UV-LIGA microfabrication of 220 GHz sheet beam amplifier gratings with SU-8 photoresists

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14. ABSTRACT

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UV-LIGA microfabrication of 220 GHz sheet beam amplifier gratings with SU-8 photoresists

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Abstract
Microfabrication techniques have been developed using ultraviolet photolithography (UV-LIGA) with SU-8 photoresists to create advanced sheet beam amplifier circuits for the next generation of vacuum electron traveling wave amplifiers in the 210–220 GHz (G-band) frequency regime. We describe methods that have led to successfully fabricated millimeter wave circuits, including applying ultra-thick SU-8 photoresist layers on copper, copper electroforming solutions, and the challenging removal of the SU-8 photoresists. A table of experimental liquid SU-8 removal chemistries and results is also presented.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Microfabrication techniques are quickly gaining interest for advancement of vacuum electron devices (VEDs), particularly for the fabrication of sub-wavelength slow-wave circuits [1–3]. VEDs remain at the forefront of the figure of merit, f^2P_{ave}, for average power generation P_{ave} at frequencies f in the millimeter and sub-millimeter wavelength ranges [4, 5]. At these frequency ranges, low microwave loss and high thermal conductivity become increasingly important for handling high power densities [6]. For that reason, microfabrication of vacuum-compatible, all-copper circuits is of high importance. Ultraviolet photolithography (UV-LIGA) [7, 8] provides the accuracy of photolithographic techniques in conjunction with the ability to electroform copper to meet these unique needs.

The push toward higher power-bandwidth products has placed a focus on spatially distributed electron beams, such as large aspect ratio sheet beams and multiple beam devices [9, 10]. These types of distributed beam devices are particularly amenable to photolithographic microfabrication techniques due to their reliance on planar interaction circuits.

The design of this traveling-wave amplifier centers on a simple grating over which a sheet electron beam passes [11]. Figure 1 shows the geometry of the device, and the design parameters are listed in table 1. The device is predicted to achieve a linear growth rate of 33 dB cm^{-1} at 210.5 GHz, with a −3 dB bandwidth of about 0.5 GHz [11, 12].

In figure 2, frequency scaling curves are presented for the grating amplifier circuit along with a comparison of fabrication technologies. UV-LIGA in particular is an attractive technique for its potential capability for the fabrication of VEDs operating from W-band (94 GHz) up to 1 THz. Micromachining is limited in its ability to form large vertical aspect ratios and also tends to deform and stress delicate features. The sizes of features that can be fabricated by wire electrical discharge machining (WEDM) are often limited to the size of the hole that can be bored in the material to feed the wire through. EDM methods also produce a rough surface, which induces loss of microwave energy. Deep reactive ion etching (DRIE) is not effective on copper substrates, but was used to fabricate metalized silicon test pieces [11].

This paper begins with a detailed description of the process for UV-LIGA using the SU-8 photoresist. In section 3, the electroforming stage is described, followed by techniques for successful SU-8 removal in section 4.

2. The SU-8 process

UV-LIGA is a microfabrication process that allows features down to just a few microns or even less to be fabricated

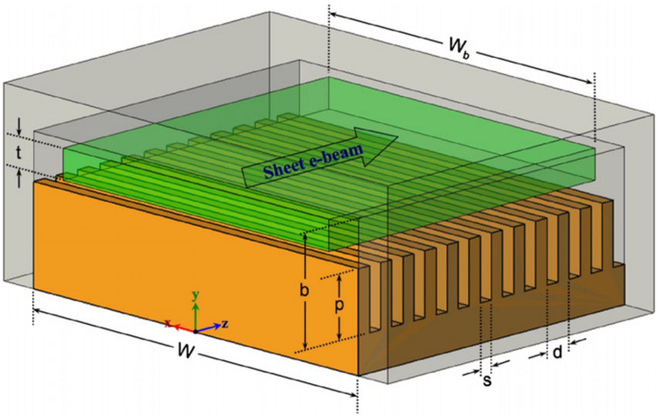

Figure 1. Perspective view of the grating amplifier geometry with a sheet electron beam passing over the grating. The assembly is contained in a waveguide (shown transparent). Design variables and axes indicated.

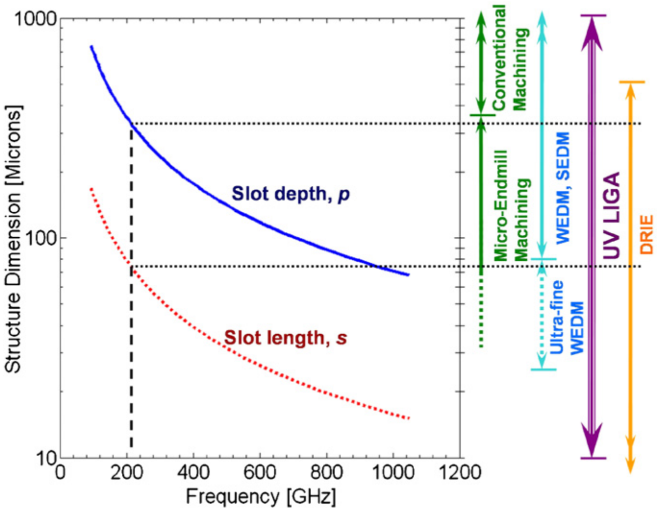

Figure 2. Frequency scaling of slot depth and length for a grating circuit, comparing fabrication technologies. UV-LIGA can potentially be used to fabricate VEDs from W-band (94 GHz) up to 1 THz.

