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LIGA-Based Microsystem Manufacturing: The Electrochemistry of Through-Mold Deposition and Material Properties

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**LIGA-Based Microsystem Manufacturing:
The Electrochemistry of Through-Mold Deposition
and
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ABSTRACT

The report presented below is to appear in *Electrochemistry at the Nanoscale*, Patrik Schmuki, Ed. Springer-Verlag, (ca. 2005). The history of the LIGA process, used for fabricating dimensional precise structures for microsystem applications, is briefly reviewed, as are the basic elements of the technology. The principal focus however, is on the unique aspects of the electrochemistry of LIGA through-mask metal deposition and the generation of the fine and uniform microstructures necessary to ensure proper functionality of LIGA components. We draw from both previously published work by external researchers in the field as well as from published and unpublished studies from within Sandia.

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Contents

Abstract	3
Figures.....	6
Tables.....	8
Introduction to LIGA Fabrication and its Applications	9
LIGA Process Flow	10
LIGA History	18
LIGA Applications	22
Electrodeposition into Deep High Aspect Ratio Features fo LIGA	27
Introduction.....	27
Workpiece and Pattern Scale Effects.....	29
Feature Scale Effects	31
Summary: Uniformity at the Workpiece, Pattern, and Feature Scales in LIGA	42
Electrodeposition in LIGA: Materials and Other Aspects.....	42
Properties and Structure of Electrodeposited Materials for LIGA-Based Microsystem Applications	45
Introduction.....	45
Measurement Techniques for Strength and Ductility	47
Grain Refinement for Improved Electrodeposit Strength.....	49
Particulate Additive Effects	71
Modulus of Electrodeposits	72
Summary: Electrodeposited Materials for LIGA-Based Microsystems	78
Other Aspects of LIGA Technology	79
Acknowledgements.....	81
References.....	83
Distribution List	91

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Figures

Figure 1	Example of Ni structures fabricated by electroplating	11
Figure 2	Schematic diagram of the LIGA process flow.....	12
Figure 3	A layout of spring prototypes used in the photolithography necessary to fabricate the gold x-ray absorbing mask.....	13
Figure 4	Process schemes for producing a thick tool bearing LIGA features for subsequent embossing or injection molding.....	17
Figure 5	X-ray absorbing masks produced.....	19
Figure 6	Patterned PMMA 12 μm in thickness.....	20
Figure 7	Patterned PMMA	21
Figure 8	Example of Ni test gear device formed from electrodeposition through a patterned PMMA mold	21
Figure 9	Example of an acceleration-sensing prototype device.....	23
Figure 10	Minimotor assembly composed of piece parts formed by through-mask plating of thick and thin UV-photoresist by workers at IBM.....	24
Figure 11	Precision position components fabricated by a LIGA-related process.....	26
Figure 12	Schematic illustration of the workpiece, pattern, and feature scales, redrawn from a similar graphic from DeBecker and West.....	28
Figure 13	Limiting current densities	33
Figure 14	Diagram of special pH electrode.....	35
Figure 15	In situ pH measurements from the pH electrode	36
Figure 16	Electrodeposited NiFe alloy: Composition dependence on deposition conditions.....	40
Figure 17	Electrodeposited NiFe alloy composition through-thickness uniformity	41
Figure 18	Correlation of Vickers hardness (VHN)	49
Figure 19	Stress strain behavior of electrodeposited and wrought Ni.	51
Figure 20	Hall-Petch behavior for electrodeposited Ni.....	52
Figure 21	Hardness dependence on Co content for an electrodeposited NiCo alloy	53
Figure 22	Stress strain behavior for as-deposited NiCo and pure Ni.....	54
Figure 23	Stress strain behavior for a series of NiMn electrodeposits.....	55
Figure 24	Co content of an electrodeposited NiCo alloy within a LIGA feature	58
Figure 25	Solute concentration for NiCo and NiMn alloys	60
Figure 26	Stress strain behavior for various anneals of Ni electrodeposited from a Watts chemistry containing 1 g/L saccharin	62
Figure 27	Stress strain behavior for Ni electrodeposited from a fresh sulfamate plating bath	64
Figure 28	Yield and ultimate strengths for Ni electrodeposited from a sulfamate electrolyte reproduced from data given by Sharpe	66
Figure 29	Effect of electrolyte filtering on stress-strain behavior for electrodeposited Ni from a sulfamate bath at 28 C and 3 mA/cm ²	67

Figure 30	Planview focused ion beam image of a nickel deposit	69
Figure 31	Effect of alumina particulate incorporation on stress-strain behavior of ED Ni plated from a sulfamate chemistry.....	72
Figure 32	Stress-strain data for Ni electrodeposited from a sulfamate chemistry	74
Figure 33	Calculated elastic moduli for Ni	76
Figure 34	Three point bend tests	77

Tables

Table 1.	Experimental Data From Griffiths <i>Et. Al.</i> ⁶²	37
Table 2.	Deposition Process Characteristics and Requirements	46
Table 3.	Electrodeposit Properties And Requirements.	46

Introduction to LIGA Fabrication and its Applications

Certain microsystem fabrication techniques are critically dependent on the electrochemistry of metal deposition into lithographically defined features that are developed in insulating molding materials. One such technique, developed originally at the Forschungszentrum Karlsruhe, Germany, is known as LIGA, the German acronym for lithography, electroplating, and replication (*lithographie, galvanoförmung, and abförmung*).¹⁻³ An example of typical miniature structures formed by plating through thick photoresist (the insulating molding materials) is shown in Figure 1. Since its inception in Germany in the 1980's, LIGA research activities have expanded throughout Europe, as well as in Asia and North America.

Thanks to the intense and collimated x-ray synchrotron radiation used in the lithography step, the definition of high aspect ratio features in thick photoresist with good dimensional fidelity is a unique attribute of the technique.⁴ For example, high aspect ratio features (i.e., the height to width ratio) as high as 100 and feature depths up to ≈ 1 mm have been realized. These features are then filled with a metal via electrodeposition through the x-ray exposed photoresist mold that is bonded to a conductive substrate (the details of the LIGA process and other LIGA-like processes will be discussed later in the chapter). The unique geometries encountered in LIGA through-mask electrodeposition present distinct challenges. This is particularly the case with respect to the resultant materials that are required to have special properties (*e.g.*, mechanical performance characteristics or magnetic properties). Consequently, a substantial portion of LIGA research is dedicated to first understand the electrochemistry of the LIGA through-mask electrodeposition process and secondly, the subsequent material properties for electrodeposited metals, alloys, and metal-matrix composites.⁵⁻⁶

Most structures fabricated with the LIGA process generally have critical lithographic dimensions on the micron scale.² In principle, submicron features are possible, but such fine features are not routinely fabricated.^{2,7} Although the physical dimensions of LIGA-fabricated components are rarely on the nanoscale, important microstructural aspects of the electrodeposit often are. For example, electrodeposited materials are well known for exhibiting fine microstructures, with grain sizes in the nm range.⁸ In fact, this is somewhat fortuitous, as a grain size on a scale much smaller than that of the physical component dimensions is usually a requisite for that component to have a spatially uniform microstructure. But, as will be discussed later, the degree of this uniformity usually depends on the presence of other species (other metal ions, additives, or

adsorbed species, for example) that may affect the deposit structure, particularly when the concentration of these species is sensitive to transport.

Our objective here is not a detailed review of the LIGA process or its technological applications; several reviews of this type are available.⁹⁻¹⁵ Instead, we will focus on the unique aspects of the electrochemistry of LIGA through-mask metal deposition and the generation of the fine and uniform microstructures necessary to ensure proper functionality of LIGA components. Before addressing these issues, brief descriptions of the LIGA process, its history, and applications will be given for those unfamiliar with the technique.

LIGA Process Flow

The general flow of the process steps necessary to create LIGA microparts is shown in Figure 2. The process consists of using synchrotron x-rays and an x-ray absorbing mask to transfer a desired pattern to a metallized wafer substrate on to which is bonded a thick, x-ray photoresist blank. This photoresist is most commonly high molecular weight polymethylmethacrylate (PMMA) which is rendered more susceptible to chemical dissolution by x-ray exposure. The resist is then “developed” using a commercial solvent to create prismatic cavities into which metal is electrodeposited. The remaining PMMA is then dissolved, and the prismatic metallic structures can be released by chemically dissolving the original metallization layer. What we have described here and show in Figure 1 is, in fact, often referred to as “direct” LIGA, wherein the final released parts are those intended to be used. Often, perhaps more typically, the final part is a monolith consisting of the electrodeposited structures attached to a backing plate (either the plating substrate itself or a top surface blank formed by overplating the mold). This “parent” tool is then used to replicate multiple generations of microparts in a variety of ways.

Figure 1 Example of Ni structures fabricated by electroplating through PMMA resist that had been patterned by x-ray lithography. This technique of using electrodeposition to deposit metal into molds that have been lithographically formed with x-ray synchrotron radiation is referred to as the LIGA technique (German for *lithographie*, *galvanoformung*, and *abformung*; in English, lithography, electroplating, and replication). The top optical shows a variety of structures still attached to the metallized substrate. The lower image is an scanning electron micrograph showing a portion of a released structure. Images courtesy of Georg Aigeldinger, Sandia National Laboratories, Livermore, California.

Figure 2 Schematic diagram of the LIGA process flow. A LIGA mold consisting of a plating base (usually a metallized wafer) with thick PMMA resist is patterned with synchrotron x-rays by using a gold x-ray absorbing mask. The features are developed and then electroplated, after which dissolution of the PMMA may take place. In the case shown here, the parts are released from the plating base to yield separate piece parts.

Pattern Layout— Before starting the LIGA process shown in Figure 2, a pattern layout must be created in order to fabricate the x-ray absorbing mask that will be used during exposure. This entails taking a desired two-dimensional device geometry from a drawing (from CAD software, for example) and distributing it across an area corresponding to the surface of a wafer substrate. An example of a pattern layout of a spring prototype is shown in Figure 3a. Unless special exposure techniques are employed,² LIGA-fabricated devices are prismatic, *i.e.* the part geometry does not vary in the *z* dimension, which is perpendicular to the substrate. Figure 3b shows the final plated LIGA component from the layout shown in Figure 3a.

Figure 3 (a) A layout of spring prototypes used in the photolithography necessary to fabricate the gold x-ray absorbing mask. The colored areas correspond to regions where thin UV resist remains after patterning for the x-ray mask. Since thick gold (several to ten's of microns) is electroplated around and through these thin resist features to form the x-ray absorbing mask, the pattern is transferred into the PMMA resist as its negative (the lack of thick gold in this region allows x-rays to impinge on the PMMA, sensitizing it for development to form open features in the resist). These features are in turn filled with electroplated metal, producing a final part after mechanical planarization and release from the substrate as shown in (b). Layout image courtesy of M. Hekmati and L. Hunter of Sandia National Laboratories, Livermore CA.

A fair amount of experience is involved in arranging the devices judiciously across the wafer so as to facilitate subsequent processing. For example, a certain minimum separation distance between features may be desired to avoid thin, fragile areas of resist. Also, since large regions of uninterrupted resist tend to lead to significant physical distortions due to swelling and thermal expansion, ancillary structures may be added to improve the dimensional fidelity of features in critical regions. Where dimensional tolerances are of particular concern, these ancillary structures are placed close to and conformal to part features. The intent is to minimize the uninterrupted length of resist immediately adjacent to these critically dimensioned structures, reducing the overall swelling and CTE-driven distortions. This also has the beneficial effect with respect to the electrodeposition process itself. By placing openings in large unpatterned areas of the resist, these ancillary features improve the homogeneity of the overall wafer with respect to the “active area density”,¹⁶ making the pattern scale current distribution more uniform. This improves the overall uniformity with respect to deposition rate which in turn, may favorably

influence material properties and structure. In Figure 3a, the moat-like features surrounding the spring geometry are an example of a structure serving these purposes, and as an added benefit, they can be used as sacrificial samples for materials analysis. One other benefit derived from these ancillary structures is the fact that they help support critical features during planarization and lapping, avoiding the tendency for fine features to lap faster (resulting in thinner in-plane dimensions) than neighboring large features. Once an acceptable layout of desired parts is obtained, one may proceed with the production of the x-ray absorbing mask.

Mask Substrate — The fabrication procedure for an x-ray mask mainly depends on the particular x-ray spectrum at the synchrotron facility. Thicker absorbers are typically needed when the x-ray energies used are relatively high, and the exact absorber thickness required for a given x-ray spectrum has been worked out by a number of groups.^{2,17-18} Electrodeposited gold is usually used as the absorbing material, although other materials and deposition processes have been investigated.² We will limit our discussion to the more common method that involves the use of electroplated gold.

For low absorber thicknesses ($<10\text{ }\mu\text{m}$), thin metallic membrane substrates can be used; this is usually the situation at synchrotron beamlines delivering a soft (low energy) x-ray spectrum. At such soft sources, the substrate must be sufficiently “transparent” to x-rays to allow them to pass through the unmasked regions. Titanium has been used as an x-ray transparent membrane for this purpose (as well as other materials).² In this instance, after patterning and deposition of the absorber gold, the titanium is partially etched away from the area of interest (usually the center of a wafer) resulting in an x-ray transparent membrane that is supported by thicker annular ring or “picture frame” of Ti. For harder x-ray sources, thicker absorbers ($>10\text{ }\mu\text{m}$) must be used, and the substrates are required to have greater mechanical integrity to support the patterned absorber gold. For this mask type, silicon and beryllium are often used as sheet substrates in thickness that can range from $100\text{ }\mu\text{m}$ to $500\text{ }\mu\text{m}$. If the substrate is not conductive, a thin metallization layer is applied. Since the x-ray spectrum employed is fairly hard in this situation, x-ray transparency in the unmasked regions is generally of less concern.

