relieve the internal stress that is generated during the polymerization process [40].

The PMMA resist was lithographically patterned using soft X-ray lithography with a bottom dose of 4 KJ/cm³ and developed with the GG developer [35]. The sample was electroplated with a sulfite-based gold electroplating solution with a final absorber thickness of 17 µm. Similar to the intermediate mask, the PMMA was stripped and mounted on an Invar frame.

Figure 3-13 shows some representative SEM pictures of the microstructures present on the two titanium membrane masks and a photo of one of these masks. The alignment markers on these masks are of the stencil-type formed by selectively etching the titanium membrane under the markers creating suspended gold cross-hairs.
Figure 3-12  High resolution *intermediate mask* patterns produced by use of a 100 KeV e-beam writer with a gold thickness of 1.8 µm: a) 700 nm-wide lines and spaces; b) 1 µm-diameter posts; c) 20 µm-diameter gear with teeth length of 1.25 µm
Figure 3-13  Ti membrane X-ray mask with 17 µm-thick gold: a) overall mask on Invar frame; b) alignment marker; c, d, e, & f) gold microstructures on mask
3.5.2 Graphite Mask Fabrication

The simplest mask fabrication method shown in Figure 3-10 may be combined with the lowest cost mask-blank material, graphite, to make the least expensive X-ray mask. In 1998, a fabrication process for X-ray masks on graphite substrates was developed at CAMD in collaboration with the Institute for Micromanufacturing (IfM) (Ruston, Louisiana) [45, 46]. Since overlay exposures were a necessity for the fabrication of the microgyrosopes, alignment markers were produced by mounting a graphite mask-blank on a glass ring and patterning the alignment markers on the optically transparent glass ring, while the microgyroscope patterns were produced on the graphite as shown in Figure 3-14 [49].

Numerous manufacturers make fine-grained and isotropic graphite sheets with relatively high strength. The density of these graphite sheets, which depends on the level of porosity, ranges from 1.4 to 2.3 g/cm³. Considering the efficiency of X-ray transmission, low density graphite (high porosity) is preferable. Table 3-5 shows the physical properties of some grades of graphite made by POCO Specialty Materials (Decatur, Texas) [122].

In order to investigate the effects of density/porosity and particle size on the fabrication process and influence on X-ray lithography, two grades of graphite (SFG-1 and DFP-3) were purchased from POCO Specialties. The initial thicknesses of the graphite substrates ranged from 200 to 260 µm with a diameter of 10 cm. Since the substrates were formed by slicing (sawing??) a block of graphite, they exhibit high surface roughness (1.5 µm Ra, 5 µm Rz). Furthermore, the sheets were porous with average densities ranging from 1.70 to 1.83 g/cm³ [122]. Since POCO makes DFP-3 by ‘densifying’ DFP-1 with a proprietary process, its properties apart from density are expected to be similar to those of DFP-1.
Figure 3-14  Graphite mask fabrication process: a) 125 µm-thick graphite disk was mounted on a glass ring using epoxy; b) 30 µm-thick SU-8 was spincoated and baked, the gap between the glass ring and the photomask was filled with glycerine to reduce diffraction and photolithographically patterned; c) the exposed SU-8 was post-exposure baked, developed, and the Cr metal layers on the glass ring was selectively etched off; d) the SU-8 mold was electroplated with gold
Table 3-5  Typical properties of POCO graphite [118]

<table>
<thead>
<tr>
<th></th>
<th>FM-1</th>
<th>SFG-1</th>
<th>DFP-1</th>
<th>DFP-3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Particle Size</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>microns</td>
<td>20</td>
<td>1</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>Coefficient of Thermal Expansion</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^{-6}$ K$^{-1}$</td>
<td>7.5</td>
<td>8.1</td>
<td>8.1</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Flexural Strength</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N/mm$^2$</td>
<td>45</td>
<td>110</td>
<td>85</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Tensile Strength</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N/mm$^2$</td>
<td>30</td>
<td>75</td>
<td>60</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Hardness</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSH</td>
<td>58</td>
<td>85</td>
<td>74</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Electrical Resistivity</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu$ ohm cm</td>
<td>1240</td>
<td>1950</td>
<td>1500</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Apparent Density</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>g/cm$^3$</td>
<td>1.70</td>
<td>1.77</td>
<td>1.77</td>
<td>1.83</td>
</tr>
<tr>
<td><strong>Thermal Conductivity</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Watts/m K</td>
<td>110</td>
<td>72</td>
<td>95</td>
<td>N/A</td>
</tr>
</tbody>
</table>

3.5.2.1 Optical Mask Fabrication

Depending on the desired resolution, an optical mask can be fabricated using an optical pattern generator (OPG), a laser writer, or an e-beam writer. OPG yields the lowest resolution, while e-beam writers produce the highest. During the course of this research, many photomasks were fabricated at CAMD while others were purchased from a variety of vendors including LSI Photomask (Tempe, Arizona), Advance Reproduction (Andover, Massachusetts), and Photronics (Austin, Texas).

A typical photomask fabrication at CAMD began with computer-aided design (CAD) layout of the desired microstructures. The mask layout was exported as DXF file (Drawing Interchange File) and ‘fractured’ into series of rectangles by using ASM2500 software (Artworks, San Jose, California). A GCA Mann 3600 optical pattern generator (DW Mann/GCA Corp, USA ) was used to write the fractured patterns with a series of rectangular flashes of UV light on top of 5” a soda lime photomask blank (Nanofilm, Wetlake Village, California) on 1000 Å-thick dark-chrome and 1 μm-thick layer of AZ1518 photoresist. The exposed photoresist was developed in a
KOH-based positive photoresist developer and the underlying chromium layer was etched with a commercial chrome etchant comprised of cerium ammonium nitrate, nitric acid, and water (Olin Corporation, Stamford, Connecticut). The remaining photoresist was stripped with a solvent and the photomask was cleaned with an acid piranha etch – a highly oxidizing mixture of sulfuric acid and hydrogen peroxide.

3.5.2.2 Graphite Surface Preparation

The fabrication of a working X-ray mask began with the preparation of the surface of the graphite substrate. To improve the surface quality and thickness uniformity, up to 70 µm of the graphite was flycut from each side of a graphite substrate until a final thickness of 125 µm was obtained. A graphite substrate prepared in this manner typically showed an average surface roughness of 800 nm. The graphite sheet was cut into a 6 cm-diameter disk and thoroughly cleaned with acetone and isopropyl alcohol, and mounted on a glass ring using a two-part high temperature epoxy called of J-B Weld (J-B Weld Company, Sulphur Springs, TX) and cured in an oven for 5 hr at 80 °C.

3.5.2.3 Photolithography

The prime consideration in choosing a photoresist for X-ray mask fabrication was the thickness and sidewall profile of the resulting photoresist mold. A photoresist thickness of at least 10 µm was required for a typical working mask, while the sidewall slope needed to be minimized. High-aspect ratio microstructures with nearly vertical sidewalls can be obtained with SU-8 photoresist by using contact UV lithography in the range of 350-450 nm wavelength [129, 130]. SU-8 photoresist was found to satisfy both the thickness and sidewall slope requirements needs of graphite based X-ray masks [128].

SU-8 with various viscosities (designated by suffixes) can be purchased from MicroChem Corp. (Newton, Massachusetts) [72]. SU-8 5 and SU-8 25 were selected to provide adequate
thickness for the fabrication of DXRL and UDXRL X-ray masks, respectively. Optimized SU-8 processing conditions were used to apply photoresist layers from 15 µm (SU-8 5) to 55 µm (SU-8 25) in thickness on the graphite substrates [131]. Exposure was carried using an Oriel contact aligner (Newport Corporation, Irvine, California) with a 350-550 nm band pass filter. Since the top surface of the graphite wafer sits approximately 125 µm above the surface of the glass frame, glycerin, a material with a similar refractive index to SU-8, was employed to reduce the loss of resolution due to diffraction [132]. Post exposure bake (PEB) was carried out in a convection oven and the sample was developed by immersion in a standard propylene glycol monomethyl ether acetate (PGMEA) based SU-8 developer made by MicroChem Corp. After the sample was completely developed, it was rinsed with isopropyl alcohol and DI water, blow-dried with nitrogen, and dry-etched with oxygen plasma for several minutes.

Typically, the thickness of a spincoated layer of photoresist is inversely proportional to the spin speed. However, the thickness of the SU-8 on graphite was found to be consistently less than the predicted thickness. Table 3-6 shows a comparison of the thickness of SU-8 on various substrates. Due to the high porosity of the graphite, some of the photoresist material was absorbed by the graphite, reducing the resulting thickness. Since SFG-1 has a higher porosity than DFP-3, the final thickness of the SU-8 on SFG-1 was thinner than on DFP-3.

Table 3-6 Comparison of the thickness of SU 8 25 processed on various grades of graphite substrates

<table>
<thead>
<tr>
<th>Spin Speed (RPM)</th>
<th>Silicon wafer (µm)</th>
<th>SFG-1 (µm)</th>
<th>DFP-3 (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>65</td>
<td>36</td>
<td>55</td>
</tr>
<tr>
<td>1300</td>
<td>50</td>
<td>25</td>
<td>44</td>
</tr>
<tr>
<td>1500</td>
<td>45</td>
<td>25</td>
<td>35</td>
</tr>
</tbody>
</table>
Figure 3-15a shows an SEM of a 35 μm SU-8 pattern on a graphite substrate. A CD of 5 μm was achieved for a maximum thickness of 15 μm, while for 55 μm-thick layers, the CD was 10 μm. The problem encountered most often during SU-8 processing was the loss of adhesion of the SU-8 microstructures to the substrate during development, which was a direct result of the porosity of the substrates. The SU-8 developer was able to penetrate the graphite substrates during development and attack the cross-linked SU-8 features at the interface between the SU-8 and the graphite causing the loss of adhesion.

### 3.5.2.4 Gold Electroplating

A commercial gold sulfite-based electroplating solution, TG25 E (Technic, Inc., Cranston, Rhode Island) was used to electroplate the absorber patterns on the lithographically patterned graphite substrates. The solution was operated at a neutral pH, 45 ºC, and current density of 2 mA/cm². The gold electroplating process is discussed further in Chapter 4. Figure 3-15b and c show SEM images of gold microgyroscope patterns on a graphite substrate after the removal of the SU-8 photoresist. The sidewalls are smooth and vertical and exhibit no under plating.

### 3.5.3 Glass Mask Fabrication

Borosilicate glass is a natural candidate for use as a mask-blank due to its optical transparency and relatively low density. Previously, Kupka et al successfully produced X-ray masks on 25 μm-thick glass membranes that were formed by etching borosilicate glass with an initial thickness 80 μm using hydrogen fluoride [124]. As part of this research, an alternative method was developed. D263 T borosilicate glass films (100 mm-diameter, 30 μm-thick) were obtained from Schott AG (Mainz, Germany) and mounted in tension on carrier frames and used as mask-blanks. The fabrication process sequence of X-ray masks on glass mask-blanks is shown schematically in Figure 3-16 and discussed below.
Figure 3-15  X-ray mask patterns made of SU-8 and gold on DFP-3 graphite: a) 15 µm-thick SU-8 pattern on graphite; b) 8 µm-thick electroplated gold after SU-8 removal; c) 35 µm-thick gold absorber electroformed into a 55 µm SU-8 25 mold after the SU-8 removal
Figure 3-16 X-ray mask fabrication process on glass membranes: a) 30 µm-thick borosilicate glass film with a diameter of 100 mm was mounted on an Invar ring and a standard Cr/Au; b) 20 µm-thick layer of SPR-220-7® positive photoresist was spincoated, baked and lithographically patterned with a contact UV aligner; c) the photoresist mold was electroplated with gold; d) the photoresist was removed and the Cr/Au plating base wet-etched to form the alignment markers.
3.5.3.1 Membrane Formation

As discussed in Section 3.4.1, mask membranes need to be mounted in tension on carrier rings or formed in situ with some level of tensile stress to provide good thermomechanical stability during X-ray exposure. 30 µm-thick D 263 borosilicate glass films with 100 mm diameter were purchased from Schott AG. Since the glass films were purchased as free-standing sheets, a method that took advantage of the difference in the coefficient of thermal expansion (CTE) of the glass film and an appropriately selected mask frame was devised. The glass film was bonded to an Invar ring at greater than room temperature. When the mounted membrane was allowed to cool down to room temperature, a tensile stress developed in the mounted membrane as a result of the mismatch in CTE between the glass (7.2x10⁻⁶ /K) and the Invar mask frame (1.5x10⁻⁶ /K) [50], [124].