Table 1. Grating amplifier design parameters.

Grating period	d	150 μm
Slot length	s	75 μm
Slot depth	p	333 μm
Beam tunnel	b-p	250 μm
Grating width	W	2.2 mm
Beam width	W_b	1.8 mm
Beam thickness	t	160 μm
Beam voltage	V_0	19 kV
Beam current	I_0	0.5 A

using an inexpensive UV source. Figure 3 illustrates the UV-LIGA process for creating grating circuits. A custom photolithography mask was purchased according to the specifications in table 1.

SU-8, an epoxy-based photoresist, was chosen because of its high viscosity, ability to be coated in extremely thick layers over 1 mm and demonstrated capability for high aspect ratios and fine features [8]. For spin coating, the very viscous SU-8 2150 can be used and can produce decent single coatings, but the best results were achieved using SU-8 3050 with methods described below.

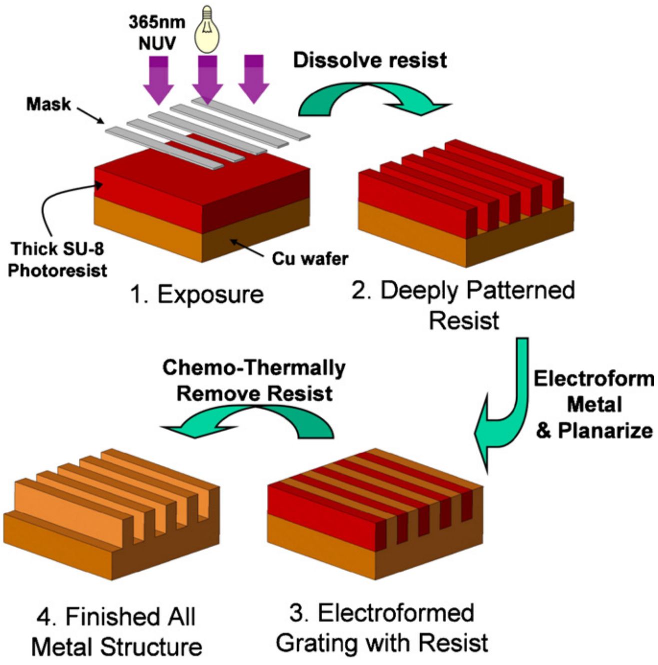

Figure 3. The UV-LIGA process for creating an all-copper grating: (1) SU-8 is deposited on a polished copper wafer and exposed with UV, (2) the unexposed SU-8 is removed, (3) copper is electroformed up between the crosslinked SU-8 patterns, (4) the SU-8 is removed.

The SU-8 molecule is exposed efficiently by 365 nm NUV from the I-line of a mercury arc lamp. It contains a photo-activated superacid, fluoroantimonic acid ($HSbF_6$) that begins a polymer crosslinking reaction to harden the epoxy during a post-exposure bake (PEB).

2.1. Polishing copper wafers

Due to the difference in mechanical properties of copper as compared to silicon, the techniques for polishing copper are somewhat different. Starting with 3 mm (1/8 inch) thick oxygen-free high-conductivity (OFHC) copper plates, a 100 mm diameter wafer is cut out by WEDM using an ONA AE300 WEDM machine. The wafers are ground on both sides using successively finer SiC-based sandpaper, 180, 320 and 600 grit, to obtain flat surfaces on both sides using a Buehler PowerPro^{TM} 3000 grinder/polisher with de-ionized water as a lubricant. Finally, Buehler MetaDI Supreme® water-based diamond suspension solutions are used on one side in decreasing sizes of 9, 3 and 1 μm for 3–5 min at the lowest counter-rotating speeds to prevent the copper surface from heating and oxidizing. No additional water is used at this polishing stage. A polished surface is important because it tends to reflect the UV directly back along the path it originated from, whereas a rough surface can scatter UV causing thickened or deformed structures.

The wafers are cleaned with de-ionized water, and then heated to 50 °C before cleaning with acetone and methanol. Dehydration continues at 50 °C for about 10 min. At no point should the temperature of the copper rise above 70–80 °C in air, which promotes the formation of an orange-colored oxide that results in poor adhesion with the SU-8 2000-series photoresists. The SU-8 3000-series photoresists were found to adhere much better to the difficult copper surface, while the SU-8 2000 series adheres most strongly to titanium, but only weakly to copper [13]. On the other hand, it was observed that the SU-8 3000 series is more difficult to remove chemically.