Mask Photoresist — The next step, the patterning of photoresist, is the same for either approach. Commercially available photoresist of a desired thickness is patterned by standard contact UV lithography to define the pattern layout geometry on the mask. Where the gold is deposited (whether as the positive or negative of the feature to be fabricated) depends on the development characteristics of the mold photoresist used to pattern the structures to be electroformed. This is the so called “tone” of the mask. Regardless, only the active (electrically conductive) areas

receive the plated gold. The thickness of the resist must be about 25 % higher than the target thickness of the deposited gold so as to not overplate the resist (which would reduce the dimensional fidelity of the final electrodeposited structures). Sulfite baths are often used for the gold deposition to avoid damaging the UV mask photoresist. After gold deposition, the resist is usually removed from the mask by dissolution in a solvent.

Since high precision patterning of UV photoresist becomes more difficult with increasing resist thickness,² thin absorbers on membrane masks yield the greatest precision for small features. Sheet substrate masks with thicker absorber gold may be mechanically more robust, but tend to be used for less demanding, more routine LIGA prototyping where high tolerances are less critical. These sheet substrate masks are convenient as the entire wafer area is available for processing, whereas for membrane masks, only the thinned region may be used. Generally speaking, for mask resist measuring a few microns in thickness, features may be reliably defined down to about a micron in width, although process limits will vary with lithography infrastructure at a given laboratory.² More advanced techniques for defining finer features for submicron LIGA will be discussed at a later point.^{2,7}

Mold Exposure— After an x-ray mask is in hand, the next step in the LIGA process is the exposure at a synchrotron to produce molds for the subsequent electrodeposition step. The molds, consisting of wafers bearing PMMA photoresist of a desired thickness, must be prepared in advance. This entails the bonding of a disk of PMMA to the wafer that has been metallized with a conductive seed layer for subsequent electrodeposition. The exposure of these molds necessitates a substantial level of infrastructure. At a minimum, an apparatus for holding and translating the mold so as to expose the entire wafer to the x-ray beam is required. More sophisticated equipment is necessary for more advanced exposure techniques, such as angled exposures to produce graded sidewalls, or alignment tools for multilevel processing that require multiple masks and x-ray exposures.² The mask is placed between the x-ray source and the mold, allowing the x-rays to pass through the areas where there is no gold absorber. The x-rays that pass through the mask impinge on the PMMA, scissioning the PMMA polymer chains, thereby sensitizing it to dissolution in the subsequent development step. The exposure times are dictated by the characteristics of the x-ray source, beamline parameters (mirrors and filters), mask substrate material and thickness, and finally, the thickness of the PMMA resist.¹⁷

Mold Development and Seed Layer Preparation— After exposure, the x-ray exposed regions of the PMMA may be dissolved by immersion of the mold in an appropriate chemical developer. Developers are mixtures of various organic solvents formulated to selectively dissolve the

exposed PMMA while leaving behind undissolved, unexposed PMMA. In this way the geometry of the discrete structures on the mold are defined. Dissolution times depend on the mold thickness and specific development conditions, but typically range from a few minutes to several hours. When development is complete (confirmation may necessitate observing features under a microscope to check for residual PMMA at the bottom of the exposed mold features), the mold is rinsed with deionized water and dried.

Depending on the metallization applied to the wafer, certain dry or wet etching processes may be necessary after development to fully reveal the desired metal seed layer. A number of materials have been used as conductive seed surfaces in LIGA.¹⁹⁻²⁰ Since the x-rays may interact with the seed layer material during exposure, some consideration must be given to the choice of metal used. These interactions often involve the emission of secondary radiation that may damage (overexpose) the PMMA/wafer interface. These aspects will be discussed in more detail in the electrodeposition section.

Electrodeposition—In order for the electrodeposition reaction to start, the seed surface must be first wetted by the electrolyte. This is usually accomplished by immersing the mold in water that has been de-aerated, as condensed gases in aerated water may form bubbles within the developed cavities of the mold. The container of water with the immersed mold is then placed in a chamber where a vacuum is used to facilitate the penetration of water into the mold features. A surfactant may be added to the water to lower its surface tension, further facilitating the wetting of the features. After the features are filled with water, the mold is then placed in the desired bath for electrodeposition, where the water in the features mixes with the bulk electrolyte. Depending on the feature geometry, some time is given for this mixing to occur before the electrodeposition of the mold is started.

Planarization and Release—Electrodeposition is complete when all of the patterned features exhibit some degree of overplating. Due to wafer and pattern scale effects, the local deposition rate varies from point to point on the wafer, so the extent of overplating varies across the mold. This overplating must be removed mechanically, by grinding and/or lapping off the excess metal. Grinding is followed by a planarization step, yielding a mold with both the final desired thickness and an appropriate surface finish. After planarization, the PMMA is dissolved in a solvent such as acetone if the parts are to be freed from the wafer and used individually (direct LIGA).

However, in some cases, a new, thick metal layer is deposited on top of the planarized surface to form a structural backing on top of the plated features in order to use the LIGA mold as an embossing tool for replication. Another way to accomplish the same end is by simply allowing the electrodeposited metal to grow completely out of the features, coalesce, and form into a monolithic metal disk. These latter two approaches are illustrated schematically in Figure 4.

Figure 4 Process schemes for producing a thick tool bearing LIGA features for subsequent embossing or injection molding.

(top) The LIGA mold is planarized so a new metal seed layer may be applied to the top of the mold, typically by vacuum deposition. A layer of thick Ni is then electroplated over the seed layer, after which the resist is dissolved and the substrate removed (either chemically or mechanically).

(bottom) Electrodeposition is allowed to continue up and out of the resist until the overplated regions coalesce into a solid Ni piece. The substrate is removed as described in the prior approach. For this technique to work, it is necessary for the parts to be located close to one another so the overplated regions can join together.

After dissolution of the PMMA, if the plated features are going to be used as individual microparts themselves, the plating base layer must be dissolved to liberate the individual structures. Since copper is often used as a plating base and the LIGA structures themselves are often Ni or Ni alloys, chemical solutions selective to Cu may be used to dissolve the plating base, leaving the Ni unaffected. The microparts may then be collected and sorted for post-processing metrology or testing required for the desired application.

LIGA History

Electrodeposition into features defined in resist by electron beam and x-ray lithography was first explored in the late 1960's and early 70's by Romankiw and coworkers at IBM.²¹ Also, the through-mask plating technology for producing gold x-ray masks necessary for x-ray exposures was developed by the same workers during this period. At the same time, through-mask electroplating was already becoming a preferred technique for the realization of patterned metal structures in the electronics industry for packaging and memory applications. It was thought possible that x-ray lithography would become necessary to replace optical lithography for features less than one micron. Romankiw gives a thorough review of the role of through-mask electroplating in the early stages of e-beam and x-ray lithography.²¹ Figure 5 shows one of the earliest x-ray masks fabricated by Romankiw and coworkers by through-mask electroplating of gold using first an e-beam fabricated mask and subsequent x-ray lithography. The x-ray sources used up to 1973 by the group at IBM were laboratory sources and hence low power. That year, high power x-rays from a synchrotron in Hamburg, Germany were employed by the IBM group to fabricate features in PMMA resist 12 μm thick and 1 μm wide. The separation between the features was 0.1 μm . Gold was electrodeposited to a thickness of 6 μm to fill the features, resulting in the first through-mask deposited structures in PMMA patterned with synchrotron radiation. These structures are shown in Figure 6. Since such high aspect ratio features were not required for electronic devices, subsequent work by the group at IBM focused on thin structures having small lateral dimensions.

Figure 5 X-ray absorbing masks produced by Romankiw *et. al.* by gold electrodeposition.¹⁹ Photoresist patterns are on the left, while electroplated gold patterns are shown on the right. The top two images are from the original e-beam fabricated mask, resulting in an x-ray negative copy in the middle. The pattern was inverted another time to return to the original tone in the bottom two images. Micrographs reproduced from ref. 21 courtesy of Elsevier.

Figure 6 Patterned PMMA 12 μm in thickness (left) exposed at the DESY accelerator in Hamburg and corresponding electroplated gold structures (right) as shown by Romankiw in ref. 21. The resist pattern linewidths are 1 μm with 100 nm spacers, resulting in electroplated gold structures spaced 100 nm apart. Micrographs reproduced from ref. 21 courtesy of Elsevier.

By the early 1980's, investigations involving the fabrication of structures using features defined in thick PMMA resist by x-ray synchrotron radiation and subsequent electrodeposition were in progress at the Forschungszentrum Karlsruhe (FZK), in Karlsruhe, Germany. In this case, the researchers were not interested in the fabrication of electronic or magnetic devices but instead in structures meant to be used for the isotopic separation of uranium.¹ Apparently, the critical features of the device needed to be not only very narrow but also very tall (i.e., high aspect ratio) for the separation process to work. X-ray lithography, with its capability to precisely form features having very small lateral dimensions in thick resist, was thus understandably an attractive fabrication technique for such structures. An example of one of the first devices fabricated at FZK is shown in Figure 7. The potential of the technique relative to the fabrication of structures for microsystems became apparent, and work continued on electroplating through PMMA resist to produce structures for other applications.^{3,4,22}

Figure 7 Patterned PMMA (left) and corresponding through-mold plated Ni nozzle structures for gas isotope separation (right) fabricated at the Forschungszentrum Karlsruhe.¹ The openings in the Ni of closest approach are about 3 μm . Micrographs reproduced courtesy of Springer-Verlag.

Figure 8 Example of Ni test gear device formed from electrodeposition through a patterned PMMA mold. Micrograph courtesy of Georg Aigeldinger, Sandia National Laboratories, Livermore, California.

Furthermore, the researchers at FZK were interested in using x-ray lithography to form a metal master tool that would be subsequently used to mass-produce structures (presumably plastic) *via* embossing or injection molding processes. Thus, the German acronym LIGA, used generally to refer to electroplating through thick resist to form metal structures, includes the word *abformung*, indicating the intention of using the metal structures as a tool to mass produce or replicate patterns.

Subsequent to the establishment of the LIGA process at FZK in the early 1980's, x-ray lithography efforts elsewhere in the world began to appear, naturally centered at synchrotron facilities in Europe, Asia, and North America. Since then, a large body of LIGA research has been published in the literature and presented at international conferences. An attempt to comprehensively summarize the LIGA work that has been done over two decades would be beyond the scope of this chapter; thus, only a relatively small number of articles and presentations are referenced where appropriate to the topic at hand.

It must be noted that many researchers worldwide (the current authors and their colleagues included) use x-ray lithography as a tool for fabricating a mold of structures, with the intention of using the electroplated parts separately in some sort of assembly (usually a microsystem). Although such a process does not involve the replication (*abformung*) step, practitioners still typically use the term LIGA to describe their work (occasionally this is referred to as “direct LIGA” as we have previously indicated). Since synchrotron radiation is usually necessary for the thick resist exposure step, a large fraction of LIGA research groups are located in academic institutions or government-sponsored national laboratories. However, commercial companies have established their presence at such facilities, and some notable examples will be mentioned in the next section discussing applications of LIGA technology.

LIGA Applications

In surveying the numerous articles and presentations involving the use of the LIGA technique, it is evident that an equally large number of applications for LIGA-enabled structures have been proposed. However, over the course of the technology's twenty-year or so history, only a few of these proposed applications have been developed into commercial products. The need for an x-ray synchrotron source, no doubt an issue for those wishing to adapt the technology for larger-scale production, has been alleviated somewhat by the fact that most synchrotron facilities have active programs for allowing access by researchers and industry.¹⁴ In this section, we will discuss only the most popularly reported applications, with some emphasis on those that have been commercially realized to give the reader a general idea of the types of applications of interest. Good reviews are available for those interested in more detailed treatments of LIGA applications.^{2,11,13-15}

One of the most commonly discussed applications of structures fabricated *via* the LIGA process involves mechanical devices. Since lateral geometries in LIGA are defined lithographically,

very high dimensional fidelity is theoretically possible across large areas, enabling the batch fabrication of large numbers of precision structures simultaneously. Moreover, deep, high aspect ratio structures are possible if thick resist is used, desirable for structures to be used as active devices transmitting useful amounts of mechanical energy.[†] For example the amount of torque that a micromotor can deliver is directly proportional to the height of the motor itself. Further, the use of electrodeposition as an additive materials fabrication technique offers the possibility of a large materials set with interesting mechanical, magnetic, and electrical properties as compared to subtractive materials fabrication techniques such as silicon surface micromachining (some challenges in taking advantage of this potential materials set will be discussed in detail later).

Gears, actuators, rotors, and drivers have been fabricated *via* the LIGA method for a large variety of purposes (see ref. 15 and references cited therein). Figures 1 and 8 show examples of LIGA structures fabricated from Ni-based electrodeposits at Sandia National Laboratories, Livermore (SNL), CA. Mechanical structures designed as sensors (motion, magnetic, pressure) have also been fabricated *via* the LIGA process. An SNL Ni accelerometer prototype device is shown in Figure 9. Other LIGA researchers have fabricated similar structures; see for example, ref. 23 by Qu *et. al.* Christenson and Guckel have demonstrated several different types of mechanical devices, including linear and rotational actuators and micromotors.²⁴ An example of a mini-motor assembly is shown in Figure 10.²⁵ This device was fabricated by the group at IBM using optical lithography and through-mask plating. More examples of such devices can be found in Madou.²

Figure 9 Example of an acceleration-sensing prototype device fabricated by the LIGA process at Sandia National Laboratories, Livermore, California. The long, slender flexures are 25 μm wide and 250 μm tall; the entire width of the device is approximately 3 cm. A portion of the device is anchored in place, while another is free to move by the bending of the flexures, allowing for the sensing of acceleration. The device above is made of high-strength Ni.

[†] This is an important characteristic that distinguishes LIGA-fabricated microdevices from silicon MEMS technology.