Desta et al. presented a simple analytical equation to estimate the stress generated after the formation of the membrane [50]. Since the frame was significantly thicker (6 mm) than the membrane (30 µm), all of the deformation due to the mismatch in thermal expansion was assumed to occur in the glass membrane. In a perfectly formed circular membrane, all of the stress components except \( \sigma_{rr} \) and \( \sigma_{\theta\theta} \) were zero in the stress-strain relationship. Assuming that the strain component in the thickness direction, \( \varepsilon_{zz} \), was much larger than the other two components, the axisymmetric stresses were written as

\[
\sigma_{rr} = \sigma_{\theta\theta} = \frac{E \alpha \Delta T}{1 - \nu},
\]

where \( E \), \( \alpha \), and \( \nu \) are the modulus of elasticity, coefficient of thermal expansion, and Poisson’s ratio of the glass, respectively and \( \Delta T = (T_{bonding} - T_{room}) \), the change in temperature during bonding. The membrane stress as a function of bonding temperature is shown in Figure 3-17.
Figure 3-17  Stress generated in a 30 µm-thick borosilicate glass membrane after bonding to an Invar ring at an elevated temperatures and cooled to an ambient temperature of 20 °C (Properties of D263 borosilicate glass: $\alpha=7.2 \times 10^{-6}/K$; $\nu=0.208$; $E=72.9$ GPa; $\sigma_{\text{yield}}=70$ MPa)
The inequality shown in Equation 3-4 and a factor of safety of 1.5 were used to determine the lower- and upper-bound for the membrane stress as 34 MPa and 47 MPa, respectively. The use of a factor of safety of 1.5 was deemed to be sufficient to prevent the membrane from damage and the maximum allowable bonding temperature of 89 °C was used to form the membrane with a projected tensile stress of approximately 47 MPa. The glass film was bonded to the Invar frame by use of J-B Weld and cured at 89 °C for 4 hr; J-B Weld (J-B Weld Company, Sulphur Springs, Texas) was reported to withstand temperatures up to 260 °C with 0% shrinkage by its manufacturer.

3.5.3.2 Photolithography

Although SU-8 photoresist yielded the best quality microstructures in terms of sidewall slope for thicknesses ranging from 10 µm to 50 µm, its residue-free removal is difficult [77-79, 133]. Unlike the graphite mask fabrication process presented in Section 3.5.2, the photoresist must be removed and the plating base selectively etched to form the alignment markers. Thus, an easily removal i-line positive tone photoresist, SPR® 220-7® (Shipley Company, Marlborough, MA), was used on the glass mask-blanks. After the membrane was cleaned and a Cr/Au plating base deposited by e-beam evaporation, a 15 µm-thick layer of SPR photoresist was spincoated and baked at 80 °C in a convection oven. The photoresist layer was exposed using a Quintel UL7000 contact aligner and a photomask fabricated at CAMD. The exposed photoresist was developed by soaking in MF 84MX developer (Shipley company, Inc., Marlboro, Massachusetts) rinsed with DI water and blow dried with nitrogen.

3.5.3.3 Gold Electroplating

A sulfite based gold electroplating bath, TG-25E (Technic, Inc., Cranston, Rhode Island), was used to electroplate 5.5 µm-thick gold into the SPR photoresist mold at 45 °C, 6.5 pH, and
current density of 1 mA/cm². The concentration and pH of the solution were monitored and adjusted between processes runs. **Figure 3-18** shows a glass-based X-ray mask.

**Figure 3-18**  Glass membrane X-ray mask: a) 30 µm-thick glass on 100 mm-diameter Invar ring with 5.5 µm-thick gold; b) 200 µm by 200 µm checker gold pattern; c) alignment marker
3.5.4 Silicon Nitride Mask Fabrication

Silicon nitride is widely used in MEMS as a dielectric material, a passivation layer to protect from water and alkali ions, and a structural material; because of its high etch resistance to chemicals, it is also used as an etch mask for silicon [134]. The high strength, excellent radiation stability, and short optical length of silicon nitride were found to be desirable for X-ray mask-blanks. Sandia National Laboratories (Albuquerque, New Mexico) and Honeywell FMT (Kansas City, Kansas) used silicon nitride masks extensively. The standard fabrication methods used at Sandia and Honeywell involved the formation of four 2.2 cm by 3.4 cm rectangular membranes with thicknesses of 1 µm on a 100 mm-diameter silicon substrate followed by photolithography and gold electroplating. However, these membranes were very fragile and susceptible to breakage during photolithography. A more robust process was developed whereby the lithography and gold electroplating were performed prior to the membrane formation and the membranes were formed by back-etching the silicon substrate. The process sequence is summarized in Figure 3-19 and presented below.

3.5.4.1 Substrate Preparation

The Delft Institute of Microelectronics and Submicronotechnology (DIMES) at the Delft University of Technology (Delft, The Netherlands) has been providing silicon nitride deposition service for X-ray masks for over a decade. Prime grade 100 mm-diameter, 525 µm-thick silicon wafers were cleaned, dehydrated, and deposited (front and back) with 1 µm-thick silicon-rich nitride using a low pressure chemical vapor deposition (LPCVD) process at DIMES. The silicon nitride deposition was carried out at 850 °C using a combination of dichlorosilane and ammonia gasses; the reaction is summarized as

\[ 3SiCl_2H_2 + 4NH_3 \rightarrow Si_3N_4 + 6HCL + 6H_2. \]
Figure 3-19  X-ray mask fabrication process on silicon nitride mask-blanks: a) Silicon wafer covered with 1 μm-thick silicon nitride on both side and Ti/Au plating on the front side; b) wafer was coated with a negative tone resist and patterned by UV lithography; c) gold was electroplated into the photoresist mold; d) the first layer of photoresist was removed and the wafers covered with a positive tone resist on both sides. The backside was lithographically patterned; e) the silicon nitride on the backside was dry-etched and used as an etch mask for the ensuing anisotropic wet etch of the silicon substrate. The plating base was etched to form transparent alignment windows.
The silicon nitride films had a silicon/nitrogen ratio of 0.95 with no detectable hydrogen content [135]. The silicon nitride stress can be controlled from zero to several hundred MPa by varying the deposition conditions. The standard silicon-rich nitride deposited by DIMES for mask-blanks had a tensile stress of 80 MPa.

The maximum operational temperature of a silicon nitride membrane was estimated by rearranging Equation 3-6 to obtain

\[ \Delta T_{\text{max}} = \frac{\sigma_{\text{membrane}}(1 - \nu)}{\alpha E}. \]

Khakani et al. presented a range of typical values for the properties of a myriad of mask-blank materials including LPCVD silicon-rich nitride [120]. Using the highest \( \nu, \alpha, \) and \( E, \) the “lowest” \( \Delta T_{\text{max}} \) was estimated to be 25 °C, which was higher than the empirical \( \Delta T_{\text{max}} \) of 10 °C reported by Vladimirsky et al. [118].

Since silicon nitride has very high resistivity (~\( 10^{16} \) Ωcm), a bi-metallic layer of 100 Å Cr/300 Å Au was deposited by e-beam evaporation to serve as an electroplating base.

### 3.5.4.2 Photolithography

A chemically amplified negative tone photoresist, NFR-015® (JSR Microelectronic, Inc., Sunyvale, California), was used to create the photoresist mold for electroplating on the silicon nitride mask-blanks. NFR-015® photoresist was spincoated on the Cr/Au plating base and softbaked in an oven to yield a thickness of 12 µm; the process was repeated over the first layer of NFR-015® resulting in a final thickness of 30 µm. The photoresist was exposed with a photomask made at CAMD using a Quintel UL7000 contact aligner (Quintel Corp., Morgan Hill, California). Post exposure bake was performed on a hot plate and the sample was developed with an positive photoresist developer solution. The softbake, exposure, post exposure, and
development parameters were optimized by using a series of half-factorial experiments to yield the smallest sidewall slope.

3.5.4.3 Gold Electroplating

The lithographically patterned silicon nitride mask-blank was electroplated with 17 µm-thick gold (Figure 3-20) using Neutronex 309® (Cookson Electronics, West Haven, Connecticut). The solution was operated at a pH of 9.5, a bath temperature of 50 °C, and pulse electroplating mode with an average current density of 1.5 mA/cm² resulting in a plating rate of 5.5 µm/hr with a tensile stress in the range of 10 to 20 MPa. The gold electroplating process is discussed further in Chapter 4.

3.5.4.4 Silicon Nitride Etch Mask Formation

Since the backside of the mask-blank was also covered with silicon nitride, it needed to be patterned to create an etch mask for the subsequent silicon anisotropic wet-etch. First, the remaining NFR-015® photoresist was removed from the front side with Dynasolve 185 (Dynaloy, Indianapolis, Indiana) and dried in an oven. S1827® positive photoresist (Shipley Company, Marlborough, Massachusetts) was spincoated on the backside of the sample and baked in an oven. Front-to-back alignment was used to align a photomask with etch windows on the backside of the sample to the absorber features on the front side and patterned using photolithography. A layer of thick positive photoresist (SJR 5740®) was spincoated on the front side and baked in an oven to protect the gold pattern from damage during the subsequent processing step. The silicon nitride on the backside was reactive ion etched at the Nanofabrication Center (University of Minnesota, Minnesota) using a combination of SF₆ and He gases through the etch mask created by the S1827® photoresist layer. The remaining photoresist was stripped by use of acetone and isopropanol.
Figure 3-20  Silicon nitride membrane X-ray mask: a) backside of a mask with 7 windows; b) alignment marker; c-f) gold microstructures
3.5.4.5 Silicon Wet Etch

An apparatus was designed and built using quartz for KOH etch as shown in Figure 3-21a, while a substrate holder (Figure 3-21b) purchased from A.M.M.T. (Frankenthal, Germany) was used to prevent the KOH solution from coming in contact with the front side of the sample. The silicon was back etched with 30 w.t.% KOH in DI water at 100 °C. The etch rate at these conditions was approximately 200 µm/hr. Since the etch rate of silicon nitride in KOH was several orders of magnitude less than for silicon, its effect on the silicon nitride was negligible [134].

3.5.4.6 Alignment Marker Patterning

As the final step of the silicon nitride mask fabrication process, the Cr/Au plating base on the silicon nitride surrounding the alignment markers was selectively etched using a potassium iodide-based gold etchant followed by a chrome etchant to obtain transparent windows around the electroplated gold alignment markers. Figure 3-20a shows a seven window silicon nitride mask with 17 µm-thick gold.

3.6 Results and Conclusions

X-ray masks for multi-level LIGA on various types of substrates were studied as part of this research and fabrication processes were developed for three types of mask-blanks. Two titanium-based X-ray masks were also purchased from IMT (Karlsruhe, Germany) and had 2.8 µm-thick titanium membranes with 17 µm and 22 µm gold. The titanium membrane masks were fabricated at IMT with a two step process consisting of a high resolution intermediate mask and soft XRL with the intermediate mask to produce a working mask. Since e-beam lithography and X-ray lithography were used for the intermediate and working masks, respectively, the titanium masks had the highest resolution among all the masks studied as part of this research.
Figure 3-21  Apparatus used for wet-etching silicon in KOH solution for making silicon nitride mask membranes: a) substrate holder to protect the gold pattern on the front side of the wafer during etch; b) quartz tank including a reflux condenser to reduce water loss because of evaporation
Low resolution fabrication processes were developed for rigid-graphite, borosilicate glass, and silicon nitride mask-blanks. In case of graphite, the optically opaque substrate was mounted on a glass carrier ring and alignment markers were patterned on the glass ring while the microstructures were patterned on the graphite. SU-8 resist was used as a photoresist mold in which gold is electroplated to form the absorber pattern.

A process was developed for mounting 30 µm-thick glass on an Invar ring with a pre-determined level of tensile stress. A positive photoresist on a Ti/Au plating base is used as a mold to electroplate the absorber layer. Since no attempt was made to control the internal stress of the gold, most masks fabricated in this manner broke as soon as they were removed from the electroplating bath and rinsed with water. Latter experiments (Chapter 4) show that under the conditions used to electroplate the glass mask-blanks, the gold had a highly compressive residual stress, which may have caused the breakage. The Ti/Au plating base was etched to create gold alignment markers on the optically transparent glass.

A silicon nitride-based mask fabrication process, which is used extensively at Sandia National Laboratories (Albuquerque, NM) and Honeywell FMT (Kansas City, Kansas), was modified and made more robust by changing the processing sequence. First, the photolithography and gold electroplating are carried out on silicon wafers covered with low stress LPCVD silicon-rich nitride. A silicon wet-etch is performed as a last step in the mask fabrication process sequence to avoid handling of a very fragile (1 µm-thick) silicon nitride membrane. Optical microscope inspection before and after the silicon etch revealed that many patterns with high lateral-aspect ratio were damaged by the wet etch process. Subsequent experiments presented in Chapter 4 show that the internal stress of the gold layer changes from tensile to compressive as a result of the extended stay at 100 °C during the wet-etch. Highly compressive stresses caused buckling in thin cantilever-like structures.
The working masks were used to expose high molecular weight PMMA resist with a thickness of 50 µm and developed using GG developer. The width of a set of ten resist lines 10 µm-wide were measured by use of a Nikon M22U Measuroscope equipped with a Quadra Check 400 coordinate measurement system and shown in Figure 3-22 and summarized in Table 3-7. As expected, the titanium membrane masks made with the two step high-resolution mask fabrication process have the best line width control with an accuracy of -0.6 µm. The low-resolution fabrication processes with the thick positive photoresist (SPR 220-7) and the negative photoresist (NFR-015) have accuracies of +2.6 µm and +2.3 µm respectively. The low-resolution method on graphite yielded the worst accuracy of -3.0 µm.

The line width control was not dependent on the mask-blank materials but rather the photoresist used. At every step of the lithographic processes, beginning from the mask fabrication to the test exposure, a resolution loss occurred. For some photoresists, the resolution loss resulted in an increase in line width, while for others it resulted in a decrease.