2.2. *Thick SU-8 layer deposition and soft baking*

Several methods were investigated for applying SU-8 photoresist in ultra-thick layers. Thin layers up to tens of microns are easy to achieve by simply spinning off excess photoresist [14], but for ultra-thick layers, this technique requires ultra-viscous photoresist, such as SU-8 2150, and low spinning speeds. Such a combination of parameters often results in wavy, uneven depositions. Multiple layers can be deposited by spinning, but this is time consuming, increases uncertainties and is not attractive for industrial scaling due to the large amounts of wasted photoresists.

Standard spinning techniques require the use of edge bead remover (EBR) chemicals to prevent a bead of excess photoresist from forming at the edge of the wafer due to discontinuous shear forces. Such chemicals are often highly flammable and somewhat undesirable to use. In addition, due to the extremely high viscosity of SU-8 as it is thrown off of the wafer by centrifugal force, tiny fibers of SU-8 were observed to form, which then catch air currents and often land on the wafer surface. Upon soft baking, these fibers caused very large craters to form on the surface of the SU-8. The mechanism for this cratering effect is not understood. Even under the best conditions without craters, variations in SU-8 thickness of ±5% were unavoidable after soft baking.

An improved spinning chuck was fabricated to alleviate all of the above problems and simultaneously improve flatness. This chuck features an extended flat region past the wafer to eliminate the discontinuity at the wafer edge. The wafer thus appears larger and prevents the edge bead from forming on the actual wafer, halting the need for the EBR chemicals entirely. Finally, a catch at the edge of the chuck prevents fibers from forming by simply catching the displaced SU-8, which can then be recycled since EBR was not used. The variation in thickness was observed to be reduced to about ±3%. Figure 4(*a*) shows a diagram and photograph of this improved spinning chuck. Recessed chucks have been used industrially for quite some time to improve flatness [15]. This chuck adds a catch mechanism to prevent the viscous SU-8 from leaving the chuck, thereby preventing SU-8 fiber formations.

In an effort to simplify the process further and improve flatness, a gravity-flattening method was developed that (a) uses the minimal amount of photoresist, thus producing no waste, (b) reduces or eliminates clean-up, (c) produces a flatter coating and (d) is industrially realizable. Figure 4(*b*) shows the process diagrammatically. Heat a 100 mm wafer to 50 °C on a carefully leveled hotplate and apply about 4 ml of SU-8 3050 to the center in a spiral pattern to form a round, flat circle. Tilt the wafer at about 45–60° and slowly rotate it until the SU-8 has flowed within about 2–4 mm of the edge of the wafer. Using an eyedropper, apply 1 ml of SU-8 thinner (cyclopentanone) to the surface to reduce surface tension and cover the wafer for 30 min at 50 °C. Uncover the wafer and soft bake up to 100 °C at 2.5 °C min^{-1}. Hold at 100 °C for 2 h, then ramp down at 1.5 °C min^{-1} or less to room temperature (RT). It has been found that without the use of the thinner, highly viscous SU-8 does not adequately reflow to form a flat surface due to solvent evaporation at the surface, which effectively freezes the surface in place [16]. The added solvent and its vapors prevent the surface from freezing in place. While less viscous SU-8 products would tend to flow better, they are not amenable to the formation of thick layers due to inadequate surface tension.

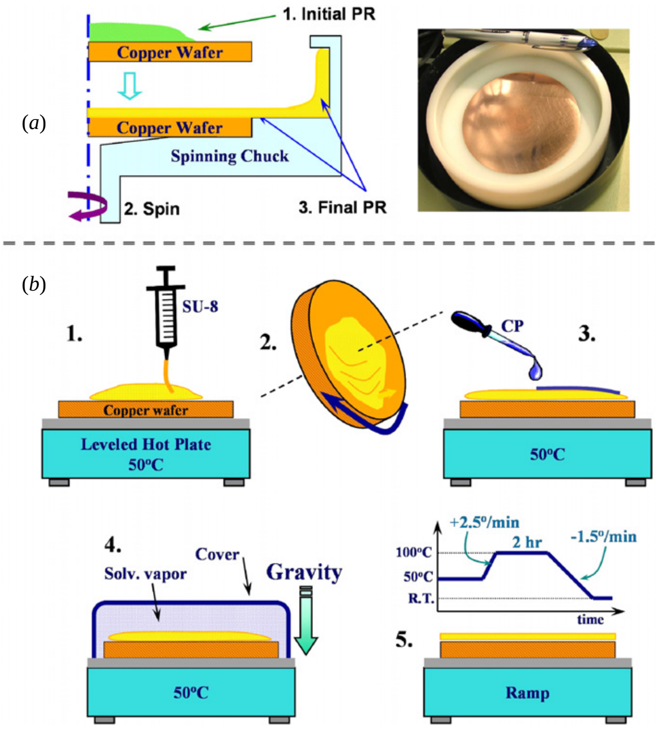

Figure 4. (*a*) The improved spinning chuck uses an extended area level with the copper wafer to eliminate the edge bead. A catch at the edge prevents fiber formation. (*b*) The gravity-assisted deposition technique: (1) apply 4 ml SU-8 3050 to a warm, level wafer, (2) rotate at an angle to spread it within 3 mm of edge, (3) drop 1 ml cyclopentanone on top, (4) cover for 30 min to level, (5) uncover and soft bake with profile.