Figure 10 Minimotor assembly composed of piece parts formed by through-mask plating of thick and thin UV-photoresist by workers at IBM.²⁵ Electroplated copper and a nickel-iron alloy was necessary for its fabrication. The plated Cu coils are 60 μm wide. Photograph reproduced with permission of the IBM Journal of Research and Development.

Another area of application for LIGA-fabricated devices is in the field of optical systems and communications. The ability to produce thick structures that are highly parallel, with optical quality sidewall roughness is useful in the fabrication of gratings, waveguides and lenses.¹⁵ These structures can be made from polymers that are directly patterned with x-rays, developed and used immediately afterwards. LIGA-fabricated structures have been developed for collimating grids for high resolution solar imaging missions²⁶ and adaptive optics systems in astronomy.²⁷ LIGA has enabled various connecting and mounting systems for optical fibers and components.^{2,15} The LIGA technique has been used to fabricate metal transmission lines with applications in the field of microwave and millimeter-wave integrated circuits.²⁸

The last area that can be broadly grouped as a LIGA application field is biological applications and microfluidics.^{15,29} LIGA tools for embossing patterns into plastic structures to be used as platforms in disposable biological or medical applications (“biochips” or “lab-on-a-chip” devices) are of special interest since such approaches are low in cost as compared to the direct

LIGA route.³⁰ LIGA tools have also been employed for the microstructuring of composite materials used as artificial bone analogues to improve bone cell growth conditions.³¹ A range of microfluidic devices have been proposed, such as microreactors, micropumps, nozzles, and microvalves.³²⁻³⁴ Both direct LIGA and the molding of plastic with a LIGA tool have been used for microfluidic device fabrication.³⁵

A few more applications that don't fit into the above categories are worth mentioning due to their unique use of LIGA technology. Spinnerets for synthetic microfiber production have been fabricated by LIGA to make high aspect ratio, narrow features of arbitrary prismatic cross section.^{2,13} These are essentially nozzles for the extrusion of polymer material; the LIGA technique allows for finer features with smooth sidewalls as compared to conventional fabrication methods. The simultaneous batch production of large numbers of nozzle structures is more rapid than conventional machining where one structure is formed at a time.

Microscale cross-flow heat exchangers have been fabricated using a LIGA embossing tool and subsequent replication steps to form Ni metal microstructures with higher heat transfer/volume ratios than conventional devices.³⁶ The possibility of using LIGA to form small Ni structures with micro-scale barbs for tagging has been explored and could be useful for military and law enforcement applications.³⁷ In the area of defense, industry is studying the use of LIGA technology to fabricate fusing devices for munitions.³⁸

Some progress has been made in the last few years in the development of LIGA-fabricated devices for commercial products. A number of optical, mechanical, and fluidic products are available from STEAG microParts, GmbH.³⁹ This company uses advanced injection molding techniques in combination with LIGA technology to make inhalers, microspectrometers, and lab-on-a-chip reaction platforms, as well as other microfluidic products. Zero-backlash gears and other precision positioning systems are fabricated by Micromotion GmbH using a LIGA-related technique (see Figure 11).⁴⁰ LIGA technology has been employed to make optical fiber connectors by Spinner GmbH in collaboration with FZK.¹⁵ In the U.S., Axsun Technologies, Inc., uses the LIGA technique to make alignment structures for photonics systems.³⁸

Figure 11 Precision position components fabricated by a LIGA-related process commercially available from Micromotion GmbH. Bottom image is a closeup of the gear assembly in the top photo. Photographs courtesy of Micromotion, GmbH.

As evidenced by this wide range of applications, the unique capability of the LIGA and LIGA-related techniques to fabricate high aspect ratio structures with a range of useful geometries has been known for several years. More recently, groups working on LIGA technology have started to focus on the fabrication of structures with special material properties. This often necessitates the consideration of materials other than electrodeposited Ni, in contrast to most of the examples discussed in this section. In the next section, we will discuss the unique challenges posed by the geometries encountered in the LIGA process during the electrodeposition of Ni and Ni alloys with special properties.

Electrodeposition into Deep High Aspect Ratio Features for LIGA

Introduction

The science and process sensitivities of electrodeposition through thin resist[‡] used to produce metallic conducting interconnects, packaging and contacts for the microelectronics industry have been much discussed.¹⁶ In contrast, electrodeposition through thick resist for deep, high aspect ratio LIGA features has received relatively little attention (although we note that one study involving design rules for the LIGA electrodeposition step has recently become available⁴¹). In surveying the literature where electrodeposition through patterned photoresist is discussed, it is evident that the microelectronics industry has devoted a significant amount of experimental and modeling resources to understanding through-mask electrodeposition (more detailed reviews of these developments are available).^{16,42} A central theme of the prior literature is the classification of three length scales over which electrochemical processes occur; the first, the workpiece scale, involves the distribution of current over the scale of the substrate or wafer; the second, the pattern scale, involves the distribution of current between features defined in the insulating photoresist; the third, the feature scale, involves the distribution of current to and within an individual opening or feature in the resist. These three scales are depicted in Figure 12 after DeBecker and West.⁴³ As will be discussed later, the principles governing the deposition of a metal structure or film having uniform thickness and properties over all these scales (usually desired for all electrodeposition processes) are largely the same, regardless of the final application. In terms of attaining uniformity *across* a substrate, the prior literature regarding the workpiece and pattern scales for electrodeposition through thin resist is directly applicable to electrodeposition through thick resist.

[‡] We define “thin” resist loosely as less than several microns, while “thick” resist is considered to be hundreds of microns to several millimeters.

Figure 12 Schematic illustration of the workpiece, pattern, and feature scales, redrawn from a similar graphic from DeBecker and West.⁴³ Groups of features are distributed across the substrate; these groups consist of a patterned array of features. The feature scale involves a single feature and its internal uniformity.

The important difference regarding metal deposition through thin and thick resist comes when *through-thickness* uniformity is considered; as the electrodeposited metal films for microelectronics are usually only a few to several microns in thickness, appreciable through-thickness variations in film structure do not usually occur since the thickness is so small. Moreover, any small microstructural deviation that may be present through the film thickness does not usually critically impact the function of the electrodeposited metal film in microelectronics. But in contrast to the thin films employed in microelectronics, large variations in deposit microstructure may occur over the hundreds of microns that comprise the through-mask electrodeposited thick films in LIGA. Since most of the issues in attaining uniformity across the substrate are similar to those in microelectronics, we will focus discussion rather on attaining through-thickness uniformity in structures electrodeposited through thick resist, a challenging aspect unique to LIGA.

Besides differences in resist and metal thicknesses, another major difference between films electrodeposited for microelectronics and microsystem applications lies in the choice of materials. In microelectronics, the metal films are serving as conductors or contacts; hence, materials such as copper, gold, and lead-tin alloys (more recently lead-free alternatives are under

development) have attractive physical properties and are widely employed. In microsystems, the thick metal structures are typically serving as components in some mechanical device or as a replication mold; the mechanical properties are thus of most interest in these situations. Electrodeposited nickel has a long history of use as a structural material since its mechanical properties may be tailored by the use of alloying elements and electrolyte bath additives (both organic and inorganic).^{8,44} Depending on deposition conditions and chemistries, Ni may be electrodeposited with low stress, making thick films possible. The generally good corrosion resistance of electrodeposited Ni also makes it attractive for mechanical applications in a wide variety of environments. The material properties of Ni and Ni alloys will be discussed in more detail later in the chapter. In comparing electrodeposition processes for thin and thick resists, we will keep in mind that the materials that are deposited into these lithographic molds may have very different deposition characteristics as well.

Workpiece and Pattern Scale Effects

In prior treatments of through-mask electrodeposition, the first length scale often identified is the workpiece scale; this is usually the characteristic length of the substrate (or wafer) itself onto which resist defining the desired structures has been applied. Variations in the local current density typically occur over the workpiece scale. The cell geometry, the size of the substrate, and other deposition parameters dictate the uniformity across the substrate; the degree of this uniformity may be described by the Wagner number, a dimensionless parameter that has been discussed in more detail previously.¹⁶ Generally speaking, if no measures are taken to improve the current distribution across the wafer, regions close to the edge will have a locally higher current density than areas near the center of the substrate.

A few different approaches may be used to render the current distribution across the wafer more uniform. The appropriate placement of insulating shields with respect to the wafer may result in a more uniform current distribution.⁴⁵ The use of auxiliary electrodes (also known as thief electrodes) in minimizing variations across the workpiece has been discussed previously.⁴⁶ For example, another cathode placed around the workpiece (as a type of surrounding “frame”) may improve the workpiece current distribution significantly. In industrial plating tools, all these aspects are carefully considered in optimizing the wafer scale uniformity. Obviously, since a large number of wafers are typically run under fixed conditions in the microelectronics industry, a fair amount of time and effort is spent in finding the optimal cell geometry and deposition conditions. These approaches for homogenizing the wafer scale

uniformity are directly applicable to electrodeposition through thick resist in LIGA, and have in some cases been adopted.⁴⁵

The second length scale is referred to as the pattern scale. The relative amounts of exposed active metal and insulating photoresist may vary across the substrate due to the geometry and layout of the pattern defining the structures to be electrodeposited. Thus, the “active area density” varies depending on essentially the distribution of the insulating resist material. This leads to variations in the local current density (the deposition rate) depending on the local pattern geometry in the resist. Mehdizadeh *et. al.* studied this problem for electrodeposition through photoresist having various pattern densities.⁴⁷ West *et. al.* considered the effect of patterning on multiple electrodes of disks and lines.⁴⁸ These and other studies^{16,49} may be drawn upon in designing layouts where pattern scale effects are minimized.

In our experience, LIGA pattern layouts that consist of an array of uniformly spaced features having similar dimensions are not commonly encountered; instead, patterns tend to consist of fine features (dense resist areas) located in close proximity to large, open areas of exposed seed metal (defining a wide, low aspect ratio feature). Thus, pattern scale effects must be managed on a fairly routine basis. Although it may not be possible to alter the particular part geometry and size (necessary for the device function), some discretion may be exercised in distributing the features in the resist defining the part geometry so as to mitigate pattern scale effects. Moreover, sacrificial features (openings in the resist) may be added to the pattern to break up areas that have long runs of uninterrupted insulating resist, resulting in a more uniform active area density distribution.⁴⁶⁻⁴⁷ This practice of inserting sacrificial “moats” or “frames” around features where dimensional fidelity is critical was previously mentioned with regard to minimizing dimensional errors due to PMMA swelling and thermal expansion after immersion in the electroplating bath.⁵⁰ It is somewhat fortuitous the same measures that aid in minimizing these dimensional errors in LIGA also may help in rendering the pattern scale current distribution more uniform. Mehdizadeh *et. al.* have discussed the possibility of carefully considering the wafer and pattern scale current distribution and arranging features in the resist across the workpiece so as to attain a more balanced current distribution.⁴⁷ Even when detailed current distribution models are unavailable, past experience can be a useful guide in judiciously arranging the part layout to avoid uneven distributions of current at the pattern scale.

Feature Scale Effects

As mentioned previously, the similarity between microelectronics processing and LIGA through-mask electrodeposition diminishes as one moves from the workpiece and pattern to the feature scale. The principal reason for this is the large resist thicknesses typically employed for x-ray lithography. As pointed out by Dukovic,¹⁶ at the feature scale, the dimensions of the lithographic features are usually small enough (microns) that electrical field effects become less important, and the influence of the concentration field of the reacting species grows in determining the feature scale current distribution. Since mixing is limited inside the feature due to the presence of the surrounding resist material, the concentration of a reacting species may vary with position within the feature. Another aspect that must be considered for both thin and thick resists is that as deposition proceeds, the feature geometry changes as the deposited metal fills the feature. Generally speaking, obtaining good mixing inside lithographic features becomes more difficult with increasing resist thickness.

When the electrodeposition reaction involves just a single metal cation, variations in its concentration inside the feature typically result in variations in the local rate of deposition and therefore deposit thickness.⁵¹ The deposition characteristics of copper, gold, and tin alloys through relatively thin resists (less than 20 microns) for bump structures have been considered with attention to the thickness distribution of the deposit within a single feature.⁵²⁻⁵⁷ It is desirable that these bump structures have good as-plated uniformity for subsequent packaging processing. Another example of an important feature scale electrodeposition problem is the case of copper Damascene electrodeposition for copper interconnects;⁵⁸ for this process, proprietary electrolyte bath additives and active feature sidewalls lead to more complicated feature-filling behavior, despite the fact that only a single elemental species is being deposited.^{59,60} The understanding and control of through-mask electrodeposition at the feature scale has undoubtedly been important in enabling the use of these processes for the large-scale manufacturing of microelectronics packaging and copper interconnects.^{16,42}

In the case of electrodeposition through thick resist for LIGA, the importance of the feature scale is not its influence on the local deposit thickness uniformity (the wafer is planarized after plating, removing thickness variations across the wafer at all scales). Rather, it is the more serious issue of poor mixing in the mold features themselves due to their small widths and large heights. This has broad implications with respect to the potential for variations in the concentrations of electrolyte species that may, in turn, impact the local deposit composition, morphology, and properties. For example, if additives or other metal species are present as alloying elements,

profound changes may occur through the thickness owing to the constantly changing feature geometry that accompanies the metal growth. If the concentration of one of these species is close to zero at the feature bottom (due to its rapid incorporation into the deposit, for example), large changes in the flux of this species will occur as the deposit grows and the diffusion length from the bulk electrolyte shortens. The resulting non-uniform deposit morphology or alloy composition may be unacceptable for some applications. The electrodeposition of the NiCo and NiMn systems and the resulting feature scale uniformity will be contrasted to demonstrate the importance of transport into LIGA features later in the chapter.