Table 3-7 Summary of the X-ray mask technologies for multi-level high aspect ratio LIGA

<table>
<thead>
<tr>
<th>Material</th>
<th>Mask-Blank Thickness (µm)</th>
<th>Effective Transp.</th>
<th>Photoresist Type</th>
<th>Gold Thickness (µm)</th>
<th>Line Width Control (µm ±1)</th>
<th>Sidewall Roughness (nm Ra)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>2.8</td>
<td>60%</td>
<td>PMMA</td>
<td>17 - 22</td>
<td>-0.6</td>
<td>30</td>
</tr>
<tr>
<td>Graphite</td>
<td>125</td>
<td>75%</td>
<td>SU-8®</td>
<td>15</td>
<td>-3.0</td>
<td>250</td>
</tr>
<tr>
<td>Borosilicate glass</td>
<td>30</td>
<td>40%</td>
<td>SPR 220-7®</td>
<td>5.5</td>
<td>+2.6</td>
<td>70</td>
</tr>
<tr>
<td>Silicon nitride</td>
<td>1</td>
<td>95%</td>
<td>NFR-015®</td>
<td>17</td>
<td>+2.3</td>
<td>60</td>
</tr>
<tr>
<td>Vitreous carbon</td>
<td>200</td>
<td>62%</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>80</td>
</tr>
</tbody>
</table>
Figure 3-22  Line width variation of 10 µm-wide PMMA test exposure for various mask fabrication processes: measurement was performed by use of a Nikon M22U Measuroscope equipped with a Quadra Check 400 coordinate measurement system. The error bars indicate the measurement error of ± 0.5 µm
Figure 3-23 illustrates the resolution loss for PMMA, SU-8®, SPR-220® and NFR-015® photoresists. PMMA is a positive tone resist and it was used for both the intermediate mask and working mask of the titanium membrane mask with e-beam and X-ray lithography, both of which have submicron resolutions. As expected, the two titanium masks exhibited the lowest average resolution loss of -0.6 µm for 10 µm-wide lines.

SU-8®, SPR 220®, and NFR-015® were used in the low-resolution methods for graphite, glass, and silicon nitride mask-blanks respectively. As can be seen in Figure 3-23, SU-8® behaved in a different manner than the other two photoresists; the line width of the SU-8 grew after UV exposure as opposed to the decrease in line width that resulted in the NFR-015® and SPR 220®. As the SU-8® was exposed to UV light, a so called Lewis acid was generated from the photo-acid generator (PAG) that was present in the photoresist formulation. During the subsequent post exposure bake (PEB) step, the SU-8 cross-linked to form an insoluble epoxy but the elevated PEB temperature also promoted the diffusion of the Lewis acid to the adjacent non-exposed regions. This mechanism caused the line width of the photoresist to get larger, which resulted in a decrease in the width of gold. During the X-ray lithography of the test exposure, an additional loss in the width of the PMMA was obtained. The combination of the two losses in line width resulted in the worst resolution loss of -3.0.

SPR 220® and NFR-015® shrank in width during photolithography, resulting in an increase in the width of the electrodeposited gold. However, the PMMA line width decreased during the ensuing X-ray lithography and a combination of the increase in gold width and decrease in PMMA width resulted in a resolution loss of +2.6 µm and +2.3 µm for SPR 220® and NFR-015®, respectively.
Figure 3-23  Propagation of line width error during X-ray mask fabrication: a) mask fabricated with SU-8® photoresist; b) mask fabricated with SPR 220-7® photoresist (Although NFR-015® is a negative-tone photoresist, it behaved similar to SPR 220-7® in terms of line width control)
The sidewall roughness of the test structures were measured by use of a WYKO NT3300 optical profiler (Veeco Instruments Inc., Woodbury, New York) and tabulated on Table 3-7. Significant differences in the sidewall surface roughness were observed. The lowest average roughness of 30 nm Ra was obtained with titanium mask-blanks while the highest was obtained with graphite mask-blanks.

To isolate the cause of the surface roughness, an experiment was devised as shown in Figure 3-24. High molecular weight PMMA sheets were patterned by use of X-ray lithography through a titanium membrane mask with the various mask-blank materials inserted as filters between the titanium membrane X-ray mask and the PMMA sheet. The test samples were developed and their sidewall surface roughness measured. The results were similar to those shown in Table 3-7, which indicated that the main source of surface roughness was the mask-blank material and not the fabrication process.

The high surface roughness of microstructures produced by rigid graphite was probably a result of its morphology, which was composed of particles from 1 µm to 4 µm in size. Small angle scattering can occur along the grain boundaries resulting in high roughness along the plane perpendicular to the incident radiation. Vitreous carbon on the other hand is an amorphous material and its X-ray diffraction only shows a ‘halo;’ as expected, vitreous carbon produced a sidewall surface roughness of about 80 nm Ra— lower than standard graphite mask-blanks. The other two amorphous materials, silicon nitride and borosilicate glass also show low surface roughness of 60 nm and 70 nm Ra respectively.

All attempts at fabricating X-ray masks on vitreous carbon with e-beam evaporated Cr/Au plating base failed as a result of adhesion loss between the Cr/Au plating base and the vitreous carbon substrates. Deposition of chromium and diamond like carbon (Cr-DLC) assisted by a magnetron were attempted with promising results. Preliminary experiments showed that low
stress (20 MPa) gold electroplated on Cr-DLC films does not peel off. Vitreous carbon can be combined with the fabrication process developed for graphite substrates to produce X-ray masks suitable for multi-level LIGA. The low cost, non-toxicity, and low microstructure sidewall surface roughness of vitreous carbon makes it an ideal candidate to replace beryllium for the next generation of X-ray masks.

Figure 3-24  Experimental setup to measure the sidewall surface roughness of microstructures caused by the mask-blank material during X-ray (a titanium membrane X-ray mask is used as a benchmark)
Chapter 4 Gold Electroplating for X-Ray Masks

4.1 Introduction

Circa 1803, the Italian chemist Luigi Brugnatelli and the Briton William Cruikshank working independently, revolutionized the method of formation of thin gold layers by using voltaic piles as current sources to deposit it. In 1805, Brugnatelli wrote in the Belgian Journal of Physics and Chemistry,

"I have lately gilt in a complete manner two large silver medals, by bringing them into communication by means of a steel wire, with a negative pole of a voltaic pile, and keeping them one after the other immersed in ammoniuret of gold newly made and well saturated" [136].

Gold was likely the first metal ever electroplated and two hundred years later, one can say that the art and science of gold electroplating is well understood.

The primary absorber material for X-ray masks since the early days of LIGA has been electrodeposited gold. The requisite properties of the electroplated gold for X-ray masks were few: high density, fine-grain, and low-stress are desirable. The electroplating solutions and operating conditions must be compatible with novalak, polyimide, and epoxy-like photoresists as well as a multitude of mask-blank materials including beryllium, titanium, glass, silicon nitride, and graphite. Moderate pH, temperature, and agitation were the preferred electroplating conditions. Many commercial solutions that meet these requirements are available. The following sections present three types of gold electroplating solutions, the process optimization for forming X-ray mask absorbers, and measurement of relevant material properties.
4.2 Gold Plating Solutions

The most common type of gold electroplating solution is the potassium gold (I) cyanide K(Au(CN)_2) bath, which was first developed in the 1840s [109]. However, this bath had poor compatibility with novalak photoresists. The addition of acid to cyanide solutions also produced hydrogen cyanide, a highly poisonous gas. Cyanide based electrolytes were readily rejected from use because of photoresist incompatibility and toxicity issues. Sulfite-based electroplating solutions presented safer alternatives to cyanide-based baths. Thus, three types of commercially available sulfite-based [(Au(SO_3)_2)^{3-}] electroplating solutions were used during the course of this research; in chronological order of use, they were TECHNI-GOLD 25 (TG 25), TECHNI-GOLD 25 E (TG 25E), and NEUTRONEX 309. The first two solutions were purchased from Technic, Inc. of Cranston, Rhode Island while the NEUTRONEX solution was purchased from Enthone, Inc. of West Haven, Connecticut. The electroplating conditions for the three solutions supplied by their respective manufacturers are shown in Table 4-1.

4.2.1 TECHNI GOLD 25 and TECHNI GOLD 25E

TG-25 and TG-25E are stabilized sulfite gold electroplating solutions with similar operating conditions (except pH) and deposit characteristics; they were obtained from their manufacturer (Technic, Inc.) in ready-to-use form. TG 25 operated at high pH (numeric range), while TG 25E worked well from slightly acidic to neutral pH; both solutions worked well with gold concentration from 8 g/L to 16 g/L. When used without additives, these baths produced very soft and bright deposits. An arsenic-containing additive (Additive A) can be used to increase the brightness without affecting the hardness, while an organic brightening agent (Additive E) increased both the brightness and hardness of deposits [137, 138].
Table 4-1  Gold electroplating [137-139]

<table>
<thead>
<tr>
<th></th>
<th>TECHNI-GOLD 25</th>
<th>TECHNI-GOLD 25 E</th>
<th>NEUTRONEX 309</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Technic, Inc.</td>
<td>Technic, Inc.</td>
<td>Enthone, Inc.</td>
</tr>
<tr>
<td>Gold concentration</td>
<td>8 – 16 g/L</td>
<td>8 – 16 g/L</td>
<td>8 – 12 g/L</td>
</tr>
<tr>
<td>pH</td>
<td>9.5 – 10.0</td>
<td>6.0 – 7.0 [6.5]</td>
<td>9.2 – 9.8</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>10 – 30 °Baumè</td>
<td>10 – 30 °Baumè</td>
<td>10 – 30 °Baumè</td>
</tr>
<tr>
<td>Anode</td>
<td>Platinized electrode</td>
<td>Platinized electrode</td>
<td>Platinized electrode</td>
</tr>
<tr>
<td>Anode-to-cathode area ratio</td>
<td>≥ 1:1</td>
<td>≥ 1:1</td>
<td>≥ 2:1</td>
</tr>
<tr>
<td>Temperature</td>
<td>49 – 71 °C</td>
<td>43 – 71 °C</td>
<td>35 – 55 °C</td>
</tr>
<tr>
<td>Agitation</td>
<td>Moderate to vigorous</td>
<td>Moderate to vigorous</td>
<td>Moderate</td>
</tr>
<tr>
<td>Current Density</td>
<td>1.1 – 8.6 mA/cm²</td>
<td>1.1 – 8.6 mA/cm²</td>
<td>1.1 – 5.4 mA/cm²</td>
</tr>
</tbody>
</table>

4.2.1.1  Maintenance

Gold electroplating systems typically use non-replenishing platinized anodes, so the concentration of the gold needed to be determined and kept within the optimal range of operation by the periodic addition of gold salt. Gold concentration can be determined accurately using gravimetry, atomic absorption spectroscopy (AA), or inductively coupled plasma (ICP) spectroscopy. A simpler method of determining the amount of gold plated out of the solution by keeping track of the total ampere-hours passed through the solution between gold replenishments was used in this research. Following the recommendation of Technic, the plating solutions were replenished at a rate of 1 Tr Oz of gold for every 4 ampere-hours of charge supplied during electroplating and the concentration was kept in the range of 90 % - 100 %.

The pH of the Techni-Gold solutions were controlled by the addition of 20 % – 40 % sodium hydroxide or TECHNI-GOLD 25 Acid Adjusting Salt E. The concentration of sulfate in these baths increased over time, which was readily detected by an increase in the specific gravity. Although precipitation with calcium- or barium-acetate could have been used to
decrease the sulfate content [137], the solutions were simply discarded when the sulfate content exceeded 30 °Baumè.

The TG solutions contain sodium sulfite as a conductive salt, whose concentration must be monitored and replenished to maintain chemical stability. The manufacturer supplied a titration method, which was used to determine the concentration of the sodium sulfite. Anhydrous Na₂SO₃ was used to control the initial concentration (50 g/L) within 10 % [140]. Alternatively, maintaining a high sulfite concentration by adding 7.5 g/L of anhydrous sodium sulfite before first-use eliminated the need to analyze the sulfite content and simplifying the maintenance procedure [141]; both TG 25 and TG 25E solutions functioned well with high sulfite concentrations with no apparent side effects.

The concentration of the stabilizer in the TG solutions was determined using UV absorption spectroscopy at 266 nm and replenished to keep the stabilizer content within the optimal range of 9 – 12 g/L [142].

Occasionally, organic contaminants, mainly from photoresist dissolution, caused reduction in electroplating rate and a significant increase in stress. When significant deviations in deposit characteristics were observed, the solutions were mixed with activated carbon (100 g/L) and heated to 80 °C for 1 hr after which they were cooled to room temperature and filtered with a series of 5 and 0.5 µm-pore PTFE filters. The activated carbon successfully absorbed organic contaminants and restored deposit characteristics to nominal.

