Electroforming of Thick Layers from Sulfite Gold Alloys in the LIGA Process

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Abstract

This paper presents advancements of sulfite-based gold electroforming process steps within the LIGA microfabrication process. Emerging applications such as waveguide filters, RF MEMS resonators, and decorative mechanical high precision devices require taller and more homogeneous Au layers with improved material properties. Therefore, three different electrolytes are evaluated by adding hardeners (cadmium, palladium, and copper) and grain refiners (arsenic and antimony) to sulfite electrolytes. For thick metal layers of 250 µm, best results with regard to thickness distribution, material properties, colour, bath handling, etc. were achieved with a ternary alloying system of gold-cadmium-arsenic.

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1 Introduction

Gold electroforming plays a key role in the LIGA process. LIGA[1,2] (Fig. 1), a German acronym consisting of the letters **LI** (Röntgen-Lithografie meaning X-ray lithography), **G** (Galvanik meaning electroforming) and **A** (Abformung meaning molding). It has been developed at Forschungszentrum Karlsruhe, offering the possibility to manufacture microstructures with high aspect ratios (structure height-to-minimum feature size ratio) from a variety of materials (plastics, metals, and ceramics). In the electroforming step, on one substrate both small gaps and large structures have to be filled with metal up to the same height. Usually, metal microstructures of nickel, nickel alloys, copper and gold are electroformed in the LIGA process.

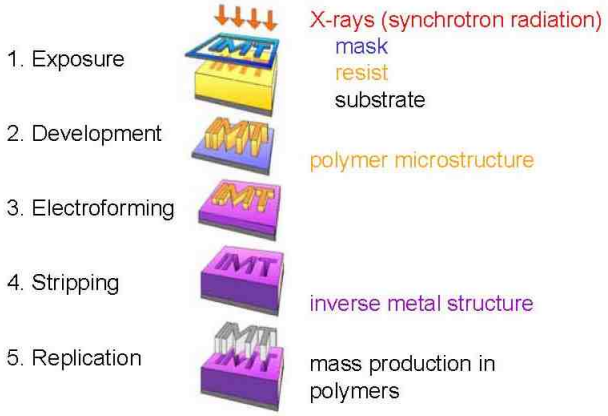


Fig. 1 Process Steps of the LIGA Microfabrication Technique

Gold with a high atomic number (Z=79) enables to manufacture high-quality X-ray mask absorbers. At Forschungszentrum Karlsruhe, Institut für Mikrostrukturtechnik (IMT), a gold sulfite electrolyte-based 'standard' process has been devoleped to produce soft, pore-free metal layers with low residual stress and a typical thickness between 2.5 µm and 25 µm. This process is compatible with positive tone resists such as polymethylmethacrylate (PMMA).

It was found to be advantageous over cyanide-based electrolytes and will be pursued in this work despite its poor macro throwing power under standard conditions. DC-plating of gold layers exceeding 70 µm thickness therefore results in inhomogeneous thickness distributions with variations of more than 40 %. This is acceptable for mask fabrication.

New applications such as decorative parts for watches or infrared filters extend the usage of gold to the fabrication of the micro components themselves. Compared to mask fabrication, relatively thick layers are required, and modifications of the existing standard process become necessary. Additional requirements include a more homogeneous thickness distribution, increased hardness, better surface finishing, less structure defects, and improved colour and bath/electrolyte handling.

Using pulse plating and a modified bath chemistry enabled the production of homogenous layers with a thickness over 150 µm. Hardeners (cadmium, palladium, and copper) and grain refiners (arsenic and antimony) increased the hardness of the gold parts over 200 $HV_{0.1}$ without changing the yellow gold colour.

2 The new Process

Screening of literature (scientific papers, reviews, patents, company literature) regarding layers with a hardness of more than 150 HV and a thickness of more than 10 µm, electrodeposited from non-cyanide electrolytes and hardened without dispersion additives ore subsequent process steps such as malleablizing/annealing, was performed. Two approaches for hardening the gold layers electroplated from an aqueous solution were found, i.e. solid solution strengthening and grain boundary hardening.