Interesting experiments involving the feature scale were carried out by Leyendecker *et. al.*⁶¹ These authors studied the effect of thick photoresist on mass transport and on the pH within a LIGA feature using special electrodes. In the first series of experiments, a rotating disk electrode masked by an insulating patterned polymer layer of various thicknesses and feature sizes is employed to study a model redox reaction occurring under transport control. The aqueous electrolyte consists of 2 mM potassium ferro- and ferri-cyanide each in 1 M potassium chloride at 25 °C. Results of their experiments are reproduced in Figure 13; although various geometries were investigated, they present results for a constant hole diameter of 200 μm and resist heights of 100, 200, and 500 μm (in addition to an unmasked electrode).

Figure 13 Limiting current densities for ferri-ferro cyanide redox couple on bare and patterned rotating disk electrodes replotted from the results of Leyendecker *et. al.*⁶¹ Feature hole diameter is 200 μ m. The presence of the resist has a large effect on the transport of species to the feature bottom, even for an aspect ratio of one. Solid points are the bare rotating disk electrode, while the hollow points are electrodes patterned with resists of various thicknesses as indicated.

In the case of an unpatterned, bare rotating disk, good linearity is obtained as expected by plotting the limiting current density as a function of the square root of the electrode rotation rate, $\Omega^{0.5}$. When the electrode is covered with photoresist, the difficulty in generating mixing into the features becomes evident. For a hole diameter of 200 μ m and a resist height of 100 μ m (an aspect ratio of 0.5) the measured limiting current densities are close to those on the bare electrode. But for a resist thickness of 200 μ m (aspect ratio 1), the measured limiting current densities are much lower than for unpatterned electrodes and the electrode with 100 μ m of resist. Even at this modest aspect ratio, increasing the electrode rotation rate becomes less effective at transporting reactant to the electrode surface, resulting in a flatter curve for the 200 μ m thick resist in Figure 13. When the resist thickness becomes 500 μ m (aspect ratio 2.5), almost no increase is obtained in the limiting current density with increasing rotation rate. This is somewhat

surprising, since if metal deposition through thick resist occurred under transport control, one would expect impractically low deposition rates to be necessary for the deep, high aspect ratio features used in LIGA process. In fact, structures with aspect ratios of 10 having appreciable thicknesses (hundreds of microns) are not uncommon, and, while on the low end of the current density operating range, these structures are typically deposited at rates that are not drastically lower than those conventionally used in electroplating and electroforming. The reasons for this seeming discrepancy will become apparent when other modes of transport are discussed.

In the same paper,⁶¹ Leyendecker *et. al.* perform a second series of experiments investigating the pH behavior within a deep, high aspect ratio feature as Ni is electroplated into the feature. As the current efficiency during Ni electrodeposition is not always 100%, the pH may rise close to the cathode surface (especially in a feature in thick resist), resulting in the presence of adsorbed hydroxide species that may affect the deposit morphology. Since Ni is often electrodeposited for LIGA applications, these experiments are highly relevant.

Special PMMA structures were fabricated by laminating three 10 μm thick antimony metal foils in between 240 μm thick PMMA layers; the laminated structure was then bonded to a metal substrate. Microholes were drilled through the layers until the conducting substrate was reached. The final structure thus consists of a metal plating base with four levels of PMMA separated by the antimony sheets, through which arrays of microholes are drilled, the entire piece approximately 1000 μm in thickness. Figure 14 is a schematic diagram of the laminated structure taken after Leyendecker *et. al.*⁶¹ The antimony metal acts as a pH sensor due to the pH-dependent equilibrium with its oxide. The Sb/Sb₂O₃ system has been used previously as a pH probe. By monitoring the potential between the antimony sheets and a reference antimony electrode in the bulk electrolyte, the authors could study *in situ* the pH in the LIGA feature as Ni electrodeposition occurred. This is the only study of its kind in the literature of which the current authors are aware.

Figure 14 Diagram of special pH electrode used by Leyendecker *et. al.*,⁶¹ redrawn after a similar sketch that was reported.⁶¹ Feature hole diameters of 200, 100, and 50 μm were considered. The Sb sheets embedded in the PMMA resist function as *in situ* pH electrodes, allowing for the monitoring of local pH within the features as electrodeposition proceeds from the cathode at the bottom of the features.

Results of filling these features were given in this paper for the 200 μm dia microholes. They are reproduced in Figure 15. Nickel is deposited into the features at 50 mA/cm^2 from a sulfamate bath (76 g/L Ni and 40 g/L boric acid) at 52 $^{\circ}\text{C}$ and a bulk pH of 3.8. Since the exact depth of the drilled features was not known (the drilling proceeded some distance into the bulk metal piece used as the plating base), deposition occurs until the first Sb layer is overgrown. At that point, plating is stopped (the position of the Ni deposit surface within the features is then known) and the experiment paused until the pH in the feature returns to the bulk pH. Then, plating resumes, with the potential of the 2nd Sb layer monitored until the growing Ni deposit reaches this Sb layer. Ni deposition continues from that point with the potential of the 3rd Sb layer then being monitored until it too is overgrown by the Ni deposit. Thus, the zero value on the x ordinate in Figure 15 represents the point when the Ni is even with the first Sb layer (about 750 μm from the feature mouth into the bulk electrolyte). The plotted values represent the pH measured at the respective Sb layers (fixed in position) as the Ni fills the features in the laminated structure. The pH at the 2nd Sb layer (500 μm from the feature mouth) is as high as 5.5 when the Ni deposition begins. As it grows, the 2nd Sb layer pH value drops towards 4.5. After the Ni deposit grows past the 2nd Sb layer, the 3rd Sb layer (itself 250 μm from the feature mouth) is monitored. The measured pH values at the 3rd Sb layer are just slightly higher than the bulk value of 3.8. Finally, when the Ni deposit has grown to a point just below the depth of the 3rd Sb layer, the pH at that position is close to that in the bulk.

Figure 15 In situ pH measurements from the pH electrode structure shown in the previous figure, replotted from Leynacker *et. al.*⁶¹ In this case, the hole diameter of all features is 200 μm. The inset helps one visualize the position of the Sb pH electrode layers with respect to the growing Ni deposit. A Ni sulfamate bath was used operating at 50 °C and a current density of 50 mA/cm².

These results are important for a number of reasons. First of all, although the PMMA feature thickness corresponding to the zero position on the x axis is 750 μm, the aspect ratio of this feature is only 3.75, which is not considered to be very aggressive for LIGA electrodeposition (aspect ratios of 10 to 15 approach the high end of what is commonly fabricated). Despite this modest aspect ratio, the measured pH 500 μm from the feature mouth is as high as 5.5; if the pH near the growing Ni surface is this high or higher (a likely case, since protons are consumed at the interface) the deposit morphology could be profoundly influenced. Deposition at high pH values has been typically associated with high hardnesses and the possible incorporation of oxygen into the deposit, presumably from hydroxide species adsorbed at the deposit surface.^{8,44,62-63} As the deposit grows, the microstructure of the deposit may therefore change as the feature opening is approached and the pH drops towards its value in the bulk electrolyte. If the pH value reaches extremely high values, the impurities in the deposit from hydroxide species may compromise its material properties. Another issue is that the increasing pH is indicative of hydrogen generation within the feature; if the hydrogen trapped within the feature accumulates

and forms a bubble, it may be occluded into the deposit as a defect that can lead to failure. These issues are of real concern for structures that will be used in mechanical applications, especially for structures having aspect ratios more extreme than those considered in Figure 15.

Another series of experiments relevant to the feature scale in LIGA involving transport limitations is reported on by Griffiths *et. al.*⁶⁴ They use a commercial Ni sulfamate plating electrolyte to deposit Ni into features drilled into PMMA. A single piece of Cu foil attached to one side of the PMMA acts as the substrate, from which the deposited Ni structures could be removed for weighing in the determination of the current efficiency. Current densities range from 1.1 to 108 mA/cm², and an electrolyte temperature of 38 °C is employed. The drilled holes have diameters of 1.7, 3.2 and 6.4 mm and depths from 17 to 42 mm. They also calculate the Sherwood number (the ratio between the measured current to the diffusion-limited current) for each case.

The experimental results are surprising in that the Sherwood numbers are all between 10 and 100, indicating a much larger deposition current than expected based upon the diffusion-limited case. The data for the experimental conditions they reported are reproduced in Table 1.⁶⁴ Measured current efficiencies indicate that hydrogen evolution

TABLE 1. EXPERIMENTAL DATA FROM GRIFFITHS *ET. AL.*⁶²

Cavity Diameter (mm)	Feature Aspect Ratio	Current Density (mA/cm ²)	Current Efficiency	Sherwood Number
1.7	10	11	99.7	48.0
1.7	15	86	96.4	82.2
1.7	25	86	89.6	137.5
3.18	8	86	99.5	82.2
6.35	1.6	108	100.9	41.1

accounts for only a few percent of the total current (except in one case, where the current efficiency was only 89%), suggesting that the large current densities are associated with the metal deposition reaction itself. They also indicate their results were reproducible, further suggesting that the observed behavior was not due to hydrogen evolution. The authors explain the unexpectedly high currents as resulting from enhanced transport of the reacting metal ion due to natural convection in the feature driven by its depletion at the substrate. This hypothesis is

further supported by the fact that when the experimental cell was inverted, the measured currents were an order of magnitude less than with the deposition surface facing up.

These authors go on to demonstrate by numerical modeling that flow across the top of the features cannot support the transport of the reacting metal ions at the observed rates, and that instead buoyancy-driven flows are probably important in allowing such high deposition rates.⁶⁴ Nilson and Griffiths present more detailed calculations of natural convection in high aspect ratio trenches in a subsequent article.⁶⁵ They find that the relative importance of natural convection depends on the feature geometry and the inclination of the substrate. The authors conclude that some mixing from natural convection is expected to occur in features having aspect ratios less than 1.2, 6.6, and 37 for resist thicknesses of 0.1, 1.0, and 10 mm, respectively. Thus, natural convection becomes important for a wider range of feature aspect ratios as the resist thickness increases. Since resist thicknesses in microelectronics are usually only tens of microns or less, the importance of convective flow had not been widely discussed until electrodeposition into deep LIGA features was considered. It is interesting to contrast the findings of Leyendecker *et al.*,⁶¹ discussed at the beginning of this section, with those of Griffiths *et al.*⁶⁴ In the former case, the insulating PMMA mask was shown to have strongly diminished mixing, resulting in lower transport rates of the reacting ions, while in the latter case, buoyancy-driven transport rates into deep high aspect ratio features higher than those expected from pure diffusion control were observed. Since Leyendecker *et al.* used a redox couple to measure transport rates through microstructured electrodes, they were not able to benefit from potential buoyancy-driven flows induced by the consumption of metal ions at the feature bottom.

Another series of studies focusing on feature scale uniformity in LIGA was carried out by Schwartz and coworkers.⁶⁶⁻⁶⁸ Leith *et al.* considered the electrodeposition of NiFe at 23 °C from sulfamate-chloride chemistries having various ratios of Ni to Fe electrolyte loadings.⁶⁷ They pointed out that the plating characteristics of an electrolyte must be carefully considered before employing it for through-mask electrodeposition using thick resist. They found that electrolytes having less dissolved iron (for example, 20:1 Ni²⁺:Fe²⁺ as opposed to 10:1 and 5:1 also considered in their study) are less sensitive to mixing variations at relatively high current densities, suggesting that they would be more suitable for the electrodeposition of LIGA structures. Leith and Schwartz also describe a cell designed to maximize workpiece and pattern scale uniformity, using the NiFe system (since it is a challenging system for uniformity) to demonstrate good uniformity across the wafer.⁶⁷ The through thickness uniformity was not investigated in this study.⁶⁷ In another article, Wang *et al.* used an electrolyte with a 10:1 Ni²⁺:Fe²⁺ loading (where the deposited NiFe alloy composition is more sensitive to mixing) to

study convective-diffusion conditions during the through-mask deposition of LIGA structures.⁶⁸ They term the approach “process archaeology” since the plated structure was planarized to half its deposited thickness for compositional analysis *via* energy dispersive x-ray analysis.⁶⁸ By observing in plan view the planarized structures, regions in the feature where locally high degrees of mixing occur could be easily identified since the Fe content of the alloy increases with mixing. In this case, the authors were using the transport-sensitive deposition kinetics of the Fe as a type of “tracer” tool to study the mixing within small cavities such as LIGA resist features.

Another group of authors also considered the NiFe system to focus on the feature scale uniformity of through-mask deposited LIGA structures. Thommes *et. al.* used a sulfate-based NiFe electrolyte at 50 °C with a $\text{Ni}^{2+}:\text{Fe}^{2+}$ ratio of about 12:1 to deposit NiFe structures at 5 mA/cm² with good through-thickness uniformity.⁶⁹ Figure 16, reproduced from their data, shows the compositional behavior of the deposition system using a rotating disk electrode. It is clear from Figure 16 that for low current densities the electrode rotation rate does not influence the deposited alloy composition, suggesting that under these conditions the alloy composition is not greatly influenced by the amount of mixing. This relative insensitivity to mixing would appear promising for the feature scale uniformity of LIGA NiFe structures.

Figure 16 Electrodeposited NiFe alloy: Composition dependence on deposition conditions, for conditions given by and replotted from Thommes *et. al.*⁶⁹ The relative compositional insensitivity at low current densities suggests that the system may be appropriate for the electrodeposition of uniform, high aspect ratio structures.

The suitability of the authors' deposition conditions for the electrodeposition of uniform high aspect ratio NiFe microstructures is evidenced by the through-thickness compositional data shown in Figure 17. For a resist thickness of 180 μm and a feature linewidth of 8 μm (aspect ratio 22.5), the authors obtain very good NiFe alloy uniformity throughout the entire structure thickness using a deposition current density of 5 mA/cm^2 . Through-thickness uniformity suffers at higher deposition current densities. Figure 17 also shows experimental results for deposition at 14 mA/cm^2 using the same feature geometry. The Fe content increases through the deposit as the top PMMA surface is approached, varying from about 20% to 50% across the thickness. Though not shown here, the authors filled cylindrical features with a diameter of 5 μm and a height of 90 μm depositing NiFe at 5 mA/cm^2 . They show similarly good results as for the structure in Figure 17 deposited at the same current density.