4.2.2 NEUTRONEX 309

NEUTRONEX 309 was a sulfite-based gold electroplating solution that operated at high pH (9.5-10). Unlike most gold electrolytes that use arsenic-containing additives for grain refinement, NEUTRONEX 309 used a thallium-based additive. The electrolyte was available in different formulations including a thallium-free solution. Direct current electroplating was reported to
require the addition of thallium in concentrations of up to 800 ppm to obtain fine grain deposits but the need for thallium could be reduced or even eliminated by using pulse-plating [139]. NEUTRONEX 309 was obtained from Enthone, Inc. as a kit containing the following:

- **NEUTRONEX 309 MAKE UP TF**: a thallium-free ready-to-use solution with 10.25 g/L of gold concentration,
- **K4P**: potassium phosphate additive to increase the conductivity of the solution as well as complex metallic impurities, and
- **NEUTRONEX 309 BRIGHTENER**: a thallium based additive used to refine the grain (10 g/L thallium).

### 4.2.2.1 Maintenance

The gold concentration of the NEUTRONEX 309 was controlled by simply tracking the total ampere-hours supplied between replenishments. The total gold consumed was calculated based on the empirical plating rate and the total ampere-hours of current passed through the solution, which was then restored using the following replenishers [139]:

- **NEUTRONEX 309 REPLENISHER A**: used to replenish the gold consumed during plating; contains 62.2 grams of gold complex per 800 mL of solution
- **NEUTRONEX 309 REPLENISHER B**: contains 20 mL/L of NEUTRONEX 309 BRIGHTENER (a thallium based grain refiner).

The pH of NEUTRONEX 309 was maintained at 9.8 ± 0.5 at room temperature with 5 % reagent grade sulfuric acid to lower the pH or 20 % reagent grade solution of sodium hydroxide to increase the pH. The specific gravity of the solution was measured occasionally to insure that the allowable range of 13 – 30° Baumé was not exceeded. A specific gravity of greater than 30° Baumé indicated that the solution needed to be either replaced or regenerated [139].
The conducting salt and K4P Additive concentrations were determined periodically using of analytical procedures supplied by Enthone, Inc. The conducting salt was maintained at 30 g/L ± 5 g/L, while the K4P concentration was kept at 50 g/L ± 5 g/L [139].

When a significant deviation in plating rate or stress of a deposit was observed, the solution was filtered through an activated carbon filter cartridge at 55 °C to remove organic contaminants and the K4P replenished.

4.3 Gold Plating Apparatuses

Two types of gold electroplating systems were designed and assembled for X-ray masks first at LSU µSET lab and later at CAMD. The first was a beaker-based plating system with an isothermal water bath to control the temperature, while the second was a fountain electroplating system. Figure 4-1 and Figure 4-2 show the two electroplating systems and their respective components. Descriptions of the two systems follow.

4.3.1 Beaker-Type Electroplating System

Two beaker-type plating systems (Figure 4-1) were setup at the µSET lab and CAMD. The gold electrolytes were contained in either 4 L rectangular quartz tanks or cylindrical Pyrex beakers. The gold plating solutions were heated and maintained within 1 °C of the desired temperature by use of isothermal water baths and agitated at moderate rates with submersible magnetic stirrers. Platinized titanium or niobium mesh anodes (Technic Inc., Rhode Island) were used as counter electrodes while the substrates were mounted parallel to the counter electrodes by use of custom made Plexiglas substrate holders. The distance between the anodes and cathodes were maintained in the range of 8 to 10 cm.
Figure 4-1  Beaker-type gold electroplating apparatus for X-ray masks with an isothermal water bath
Figure 4-2  Fountain gold electroplating system
4.3.2 Fountain Electroplating System

A fountain gold electroplating system (Figure 4-2) was designed and built at CAMD with assistance from BESSY GmbH (Berlin, Germany). The conditioning tank was made of CPVC and had a minimum operational fluid volume of 7.5 L. The electrolyte was heated and kept within 1 °C of the desired temperature with a 1000 W Teflon coated resistive heater and a PID controller. During use, the solution was pumped out of the conditioning tank, filtered with a 0.5 µm polypropylene filter cartridge, pumped into a vertical column plating chamber, flowed over the surface of a 100 mm-diameter substrate, and over-flowed back into the conditioning tank. The flow rate was regulated by using two three-way valves such that a continuous flow over the substrate was maintained.

4.3.3 Power Supplies

An EG&G Model 273A potentiostat/galvanostat (Princeton Applied Research) was used for all electroplating experiments performed at the µSET Lab. At CAMD, a Valhala current calibrator (Valhalla Scientific, San Diego, California) in conjunction with an HP 355 function generator (Hewlett-Packard Development Company, Palo Alto, California) were used for both pulse and DC plating.

4.4 Experimental

In the early stages of this work, TG 25 was used to electroplate X-ray masks. Only the plating rate of TG 25 was characterized as a function of current density and many masks were electroplated. However, the high pH of TG 25 was detrimental to AZ 4620®, a novalak-based positive tone photoresist. When TG 25E, a neutral pH version of TG 25 was made available by Technic, Inc., it replaced the latter. After determining the use, maintenance, and plating rate of TG 25E, all X-ray masks at LSU were electroplated using TG 25E. Later, the need to minimize the internal stress of deposits initiated the study of the internal stress of deposits as a function of
current density and solution temperature. The inadequate level of stress control and solution stability with the Technic baths led to the study and adoption of NEUTRONEX 309. The following sections describe the experimental studies performed to characterize TG 25E and NEUTRONEX 309.

4.4.1 Electroplating Rate

Using Faraday’s law, one can show that the theoretical electroplating rate in an electrochemical cell is only a function of the electroplating current density, \( J \), such that

\[
PlatingRate = \frac{m_w J}{nF\rho},
\]

where \( m_w \) is the atomic weight, \( n \) is the number of electrons required to deposit one atom, \( F \) is the Faraday constant, and \( \rho \) is the density of the deposited material. However, other factors such as temperature, pH, and composition affect the throwing-power of an electroplating solution and the plating rate. The electroplating rates of TG 25, TG 25E and NEUTRONEX 309 plating solutions were studied as functions of current density and plating temperature by using the beaker-type electroplating setup.

The electroplating rate of TG 25 was determined by electroplating for a specified amount of time on silicon wafers with a Cr/Au plating base and masked with insulating tape. The thicknesses of the deposits were measured by use of an Alpha-Step 500 Profiler (KLA Tencor, San Jose, California). The densities of the films were also calculated by measuring the weight of the deposits with a high precision weighing balance.

The plating rates of TG 25E and NEUTRONEX 309 were determined using a slightly different method. The mass of metallic stress test strips were determined with a precision weighing balance and electroplated with gold at 45 °C, 50 °C, and 55 °C with current densities from 1 to 3 mA/cm². The mass of the test strips were measured again and the electroplating rates
were determined by assuming that the densities of the deposited layers were equal to that of bulk-gold (19.3 g/cm³).

The electroplating rates of TG 25E and NEUTRONEX 309 are shown in Figure 4-3. At low current density, the plating rate of the two solutions showed little dependence on the temperature. As the current density was increased and the temperature was lowered, a slight reduction in the throwing-power of the solution resulted in a decrease in plating rate. For example, when the temperature was lowered from 55 °C to 45 °C, the plating rate of TG 25E at 3 mA/cm² decreased from 11.7 µm/hr to 11.2 µm/hr. No difference in the plating rates were observed between the two Techni Gold solutions.

4.4.2 Thickness Uniformity

The thickness uniformity of electroplated layers was dependent on a variety of factors including the anode/cathode configuration, geometry and distribution of the features [143, 144], additives (leveling agents) [109, 145], and electroplating mode (DC vs. pulse; potentiostatic vs. galvanostatic) [49, 146, 147]. Since it was impractical to optimize all these factors for each X-ray mask, two factors that were expected to have the strongest influence on the thickness uniformity, the anode-cathode configuration and electroplating mode, were studied using the NEUTRONEX 309 solution. The thickness uniformities of the two electroplating systems and the total thickness variation (TTV‡‡), were determined by electroplating 5 µm gold into 10 µm-thick photoresist patterns on a series of five 100 mm-diameter silicon wafers with chromium/gold plating base. The thicknesses were measured at nine points on each wafer using an Alpha-Step 500 Profiler (KLA Tencor, San Jose, California); the results are summarized in Table 4-2.

‡‡ The Total Thickness Variation (TTV) is defined as the maximum thickness variation (maximum-minimum) divided by the average thickness.
Figure 4-3  Gold electroplating rate in TG 25E and NEUTRONEX 309 solutions from 45 °C to 55 °C [the error bars (± 0.1) are not shown for the sake of clarity]
Table 4-2  Thickness uniformity of deposits made using beaker-type and fountain electroplating systems at 1 mA/cm² and 50 °C

<table>
<thead>
<tr>
<th>Plating Mode</th>
<th>Beaker-Type Plating System</th>
<th>Fountain Plating System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct-current</td>
<td>21%</td>
<td>8%</td>
</tr>
<tr>
<td>Pulse plating</td>
<td>13%</td>
<td>6%</td>
</tr>
</tbody>
</table>

For direct current plating, the beaker-type electroplating system with DC plating yielded the worst result of 21 % total thickness variation (TTV), while the fountain plating system yielded a TTV of 8 %. Pulse plating improved the TTV in both types of electroplating systems.

4.4.3  Internal Stress of Electrodeposited Layers

The causes of internal stress include the mismatch in coefficient of thermal expansion between the absorber and mask-blank, inclusion of bath components including organic and inorganic contaminants in the deposits, phase transformation, and growth dynamics. In X-ray masks, excessively high stress may cause delamination of the absorber layer from the mask substrate, pattern distortion [148, 149], or breakage of the mask substrate [50]. The methods of stress control include the use of additives, bath temperature, solution pH, and plating mode (direct-current vs. pulse) [150]. In this work, the solution compositions were kept within acceptable ranges and the effects of current density and temperature on the internal stress of the deposits were investigated.

4.4.3.1  Measurement Technique

In 1909, George J. Stoney published a method of stress measurement in electrodeposited thin films based on the deflection of beams on which the thin films had been deposited [151]. Other methods based on X-ray diffraction [152] and holographic techniques [153] have also been used to characterize film stress but Stoney’s remains the basis for most methods.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method of measurement</th>
<th>Method of control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold concentration</td>
<td>Track the total ampere-hour used</td>
<td>Replenish with gold salt</td>
</tr>
<tr>
<td>Conducting salt</td>
<td>Titration</td>
<td>Replenish with conducting salt</td>
</tr>
<tr>
<td>Additives</td>
<td>UV absorption, titration</td>
<td>Replenish with additives</td>
</tr>
<tr>
<td>Organic contaminants</td>
<td>Change in stress and/or plating rate</td>
<td>Filter with activated carbon</td>
</tr>
<tr>
<td>pH</td>
<td>Measure with pH meter</td>
<td>Adjust with base, acid, or acid adjusting salt</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>Measure with hydrometer</td>
<td>Replace solution</td>
</tr>
</tbody>
</table>

Stoney’s method has resulted in what is commonly referred to as Stoney’s equation, 

\[ \sigma_f = \frac{1}{6R} \frac{E_s t_s^2}{(1-\nu_s)t_f}, \tag{4-2} \]

where \( \sigma_f \) is the stress in the deposited film, \( R \) is radius of curvature, \( t_s \) is the thickness, \( E_s \), is the modulus of elasticity, and \( \nu_s \) is the Poisson’s ratio of the substrate, while \( t_f \) is the thickness of the deposited film [154]. Stoney’s equation can also be expressed in terms of the tip deflection instead of the radius of curvature, which is the inverse of the second derivative of the deflection such that

\[ R = \left( \frac{d^2 y}{dx^2} \right)^{-1} \Rightarrow y(x) = \frac{x^2}{2R}. \tag{4-3} \]

For a beam of length \( L \) and small tip deflection \( \delta \), the radius of curvature is simply written as \( R = L^2 / 2\delta \). Substituting for the radius of curvature in Equation 4-2 results in the following:

\[ \sigma_f = \frac{\delta}{3} \left( \frac{E_s t_s^2}{1-\nu_s} \right) \left( \frac{1}{t_f} \right). \tag{4-4} \]

For a cantilever beam of a given configuration, \( E_s t_s^2 / (1-\nu_s) \) does not vary, so the stress is a function of only the deflection of the beam and the thickness of the film. This fact has been
exploited by many to produce practical stress measurement techniques one of which is the Stress Deposit Analyzer System (DSAS) (Specialty Testing & Development Co., Jacobus, Pennsylvania)—a simple and convenient method for measuring the average stress in an electrodeposited layer.