The thickness of the SU-8 can be measured using a microscope at about 200 magnification using only red or cleanroom-yellow lighting by looking for tiny defects in the surface and comparing that height to the uncoated extreme edge of the wafer. The resulting thickness is typically around 400 μm using this method, with a variation of only ±1% in thickness. The final thickness of the SU-8 can be calculated by taking the solids fraction into account. For SU-8 3050, which

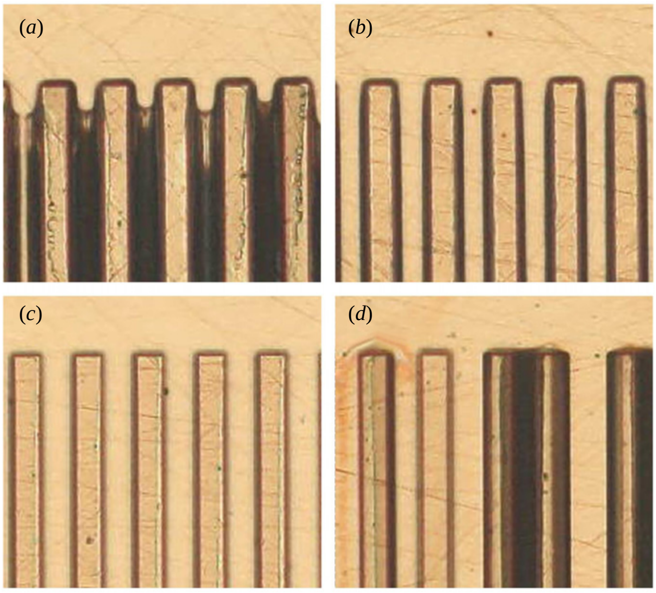

Figure 5. Photos from the same developed wafer showing the effect of varying exposure dose: (*a*) blocked vanes due to significant over-exposure, (*b*) thickened vanes due to modest over-exposure, (*c*) optimal exposure, (*d*) loose vanes due to insufficient exposure. Photos are taken perpendicular to the wafer surface.

is 75.5% solid, the final thickness on a 100 mm diameter wafer resulting from 4 ml of SU-8 3050 would be

$$h_f = \frac{V_i \alpha}{S} = \frac{4\ \mathrm{ml} * 0.755}{\pi (50\ \mathrm{mm})^2} = 385\ \mu\mathrm{m},$$

where h_f is the final thickness, V_i is the initial volume of the SU-8, α is the solids fraction and S is the surface area. Since in reality the SU-8 is not quite spread exactly to the edge, and the edge of the SU-8 is slightly rounded due to surface tension, the actual SU-8 thickness would be slightly higher.

2.3. *Ultraviolet exposure*

Proper exposure is critical to achieving a clean structure. As little as ±5% can be the difference between perfect exposure and having the structures fall off due to inadequate adhesion, which is a key issue for copper substrates. Over-exposure is manifested as a thickening of the SU-8, attributed to UV scattering, and the sidewall angles are generally 'big headed' due to higher exposure dose at the top than the bottom. Figure 5 illustrates the effect of exposure. We use a Newport model 97436-1000 500 W UV flood source. SU-8 edges appeared cleaner after installation of an Oriel model 87066 I-line filter to isolate the 365 nm range. We estimate a dose rate of 25–30 mW cm^{-2} at 365 nm. With this setup, we find that exposure doses of 6–8 mJ cm^{-2} μm^{-1} result in optimal exposure at 400 μm thickness. For thicker layers, the total exposure dose needs to increase significantly due to the exponential attenuation of the UV inside the SU-8. In addition, it is important to incrementally build up the exposure in small doses to prevent heating of the SU-8. Prolonged continuous exposures tend to result in ragged, deformed edges. Incremental exposures of 10 s followed by 30 s of cooling time has been found effective.

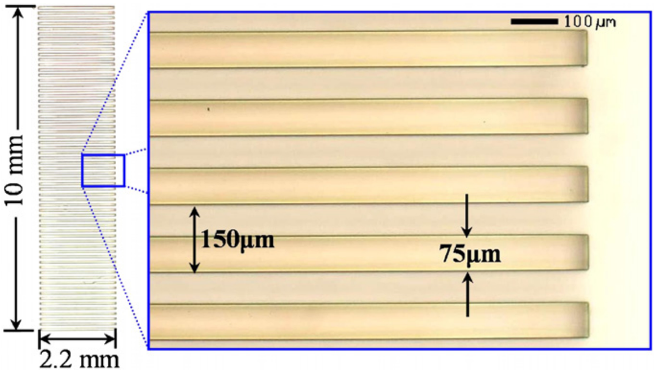

Figure 6. A photomicrograph of a finished SU-8 grating on copper showing excellent formations.