For our experiments, we chose three alloying systems[3,4,5] (Table 1). Each system comprises a minimum of one hardener (cadmium, palladium and copper) and one grain finer element (arsenic and antimony). All systems are based on a sodium disulfitioauraute complexed gold bath. One bath, 'TUI Golden Alloy', was entirely developed by IMT in cooperation with Technische Universität Illmenau, Germany. The other baths, 'AMI Golden Alloy'* and 'UMI Golden Alloy'** are commercially available, but have been modified within this study.

For the processing of test microstructures, simple laboratory equipment was used. The plating baths with a volume of 2 litres were filled into glass beakers. Inert, platinum coated titan was used as anodes. The temperature and stirring are controlled by using a stirrer-heater combined with a feedback thermometer. Stirring of the electrolyte is maintained by a magnetic bar.

DC processing was replaced by unipolar low-frequency pulse plating to reduce the negative influence of the mass transfer on the current density distribution by technically and chemically modifying the deposition. During the pulse off-time, concentration gradients and inhomogenities at the cathode surface, introduced by circulation and vorticity in the microstructures, are reduced.

* 'AMI Golden Alloy' … HELIDOR 100, AMI DODUCO GmbH, Pforzheim, Germany

** 'UMI Golden Alloy' … AURUNA 547, Umicore GmbH, Schwäbisch Gmünd, Germany

Table 1 Alloying systems

alloy	electrolyte	Au content	alloying elements	parameters	comment
Au-Sb-Cu	**TUI Golden Alloy**	25 g/l	antimony tartrate, Cu EDTA complexed	pH = 8–8,5 T = 55 °C i = 0.2–0.5 A/dm²	IMT 'standard' electrolyte for masks
Au-As-Cd	**AMI Golden Alloy**	10 g/l	As, 2 g/l Cd,	pH = 9,3 T = 55 °C i = 0.2–0.4 A/dm²	hardness 165–200 HV
Au-As-Pd-Cu	**UMI Golden Alloy**	8 g/l	2 g/l Pd, Cu, As	pH = 8,4 T = 55 °C i = 0.8–1.6 A/dm²	hardness 300 HV

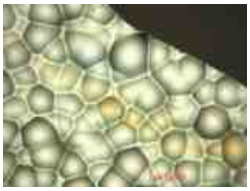
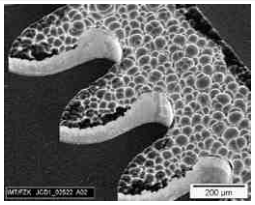
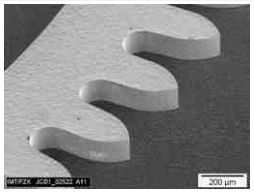
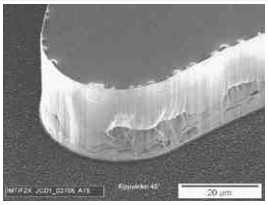
The pulse plating parameters, the pulse on-/off-times and the pulse height, and the microelectroforming parameters, the resist thickness, the metal/resist filling ratio and the layout, were adapted to the parameters of the IMT pure gold electrolyte for an optimum thickness distribution, and held constant[6,7].

For microelectroforming, it is necessary to enhance the gold content of commercial electrolytes with typically low gold content. The microelectroforming performance of the modified electrolytes listed in Table 1 was demonstrated.

3 Process Characterization and Rating

200 µm high PMMA microstructures, patterned by deep X-ray lithography, were used as templates to characterize the three different electrolytes. The templates were filled to a nominal gold height of 150 µm and examined concerning their thickness distribution, hardness, surface finish, structure defects, colour (cf. Table 2), and bath handling properties. Examination was performed with an optical microscope (thickness distribution, structure inspection), a scanning electron microscope (SEM, structure inspection), a hardness testing machine for small test load (Vickers hardness), a so-called 'nanoindenter' (Berkovich hardness, dynamic measurement), an ESEM/EDX tool (layer composition analysis), and a IC (ICP-OES, electrolyte and layer composition analysis, wet chemical method).