### 4.4.3.2 Deposit Stress Analyser System (DSAS)

A DSAS apparatus was purchased from Specialty Testing & Development Co. The apparatus consisted of disposable metallic strips on which metal was electrodeposited and a test stand to measure the deflection of the test strips (Figure 4-4). The standard test strips were insulated with photoresist everywhere except the alternating sides of the two legs. When films were deposited on the exposed parts of the test strip, the legs deflected in opposite directions. A deflection away from the electroplated film indicated compressive stress, while bending towards the electroplated film indicated tensile stress. The leg spread, $U$, was measured by use of the test stand (Figure 4-4b) on a nonlinear calibrated scale and used to determine the stress, $S$ (psi),

$$S = \frac{U}{3T}K,$$

where $U$ was double the deflection of one leg of a test strip in units of increments, $T$ was the thickness of the deposited film in inches, and $K$ was a dimensionless strip calibration constant supplied with each lot of test strips by Specialty Testing & Development[155]. By comparing **Equations 4-4** and **4-5**, one can see that the parameter $K$ depended on the thickness, modulus of elasticity, and Poisson’s ratio of the test strips. The parameter $K$ also included some unit conversion factors such that the thickness of the deposit and the deflection of a test strip can be substituted into **Equation 4-5** in inches and DSAS increments respectively to obtain the stress in psi. Stein et al have shown that the resolution of the DSAS can range from 2 MPa for 8 µm-thick films to 10 MPa for 4 µm films [150]
Figure 4-4  Deposit Stress Analyzer System (DSAS) apparatus (Specialty Testing & Development Co., Jacobus, Pennsylvania): a) beryllium-copper alloy test strip with only one side of one leg non-insulated; b) Model 683 Test Stand used to measure the deflection of a test strip with a mounted strip
A variety of test strips are marketed by Specialty Testing including beryllium-copper alloy, copper, and steel. Beryllium-copper test strips were used in this research because they showed better chemical resistance to sulfite-based gold plating solutions than copper. Although stainless steel test strips are even more chemically resistant than beryllium-copper, they were not readily available for purchase. Since the beaker-type electroplating baths were setup for electroplating from one side only, custom made test strips, where only one side of a single leg on each test strip was exposed to the electroplating solution, were used for measuring stress.

4.4.3.3 Experiments and Results

The dependence of the internal stress on the temperature (45 °C to 55 °C) and current density (1 to 3 mA/cm²) of gold films deposited with TG 25E and NEUTRONEX 309 solutions was studied by use of the DSAS. The plating solutions were formulated with 40 ppm arsenic and 30 ppm thallium grain refiners for TG 25E and NEUTRONEX 309, respectively. Since no baseline process for X-ray mask electroplating existed for the TG 25E solution, a simple DC electroplating mode was chosen and the current density was varied from 1 mA/cm² to 3 mA/cm². In order to minimize the need for a grain refiner, pulse plating (600 Hz frequency with 25 % duty cycle) was used for the NEUTRONEX 309 solution; the average current density was varied from 1 to 3 mA/cm² [139, 156]. Since age was reported to have an effect on the internal stress of the deposits in gold sulfite baths [157], five data points were taken over a period of 1 year and averaged. The beaker-type electroplating system was used for all stress measurements.

Table 4-4 Appearance of deposits made using TG 25E gold electroplating solution at various current densities

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Current Density</th>
<th>1 mA/cm²</th>
<th>2 mA/cm²</th>
<th>3 mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 °C</td>
<td>Yellow (bright)</td>
<td>Yellow (dull)</td>
<td>Brown (dark)</td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>Yellow (bright)</td>
<td>Yellow (bright)</td>
<td>Brown (dull)</td>
<td></td>
</tr>
<tr>
<td>55 °C</td>
<td>Yellow (bright)</td>
<td>Yellow (bright)</td>
<td>Yellow (dull)</td>
<td></td>
</tr>
</tbody>
</table>
Table 4-5  Appearance of deposits made using NEUTRONEX 309 gold electroplating solution

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Current Density</th>
<th>1 mA/cm²</th>
<th>1.5 mA/cm²</th>
<th>2 mA/cm²</th>
<th>3 mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 °C</td>
<td>Yellow (bright)</td>
<td>Yellow (dull)</td>
<td>Brown (dark)</td>
<td>Brown (dark)</td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>Yellow (bright)</td>
<td>Yellow (bright)</td>
<td>Brown (light)</td>
<td>Brown (dark)</td>
<td></td>
</tr>
<tr>
<td>55 °C</td>
<td>Yellow (dull)</td>
<td>Yellow (dull)</td>
<td>Yellow (dull)</td>
<td>Brown (dark)</td>
<td></td>
</tr>
</tbody>
</table>

The appearance of the deposits made for stress analysis were also noted and shown in Table 4-4 and Table 4-5. Bright yellow to dull yellow deposits were considered as “good,” while those with brownish appearances were considered undesirable. Brownish deposits were characterized by large nodules, low density, and high levels of impurities.

Figure 4-5 and Figure 4-6 show the internal stress in 2 µm-thick gold layers as measured by the DSAS technique. Figure 4-5a shows that as the current density was raised from 1 mA/cm² to 3 mA/cm², the internal stress in the TG 25E deposits changed from compressive to tensile. Plotting the same data as a function of temperature (Figure 4-5b) revealed some interesting trends. The stresses were maximum at 50 °C, compressive from 1 to 2 mA/cm², and tensile at 3 mA/cm² regardless of the solution temperature.

The internal stresses of all deposits made using the NEUTRONEX 309 were tensile and ranged from 2 12 MPa as shown in Figure 4-6. For the deposits that were judged to be “good” based on appearance, the internal stress increased when the current density was increased from 1 to 2 mA/cm². In general, an increase in temperature resulted in a decrease in internal stress.
Figure 4-5  Internal stress in 2 µm-thick gold electroplated using TECHNI GOLD 25E with 40 ppm arsenic grain refiner: a) stress as a function of current density; b) stress as a function of temperature
Figure 4-6  Internal stress in 2 µm-thick gold electroplated using NEUTRONEX 309 with 30 ppm thallium grain refiner: a) stress as a function of current density; b) stress as a function of temperature
4.5 Concluding Remarks

TG 25E and NEUTRONEX 309 were found to be suitable solutions for electroplating X-ray masks. Since TG 25E was a neutral pH bath, it was compatible with a wider variety of photoresists than NEUTRONEX 309, which operated at high pH. NEUTRONEX 309 attacked many positive tone photoresists such as SJR 5740 and AZ 4620, especially when they had not been subjected to sufficient soft bake. Hard bake of the photoresists before electroplating improved their chemical resistance.

Two types of plating systems, two beaker-type and one fountain, were constructed for electroplating X-ray masks. The TG 25E solution was used with the beaker-types while the NEUTRONEX 309 was used with the fountain plater. The use of the fountain plater as well as pulse-plating improved the thickness uniformity significantly.

The internal stress in TG 25E (40 ppm arsenic) showed a stronger dependence on current density than NEUTRONEX 309 (30 ppm thallium). The stresses in TG 25E deposits ranged from -40 to 10 MPa, whereas the stresses in NEUTRONEX 309 deposits ranged from 2 to 12 MPa. The recommended electroplating conditions, plating rate, and internal stress of deposits of the two solutions are shown in Table 4-6.

The TG 25E was used at the µSET lab and CAMD since 1996 whereas the NEUTRONEX 309 was used at CAMD for only one year. The change from TG 25E to NEUTRONEX 309 at CAMD was prompted by the short ‘life’ of the TG 25E, which could not be used for more than 6 months or 20 – 30 substrates regardless of the maintenance and care taken. In comparison, a 4 L NEUTRONEX 309 solution was used at CAMD for one year with over 100 samples electroplated before the solution was replaced. Occasionally, deviations in the plating characteristics of NEUTRONEX 309 were encountered but cleaning of the organic contaminants by activated carbon filtration and replenishment of the lacking components restored the deposit.
characteristics. Although the initial cost of NEUTRONEX 309 was higher than TG 25E, over the long term the NEUTRONEX solution was found to be a more economical as well as easier to maintain than the Technic solution. The recommended operating conditions of TG 25E and NEUTRONEX 309 solutions are shown in Table 4-6.

Table 4-6  Recommended electroplating conditions and the resulting deposit characteristics of TG 25E and NEUTRONEX 309 gold electroplating solutions for X-ray masks

<table>
<thead>
<tr>
<th></th>
<th>TG 25E</th>
<th>NEUTRONEX 309</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electroplating mode</td>
<td>Direct-current</td>
<td>Pulse</td>
</tr>
<tr>
<td>Current density (mA/cm²)</td>
<td>1</td>
<td>1.5 (average)</td>
</tr>
<tr>
<td>Frequency (Hz)</td>
<td>N/A</td>
<td>600</td>
</tr>
<tr>
<td>Duty cycle</td>
<td>N/A</td>
<td>25 %</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>pH</td>
<td>6.5</td>
<td>9.8</td>
</tr>
<tr>
<td>Agitation</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>Plating rate (µm/hr)</td>
<td>3.8</td>
<td>5.3</td>
</tr>
<tr>
<td>Internal stress (MPa)</td>
<td>-5</td>
<td>8 MPa</td>
</tr>
</tbody>
</table>
Chapter 5 Fabrication of High Aspect Ratio Microgyroscope Structures

5.1 Introduction

Two-layer fabrication processes (Figure 5-1) were developed for the LSU/SatCon microgyroscopes. The first layers consisted of 10 μm-thick wires to provide isolated electrical connections to the cylinders, drive- and sense-electrodes. The high aspect ratio (HAR) layers were made of the cylinders and sets of four drive- and four sense-electrodes around each cylinder. The HAR-layers ranged in thickness from 500 to 1500 μm. Many variations of the two-layer process were attempted through the course of this research but only the two most successful methods are presented in this dissertation. The first process sequence is called TI-1999 and a combination of a titanium membrane X-ray mask and a low precision alignment system were used to produce prototypes in 1999. The second process is called SN-2003 and used a silicon nitride membrane X-ray mask and a DEX02 scanner (Jenoptik GmbH, Jena, Germany) with a high precision semi-automatic alignment system.

In 1999, the CAMD synchrotron was regularly operated at 1.3 GeV with two days out of every two weeks being run at 1.5 GeV. The 1.5 GeV mode, which produces relatively more penetrating X-ray radiation (2.6 KeV characteristic energy), was exploited to produce microstructures as high as 1250 μm. CAMD ceased to operate the synchrotron at 1.5 GeV in 2000. As a result, all the microgyroscopes that were fabricated after 2000 including the SN-2003 series were limited to 500 μm or less in thickness.
Figure 5-1 A basic two layer process for multi-level high aspect ratio microstructures
Two additional processes were also developed as part of this work. The first is the transfer-mask technique, which uses X-ray absorber patterns that are fabricated on top of the X-ray resist itself. This method was found to be non-suitable for high aspect ratio microstructures but useful for prototyping low aspect ratio microstructures and mold insert fabrication. The transfer mask technique is discussed in the Appendix B. The second process sequence was a variation of the two-layer processes TI-1999 and SN-2003. It was used to fabricate sense- and drive-electrodes for hybrid microgyroscopes and is presented in Appendix C.

5.2 X-Ray and Photomasks

The fabrication processes of the two X-ray masks used for TI-1999 and SN-2003 were presented in Sections 3.5.1 and 3.5.4 respectively. TI-1999 used a titanium membrane X-ray mask with a membrane thickness of 2.8 µm and an X-ray absorber layer of 17 µm-thick gold. SN-2003 was fabricated at CAMD on a 1 µm-thick silicon nitride membrane with 17 µm-thick gold. The titanium membrane mask had a single membrane of 6 cm by 2 cm (Figure 3-13) while the silicon nitride mask (Figure 3-20) had seven fields of 2 cm by 2 cm.

The photomask for the wiring layer of the TI-1999 process was purchased from IMT (Karlsruhe, Germany) while the SN-2003 photomask was fabricated at CAMD. Figure 5-2 shows the CAD layouts of the two processes. Since a low precision alignment system (Figure 5-3a) was used in TI-1999, the wiring layer was designed to tolerate misalignments of as much as 10 µm. The SN-2003 wiring layer was designed for the high precision alignment of the DEX03 X-ray scanner (Figure 5-3b), which yielded alignment of +/-2 µm for high aspect ratio microstructures. The tools used in the alignment of the wiring to the HAR layers for the two fabrication series are shown in Figure 5-3.
Figure 5-2  CAD layout of the wiring layers: a) TI-1999 wiring layer super imposed with the properly aligned and misaligned microgyroscope layer; b) SN-2003 wiring layer with the wiring pad under the cylinders for improved adhesion of the cylinders to the substrate.
Figure 5-3  Alignment systems used for multi-level LIGA: a) low precision (+/-5 µm) manual alignment jig; b) DEX02 scanner with high precision (+/-1 µm) alignment capability (Jenoptik GmbH, Germany)
5.3 Substrate Selection

The conductivity, dielectric constant, and strength of various substrate materials were considered in the selection process. First, in order to provide electrical isolation of the cylinders from each one of the electrodes, the substrate needs to be a good insulator. Second, to minimize parasitic capacitance, its dielectric constant needs to be low. Third, since the substrate undergoes a variety of processing including mechanical polishing, it needed to have high strength.

Unfortunately, all three requirements could not be met by any single substrate material. The standard MEMS substrate, silicon, is a semiconductor and it is weak along its crystal planes. Quartz has low dielectric constant but at a thickness of 500 µm it is very fragile. Alumina is a good insulator and has high strength but its dielectric constant is high. After testing three substrates, it was decided to use alumina for process development and silicon passivated with a silicon nitride coating for building testable prototypes. TI-1999 structures used 100 mm-diameter, 500 µm-thick, ceramic substrates while SN-2003 substrates used 100 mm-diameter, 500 µm-thick, silicon wafers coated with 1 µm silicon-rich nitride.