2.4. *Post-exposure baking*

If the temperature is ramped too quickly, the PEB can cause cracking or delaminating of the SU-8 structures due to stresses that have not had enough time to be relieved. The much larger thermal expansion coefficient of copper as compared to silicon only exacerbates the adhesion issues, since SU-8 is known to shrink during PEB [17]. On the other hand, a PEB with slow ramp rates can effectively extend the PEB time, resulting in over-crosslinking of the SU-8, thickening of the structure and difficulty in the removal stages later. Ramping up from RT to 100 °C at 3 °C min^{-1}, holding at 100 °C for 15 min and ramping down to RT at 1 °C min^{-1} seems quite effective for layers on the order of 400–500 μm thick.

2.5. *Developing SU-8*

The MicroChem Corp. SU-8 Developer (99% 1-methoxy-2-propanol acetate, a.k.a. PGMEA), preferentially dissolves uncrosslinked SU-8 from the wafer, leaving behind the rigid SU-8 structure that was exposed to UV. We use a reciprocal motion shaker table to accelerate the developing process, which works well for the grating slot shapes. Orbital motion should be avoided, because it tends to clean only the outer edge leaving zero fluid velocity and little cleaning in the center. A figure-8 motion would perhaps be more beneficial for structures that are not linearly oriented. It has been found that two or three 30 min segments with fresh developer work well for a 400 μm thick layer. The wafer is then cleaned with the developer from a squirt bottle and finally rinsed with isopropanol and spun dry. Spot checks for residue should be performed under a microscope, and a subsequent developer wash may need to be performed. Figure 6 shows a completed SU-8 grating on copper. Developing with the wafer SU-8 side down to gain gravitational advantage, and the use of ultra- and mega-sonic agitation has been reported to speed up the development time with a concurrent decrease in feature swelling [8, 18]. Prior to electroforming, it is also advisable to pre-soak the wafer in a sulfuric acid solution to help remove any traces on the copper surface of adhesion promoters present in the SU-8 3000 series, which on occasion seem to interfere with the copper electroforming chemistry.

Table 2. DC electroforming solution.

Additive	Symbol	Concentration
Sulfuric acid	H_2SO_4	190 g l^{-1}
Copper sulfate	$CuSO_4 \cdot 5H_2O$	65 g l^{-1}
Copper chloride	$CuCl_2 \cdot 2H_2O$	120 mg l^{-1}
Polyethylene glycol (4000 mol wt)	PEG	100 ppm
Sodium (3-mercapto-1-propane) sulfonate	MPS	12.5 ppm[a]
Janus Green B	JGB	2.0 ppm[a]
Anode: OFHC copper		
Cathode: wafer to be plated		

[a] Extremely sensitive.

2.6. Double exposure option

At the end of the development process, adhesion may be somewhat strengthened by re-exposing the wafer to the UV flood source without the mask for about 30 s and baking to about 50 °C or so for 15 min. This process will help activate and more fully strengthen any SU-8 on the bottoms of the features that did not receive enough exposure.

For preservation, the wafer is stored under inert gas at room pressure to prevent any oxidation or other chemical reactions on the copper surface from progressing.

2.7. Copper electroforming

Void-free copper electroforming with fine grain size is a very challenging art for which almost all information was proprietary until around the year 2000. The main ingredients for the electroforming bath are sulfuric acid and copper sulfate, but dc electroforming will produce a very poor surface quality unless parts-per-million amounts of key additives are introduced into the bath [19–22]. A nearly optimal plate bath for dc plating tailored to these types of structures consists of the ingredients listed in table 2 in water solution.

The ideal bath should produce a very fine copper grain size of a few microns so that smooth slot walls may be formed. A coarse grain size may result in roughness and gaps in the grating that would be a detriment to the performance of the amplifier by increasing microwave losses and breaking the periodicity of the circuit. Voids in the copper deposit can trap the bath solution, which, if heated, results in bubbling deformation in the copper. Furthermore, the electron sources used in VEDs are typically very sensitive to sulfur, and outgassing from such voids could quickly poison the electron gun under vacuum [23, 24]. The competing roles of PEG and MPS along with the Janus Green B (JGB) dye in the bath are key to reducing this grain size and eliminating voids [25–28]. PEG acts as a suppressor, while MPS acts as an accelerant to enhance the speed of the copper deposition. JGB works as a grain refiner and leveling agent.

After the bath is prepared, it must go through an aging period before it plates with a fine, pore-free grain structure. This aging period is usually accomplished by plating a dummy piece of copper at controlled electrode potential. During this time, a thin film is observed to form on the anode and copper nanoparticles tend to precipitate, both of which must re-dissolve into the solution before plating can be performed. In addition, during the plating process, the JGB seems to oxidize and lose its color. Additional minute amounts of MPS and JGB may be periodically added to keep the bath in balance.