Table 2 Layer characterization

	TUI Golden Alloy	AMI Golden Alloy modified	UMI Golden Alloy modified
thickness distribution	+ 10 % / - 10 %	+ 10 % / - 10 %	nominal height not achieved
hardness [$HV_{0.1}$]	230–250	180–210	290
surface finish	surface with smooth, 5 µm large bumps	amorphous, rough surface with single/sporadic bumps	smooth surface
structure defects	blow holes, 'discoloured' structures in SEM micrographs	blow holes	convection influence visible in deposited layer, blow holes
colour	gold	gold	rose-coloured-gold
OM pictures			
SEM micrographs			
layer composition	98 wt % Au, 2 wt % Cu, Sb in the ppm range	99.5–99.8 wt % Au, 0.5-0.2 wt % Cd, As in the ppm range	approx. 90-92 wt % Au, 6-8 wt % Pd, 2 wt % Cu, As in the ppm range

To select the electrolyte that best meets the requirements of the new applications and also shows an easy bath handling (dosage, robustness, pH stability, etc.), one, two or three points were granted for the relative fulfilment of these rating criterions, see Table 3. According to the sum of all criterions, the best overall characteristic is shown by the AMI Golden Alloy modified, followed by the TUI Golden Alloy, and the UMI Golden Alloy modified.

Table 3 Electrolyte rating

	TUI Golden Alloy	AMI Golden Alloy modified	UMI Golden Alloy modified
thickness distribution	2	3	1
hardness	2	1	3
surface finish	1	3	2
structure defects	1	2	2
colour	3	3	1
electrolyte handling	1	3	1
sum	**10**	**15**	**10**

Structure defects such as blow holes were minimized by adding an organic component to reduce the influence of hydrogen deposition, see Figure 2, or by shorter pulse off-times to reduce the cadmium surface inhibition[8]. The hardness ranges between 180 $HV_{0.1}$ and 210 $HV_{0.1}$, depending on the cadmium content in the gold layers regulated by the cadmium/gold relation in the electrolyte. The Focused Ion Beam (FIB) analysis showed a fine grained structure with a grain size smaller than 300 nm produced by pulse plating which slightly reduces hardening by lattice dislocation.

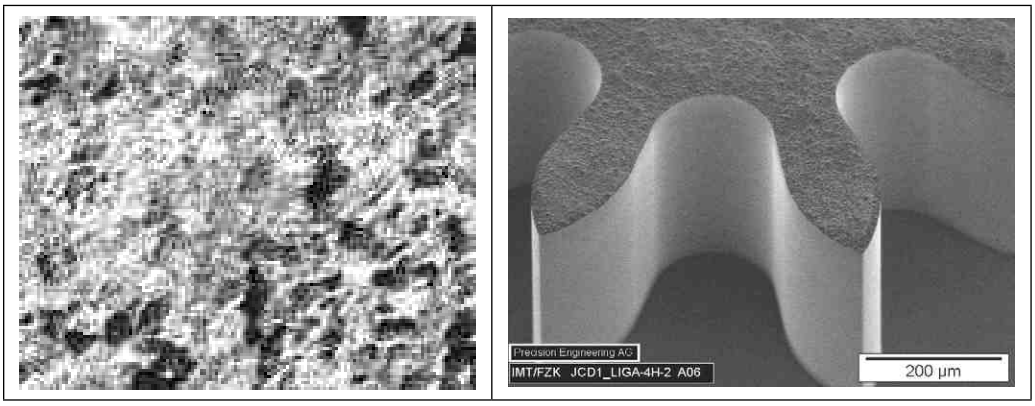


Fig. 2 Fine grained structure of Au-Cd-As with a grain size smaller than 300 nm (FIB micrograph, left) and 200 µm high micro component of a Au-Cd-As (SEM micrograph, right)

4 Conclusions

In this paper, the advancements of sulfite-based gold electroforming process steps within the LIGA microfabrication process are described that allow for new applications requiring thick homogeneous layers and improved material properties. Best results were achieved with a ternary system of gold-cadmium-arsenic with a gold content exceeding 24 carat.

5 References

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