5.3.1 Plating Base Deposition

The plating base served a dual purpose: a conductive layer for electroplating and as an adhesion layer for the X-ray resist. Since HAR microstructures need to have good adhesion to the substrate, multi-layer plating bases were used for both processes. The plating base used for TI-1999 on ceramic substrates consisted of 200 nm Ti/500 nm Cu/2 µm Ti sputtered by use of an Oxford Plasmalab 400 sputtering system (Oxford Instruments, United Kingdom). The plating base for SN-2003 consisted of 20 nm Cr/200 nm Cu/2 µm Ti deposited by use of a BJD-1800 e-beam evaporator (BOC Edwards, United Kingdom).
5.3.2 Surface Modification for PMMA Adhesion

Among the various types of metals and surface treatments that have been investigated by previous researchers, the use of wet oxidized titanium or copper have been shown to yield the strongest resist-to-substrate adhesion [44]. The top 2 µm Ti layer in each process was oxidized by use of an alkaline-peroxide treatment to form TiO₂. The composition of the alkaline-peroxide (AP) solution consisted of 0.1 M sodium hydroxide and 30% hydrogen peroxide. A one-minute soak in the AP solution at 65°C resulted in the transformation of the surface titanium layer into a porous oxide layer with increased roughness [119].

5.4 Fabrication of Wiring Layer

The substrates were spincoated with 15 µm-thick novolak based positive resist, Microposit SJR 5740® (Shipley Company, Inc., Marlboro, Massachusetts), baked in a convection oven and patterned exposed with an UV contact aligner and the wiring layer photomasks. After developing in a KOH based developer, the substrates were dried, and treated with a short cycle of oxygen plasma. The Ti/TiO₂ layers were etched by use of 1 % aqueous HF and rinsed with DI water. TI-1999 and SN-2003 series wafers were electroplated with 10 µm-thick nickel and gold, respectively.

5.5 Fabrication of HAR Cylinders and Electrodes

5.5.1 X-Ray Resist Preparation

PMMA purchased from AIN Plastics (Florida) and CQ grade from Vistacryl (United Kingdom) were used for TI-1999 and SN-2003 processes, respectively. Both types of PMMA were found to contain high molecular weight with similar sensitivity to X-ray radiation of 1600 J/cm³. The PMMA sheets were cut into disks and rectangles of various sizes and annealed in a convection oven at 80 °C for 2 hr and cooled to room temperature [158]. In addition to
relieving internal stress, the baking process also removed the residual monomers in the PMMA layer [159].

A PMMA gel was made with a combination of 15% high molecular weight PMMA powder, 85% methylmethacrylate (MMA), 1.5% benzyolperoxide (BPO), 1% dimethylanine (DMA), and 1% methacryloxypropyltrimethoxy silane (MEMO) and used to bond the annealed PMMA sheet to the oxidized titanium layer. The presence of the MEMO in the bonding gel resulted in a copolymer that contains the MEMO side groups, which in turn reacts to the hydroxyl groups of the TiO₂ surface. This resulted in a chemical bond between the PMMA and the substrate thereby minimizing stress corrosion [119]. The increased surface roughness of the titanium layer also enhanced the mechanical bond.

5.5.2 Flycutting

A Precitech Optimus flycutting machine (Keene, New Hampshire) with a diamond tools (Contour Tooling) was used to flycut the bonded PMMA to the desired height with +/- 3 µm accuracy. The resulting surface of the PMMA sheet was clear and transparent with no visible scratches.

5.5.3 X-Ray Exposure

Before the PMMA resist can be exposed with X-ray radiation, the X-ray mask must be aligned to the wiring layer and rigidly affixed. An alignment system developed for the HI-MEMS alliance by Wood et al. [160] was used to align the substrates to the X-ray mask for the TI-1999 series wafers. The performance of this alignment system was highly dependent on the user—at best, an experienced user could obtain an overlay accuracy of ± 5 µm but the repeatability was very poor. After proper alignment was achieved, the mask was rigidly clamped and the device was moved to the XRLM3 beamline at CAMD, where exposure was carried out.
Fabrication of the SN-2003 series wafers took advantage of the DEX02 scanner’s semi-automatic alignment system, which was installed at CAMD in 2001. The DEX02 used piezoelectric transducers to position the substrate while observing the alignment marker on the substrate and mask at high magnification with a CCD camera. Since sub-micrometer resolution could be obtained with piezoelectric actuators, the limiting factor in the alignment precision was found to be the quality of the alignment markers on the X-ray mask. High contrast alignment markers yielded the best results. The DEX023 was capable of performing pattern recognition and alignment in a semi-automatic manner with high contrast alignment markers.

Optimization of the exposure conditions was essential to reduce side-wall surface roughness, defects, protect the fragile X-ray masks, and enhance the development process. Some of the parameters that were considered for optimization were the bottom dose, $D_{\text{bot}}$, top-to-bottom dose ratio, $R$, and total exposure time.

The sensitivity of the two types of PMMA used in this research were experimentally determined to be about 1600 J/cm$^3$, which was adequate to cause sufficient scission in the polymer for dissolution to occur in the GG developer. However, the underlying PMMA layer created during the gluing process was highly cross-linked and could not be properly developed with 1600 J/cm$^3$. A test wafer that contains a layer of 30 µm-thick cross-linked PMMA was prepared and exposed with doses ranging from 1000 to 6000 J/cm$^3$ and determined that samples exposed with less than 3700 J/cm$^3$ could not be to develop cleanly. The dissolution rate of exposed PMMA in the developer was dependent on the dose absorbed. Since the PMMA pattern for the gyros form very high aspect ratio trenches (as much as 200), a bottom dose of 4500 J/cm$^3$ was used for all exposures to enhance the development rate.

When PMMA is exposed to high doses of X-ray radiation (>15 KJ/cm$^3$), foaming of the exposed resist was often observed as a result of the rapid formation and expulsion of gas from
with the exposed volume. The foaming was exasperated by heating during X-ray exposure. Sometimes, the “foam” layer was several hundred micrometers above the level of the unexposed resist. If the foaming is not controlled, it can damage the X-ray mask, which was usually separated from the X-ray resist only by several hundred microns. Thus, the top-to-bottom dose ratio was limited to less than or equal to 4 by inserting aluminum filters of varying thickness in front of the mask membrane.

**Table 5-1** shows the exposure doses and contrasts of exposures at 1.3 and 1.5 GeV of electron energy. The exposure times range from 2.5 hr for a 500 µm-thick PMMA exposed at 1.5 GeV to 55 hr for a 1000 µm-thick PMMA exposed at 1.3 GeV. All exposures that required more than 12 hrs were not considered feasible. Therefore, since 1.5 GeV was not available after 2001, no attempts were made at exposing layers greater than 500 µm. TI-1999 series wafers were prepared and exposed with up to 1000 µm thickness while SN-2003 wafers were exposed at 250 and 500 µm thickness.

### 5.5.4 Development

The exposure process reduced the average molecular weight of the PMMA resist from over $1 \times 10^6$ to less than $1 \times 10^4$. The exposed wafer were developed in the GG developer and rinsed in GG rinse followed by DI water rinse. The composition of the GG developer and rinse solutions are shown Table 5-2. The completion of the development of the electrodes was easily detected by using a microscope but the high aspect ratio of the cylinders prevented all attempts at inspection including SEM and optical profiling. The subsequent steps of nickel electroplating, planarization, and resist removal were needed to see the successful completion of the development step. Figure 5-4 shows a sample that was developed using the traditional method of single-soak development followed by a short rinse.
Table 5-1 Exposure conditions for PMMA at the bending magnet beamlines at CAMD: the dose ratio in all cases was adjusted to 5 by using a combination of the mask substrate and insertion of aluminum filters of various thicknesses in front of the mask. The exposure time was based on an average stored current of 100 mA.

<table>
<thead>
<tr>
<th>Energy (GeV)</th>
<th>Resist Thick. (µm)</th>
<th>Exposure Time for 5 cm scan length (hr)</th>
<th>Bottom dose (J/cm³)</th>
<th>Dose (mA/cm)</th>
<th>Contrast for 17 µm-thick gold</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>500</td>
<td>12</td>
<td>4500</td>
<td>14500</td>
<td>500</td>
</tr>
<tr>
<td>1.5</td>
<td>2.5</td>
<td>2.5</td>
<td>4500</td>
<td>2940</td>
<td>265</td>
</tr>
<tr>
<td>1.3</td>
<td>750</td>
<td>28</td>
<td>4500</td>
<td>33600</td>
<td>250</td>
</tr>
<tr>
<td>1.5</td>
<td>5</td>
<td>4500</td>
<td>5780</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>1000</td>
<td>55</td>
<td>4500</td>
<td>65300</td>
<td>135</td>
</tr>
<tr>
<td>1.5</td>
<td>9</td>
<td>4500</td>
<td>9370</td>
<td>96</td>
<td></td>
</tr>
</tbody>
</table>

Table 5-2 Composition of GG developer and GG rinse solutions

<table>
<thead>
<tr>
<th>Component</th>
<th>Developer</th>
<th>Rinse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di-ethyleneglycol monobutyl ether</td>
<td>60%</td>
<td>80%</td>
</tr>
<tr>
<td>2-Ethanolamine</td>
<td>20%</td>
<td>N/A</td>
</tr>
<tr>
<td>Morpholine</td>
<td>5%</td>
<td>N/A</td>
</tr>
<tr>
<td>DI water</td>
<td>15%</td>
<td>20%</td>
</tr>
</tbody>
</table>

Megasonic agitation during development has been shown to increase the development rate of irradiated PMMA. El-Kholi et al studied the effects of megasonic agitation on the development of various sized holes [60, 161, 162] and found a four-fold increase in the development rate of microstructures with large lateral aspect ratios. However, after the purchase of a megasonic system SONOSYS Ultraschalldsysteme (Germany), experiments at LSU revealed that megasonic agitation damaged the thin PMMA walls that defined the electrode gaps. Since the conventional single soak method was found to be inadequate for the microgyroscopes, a new scheme was devised.
Figure 5-4 Nickel microstructures used to judge the development of the PMMA:
a) 500 µm-thick pattern produced using conventional single-soak development; b) 1000 µm-thick microgyroscope structure produced using cyclic development
The temperature of the developer bath was reduced from 36°C to room temperature and a cyclic development process was adopted. Through a series of experiments, a short soak in the GG developer followed by a longer soak in the GG rinse was found to be effective. A single cycle consisting of a 20 minutes soak in the GG developer and a 40 minutes rinse in the GG rinse followed by a DI rinse was found to develop a properly irradiated PMMA resist with low aspect ratio pattern (<5) to a depth of 100 µm. To ensure no residue was left in on the developed structures, an additional cycle was added. For thicker resist layers, one additional development cycle is added for every 100 µm of PMMA. Using this scheme, a 1000 µm layer of PMMA could be completely developed in 11 hours as opposed to the 36 hours needed with the conventional single soak development process at room temperature. In addition, the total amount of time for the soak in the developer was reduced from 24 hours to 3 hours and 40 minutes. Even though this scheme worked well for low aspect ratio microstructures, a more radical development scheme was needed for aspect ratios over 100. Five cycles of 4 hours in the GG developer followed by 20 hours in the GG rinse and a DI rinse, all at room temperature, yielded complete development of 1000 µm microgyroscope patterns with cylinder wall thickness as small as 6 µm. Figure 5-4b shows a 1000 µm-tall microgyroscope structure that was produced using the cyclic development process.

5.6 Nickel Electroplating

Nickel was electroformed into the PMMA molds by using low stress nickel sulfamate baths. The composition of the baths used in the TI-1999 and SN-2003 fabrication series are shown in Table 5-3 and Table 5-4. TI-1999 used an in house built plating system with an M273 potentiostat (Princeton Applied Research, Princeton, NJ). SN-2003 wafers used a microform.200 nickel electroplating system (Technotrans America, Atlanta, Georgia) at CAMD (Figure 5-5).
Table 5-3 Composition of sulfamate based nickel electroplating bath used for TI-1999 fabrication series with *in house* plating station

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel ion concentration from Ni(HS₂SO₃) salt</td>
<td>78</td>
</tr>
<tr>
<td>Boric acid – H₃BO₄</td>
<td>37</td>
</tr>
<tr>
<td>Sodium lauryl sulfate</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 5-4 Composition of sulfamate based nickel electroplating bath used for SN-2300 fabrication series with Technotrans Plating Station

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel ion concentration from Ni(HS₂SO₃) salt</td>
<td>90</td>
</tr>
<tr>
<td>Boric acid – H₃BO₄</td>
<td>44</td>
</tr>
<tr>
<td>DK-surfactant (Technotrans)</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Both baths were operated at 52°C, pH of 3.6-3.8. TI-1999 wafers were electroplated in potentiostatic mode with voltages ranging 0.8 - 1.1 V depending on the plating area. The SN-2003 wafers were electroplated in galvanostatic mode with current densities ranging from 5 to 10 mA/cm². These sulfamate-based baths yielded considerably lower internal stress than nickel sulfate-based baths. The presence of surfactants enhanced the penetration of the plating solutions into the micro-cavities. Prior to immersion in the electroplating solutions, the substrates were immersed in DI water and vacuumed to remove the trapped air bubbles from the micro-cavities.