Figure 17 Electrodeposited NiFe alloy composition through-thickness uniformity replotted from Thommes *et. al.*⁶⁹ The structure width is 8 μm and its height is 180 μm. Deposition at the lower current density (where composition was shown to be less sensitive to mixing) leads to uniform alloy content through the structure thickness. Deposition at the higher current density, 14 mA/cm² resulted in extreme compositional gradients.

The electrodeposition process outlined by Thommes *et. al.* has been shown to be capable of producing high aspect ratio structures with good alloy through-thickness compositional uniformity.⁶⁹ To the authors' knowledge, few other studies exist of alloy deposition through thick resist where the feature scale uniformity is considered in such detail. An aspect that is likely important in explaining the good results obtained by these authors is the bath temperature; Brenner has discussed the fact that NiFe electrodeposition becomes less anomalous (and hence less transport sensitive) with increasing bath temperature.⁷⁰ Andricacos and Romankiw also discuss the importance of bath temperature as well as other process variables on electrodeposited magnetic alloy composition.⁷¹ Given the limitations in obtaining good mixing in small LIGA features, it is not surprising that achieving good feature scale uniformity for anomalous deposition systems (such as NiFe) is challenging for geometries encountered in LIGA electrodeposition.⁷⁰⁻⁷¹

New techniques are being employed for studying the electrodeposition reaction inside of small features like those fabricated by the LIGA process; for example, special microelectrodes and chronoamperometric methods have been developed to measure the local metal cation concentrations during alloy electrodeposition inside small cavities.⁷² Kuepper and Schultze study concentration variations inside of a cavity where a NiCu alloy is being electrodeposited;⁷² they also observe the formation of a Ni hydroxide and nickel oxide at the deposition surface during electrodeposition of the NiCu alloy from a sulfate electrolyte with potassium nitrate as supporting electrolyte. It is likely that specialized, *in situ* techniques such as those used by Kuepper and Schultze⁷² and others⁶¹ will yield new insights into electrodeposition into deep, high aspect ratio features.

Summary: Uniformity at the Workpiece, Pattern, and Feature Scales in LIGA

The detailed study of Thommes *et. al.* is a good example of the considerable effort required to develop an electrodeposition process capable of producing uniform structures at the feature scale for geometries encountered in LIGA electrodeposition. When mixing effects are important (as often the case in Ni-alloy deposition),⁷⁰⁻⁷¹ this is especially difficult. After some confidence in the feature-scale uniformity is attained for a given chemistry and set of deposition conditions, the uniformity at the pattern and workpiece scales must still be addressed as well. This makes LIGA through-mask electrodeposition in some ways more challenging than electrodeposition through thin resist, as the feature scale adds literally another dimension to the problem of obtaining uniformity across multiple length scales. Considerable time and effort may be saved by first characterizing the electrodeposition kinetics and the importance of mass transport for an electrodeposition process before attempting to apply it to LIGA fabrication (especially in the case of an alloy system). If a good understanding of kinetics, transport, and alloy composition is in hand, electrolytes and deposition parameters suitable for deposition through thick resist may be chosen more prudently.^{67,69} Examples of such situations will be given when the mechanical properties of electrodeposits are discussed.

Electrodeposition in LIGA: Materials and Other Aspects

Up to this point, the range and types of materials electrodeposited for LIGA applications have not been discussed in depth. In the next section, we will go into more detail on these topics in regard to requirements for LIGA-fabricated structures to be used in mechanical applications. Before doing so, we will briefly mention materials studied for other types of LIGA applications, as well as other aspects related to the integration of the electrodeposition step into the LIGA process.

Besides the study of Thommes *et. al.* discussed above as an example of feature scale uniformity,⁶⁹ the possibility of using electrodeposited NiFe structures as magnetic components in microsystems has been discussed or demonstrated in a number of articles (a sampling is given in the references);^{25,73-79} but as shown by Thommes *et. al.*,⁶⁹ some care must be taken in insuring a given deposition process will result in acceptable alloy uniformity. Chin reviews a variety of different types of magnet films besides the traditional plated iron-group alloys for applications in microsystems, discussing the potential of electrodeposition in fabricating some more exotic magnetic alloys.⁸⁰ Despite the challenges posed by the thick resist often used in LIGA, the possibility of electroplating magnetic alloys for LIGA microstructures with useful magnetic properties makes LIGA and LIGA-like processes attractive to microsystem designers. In general, such LIGA-fabricated NiFe microstructures appear to have magnetic properties that are comparable to similar bulk NiFe materials.^{75-76,78}

Compared with Ni and Ni-alloys, investigations of other electroplated materials for LIGA processing are relatively few in number; this is most likely due to the fact that Ni may be electroplated with low stress in thick films with reasonable mechanical properties, as discussed in the next section. However, copper²⁸ and gold²¹ (both of which can be plated as thick films) have been used with the LIGA process to fabricate thick plated LIGA structures. Copper is of interest of course where a high electrical conductivity is necessary, and gold is attractive when structures having a high mass are required due to its high density ($\sim 19.3 \text{ g/cm}^3$). One study reports the electrodeposition of a Bi-Te alloy into a LIGA mold to form BiTe microposts for micro-cooling probes.⁸¹

Though not discussed at length here, another important area of LIGA electrodeposition research involves the nucleation and adhesion of the plated structures to the seed layer material used as the substrate. Since the substrate is exposed to x-rays during the exposure of the PMMA resist, metallization layers between the substrate and resist (such as those commonly used as plating bases, like copper) can re-emit the x-ray radiation (*e.g.*, by fluorescence), damaging the bond at the resist-metallization interface and provoking adhesion failures during subsequent processing.⁸² Since this damage can lead to the failure of the entire LIGA mold, alternative plating bases that do not behave in such a way are thus of interest.⁸² At the Forschungszentrum Karlsruhe in Germany, an approach using TiO_2 as a plating base has been developed and successfully employed.⁸³ Other suitable plating base materials have been recommended, but electrodeposition processes where good nucleation and adhesion to the base still need to be developed for these materials.⁸²

In this section, the challenges in attaining good uniformity in deposit morphology and/or deposit alloy composition over various length scales during the LIGA electrodeposition process step was emphasized. In practice, an equally important aspect in electrodeposition for LIGA is the subject of electrolyte aging and maintenance. Although it is not the focus of this chapter, a few comments on these topics are appropriate, especially since they are little discussed in the LIGA electrodeposition literature. These aspects are particularly important if the LIGA process is to be used for the manufacturing of a product with some specified, reproducible material properties that depend on the deposit morphology and/or alloy composition. For example, sulfamate baths are very popular for the electrodeposition of Ni LIGA microstructures. But as the electrolyte is used and ages, ammonium ions (originating from the sulfamate ion) may accumulate and adsorb at the deposition surface, acting as an additive and changing the deposit morphology and hardness.⁸⁴ Moreover, it has been known from the traditional electroforming literature that sulfur-containing breakdown species (originating presumably from the sulfamate ion) may also accumulate over time, leading to changes in film stress and morphology.⁸⁵ Both of these aging effects complicate the deposition of a film with consistent morphology and stress during manufacturing. We have observed complications arising from sulfamate electrolyte aging during the deposition of a NiMn alloy from this chemistry.⁸⁶ Since the aging of electrolytes often leads to species that induce unwanted changes in the plated film microstructure and material properties that an electrodeposition process is engineered to obtain, an understanding of electrolyte aging and maintenance is critical for the use of LIGA as a manufacturing process. Before addressing these topics in more detail, we will first discuss the development of electrodeposited materials for LIGA mechanical applications in the next section.

Properties and Structure of Electrodeposited Materials for LIGA-Based Microsystem Applications

Introduction

We describe here the material characteristics necessary to successfully fabricate precision structures for microsystem applications. In particular, we focus on the electrodeposited (ED) component structures that are required to have mechanical functionality: for example, springs or flexures. In such instances, mechanical strength, ductility, fatigue life and a well characterized modulus are critical material properties that must be well understood and reproducible. These structures typically have micron scale tolerances with respect to critical dimensions and insofar as their mechanical and physical behavior are governed by their sub-micron grain size, crystallographic texture and the very high defect densities typical of electrodeposits, we may consider these materials to be nanostructured.

In this section we restrict ourselves largely to the material properties and performance of structures that are fabricated *via* the LIGA process, which we described at the beginning of this chapter. In some instances though, we refer to work based on the deposition of blanket films where LIGA prototyping processes were not employed. A number of constraints limit the range of practical electrolytes and therefore electrodeposited material systems. Some of these constraints include: (1) low bath temperatures, which often must be well below those recommended by common electrodeposition practice (necessary to reduce thermal distortions of the resist material that define the lateral dimensions of precision structures);^{50,87} (2) transport limitations - particularly important in deep, high aspect ratio features where circulation of the bulk electrolyte is impeded, being typically minimized by the use of reduced deposition rates (that is, the use of atypically low current densities);⁸⁶ (3) low intrinsic film stresses to minimize piece part distortions and survivability of the mold during plating; and (4) pH compatibility with LIGA fabricated molds and substrates and pH control (both in the bulk electrolyte as well as within narrow, stagnant cavities as was described in the previous section). These various factors are summarized in Table 2.

TABLE 2. DEPOSITION PROCESS CHARACTERISTICS AND REQUIREMENTS

Process Characteristic	Requirement
Near ambient temperature deposition	Dimensional tolerances
Cation/Impurity/Additive transport	Composition, microstructure, property uniformity in high aspect ratio features
Intrinsic film stress	Dimensional tolerances Thick section deposition
pH restrictions	Substrate/resist compatibility Effects on ED structure and properties

With regard to the properties of electrodeposits themselves, where structures have an intended mechanical functionality, the most critical material property considerations are (1) strength- as section size of microscale components decrease, the strength must increase to avoid plastic deformation; (2) ductility- structures within mechanical assemblies cannot fail in a brittle, catastrophic fashion; (3) modulus- the material stiffness is a first order input parameter in the design of a spring or flexure; and (4) fatigue- the fatigue response of an electrodeposit can be an important material property depending on the ambient or functional environment. Table 3 summarizes these requirements.

TABLE 3. ELECTRODEPOSIT PROPERTIES AND REQUIREMENTS.

Material Characteristic	Requirement
Strength	Elastic response of mechanically functional structures
Ductility	Preclude catastrophic brittle fracture
Well characterized modulus	Predictable flexural response
Fatigue	Predictable response to dynamic environments

The practical choice of ED materials compatible with all aspects of LIGA fabrication is restricted to gold, copper and nickel (and a limited number of nickel-based alloys). Notwithstanding this limited family of materials, the range of microstructures and resulting material properties is quite extensive, and it is the electrochemistry of metal deposition that is principally responsible for

defining the microstructure and properties of these materials which form the free-standing structures from which microsystem component parts are fabricated. However, with respect to the fabrication of mechanically functional structures, neither gold nor copper has suitable strength (yield strength of ED copper is typically less than 500 MPa, while even “hard” gold will rarely exhibit yield strengths that exceed 250 -300 MPa).⁸

We focus then on ED nickel and Ni-based alloys since these materials can exhibit yield strengths that range between 350 MPa and 1200 MPa, depending on electrolyte and the particular plating conditions employed. The main challenge lies in adapting approaches that have been used for years to deposit high strength Ni for industrial electroforming and electroplating to the through-mask electrodeposition of LIGA structures.

Measurement Techniques for Strength and Ductility

The strength of electrodeposits can be characterized either indirectly through surface indentation hardness testing or directly by testing net shape deposited mechanical test specimens (tensile, compression, fatigue etc.). In the former instance, yield strength, the strength parameter most meaningful with respect to the design of mechanically functional structures, can only be roughly estimated even if the general work hardening characteristics of the material are known (more typically, attempts are made to correlate “flow stress” with indentation hardness measurements). The principal difficulty is the inability to reliably characterize the “constraint” factor that relates the contact pressure under an indenter tip to an equivalent uniaxial compressive stress. This constraint factor is dependent on a host of considerations, including the geometrical shape of the indenter tip, the rate of indenter loading, and the work hardening and relaxation characteristics of the material of interest.⁸⁸ Thus, hardness measurements can only be related to the strength of a material if an explicit correlation has been derived between indentation measurements and strength measurements for each individual electrodeposit of interest.

For example, Figure 18 shows the correlation between indentation hardness and the yield and the ultimate tensile strengths (UTS) of an ED NiMn alloy where we have adjusted the deposition parameters to yield a series of deposits whose strengths vary over the wide range indicated. For the data shown here, the yield strength (in conventional SI units of MPa) follows the relationship:

$$\sigma_y \approx -300 + 3H_{25g}$$

where σ_y is the yield strength and H_{25g} is the Vickers microhardness (using a 25 g load). The UTS of these NiMn electrodeposits has a somewhat higher correlation slope. With such correlation curves, one can, with some confidence, use hardness measurements as a surrogate for yield strength, where the direct measurement of mechanical properties is impractical (due to structure geometry or size, for example). As the work hardening characteristics of each ED material system is different, in principle, a similar correlation curve would be necessary for each family of electrodeposit. Furthermore, the intrinsic ductility of an ED (or any other) material remains uncharacterized by a hardness measurement.

Figure 18 Correlation of Vickers hardness (VHN) using a 25 g load with yield and ultimate tensile strengths (UTS) determined by direct mechanical tensile testing for a series of NiMn electrodeposits. Deposition conditions were varied to produce materials having a range of strengths and hardnesses.