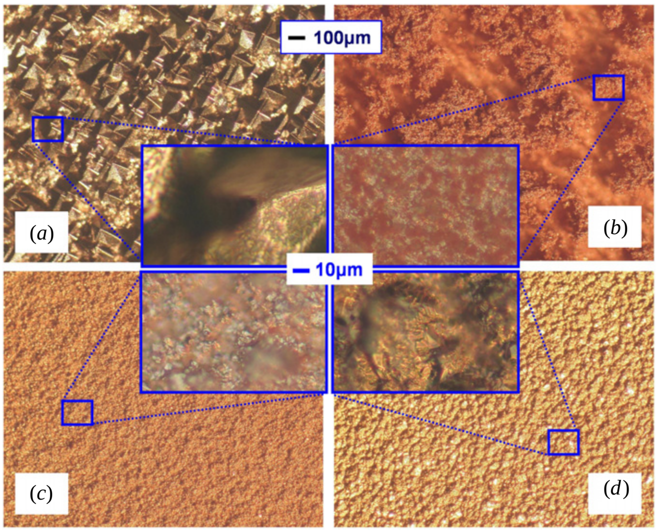

Figure 7. Photomicrograph of the various raw surface finishes after electroforming copper: (*a*) large, pyramid-shaped crystals, (*b*) porous, spongy copper, (*c*) very fine-grained copper on the verge of porosity, (*d*) non-porous with fine grain size below about 8–12 μm.

Figure 7 shows various electroformed surfaces of copper wafers prior to grinding and polishing. The wide variances in crystal structure are a result of small changes in the bath chemistry. The dc current density was 4 mA cm^{-2}, yielding a deposition rate of approximately 4 μm h^{-1}. Figure 7(*a*) shows large, pyramid-shaped copper crystals that form near the wafer edge in a 'high copper sulfate' bath with no organic additives. Figure 7(*b*) shows a highly porous, spongy copper deposited with the ingredients in table 2 without MPS or JGB (only PEG). Fine-grained crystal structures with no porosity are shown in figures 7(*c*) and (*d*). These two samples were then polished and heated to 600 °C in argon. The sample in figure 7(*c*) became grainy and dull, while the sample in figure 7(*d*) maintained a polished surface. In both cases, the largest grain sizes that could be found were at or below the 8–12 μm range, which is acceptable for a grating with a 75 μm slot size. The recipe in table 2 produced the sample in figure 7(*d*).

Figure 8 is a photomicrograph of a grating after electroforming and grinding/polishing the surface, but prior to removal of the SU-8. In this sample, grain roughness can be seen in the slots, although it is more prominent on the right-hand side of the slots. This effect is due to the direction of fluid flow caused by the magnetic stir bar in the beaker. A circular motion of the wafer has since been found to mitigate this effect.

It has been found that electroforming copper using pulsed current instead of dc current has certain advantages [29–32]. A custom pulsed power supply was built in-house to accommodate a range of pulsed current techniques in order to explore this possibility. After performing several rudimentary

Table 3. List of SU-8 removal chemistries.

Chemistry	Condition	Copper damage	Swollen/ soft	Bowed/ shriveled	Discoloration	Crazed	Crumbles	Tot. effect on SU-8
SU-8 Remover PG	3 h, 70 °C		3		1	2	2	**3**
Burning in H_2 furnace	10 m, 500 °C			4	4		3	**3**
Burning in argon furnace	30 m, 700 °C	2		3	4		2	**2**
Burning in air	20 m, 500 °C	4			*Burns to dust.*		4	**4**[a]
Pyridine (Py)	3d, RT		3		2		3	**3**
Py + acetone	1d, 55 °C		3			2	2	**2**
Py + $K_2Cr_2O_7$ + H_2O	3d, RT		3	3	2		3	**3**
Py + 1-butyl-3-methyl-imidazolium iodide	3d, RT		4	3	2	3	4	**4**
Py + propylamine, 2:1	2d, RT	1	4	3	3	4	4	**4**
Py + butylamine, 2:1	2d, 75 °C		4	4	3	3	4	**4**
Tetrahydrofuran	3d, RT		1		2	4	3	**3**
Conc. HNO_3	3d, RT	3	4	3	4		4	**4**[a]

1 = weak effect, 4 = severe effect, [blank] = no effect, [a] = concurrent moderate to severe damage to copper.