The growth rate of nickel was dependent on the local current density in the various micro-patterns. The growth rate of small features was higher than that of structures with large lateral dimensions. As a result, thickness variations of as high as 100% were observed on the wafers. Typically, small features electroplated faster than large ones due to nonlinear diffusion [163].
Figure 5-5  Nickel electroplating systems: a) in house plating system used for TI-1999 fab series; b) microform.200 plating system (Technotrans America, Atlanta, Georgia) used for SN-2003 fab series; c) rotating cathode of the microform.200
5.7 Planarization

Since the microgyroscope structures had very small footprint, they broke off the substrates very easily; therefore, it was necessary to develop a gentle polishing process in order to improve the yield. A polishing system (Figure 5-6) consisting of a 15” Engis polishing machine (Engis Corporation, Wheeling, Illinois) with a composite iron polishing wheel and a vacuum chuck with “carbide feet” (South Bay Technologies, Inc., San Clemente, California) to hold the wafers during polishing was used to planarize the wafers. The over-plated nickel was first removed by polishing with oil-based 15 µm diamond slurry. The diamond particle size was progressively decreased to 9, 6, and 3 µm until all scratches larger than 3 µm were removed. The samples were finally polished with 1 µm water-based slurry and a polishing clothe mounted to the composite iron polishing plate resulting in a mirror finish.

5.8 Resist and Plating Base Removal

Several methods were evaluated for the removal of the unexposed PMMA resist including of solvents such as acetone, di-chloromethane, and chloroform. Removal of the PMMA with solvents often left residue on the microstructures, which was difficult to remove by subsequent cleaning processes. X-ray irradiation of the remaining PMMA with 50% of the development dose followed by soaking in acetone and rinsing with IPA proved effective for TI-1999 series wafers. However, successful fabrication of SN-2003 structures was possible only by exposing and developing the remaining PMMA in steps of 100 µm-thick at a time. After the PMMA molds were completely removed, the tri-layer plating bases were selectively etched by using the etchants shown in Table 5-5, rinsed with DI water, and dried in an oven.
Table 5-5  Etchants used to remove the plating bases

<table>
<thead>
<tr>
<th>Plating Base Layer</th>
<th>Solution</th>
<th>Etch Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>0.5% HF</td>
<td>2</td>
</tr>
<tr>
<td>Copper</td>
<td>50% NH$_4$OH:50% H$_2$O$_2$ (1:1)</td>
<td>1</td>
</tr>
<tr>
<td>Chromium</td>
<td>Transene Cr etch</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Figure 5-6  Engis 15” polishing machine (Engis Corporation, Wheeling, Illinois)
5.9 Results and Discussion

Microgyroscope structures with cylinders as small as 8 µm and heights of 750 µm were fabricated as part of the TI-1999 fabrication series but devices with cylinder wall thickness of less than 8 µm were consistently destroyed most often during PMMA removal. Figure 5-7 shows a field of microgyroscope structures and a single device with a wall thickness of 10 µm. The SN-2003 fabrication series yielded similar results to TI-1999 as shown in Figure 5-8. In both cases, deformation of some of the gaps between the cylinders and the electrodes were observed. The gaps were also smaller than the width of the corresponding absorber patterns.

Loss of adhesion of the nickel microstructures to the substrates were the most common types of problems observed. Structures that appeared to be complete before the removal of the PMMA mold would wash away during stripping. Since the nickel cylinders had thin walls, their footprint was very small. In TI-1999 series wafers, the nickel cylinders had an approximately 20% contact area with the nickel wiring layer and 80% with the titanium plating base. Electrodeposited materials do not adhere well to titanium or titanium oxide. Thus, the only reliable adhesion mechanism for the microstructures was the bond between the nickel wiring layer and the nickel microstructures; this bond was not sufficient to hold most microstructures in place during processing. The wiring layer in SN-2003 series wafers was designed such that the cylinders are electroplated directly on the gold wiring layers as shown in Figure 5-8d. However, the loss of adhesion was worse on the SN-2003 series than the TI-1999 because of the decrease in the roughness of the wafers. The alumina wafers used in the TI-1999 series had typical surface roughness of 800 nm Ra while the silicon nitride wafers had less than 20 nm Ra.
Figure 5-7  TI-1999 series microgyroscope structures on 10 µm-thick wiring layer: a) a field of 750 µm microstructures; b) top view of a microstructure showing proper alignment; c) 10 µm cylinder wall thickness device; d) deformed electrode gap (2 µm)
Figure 5-8  SN-2003 series microgyroscope structure on a 10 µm-thick gold wiring layer:

a) 500 µm-tall microstructure with a cylinder wall thickness of 6 µm;

b) close-up view of the microstructure;

c) deformed drive electrode and proper sense electrode;

d) cross-section of a similar microstructure showing the proper alignment of wiring and high aspect ratio layers.
Chapter 6 Summary and Conclusions

Multi-level LIGA-based processes were developed for the fabrication of high aspect ratio microgyroscope structures. The first level was a wiring layer composed of 10 \( \mu \text{m} \)-thick metal interconnects needed to provide electrical connection to the cylinders and electrodes that make up the microgyroscope structures. The wiring layer was made by a combination of thick film photolithography and nickel or gold electroplating on a low dielectric substrate material (silicon coated with 1 \( \mu \text{m} \)-thick silicon nitride). The second level consisted of high aspect ratio cylinders and electrodes (500 – 1000 \( \mu \text{m} \)-thick) that were fabricated by a combination of deep-etch X-ray lithography and nickel electroplating.

Significant process development in the areas of X-ray exposure, development, and nickel electroplating were necessary to produce the microgyroscope structures successfully. The X-ray exposure conditions were optimized to minimize the damage caused by resist swelling. A cyclic development process (room temperature) was devised to address the difficulties involved in developing recesses with aspect ratio of as much as 250. The cyclic development process increased the speed of development for all ranges of resist thicknesses. For resist molds with aspect ratio of less than 100, cycles made of 20 minutes in GG developer followed by 40 minutes in GG rinse were found to be effective. In general, one cycle for every 100 \( \mu \text{m} \) of resist thickness was required. The high aspect ratio recesses of the microgyroscope structures required significantly different cycles. A single cycle made of 4 hr in the GG developer followed by 20 hr
in the GG rinse was required to develop a 200 µm-thick microgyroscope resist mold; structures with a thickness of 1000 µm required five cycles.

The lack of an in house X-ray mask technology was found to be a hindrance in this research and three types of X-ray masks were pursued as part of this work. A graphite mask making process with alignment markers was developed, which can also be used to make X-ray masks on other opaque substrates. Borosilicate glass-based and silicon nitride-based mask fabrication processes were also developed. To address the needs of the X-ray masks, three commercial gold electroplating solutions were evaluated and their deposit characterized including the internal stress of deposits. The NEUTRONEX 309, a sulfite-based solution, was determined to be the best solution of those investigated.

Two successful fabrication sequences were developed for the microgyroscope structures. The first sequence (TI-1999) used a titanium membrane X-ray mask purchased from IMT (Karlsruhe, Germany) while the second (SN-2003) used a silicon nitride membrane X-ray mask fabricated at CAMD. The titanium membrane mask was made by using a combination of e-beam lithography, X-ray lithography and gold electroplating, while the silicon nitride membrane mask was made with UV photolithography and gold electroplating. Test structures (50 µm-thick) made with the titanium membrane mask had a process bias of -0.6 µm and sidewall surface roughness of 30 nm Ra while the silicon nitride membrane test structures yielded 2.6 µm process bias and 70 nm Ra sidewall surface roughness.

Although both TI-1999 and SN-2003 yielded complete microgyroscope structures, the gap between the cylinders and the electrodes were deformed in some cases and always smaller than the corresponding structures on the X-ray masks. The deformation was found to be related to the
lateral aspect ratio of the resist wall that forms the gap during electroplating. Resist swelling during development resulted in stress thereby buckling the thin walls.
References


Appendix A Vibration of Cylindrical Perfect Shells

A.1 Introduction

In studying the principle of operation of a vibrating shell type gyroscope, it is necessary to consider the freely and forced vibration of shells separately. Figure A-1 shows a thin axi-symmetric cylindrical shell, where the variables \( u \), \( v \), and \( w \) represent the radial, tangential and axial displacement directions. Being a continuous elastic structure, the shell has an infinite number of natural frequencies of vibration. References [1] and [2] provide a through derivation and analysis of the equations of motion of such shells. In the following sections, the analysis of the equations of motion and nomenclature used by Fox and Leissa are closely followed.

The equation of motion of a non-rotating cylindrical shell can be written as

\[
\left\{ L(z,\theta)w(z,\theta,t) + I \frac{\partial^2 w}{\partial t^2}(z,\theta,t) \right\} = f(z,\theta,t)
\]

where \( w \) is a vector of radial (\( u \)), tangential (\( v \)), and axial (\( w \)) displacements [1]. The position of a point on the shell is defined by \( z \) and \( \theta \). The forcing function which is used to excite the shell is represented by \( f(z,\theta,t) \). The elements of the shell matrix operator, \( L(z,\theta) \), depend on the shell theory used and Leissa provides thorough discussions and derivations of the various shell theories [2].

Thus, the axial motion can be neglected and \textbf{Equation A-1} can be simplified as

\[
\frac{\rho R^2}{E} (1-\nu^2) \frac{\partial^2 u}{\partial t^2} + u + \frac{\partial v}{\partial \theta} + \frac{h^2}{12R^2} \left( u + 2 \frac{\partial^2 u}{\partial \theta^2} + \frac{\partial^4 u}{\partial \theta^4} \right) = 0
\]

\[
\frac{\rho R^2}{E} (1-\nu^2) \frac{\partial^2 v}{\partial t^2} - \frac{\partial u}{\partial \theta} - \frac{\partial^2 v}{\partial \theta^2} = 0
\]
where $\rho$, $E$, and $\nu$ are the density, Young’s modulus and Poisson’s ratio respectively while $R$ and $h$ are the mean radius and thickness of the cylinder.

The solutions of Equation A-2 have the following form:

$$u = A \cos n\theta \cos \omega_n t \quad A-3$$

$$\nu = B \sin n\theta \cos \omega t.$$  

Assuming that the wall thickness of the cylinder is much smaller than the radius, i.e., $h<<R$, and substituting Equations A-3 into A-2 and simplifying yields the following for the flexural natural frequency, $\omega_n$, and the mode shape, $A/B$:

$$\omega_n = \frac{E}{\rho R^2 (1-\nu^2)} \left( \frac{h^2}{12R^2} \right) \frac{n^2(n^2-1)^2}{(n^2+1)}$$  

$$\frac{A}{B} = -n. \quad A-4$$
Figure A-2 shows the first five circumferential nodal patterns that can result. Out of these, the most relevant mode that can be used for sensing purposes is the \( n = 2 \) mode where the free-vibration results in a standing wave.

Introduction of an angular velocity \( \Omega \) about the axis of symmetry results in the following equations of motion:

\[
\begin{align*}
\frac{\partial^2 u}{\partial t^2} - 2\Omega \frac{\partial v}{\partial t} - u\Omega^2 + v \frac{\partial v}{\partial t} + \frac{E}{\rho R^2 (1 - \nu^2)} \left[ u + \frac{\partial v}{\partial \theta} + h^2 \left( u + 2 \frac{\partial^2 u}{\partial \theta^2} + \frac{\partial^4 u}{\partial \theta^4} \right) \right] &= R\Omega^2 \\
\frac{\partial^2 v}{\partial t^2} - 2\Omega \frac{\partial v}{\partial t} - v\Omega^2 + u \frac{\partial u}{\partial t} - \frac{E}{\rho R^2 (1 - \nu^2)} \left[ \frac{\partial u}{\partial \theta} + \frac{\partial^2 v}{\partial \theta^2} \right] &= R \frac{\partial \Omega}{\partial t} 
\end{align*}
\]

(A-5)

In the above equation, \( \Omega \frac{\partial v}{\partial t} \) and \( \Omega \frac{\partial u}{\partial t} \) represent the Coriolis terms. Figure A-3 shows the nodal shift in a freely vibrating cylinder with and without rotation.

![Figure A-2](Figure A-2 shows the first five circumferential nodal patterns of an axisymmetric non-rotating cylindrical shell [2])
Figure A-3  Nodal shift caused by a rotation about the axis of symmetry in a freely vibrating thin shell cylinder

In the case where the applied angular velocity $\Omega$ is much smaller than the natural frequency of the shell ($\Omega \ll \omega_n$), the $\Omega^2$ terms can be neglected. In addition, if $\Omega$ is constant and the shell is thin, then $\partial \Omega / \partial t = 0$ and $h \ll R$. These assumptions lead to the following equation:

$$\begin{align*}
\frac{\partial^2 u}{\partial t^2} - 2 \Omega \frac{\partial v}{\partial t} + \frac{E}{\rho R^2 (1 - \nu^2)} \left[ u + \frac{\partial v}{\partial \theta} \right] &= 0 \\
\frac{\partial^2 v}{\partial t^2} - 2 \Omega \frac{\partial u}{\partial t} - \frac{E}{\rho R^2 (1 - \nu^2)} \left[ \frac{\partial u}{\partial \theta} + \frac{\partial^2 v}{\partial \theta^2} \right] &= 0
\end{align*}$$  \hfill A-6

The above equation can be satisfied by solutions of the form

$$\begin{align*}
u &= A \cos(n \theta + p_1 t) + A \sin(n \theta + p_2 t) \\
\nu &= -A \sin(n \theta + p_1 t) - A \cos(n \theta + p_2 t)
\end{align*}$$  \hfill A-7

where $p_1 \approx \frac{2n}{n^2 + 1} \Omega + \omega_n$, $p_2 \approx \frac{2n}{n^2 + 1} \Omega - \omega_n$, and the natural frequency $\omega_n$ is given by

Equation A-4. As shown in Equation A-7, the vibration of the shell is composed of two waves traveling in opposite directions but equal amplitudes. The expressions for $p_1$ and $p_2$ show that the two waves have slightly different speeds that are proportional to $\Omega$.  