With respect to the direct characterization of strength and ductility, these measurements are made directly using standard, albeit, much higher resolution, testing methodologies on test instruments that are usually appropriate for the size scale of the test specimens. Because specimen sizes are small, non-contacting, optical strain measurement systems are often employed.⁸⁹⁻⁹¹ As will be described later, it is these strain measurements that are most problematic when specimen sizes approach those of actual microsystem component structures.

Grain Refinement for Improved Electrodeposit Strength

Alloying and Organic Additives— Strength in engineering materials is derived from several sources. Common among these sources are solution strengthening, strengthening from the presence of rigid second phases or inert particle additives, and lastly grain refinement. Generally speaking, for Ni-based electrodeposits, grain size is the principal microstructural feature that governs strength; the wide range of strength that can be realized reflects the equally wide range

in grain size that is achievable. For example, Figure 19 shows tensile curves for an ultra-fine grained Ni deposited from a standard Watts bath electrolyte (nickel sulfate, nickel chloride, and boric acid) as well as that for a lower strength ED nickel deposited from a standard sulfamate bath chemistry (nickel sulfamate and boric acid). In the example shown in Figure 19, saccharin is included in the electrolyte as a stress reliever, and the resulting Watts bath-deposited Ni has a grain size on the order of 10 - 20 nm as shown in the TEM insert in Figure 19. The yield and ultimate tensile strengths (σ_y and UTS) are ≈ 1200 and 1800 MPa, respectively. This can be contrasted to the sulfamate bath ED Ni, where the grain size measured transverse to the columnar axis is on the order of 1-2 μm and the resulting yield and ultimate tensile strengths are ≈ 350 and 600 MPa. Indeed, Ebrahimi *et. al.*⁹² and Thompson⁹³ have shown that over a very wide range, nickel electrodeposits follow the Hall-Petch relationship⁹⁴ with respect to the effect of grain size on strength as illustrated in Figure 20.

Figure 19 Stress strain behavior of electrodeposited and wrought Ni. When a Watts bath is used with saccharin (a common organic additive in Ni plating) a fine grain size is obtained (see inset TEM plan view micrograph), resulting in a high-strength Ni deposit. In contrast to the fine-grained Watts deposit made with saccharin, Ni from an additive-free sulfamate bath has larger grains (see inset focused ion beam cross-sectional micrograph), resulting in a lower strength deposit. Compared to commercial purity, annealed Ni, both electrodeposits have high strength due to the fine as-deposited grain size.

Figure 20 Hall-Petch behavior for electrodeposited Ni, replotted from the data of Ebrahimi *et. al.*⁹² and Thompson.⁹³ The grain size of electrodeposited Ni is principally responsible for determining its strength.

The importance of grain size is further illustrated in Figure 21 where the Vickers hardness of ED NiCo (deposited from a 1.25 M nickel sulfamate and 0.025 M cobalt sulfamate electrolyte) is plotted against the concentration of incorporated cobalt. It is clear that the hardness, and therefore the strength, rises rapidly with cobalt concentration to a maximum of 450 VHN at approximately 40 wt. % cobalt. One is tempted to view this increased hardness as the result of solid solution strengthening since cobalt is substitutional in nickel and completely miscible at these concentrations.⁹⁵ However, the SEM micrograph inserts in Figure 21 reveal that the principal effect of cobalt is to dramatically reduce the grain size from 1-3 μm at low Co concentrations to 50 -100 nm at the maximum hardness.⁹⁶ The absence of a significant solution strengthening effect (even in this relatively high alloy content material) is further illustrated in Figure 22, where the tensile behavior of this alloy electrodeposit is compared to that of unalloyed

ED Ni plated from a sulfamate bath. The as-deposited yield strength of the NiCo alloy is ≈ 1.1 GPa, approximately 800 MPa greater than the yield strength of the pure nickel deposit. In contrast, after annealing at 700 °C for one hour, the yield strength of the alloy electrodeposit is only about 150 MPa greater than that of the nickel deposit. Thus, any contribution to the increase in mechanical properties due to solution strengthening is marginal. Even this small difference in the annealed strength most likely reflects slight differences in the final grain size of the tested material.

Figure 21 Hardness dependence on Co content for an electrodeposited NiCo alloy. The SEM cross-sectional micrographs show that the increased hardness obtained at higher Co contents arises from a refinement in the alloy grain size. (Reproduced from Yang, *et al.*⁹⁶)

Figure 22 (top) Stress strain behavior for as-deposited NiCo and pure Ni, both from sulfamate electrolytes. The as-deposited NiCo is much stronger than the pure Ni. (bottom) Both materials soften after annealing at 700 °C for one hour, but the NiCo alloy loses almost all of its strength advantage over the pure Ni after the anneal, resulting in similar stress strain behavior for both materials.

Figure 21 indicates that it takes 10's of percent of Co addition to significantly increase the strength and hardness of ED nickel. However, metallic solutes can be potent grain refiners and therefore material strengtheners in nickel electrodeposits even at very low concentrations. The work of Stephenson and others has demonstrated this for nickel-manganese electrodeposits.^{70,91,97-99} Small additions of a Mn salt to a Ni-sulfamate electrolyte result in exceptionally high strength ED Ni alloys having Mn concentrations that are typically less than 1 wt. %. In these reports, the principal effect of Mn incorporation was to reduce the grain size of the Ni-sulfamate electrodeposit by approximately 100-fold. Figure 23 illustrates effectiveness of small Mn additions to ED Ni using a sulfamate chemistry. This series of tensile curves shows the progressive increase in strength with increasing Mn concentration. As Mn is not a potent solution strengthening species, the more than two-fold increase in strength is derived from the continuing grain refinement as the solute concentration increases. Generally speaking therefore, nickel alloy electrodeposits derive their strength from the effect of the solute on suppressing grain growth during deposition (or alternatively, increasing grain nucleation) rather than from the more traditional metallurgical effects associated with solution strengthening.

Figure 23 Stress strain behavior for a series of NiMn electrodeposits. The alloy is deposited from a Ni sulfamate electrolyte containing 1-5 g/L of Mn added as Mn chloride. The reason the alloy strength increases with Mn content is the increasingly fine grain size induced by the Mn codeposition.⁹⁸⁻⁹⁹

Employing the grain refining attributes of solutes in nickel alloy electrodeposits must be approached with caution for deep, high aspect ratio, through-mold structures. The principal reason for concern arises from diffusive transport limitations of the co-depositing solute that can limit compositional and microstructural uniformity. The nickel-cobalt system affords a useful example of this limitation. Cobalt is easily deposited in uniform concentrations in bulk films over a wide range of concentration. Indeed, the hardness data shown in Figure 21 is an example of the synthesis of bulk films over a wide range of uniform, thru-thickness Co concentration. However, when filling a deep, high aspect ratio feature on a LIGA mold, the consumption of cobalt ions at the substrate surface may lead to concentration gradients in the electrolyte within the feature for this species (this was discussed previously for the NiCu system)⁷² as mixing of the electrolyte deep within high aspect ratio features is minimal.

As we discussed for the case of NiFe, the NiCo system may also exhibit what is known as anomalous codeposition, which exacerbates the problem. For anomalous systems, under certain conditions (*e.g.*, low bath temperatures), the alloying element deposits preferentially; *i.e.*, the fraction of the alloying element in the deposit is larger than that expected based on the ratios of the two metal cations in the electrolyte.⁷⁰ In the particular case of NiCo, the bath is dilute in cobalt ions, but they deposit and are thus consumed at a high rate because of the anomalously high cobalt deposition current density. Under such circumstances, the electrolyte close to the deposition surface is rapidly depleted of cobalt ions, leading to a lower than expected concentration of cobalt in the deposit. However, as the metal grows towards the top opening in the resist, the geometry of the feature changes, leading to a constantly changing set of local electrolyte conditions. For example, as the aspect ratio is reduced, the diffusive transport of cobalt ions increases, allowing for their more rapid replenishment to the deposit-electrolyte interface. The net result is a progressive increase in the concentration of solute in the alloy as the high aspect ratio feature is filled.

As an example, Figure 24a shows the evolution in concentration of cobalt in a 25 μm wide x 250 μm tall LIGA-fabricated NiCo beam. The plating conditions were set so as to yield a deposit consisting of 30 wt.%Co-70 wt.%Ni. The cobalt concentration is characterized *via* microprobe-based, wavelength dispersive spectroscopy (WDS), and in this figure the seed surface (the surface at the “bottom” of the lithographically defined feature) is to the left axis while the top of the feature is to the right. Transport limitations due to lack of mixing within the LIGA feature, as described above, result in a deposit that is severely depleted in cobalt at the base of the feature. Only as the cavity fills and the deposit-solution surface rises toward the top third of the high aspect ratio feature (where convective mixing can aid in the replenishment of the cobalt

cations) does the bulk concentration of Co approach its target concentration. Since solute content determines the grain size of the deposit, the mechanical properties of such a compositionally graded structure are correspondingly compromised as shown in Figure 24b. Here, the indentation hardness is profiled from the seed surface to the top of the feature, and it is clear that the hardness rises in direct relationship to the increase in Co concentration in close agreement to the data shown in Figure 21.

Figure 24 (a, top). Co content of an electrodeposited NiCo alloy within a LIGA feature having an aspect ratio 10 (25 μm wide, 250 μm tall). Poor mixing within the feature results in cobalt ion gradients in the electrolyte and hence in the deposited metal. **(b, bottom)** The varying Co content manifests itself in a hardness gradient across the feature height.

The NiCo system is particularly sensitive to these transport-limitation-induced effects on composition and structure since this system exhibits anomalous codeposition. Figure 25 compares its feature-filling behavior to that of the NiMn system, which is not anomalous in its deposition characteristics, for a geometry similar to that shown in Figure 24 (specifically, 32 μm

wide and 350 μm tall). Since the target concentration for the NiMn alloy was approximately 1% as compared to 30% for the NiCo alloy, we plot the concentration profile in Figure 25 normalized to the WDS-measured concentration near the seed surface for each alloy. Similarly, location from the substrate is normalized to the absolute feature height for both deposits. While the concentration of Mn solute in the NiMn deposit exhibits a measurable gradient, the Co concentration gradient in the NiCo deposit is ten-fold greater, a direct consequence of the sensitivity of the anomalous NiCo system to mixing. The increased Mn uniformity in the NiMn alloys is reflected in the enhanced uniformity of the hardness of the electrodeposit along the thickness of the deposit as shown in Figure 25. The behavior illustrated in Figure 25 demonstrates the importance of understanding how the electrochemistry of the deposition reaction influences the resulting material properties of LIGA-fabricated structures.

Figure 25 (a, top). Solute concentration for NiCo and NiMn alloys, normalized to the solute concentration at the bottom of the feature, for alloys deposited into a LIGA feature with an aspect ratio of about 10. The distance from the substrate is also normalized (for NiCo, the feature width and height is 25 and 250 μm , respectively, while for NiMn it is 32 and 350 μm , respectively). The Mn solute concentration is more uniform since the Mn deposition rate is not sensitive to mixing. **(b, bottom)** Through-thickness hardnesses for the two alloy systems normalized to the hardness at the feature bottom. The more uniform composition of the NiMn alloy results in a more uniform through-thickness hardness.

Other Additives—Other electroplating bath additives can have similarly significant effects on the grain structure of nickel electrodeposits. We have already discussed the example of the organic electrolyte additive saccharin. At concentrations of about 1 g/L and higher, saccharin reduces high film stresses obtained when depositing nickel from a Ni-Watts plating bath (nickel

sulfate, nickel chloride, and boric acid).⁸ It has the additional effect of reducing the grain size of the as-deposited material into the 10's of nanometer regime as a result of its adsorption at the deposit-solution interface. The impact of this refined grain size on the deposit's mechanical properties has already been illustrated in Figure 19, where it was shown that the as-deposited strength of the deposit exceeds that of ED Ni-sulfamate by nearly four-fold, while retaining significant ductility. However, the adsorption of the saccharin molecule and subsequent incorporation of sulfur into the deposit (the resulting sulfur concentration in a Ni-Watts deposit is on the order of 500-700 wt. ppm) have severe consequences with respect to the thermal response of the deposit. Sulfur is a well-known embrittling agent of nickel and nickel-based alloys at concentrations far lower than that present in the electrodeposit. The consequences of this sulfur incorporation is made obvious in Figure 26, which shows the effect of vacuum annealing temperature on the room temperature mechanical properties of Ni deposited from a Watts electrolyte with a saccharin additive. Ductility loss is evident in specimens annealed at temperatures as low as 200 °C. At temperatures above 200 °C, embrittlement is so severe that there is no measurable ductility. Tensile specimens simply deform elastically and then fail in a catastrophic brittle fracture. Because of this complete lack of ductility, the individual tensile curves cannot be discerned in Figure 26. As an aid to visualizing the degree to which the material is embrittled, the insert in this figure shows the tensile curve for a specimen annealed at 500 °C and then tested at room temperature. In this instance, fracture occurred at approximately 50 MPa and at a total plastic strain of less than 0.025%. Figure 26b shows the fracture surface of a tensile specimen tested to failure at room temperature after an elevated temperature anneal. The intergranular nature of the fracture is evident in this micrograph. Similar effects are found in electrodeposited Ni-Fe alloys, where the saccharin addition to the NiFe electrolyte is again required to reduced plating stress.¹⁰⁰ In this instance, there is direct evidence of the segregation of sulfur to grain boundaries after annealing at elevated temperatures. The results of these studies lead to the conclusion that, insofar as ED Ni is concerned, no sulfur-bearing electrodeposit can be expected to exhibit any significant amount of ductility, after even modest elevated temperature exposure.

Figure 26 (a, top). Stress strain behavior for various anneals of Ni electrodeposited from a Watts chemistry containing 1 g/L saccharin. The incorporation of sulfur from the saccharin additive leads to the embrittlement of the electrodeposit after thermal exposures. (b, bottom) Fracture surface of Ni test sample plated from a saccharin-containing Watts bath. The test specimen was annealed before testing, causing its brittle failure; the intergranular nature of the fracture surface is easily discernable *via* SEM.