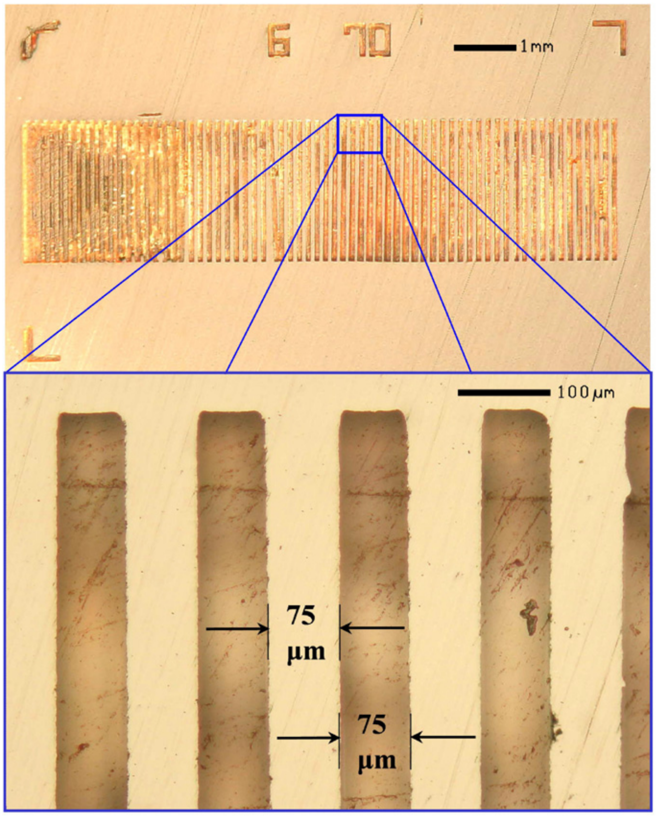

Figure 8. Photomicrograph of electroformed copper on an SU-8 grating after mechanical grinding, but prior to SU-8 removal. Some coarseness of the copper grains is evident due to the direction of fluid flow.

experiments, it has been found that, indeed, pulsed plating can produce an electroformed surface with a medium-quality copper structure in a bath containing only H_2SO_4, $CuSO_4$ and $CuCl_2$, while that very same bath grew large dendritic crystals using dc. This is a significant finding because it may allow for reduced sensitivity to bath additives, or allow for less additives, or eliminate additives altogether while producing a finer grain size. This pulsed experimental work is ongoing.

3. Removal of SU-8

The final step in the grating microfabrication is the removal of the SU-8 photoresist [33]. This is arguably the most challenging step, because no solvent has been found, published or patented that can simply dissolve SU-8 after PEB at the time of this writing. Therefore, it was found that a multi-step process could be used to remove SU-8 effectively without damaging the copper.

3.1. *Liquid chemistries*

Table 3 illustrates some of the most effective experiments that have been performed in our laboratory in order to remove SU-8. Composition ratios, when given, are for liquids by volume. Most solvent-based tests have followed a similar trajectory of first softening and swelling the SU-8, but later causing it to become very hard and brittle. It is believed that solvents such as *N*-methyl pyrrolidinone (NMP), which is the major constituent in MicroChem SU-8 Remover PG, are initially effective at expanding the free volume between the polymer chains in the cross-linked SU-8 epoxy, at least at temperatures in the range of 50–80 °C. After this structural swelling and plasticizing, however, the extremely strong $HSbF_6$ acid, which makes up almost 4% of SU-8 2150 by weight, retains sufficient chemical activity and diffusive mobility to crosslink the remaining unreacted epoxy groups and eventually re-harden the SU-8. For this reason, certain organic acids tend to further harden the SU-8: glacial acetic acid caused the SU-8 to become extremely hard rather than attacking the polymer bonds. This re-hardening process also seems to occur after several hours or at elevated temperatures (100 °C and above) in nearly all chemistries. In fact, the recommended method for dramatically hardening SU-8 is a hardbake at 200 °C. Pyridine seems to do a better job at softening the SU-8 than NMP, but it also cannot prevent the re-hardening tendency by itself. The most promising chemical treatment appears to be pyridine and butyl amine in 2:1 volume ratio refluxing at 75 °C. It is believed that the basic (proton accepting) character of primary alkyl-amines neutralizes the photo-activated $HSbF_6$ acid, preventing re-hardening. There was no damage to the copper, but severe damage to the SU-8. Tetrahydrofuran was unique in its ability to heavily craze the SU-8 surface and may be a useful pre-treatment to greatly increase the active surface area before attack with other chemistries. Concentrated nitric acid also has highly desirable effects on the SU-8, but it also imparts significant damage to the copper.

The liquid SU-8 removal chemistries tend to rely on swelling, which may be prevented by constrained structures or could cause damage to delicate structures, particularly if multi-layer UV-LIGA is being performed. Another intrinsic issue of liquid removal techniques is the need for diffusion of the reagent through the polymer solid, which is slow in high-aspect-ratio, dead-ended structures such as slots.

3.2. Burning/heating methods

By far the simplest SU-8 removal technique is burning it out in air at around 500 °C [33], but this has the extremely undesirable effect of oxidizing the copper surface into a thick layer of black cupric oxide (CuO) that spalls off. While these oxides can then be removed in a sulfuric acid solution or a hydrogen furnace, pits and swaths of missing surface up to about 20 μm deep are left where the CuO has spalled off. Clearly, this is unacceptable when a slot depth accuracy of better than 5 μm is required.