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Appendix B Fabrication of HARMS with a Transfer Mask Technique

A transfer mask (TM) is similar to a portable conformable mask (PCM) used to pattern multi-layer resists (MLR) [3]. In PCMs, a thick resist layer is applied to a substrate with varied topography. After planarization, the thick layer is coated with a thinner resist layer, which is lithographically patterned. The top layer of resist is used to pattern the underlying thick resist layer by another lithographic or etch process.

In 1995, Vladmirisky, et al. [4] adopted the PCM technique for use in the x-ray lithography of thick resists. A layer of positive resist was directly applied and lithographically patterned on a PMMA resist sheet coated with a thin layer of chromium and gold. An X-ray absorber layer made of gold was directly electroplated on the surface of the PMMA and the positive resist was removed. The PMMA sheet with the gold absorber was exposed and developed to a depth of over 200 \( \mu \text{m} \) in five sequential steps.

There are several advantages offered by the TM technique when used for deep X-ray lithography. The often tedious and expensive to make X-ray mask becomes unnecessary. In addition, since the gold absorber remains attached to the PMMA resist, the x-ray lithography can be carried out in increments; several sequences of exposures and developments can be used to pattern thick resist layers. Since highly penetrating X-ray radiation is not needed for thinner resist layers, this approach can be used to expose thick resist layers with soft x-ray sources.

**Figure B-1** shows the dose distributions of a 500 \( \mu \text{m} \) PMMA resist exposed with a single exposure step and a five-cycle exposure/development process. **Table B-1** shows a comparison of the exposure conditions of a 500 \( \mu \text{m} \) PMMA resist layer for a single and multiple exposure/development conditions at 1.3 GeV at the XRLM3 beamline at CAMD.
A total dose of 12640 mA.min/cm is required to fully expose the resist layer with an absorbed dose of 2500 J/cm³ at the bottom of the resist as opposed to 2342 mA.min/cm if the exposures and developments are performed in increments of 100 µm at a time. In terms of the exposure time, this translates into a reduction of exposure time from 2 hr/cm to 40 min/cm. Since the lithography step of a TM is done in a UV aligner, multi-level structures can be made without alignment capabilities.

The micro-gyros jointly proposed by SatCon Technologies and the LSU ME require precision alignment of the wiring layer to the LIGA layer. In 1995, alignment and X-ray mask manufacturing capabilities for x-ray lithography did not exist at LSU. Thus, the TM technique was chosen for the fabrication of prototype devices. Figure B-2 shows the schematic of the proposed fabrication process.
Table B-I  Comparison of single and multiple exposure/development schemes with a BOM

<table>
<thead>
<tr>
<th></th>
<th>Single exposure and development</th>
<th>Multiple exposure and development</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mask membrane</td>
<td>2.2 µm titanium</td>
<td>None</td>
</tr>
<tr>
<td>Filters</td>
<td>21 µm aluminum</td>
<td>6 µm aluminum</td>
</tr>
<tr>
<td>Top to bottom dose ratio</td>
<td>4.72</td>
<td>1.9-2.5</td>
</tr>
<tr>
<td>Bottom dose</td>
<td>2500 J/cm³</td>
<td>2500 J/cm³</td>
</tr>
<tr>
<td>Number of cycles</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Total dose required (1.3 GeV)</td>
<td>12640 mA.min/cm</td>
<td>2342 mA.min/cm</td>
</tr>
</tbody>
</table>

Application of the BOM technique for the fabrication of the 500 µm micro-gyros was problematic in many ways.

- After spincoating, the photoresist used to build the BOM must be baked either on a hot plate or in a convection oven. The mismatch in the thermal coefficient of expansion (CTE) between the substrate and the PMMA layer often resulted in the de-bonding of the resist layer.

- The gold absorber layer used in this process was 4-6 µm. For best result, at least 10 µm of gold must be used.

- During exposure, insufficient filtration was used. This caused the absorber layer to heat-up and peel off due to the mismatch in the CTE of gold and PMMA.

Since no viable solutions were found at the time, the TM technique was abandoned in favor of the conventional LIGA process.
Appendix C Fabrication of Components for Hybrid Microgyroscopes

C.1 Introduction

The fabrication of testable micro-gyros with the LIGA process was plagued with three major problems: 1) adhesion of the nickel cylinders to the substrate, 2) reduction of the electrode/cylinder gaps to a substantially smaller width than designed and 3) buckling of the gap defining resist. In order to overcome these problems, the micro-gyros were re-designed by SatCon Technologies. The revised gyros were substantially larger and the cylinders and electrodes were to be fabricated separately and assembled together. The cylinders with a height of 6000 \( \mu \text{m} \) tall and 75 \( \mu \text{m} \) wall thickness were made by use of a high precision lathe. The electrodes were 1000 \( \mu \text{m} \) tall and were made by the LIGA process. The following sections describe the process development and fabrication of the LIGA based components.

C.1 Process Sequence

Figure C-1 shows the two types of electrode configurations. In the first configuration, eight electrodes were placed at 45° intervals while a cylinder-stand with an interior hole was located at the center. In the second configuration, only six electrodes were placed around the center post. Two of the electrodes were moved into the interior of the cylinder and combined with the cylinder-stand to form a single structure. Since the cylinders and electrodes are made separately, the buckling of the gaps can be eliminated.
Figure C-1 X-ray mask for the fabrication of hybrid-gyros using the LIGA process: a) electrode layout; b) graphite mask with alignment markers

C.1.1 Photo- and X-ray Masks

The optical masks for the wiring/adhesion and the LIGA layers were purchased from LSI Photomask (Tempe, AZ). Since the state of the art titanium membrane x-ray masks take 6 to 12 months to procure from IMT, Germany, a substantial effort was made to create a reliable but
inexpensive x-ray mask technology. The key factor that contributes to the reliability and cost of x-ray masks is the type of membrane used. In the past, titanium, silicon, silicon nitride, silicon carbide, kapton, beryllium, and graphite have all been used for making x-ray masks. The thickness of the membrane for an x-ray mask is determined by the transmission and stability of the material to hard x-ray radiation. In order to form mask membranes that have acceptable transmission to the spectrum of radiation at CAMD’s bending magnet microfabrication beamlines, the thickness of titanium, silicon, and silicon-based membranes must be less than 10 µm. On the other hand, thick graphite and beryllium substrates can be used as substrates for mask; very hard x-ray sources such as the NSLS in Brookhaven use masks with 100-500 µm thick Si wafers as mask substrates.

C.1.1.1 Performance of X-Ray Masks with Graphite Membranes

Features as small as 6 µm were produced on graphite based x-ray masks with absorber thickness of 10 µm; smaller structures were often difficult to adhere to the surface of the graphite.

Exposures made with graphite membrane X-ray mask typically showed higher surface roughness than those patterned with titanium, beryllium and silicon based membranes. In order to isolate the impact of the graphite substrate on the increased sidewall roughness a series of exposures were done using a titanium x-ray mask with DFP-3 and SFG-1 graphite substrates as filters. These filters were placed between the mask and the resist surface. Both the mask/filter and filter/resist proximity gaps were approximately 150 µm. Exposures were done into 300 µm thick PMMA sheets bonded to Silicon wafers. The structures were released from the wafers during the development and the sidewall roughness was measured using a WYKO interferometer (Figure 5.7). As expected, the structures exposed with the titanium mask only showed a surface
roughness of 39 nm while the SFG-1 and DFP-3 showed surface roughness of 200 nm and 250 nm Ra.

Figure C-2  Sidewall roughness of 300 µm-high PMMA microstructure patterned by use of a titanium membrane X-ray mask and a 125 µm-thick SFG-1 graphite substrate used as a filter: a) Resist patterned with a titanium membrane mask; b) Resist patterned with a titanium membrane mask and SFG-1 graphite placed between the PMMA and the titanium membrane mask
C.2 Wiring Layer

The primary purpose of the wiring layer for the hybrid-gyros was to provide an external electrical interface to the devices. In addition, the large nickel wiring pads also allowed nickel-to-nickel bond to the LIGA structures thereby improving the adhesion. To fabricate the wiring layer, a ceramic substrate (95.9% alumina) was sputter coated with 2000 Å titanium followed by 2 µm copper. 8 µm of a positive resist was lithographically patterned on the copper layer. The surface was de-scummed, activated with a commercial activation solution and electroplated with 3-4 µm of nickel by use of a nickel sulfamate bath. The remaining positive resist was stripped by use of acetone.

C.3 X-Ray Lithography

In order to improve the adhesion of the PMMA layer to the plating base, the top layer of copper was soaked in a hot alkaline solution to form black copper oxide. The alkaline solution consisted of NaClO₂, NaOH, Na₂CO₃, and NaCl and the treatment was done at 95°C. 1100 µm thick PMMA resist layers were bonded to the black oxide surface using PMMA gel and pressed for 5 hours. The x-ray mask fabricated for this process was aligned to the substrate with the HI-MEMS Alliance manual aligner and exposed at XRLM3 at 1.5 GeV. 12 cycles of a 20-minute soak in the GG developer followed by 40 minutes in the GG rinse were used to fully develop the irradiated resist.

C.4 Electroforming of LIGA Structures

During the first fabrication run of the hybrid-gyros, the LIGA components were electroplated by using a nickel sulfamate bath. However, the ensuing planarization step revealed a new problem. Since the thickness of the electrode stand and the electrodes needed to be within 10 µm, fly cutting was attempted as a form of planarization. While flycutting, several of the structures fractured at approximately 100 µm and 300 µm from the bottom of the substrate.
Figure C.3 shows one of the components that fractured at a height of 100 µm. A close observation of the plating activities revealed that the fracture points in time correspond to a change in the plating conditions made including pH, solution level, and current density adjustments. Any discrete changes in the plating conditions that occur during electroforming created discontinuities in the grain structure causing failure.

A new plating setup with two tanks was designed and built—a deposition tank and a conditioning tank where pH adjustments were made. The plating solution was continuously filtered and circulated between the deposition and conditioning tank. A float switch was used to sense the level of the solution in the conditioning tank and open a valve to add DI water. The new setup was able to produce reliable and defect free nickel structures.

C.5 Planarization, Resist Stripping, Dicing, and Plating Base Removal

Manual polishing of the samples with 600 grit carbide paper was used to remove the excess nickel material. After the level of the resist was reached, higher grit carbide and diamond papers were used to improve the surface finish and obtain burr-free structures. The PMMA mold was irradiated with a bottom dose of 500 J/cm³ and dissolved with acetone. A commercial wafer dicing company, Sawtech, Inc. (Garland, Texas), diced the ceramic wafers into separate die. The black copper oxide and copper layers were removed with a combination of ammonium hydroxide and hydrogen peroxide, a selective copper etchant. The final titanium layer was etched by use of 2% HF solution.
Figure C-3  Microgyroscope components fractured during planarization: a) wiring layer overall view; b) wiring layer is partially de-bonded
C.2 Results and Discussion

Figure C-4 shows a representative sample of hybrid-gyro components. These components had very strong adhesion to the ceramic substrates to the extent that any mechanical failure that occurred was due to failure in the bulk ceramic; Figure C-5 illustrates this point well. SatCon Technologies assembled some of the hybrid-gyro components with cylinders of 6000 µm height and 75 µm wall thicknesses. Preliminary tests revealed the unexpected existence of two resonance frequencies close to each other. A possible cause for the double resonance frequencies is eccentricity in either the electrodes or assembly of the cylinder with the electrodes.

Figure C-4 LIGA components for a hybrid-gyro: a) All-outer electrode design; b) 6-outer and 2-inner electrode design
Figure C-5  Fractured substrate shows that the adhesion between the electroplated nickel and the copper plating base is relatively strong

References


Vita

Yohannes Mamo Desta was born in Dessie, Ethiopia, on December 31, 1969. After completing high school in Kingston, Jamaica, he moved to Prescott, Arizona, where he attended Embry Riddle Aeronautical University and graduated with a bachelor of science in aerospace engineering (magna cum laude) in 1991.

He joined the Department of Mechanical Engineering at Louisiana State University in 1992 as an M.S. candidate and the MicroSystems Engineering Team (µSET) in 1993, where he began R&D in LIGA under the supervision of Dr. Michael C. Murphy. In 1997, he was accepted into the Ph.D. program at the Dept. of Mechanical Engineering and hired as a full-time research associate in 1999.

In 2000, he was hired at the Center for Advanced Microstructures and Devices (CAMD) at Louisiana State University, where he continued research in X-ray mask fabrication, ultra-deep X-ray lithography, and electroplating. Currently, he is a senior research associate and manager of the MEMS/LIGA Services at CAMD.