Even unintentional additives to a plating bath can result in significant changes to the resulting structure and properties of electrodeposited materials. Deposition of through-mold structures from Ni-sulfamate baths affords an example of this. Ni-sulfamate is an attractive electrolyte for use in LIGA fabrication for a variety of reasons. From a properly conditioned bath, deposition can occur at relatively high rates due to its high current efficiency, and the resulting nickel deposits exhibit good ductility and low internal film stress (an important consideration when fabricating high precision micro-component structures where elastic distortions can compromise dimensional fidelity). However, hydrolysis of the sulfamate ion may result in the build-up of sulfate and ammonium ion,^{85,101-102} the latter of which acts effectively as an unintended additive species. This may occur over the natural age of the plating bath, or if the temperature of the nickel sulfamate concentrate makeup solution or Ni sulfamate plating bath exceeds 60 °C for extended periods.

The ammonium decomposition product in nickel sulfamate plating baths affects the intrinsic film stress, the crystallographic film texture, as well as the film grain structure and mechanical properties. Lin *et. al.*⁸⁴ reported that film stress rises from about 22 MPa in the absence of ammonium to over 45 MPa at ammonium ion concentrations of approx. 250 wt. ppm. At the same time, the <001> texture, characteristic of the free-growth mode of Ni-sulfamate deposits, is suppressed in favor of an “inhibited” growth mode, giving rise to a <011> characteristic texture. Such texture changes can affect the elastic response of through-mold structures and will be discussed later in this section. With respect to mechanical strength, though, the presence of ammonium ion has important implications. Figure 27 compares the microstructure and tensile behavior of LIGA fabricated mechanical test specimens plated from a freshly prepared Ni-sulfamate electrolyte to that of a specimen fabricated from an “aged” electrolyte (that is, after several hundred A-hrs of prior use). In both cases, the deposition conditions are identical, with respect to plating temperature, current density, pH and plating cell geometry. In the former instance, the microstructure and tensile behavior is as expected; a coarse, columnar grain structure giving rise to a yield strength of ≈ 300 MPa. In the later instance, the presence of approximately 150 wt. ppm of ammonium results in drastically refined grain size, and as a result, a nearly 3-fold increase in yield strength to 800 MPa.

Figure 27 Stress strain behavior for Ni electrodeposited from a fresh sulfamate plating bath (dashed line) and an identical bath that has ≈ 150 ppm ammonium ion due to several hundred A-hours of use. The accompanying SEM cross-sectional micrographs show that the higher strength of the Ni from the ammonium-containing bath is due to its finer grain structure.

The mechanism by which additives and alloying species can influence the structure and properties of nickel electrodeposits is a subject of much discussion. Some qualitative understanding of the phenomenon can be drawn from the proposition that any adsorbed species, be it a foreign codepositing metal cation or a chemical constituent of the plating bath (inorganic or organic) may interfere with the usual nucleation and growth of the electrodeposited film, resulting in a grain structure much different than that obtained in the absence of such species.¹⁰³⁻¹⁰⁵ Sometimes, the potency of the interfering species may be ascertained by studying its effects on the metal deposition reaction kinetics; a species that strongly prevents the deposition reaction from occurring is thought to have a strong inhibitive effect on the film growth, resulting in a finer-grained film.¹⁰⁵ Thus, additives are sometimes classified by their inhibitive effects on film growth, but it is clear that their impact on the nucleation process can strongly influence the final film microstructure as well.¹⁰³⁻¹⁰⁵

Current Density Control—Beyond the intentional or unintentional incorporation of alloy or chemical additives, plating process parameters can have a significant effect on the structure and properties of nickel electrodeposits. For example, the imposed current density during deposition can have a profound impact on grain size. Zentner et. al.¹⁰⁶ have shown that, for bulk ED Watts nickel (nickel sulfate + nickel chloride) deposited at pH 3.0 and at 55°C, grain size first increases as current density increases to intermediate levels. Under these conditions, the deposit develops an exaggerated coarse columnar grain structure. However, as current density continues to increase, the trend reverses, such that the grain size becomes finer overall. This behavior is sometimes rationalized as being governed first by the inhibiting effect of weakly adsorbed species in the electrolyte at very low current densities (such species may be effective inhibitors despite being weakly adsorbed since the driving force for film growth is low) that are overwhelmed as current densities and overpotentials increase to intermediate levels where the metal deposition rate is correspondingly higher. At these intermediate current densities deposition is said to be “uninhibited” and coarser grained microstructures are favored. Ultimately, at the very highest current densities, nucleation once again dominates; the net result is a reversal in the trend to favor more crystallite (grain) nucleation at very high deposition rates.

The response to applied current density (in terms of strength) can be seen in other reports in the literature, although the trends are not always consistent. For example, Sharpe reported that both the yield and ultimate tensile (UTS) strengths decreased monotonically with increasing current density across the range of 3 to 50 mA/cm² for through-mold ED Ni tensile specimens plated from a sulfamate chemistry, as shown in Figure 28a.⁸⁹ Such behavior is easily explained based on conditions that promote uninhibited growth of the deposit with a corresponding increase in grain size of ED Ni at these intermediate current densities. However, the work of Kim and Weil run counter to this, as shown in Figure 28b, which suggests no strong trend at applied current densities between 3 and 25 mA/cm² for ED Ni plated from a sulfate chemistry.¹⁰⁷ A clear increase in yield strength is noted at a current density of 50 mA/cm², however, and pulse plated deposits exhibit higher strengths than direct-current deposits. Pulse plating has long been considered a method for encouraging nucleation and thus finer-grained deposits as we will discuss shortly. Safranek reports similarly contradictory results for ED Ni-Sulfamate, with the strength trending in opposite directions with increasing current densities between 200 and 600 mA/cm².⁸

Figure 28 (a, top) Yield and ultimate strengths for Ni electrodeposited from a sulfamate electrolyte reproduced from data given by Sharpe.⁸⁹ Strength decreases with increasing current density under these conditions. (b, bottom) Yield strength data reproduced from Weil and Kim who used a sulfate chemistry for Ni electrodeposition.¹⁰⁷ Their results for DC deposits show no strong dependence of yield strength on current density for low deposition rates, with an increase occurring at 50 mA/cm². Their pulse-plated deposits are stronger than those plated using DC, with strength trending higher with higher peak current densities.

Such inconsistencies are not uncommon when reviewing the literature and illustrate the fact that broad assumptions as to particular effects of current density may not be drawn between different electrolyte systems (sulfamate vs. sulfate, for example). Indeed, even for a single electrolyte, the potential effects of even the smallest variation in other deposition process variables such as bath age (discussed above), chemistry, pH and temperature may overwhelm the effect of current density. A graphic example of the impact of even minor changes in deposition process parameters is shown in Figure 29, where the tensile behavior of ED Ni is shown for through-mold test specimen plated from a sulfamate chemistry at 28 °C and at 3 mA/cm². The only difference in the plating processes for the two results shown is the circulation pump driven passage of the electrolyte through a 5 µm debris filter in one instance but not the other.

Figure 29 Effect of electrolyte filtering on stress-strain behavior for electrodeposited Ni from a sulfamate bath at 28 C and 3 mA/cm². The passage of the bath through the filter at lower temperatures is thought to lead to the formation of polyborate species that refine the grain structure at low deposition rates, resulting in higher strength Ni.⁸⁶

Filtration is a common industrial practice and has not been thought to influence the *electrochemistry* of deposition. However, it is evident that the properties and microstructure of the deposits are profoundly affected by the presence or absence of such filtration under certain conditions. ED Ni specimens plated from a filtered sulfamate bath exhibit a relatively high yield and ultimate tensile strength (700 MPa and 950 MPa respectively), while specimens made from an unfiltered bath exhibit corresponding strengths equal to about half of these values; these lower strengths seen for the unfiltered electrolyte are more in line with expectations from the literature for the sulfamate chemistry.⁸ The differences observed in the mechanical properties are reflected in the microstructures shown in Figures 30a and b, where the deposit from the filtered bath exhibits about a 5-10-fold decrease in grain size. The inverse pole figure inserts in Figure 30 reveal even more unexpectedly a change in the characteristic texture of ED Ni-sulfamate from $\langle 001 \rangle$ in Figure 30b to $\langle 011 \rangle$ in Figure 30a. These effects are dependent on the boric acid content and occur most profoundly at lower bath temperatures ($<40\text{ }^{\circ}\text{C}$) and current densities ($<5\text{ mA/cm}^2$); we thus postulate that precipitation of the boric acid during passage through the filter leads to the formation of polyborates, which in turn act as weak inhibitors at low deposition rates.⁸⁶

a

b

Figure 30 (a, top) Planview focused ion beam image of a nickel deposit from a filtered sulfamate electrolyte at 3 mA/cm^2 and 28°C reveals a fine grain structure with a predominantly $\langle 011 \rangle$ texture (inset inverse pole figure). (b, bottom) Same as in (a), but from an unfiltered electrolyte. The nickel deposit instead has a coarse grain structure with a $\langle 001 \rangle$ texture. (Microscopy and texture courtesy of J. Michael and A. Talin, Sandia National Laboratories)

As mentioned previously, pulsed deposition schemes are also used to influence deposit properties and structure through current density manipulation. Square-wave pulses, in which the deposition current is on for a given time followed by an interval in which no current flows, are most often used. Additional control over the properties of deposits relative to constant, direct current (DC) deposition results because it is possible to independently vary the current density, the pulse frequency and the duty cycle (the ratio of the on-time to the pulse period, *i.e.* the sum of the on-time and the off-time). The properties of such pulsed plated (PP) deposits can be manipulated in theory because the accompanying higher peak current densities result in higher nucleation rates and thus in grain refinement, as we and others have discussed.¹⁰⁸⁻¹¹¹ Brighter deposits, typically an indication of a fine-grained deposit, frequently result.¹¹² Figure 28b shows additional work of Kim and Weil illustrating the effect of current density-induced grain refinement for pulse deposited Ni-sulfate at peak current densities up to 200 mA/cm². At lower mean current densities, it is still possible to find reports where the reverse trend is observed. Fritz and co-workers¹¹³ reported continuously decreasing indentation hardness for pulse deposited ED Ni plated from a sulfamate electrolyte at 40 °C and a pH of 3.2 between mean current densities of 2 mA/cm² and 20 mA/cm²; as expected, the lower observed hardness values are accompanied by an increase in the grain size.

pH and Temperature Control— Other processing parameters can affect the structure and properties of ED nickel. Safranek has compiled results from many sources and shown that for ED nickel chloride, sulfate, sulfamate and Watts type deposits, hardness generally rises with increasing pH.⁸ The effects tend to be small between pH values of 1 to 4 but then rise rapidly as pH is increased to values of about 5 or higher.^{106,114} Since hydroxide species start to precipitate at about this pH for most Ni plating baths, the increases in hardness observed at pH values of 4.5 and higher are likely due to adsorbed metal hydroxide species acting as inhibitors.^{8,115} Conversely, increasing deposition temperature generally results in decreased strength of electrodeposits. Phillips and Clifton reported a decrease of almost 50% in the UTS of Watts nickel deposits plated at 60 °C relative to deposits plated at 25 °C.¹¹⁶ Such changes may be due to the adsorption-desorption kinetics of a potentially inhibiting electrolyte species; for example, the adsorption and subsequent effects of the electrolyte bath additive saccharin has been shown to be very temperature dependent.¹¹⁷ However, as with the earlier discussion regarding current density effects on material properties, identifying consistent trends from the literature with respect to temperature and pH effects is often problematic, since the final characteristics of any electrodeposit are the result of the interactions of many processing variables.

Particulate Additive Effects

A path towards enhanced mechanical strength that is independent of deposition parameters and electrolyte chemistry is found through the physical incorporation of an inert, particulate dispersoid, typically a hard oxide such as alumina (Al_2O_3), into the host nickel electrodeposit, creating an oxide dispersion strengthened (ODS) particulate composite. The source of the strength increase is the Orowan hardening phenomena wherein the distributed particulates act as barriers to dislocation motion within the metal matrix.¹¹⁸⁻¹¹⁹ Additional benefits can be realized if the particulate microstructure acts to pin the grain boundaries, thereby rendering the deposit less sensitive to anneal softening. The ability to successfully co-deposit a particulate in both thin and thick electrodeposited films has been demonstrated previously by a number of groups.¹²⁰⁻¹²⁵ More recently, we have demonstrated the ability to uniformly incorporate a 10 nm (avg. diameter) Al_2O_3 particulate into through-mold electrodeposited structures.¹²⁶ The use of such a small diameter particulate is necessary in order to insure that the transport of this hardening constituent is not impeded within the narrow, high aspect ratio channels that are typical of LIGA-fabricated structures. Figure 31 shows the influence of a uniform distribution of oxide particles co-deposited with nickel from a nickel sulfamate bath. In the as-deposited condition, the ODS electrodeposit exhibits a 50% increase in both the yield and ultimate tensile strengths. Because the oxide particulates also act to pin grain boundaries as suggested above, resistance to anneal softening is also realized. The two traces in Figure 31 labeled as “annealed 600C” represent the tensile behavior after a 1 hr. vacuum annealing treatment, and it is evident that the ODS deposit suffered only negligible loss in strength while the baseline ED Ni plated from sulfamate bath suffered a 75% loss in yield strength.

Figure 31 Effect of alumina particulate incorporation on stress-strain behavior of ED Ni plated from a sulfamate chemistry.¹²⁶ The incorporated particulate strengthens the plated Ni; ED Ni plated under the same conditions but without the particulate is shown for comparison. The particulate also allows the plated Ni to retain much of its strength after a 600 °C anneal as compared to the particulate-free Ni.

While dispersion strengthening is clearly an effective means to increase the mechanical performance of Ni-based electrodeposits, significant hurdles remain with respect to implementing the appropriate plating processes in LIGA-based fabrication. Principal among these would be the potentially problematic effects of routine particle filtration of the plating bath, a routine procedure. As commented earlier, this filtering is employed to remove unintended species resulting from accidental contamination which would lead to internal defects in the plated material (*e.g.*, dissolved anode particulate). Such filtering media would have to be carefully sized to minimize any tendency for it to strip the intentionally added particulate out of the bath, compromising the original intent of the process.

Modulus of Electrodeposits

Because many LIGA-based microsystem components have a mechanical functionality, the elastic modulus of electrodeposits is often a first order design parameter. For example, the elastic modulus is required to predict the elastic displacement of a spring-type structure.

Handbook or literature values for modulus cannot be assumed, since these are typically based on randomly oriented polycrystalline materials. In contrast, most ED nickel materials exhibit out-of-plane (parallel to the growth direction) crystallographic texture. For very thin films (<10 microns), there can be significant in-plane texture as well (in-plane being normal to the growth direction of the electrodeposit), depending on the character of the seed surface substrate.¹²⁷ For thicker deposits (> 50 microns) any in-plane texture usually disappears, leaving a material that is randomly oriented within the plane. However, the out-of-plane texture can remain strong, and the particular crystallographic orientation and texture strength depends on the ED material system, the deposition parameters and the chemistry (chemical purity) of the electrolyte. As a result, it is often necessary to explicitly characterize the in-plane modulus of through-mold electrodeposited structures not only for each material system, but also when there are even minor changes in deposition conditions.

Some work has been reported in the literature where modulus has been determined through the characterization of the resonance behavior electroformed structures.¹²⁸⁻¹²⁹ In the work of Shi *et.al.*,¹²⁸ a modulus of 110 GPa is reported for electroformed Ni resonators, which is compared to a literature value of 140 GPa for electroplated Ni. This data appears to be insupportably low (see the discussion below) and undoubtedly suffers from the inability to determine critical specimen dimensions with sufficient accuracy. Beyond this, the authors do not indicate the ED Ni system employed or the particular deposition parameters. In another study by Majjad *et. al.*,¹²⁹ the authors do not indicate the ED Ni system studied, but the values they report (approx. 195 GPa) are in agreement with companion studies employing apparently the same material and are more in line with expected values for a range of likely Ni deposit systems.

Most often, the modulus of a material is determined in a straightforward fashion from the initial linear loading slope of a mechanical test specimen. From such testing, the modulus of ED Ni-sulfamate has been variously reported from low values of approximately 90 GPa to as high as 208 GPa.^{90,130} Accurate characterization of the elastic modulus of LIGA-fabricated test specimens in this fashion is made difficult by two principal factors, the specimen size and alignment considerations. With respect to the former, material test specimens fabricated using LIGA techniques have characteristically small dimensions. For example, gauge sections of lithographically patterned tensile specimens range from a few hundred microns to a few millimeters in length. As a result, the elastic deformation range over which the modulus is measured is quite small. This point is illustrated in Figure 32, which shows a typical tensile test curve for ED-Ni deposited from a sulfamate electrolyte at 50 °C.¹²⁶ While the overall curve is unremarkable, for this relatively soft electrodeposit (yield strength on the order of 400

MPa), the insert in Figure 32 shows that the total elastic elongation of a test specimen having a 3 mm gage length is only approximately 4 μm . If we presume that 25- 50 unique data points are necessary to adequately define the initial loading slope, then the required displacement resolution is on the order of 200 nm. Accurate and reproducible measurements with non-contacting extensometry (necessary because of the inability to mechanically attach displacement transducers to these very small test specimens) at this resolution are quite difficult. Some groups have had good success with custom-built instruments using interferometric techniques (Sharpe and co-workers,⁸⁹ for example), but there are few commercial devices that have sufficient accuracy for these types of measurements.

Figure 32 Stress-strain data for Ni electrodeposited from a sulfamate chemistry.¹²⁶ The measured displacements in the elastic region, necessary for the determination of the elastic modulus by this method, are very small, thus limiting the accuracy of moduli determined in this fashion.

With respect to the latter consideration, the very small loads required to deform these small specimens preclude the use of alignment fixtures. The resulting off-axis bending can mask the true linear loading slope and can result in significant uncertainty in the calculation of the modulus. Thus, even when displacement-measuring instruments with sufficient resolution are available, one must approach the use of the initial tensile loading slope with great caution.

We have instituted a 3-point bending test procedure that obviates these problems. These tests are performed on LIGA-fabricated, rectangular beams of uniform cross-section and the modulus is extracted from the centerline deflection and the deflection load according to:

$$E = \frac{P \cdot L^3}{4\Delta x \cdot w \cdot h^3}$$

where E is the modulus, P is the centerline flexure load, L is the support span length, x is the centerline displacement, w is the specimen width and h is the thickness of the beam parallel to the displacement line. Because the applied loads are small, the system and fixture compliance (with respect to displacement measurement) are negligible. Therefore, centerline displacement can be monitored by the optical encoder of the cross-head drive mechanism that is present in any modern mechanical test instrument. Since the specimen is point-loaded, alignment requirements are far less critical than is the case for conventional uniaxial mechanical testing. Results, presented below, generally show less than about 1 % standard deviation in the computed modulus when 6-10 replicate measurements are performed on individual specimens — far less variability than that typically found in the literature.

For the majority of microsystem applications where the mechanical response of component structures is required, design considerations are most often concerned with the in-plane modulus. Hemker and Last showed that the in-plane modulus of an electrodeposit that exhibits out-of-plane texture can be modeled by averaging over all possible directions in the plane of the electrodeposit (assuming that the plane of the electrodeposit is the plane of the texture).¹³¹ The calculation is simplified by the fact that the in-plane texture is typically random as described above.

For ED nickel deposited from sulfamate and sulfate solutions under conventional deposition conditions, the as-deposited structures most typically have a <001> out-of-plane texture and exhibit either no or only weak in-plane texture. Following Hemker and Last,¹³¹ the in-plane directional dependence of E on the (001) plane is:

$$E(\theta) = \{S_{11}(\cos^4 \theta + \sin^4 \theta) + (2S_{12} + S_{44})\cos^2 \theta \sin^2 \theta\}^{-1}$$

where $S_{11}=0.00734 \text{ GPa}^{-1}$, $S_{12}=-0.00274 \text{ GPa}^{-1}$ and $S_{44}=0.00802 \text{ GPa}^{-1}$ are the relevant compliances¹³² and θ is the angle from the [001] direction on the (001) plane. E for a <001> textured material is shown as a function of θ in Figure 33 along with that for a <011> textured

deposit since these are the most relevant texture considerations for ED Ni-sulfamate. For the $\langle 001 \rangle$ preferred texture, the modulus reaches a maximum of 323 GPa along the $\langle 011 \rangle$ directions and exhibits minimum values of 137 GPa along the $\langle 001 \rangle$ directions. Thus, it can be concluded that in no instance can the modulus of an electrodeposit with a preferred $\langle 001 \rangle$ out-of-plane texture ever exhibit a modulus either greater than 323 or less than 137 GPa regardless of the extent of in-plane texture. Hemker and Last further indicate that, since bulk film Ni-sulfamate is randomly oriented in-plane, it is appropriate to average the curves in Figure 33. Such averaging yields a value for E for $\langle 001 \rangle$ textured deposits of 178 GPa assuming a Voigt solid model¹³³ or a somewhat lower value of 172 GPa assuming a Reuss solid model.¹³⁴ For a deposit with a preferred $\langle 011 \rangle$ texture, Figure 33 shows that $E(\theta)$ exhibits a different periodicity with respect to the in-plane direction, with average moduli of 230 GPa and 210 GPa, respectively, depending on the solid model used.

Figure 33 Calculated elastic moduli for Ni, taken after Hemker and Last.¹³¹

We have shown that the crystallographic texture developed in an electrodeposit is influenced by deposition processing parameters. Based on Figure 33, the modulus of differently textured ED Ni structures should be measurable. Figure 34 shows representative results for modulus measurements performed as described earlier. The slope of each curve represents the modulus for two different ED Ni-sulfamate films deposited using deposition conditions such that in one

instance the preferred texture is $\langle 001 \rangle$, while in the other instance the preferred texture is $\langle 011 \rangle$. In the former case the $\langle 001 \rangle$ textured material exhibits a modulus of 153.2 ± 1.4 GPa, while in the later case, the modulus is 186.9 ± 1.8 GPa. It is evident that, while the trends agree with the modulus calculations presented in Figure 33, the absolute values in each case are significantly lower than expected. One possible explanation for these discrepancies may be associated with the assumption that these deposits have no in-plane texture. Any significant in-plane texture component may skew the measured modulus of these materials to values that are lower or higher than the predicted Reuss or Voigt averages. More likely, the above consideration of modulus does not account for the high fraction of material associated with grain boundaries in these very fine grained electrodeposits. A high “volume fraction” of disordered grain boundary may lead to a material that is overall, more compliant. Studies like those of Hemker and the experimental work presented here, suggest that additional work is appropriate with respect to understanding the relationship between the structure of electrodeposits and physical properties such as modulus.

Figure 34 Three point bend tests for $\langle 001 \rangle$ and $\langle 011 \rangle$ textured ED Ni. The difference in film texture is reflected in the moduli determined from this measurement.

Summary: Electrodeposited Materials for LIGA-Based Microsystems

We have attempted to summarize and discuss the important characteristics of electrodeposited materials used for LIGA-based applications, and the ways in which these characteristics may be manipulated to obtain material properties desirable for such applications. For the mechanical applications discussed here, a material with a uniformly nano-sized grain structure is ideal; while this can be done in a fairly straightforward fashion for blanket electrodeposited films, it is quite challenging to do so when electrodepositing into deep, high aspect ratio features formed by x-ray lithography. A variety of processing parameters, ranging from the bulk chemistry of the electrolyte, the effect of adsorbed species on the nucleation and growth of the depositing film, to mass transport limitations in deep cavities, all can have a strong effect on the microstructure and material properties of the through-mold deposited structures. We have only discussed Ni and Ni alloys here, but it is certain that similar challenges exist in integrating electrodeposition processes for other materials with LIGA processing. As interest develops for new materials necessary for new applications of LIGA technology, such materials and process development for LIGA will ensue.^{11,15}

Other Aspects of LIGA Technology

In this final section, we address some miscellaneous aspects of LIGA technology that do not explicitly involve electrodeposition, but are worth mentioning for completeness. They entail the areas of replication, alternative resists for LIGA, and x-ray lithography at the nano-scale.

As mentioned in the introductory section, when the LIGA process was developed, a major interest was the use of the lithographically patterned mold as a means to make a thick, electroplated monolithic metal master tool for subsequent replication. This plated Ni tool, bearing the lithographically-defined pattern, would in turn be used to inexpensively mass-produce plastic parts *via* embossing or injection molding.¹³⁵⁻¹³⁷ As discussed in the LIGA applications section, replication is an important technique in LIGA technology that is used to this day in the low-cost fabrication of commercial products.³⁹ Other variants of the replication technique, such as the electroforming of lost plastic molds (the plating of molded plastic substrates) and the casting of metal powders into ceramic molds (obtained from plastic parts made from a metal LIGA mold) to form solid microparts have been discussed by Ruprecht *et al.*¹³⁸ The lost plastic mold approach is very attractive from a cost standpoint, but structures electroformed from these substrates typically have small internal voids (the plastic mold sidewalls become electrically active after the necessary metallization layer is vacuum deposited; electrically conductive plastic molds present the same problem).¹³⁸⁻¹³⁹ More recent work has shown greater success with respect to obtaining defect-free material with mechanical properties comparable to direct LIGA fabricated test structures.¹⁴⁰ Ruprecht *et al.*¹³⁸ also describe the challenges in obtaining fully dense metal structures with minimal shrinkage by casting metal powders into ceramic molds derived from LIGA masters.

While replicating large numbers of parts with a single master tool lowers the overall cost of the LIGA process, another way to achieve this end is to use a resist that may be prepared using standard UV exposure equipment, obviating the need for x-ray synchrotron access. Since collimated x-rays are not used, the lithographic dimensional fidelity is not as high as that obtained with the true LIGA process. Wafers bearing patterned resist may be electroplated as in the normal LIGA process to produce through-mask plated structures.¹⁴¹ Another complication is the removal of some of the thick UV resists typically employed, such as SU8; whereas PMMA may be dissolved in standard organic solvents like acetone, for example, resists such as SU8 usually do not dissolve in such solvents due to its high degree of cross-linking.¹⁴² Dentinger *et al.* reviews some of the prior methods for SU8 removal and presents some new routes for the

removal of this resist.¹⁴² Although thick resist such as SU8 have been widely used as a process tool for fabricating LIGA-like structures, there are limitations with regard to dimensional precision at large resist thicknesses that must be mitigated by careful resist process control.¹⁴³⁻¹⁴⁶

Most LIGA research has focused on structures whose lateral critical dimensions are on the micron scale. In principle, it is possible to fabricate structures that have lateral critical dimensions that are less than a micron, but this has not been much explored. A possible reason why the LIGA process has not been employed frequently at the submicron scale involves the typical PMMA resist thickness; since resist is usually hundreds of microns in thickness, submicron features are difficult to fabricate and process. Nonetheless, some work is being done at a submicron feature scale using x-ray lithography, typically using fairly thin PMMA resist.¹⁴⁷⁻¹⁴⁸ The gold-absorbing masks must be carefully fabricated, and synchrotron radiation with the appropriate characteristics must be used to insure high resolution and fidelity at submicron scales.¹⁴⁹ Recently, x-ray and nanoimprint lithography have been used together to fabricate three dimensional structures patterned over different length scales.¹⁴⁸

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