SU-8 can also be partially carbonized in a hydrogen furnace without the presence of oxygen, but instead of completely burning out into dust, the SU-8 just shrivels significantly and partially remains as a carbonized solid in the slots. Since the hydrogen cleans the copper simultaneously, it is a useful finishing step in the removal of SU-8. The experiment was also tried in argon at 700 °C, but with much less satisfactory results due to significant grain growth in the copper at high temperatures.

Figure 9 shows a hybrid process sequence that removed nearly all of the SU-8 from a grating structure. First, the grating was placed in MicroChem Remover PG for 3 h at 80 °C, which resulted in softening, swelling and partial removal of the SU-8 (figure 9(*a*)). Next, the grating was placed in the hydrogen furnace at 500 °C for 10 min, which shriveled and burned out much of the SU-8 (figure 9(*b*)). After an ultrasonic bath in Microclean 90® and water, only half of a dozen blackened bits of SU-8 remained. The remaining SU-8 residue was cleaned using hydrogen plasma.

3.3. Plasma methods

A plasma ashing chamber has been fabricated to study the effects of reactive gas plasma on SU-8 removal. A block diagram of this device is shown in figure 10. The present experimental work involves hydrogen, oxygen and tetrafluoromethane (CF_4) plasmas. Removal is reported to be most effective when both fluorine and oxygen species are present [33]. The current unit allows plasma to be generated by an RF source in the range of 10–20 MHz at up to about 50 W, with the option of a dc offset from 0 to ±3 kV. Pressures in the range of 100 mTorr (calibrated in air) are most often used. It has been found that substrate temperatures of at least 200 °C are needed to effectively attack SU-8.

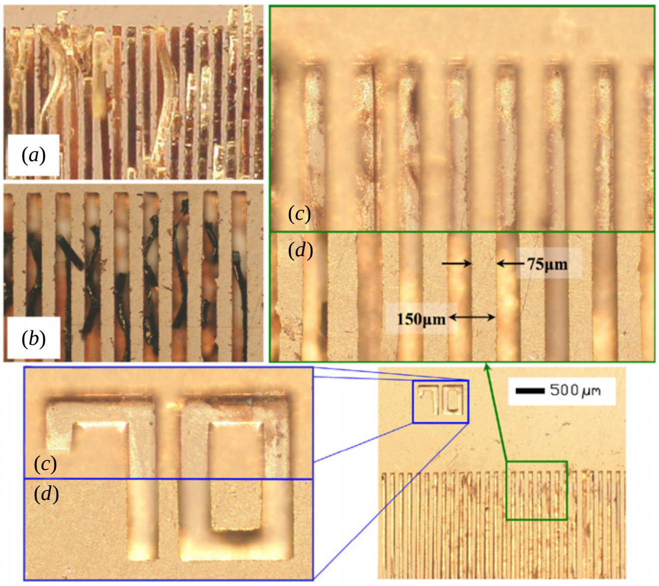

Figure 9. Photomicrograph of a grating after sequential stages of SU-8 removal. (*a*) After 3 h in SU-8 Remover PG at 80 °C, (*b*) after burning in a hydrogen tube furnace at 500 °C. (*c*) indicates focus on the bottoms of the respective slots, (*d*) indicates focus on the top surfaces after ultrasonic cleaning and plasma ashing.

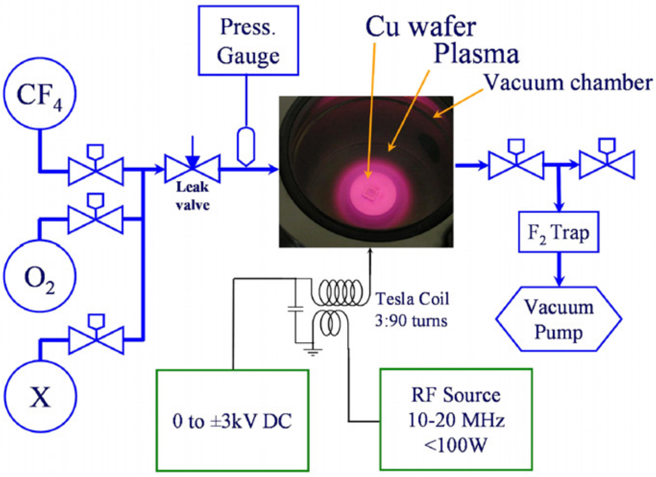

Figure 10. Plasma asher system block diagram, showing various input gases and RF/dc hybrid system. ‘X’ is a purge gas or hydrogen.

An alternate method exists whereby very high power plasma of reactive gases (often O_2 and CF_4) is generated in a separate water-cooled reactor to completely ionize the gases. The distance from the plasma tube to the sample is long enough that the ions can be neutralized, but not so long that monatomic species recombine. Thus, the resulting monatomic reactive species are allowed to flow over the sample. This is the chemical downstream etching (CDE) method, which often makes use of a 1 kW, 2.45 GHz magnetron power source to generate the plasma [33–35]. Removal rates show a ten-fold improvement over the plasma chamber method for some types of photoresists. This technique was not utilized in the current experiments, but is under consideration for future experiments.

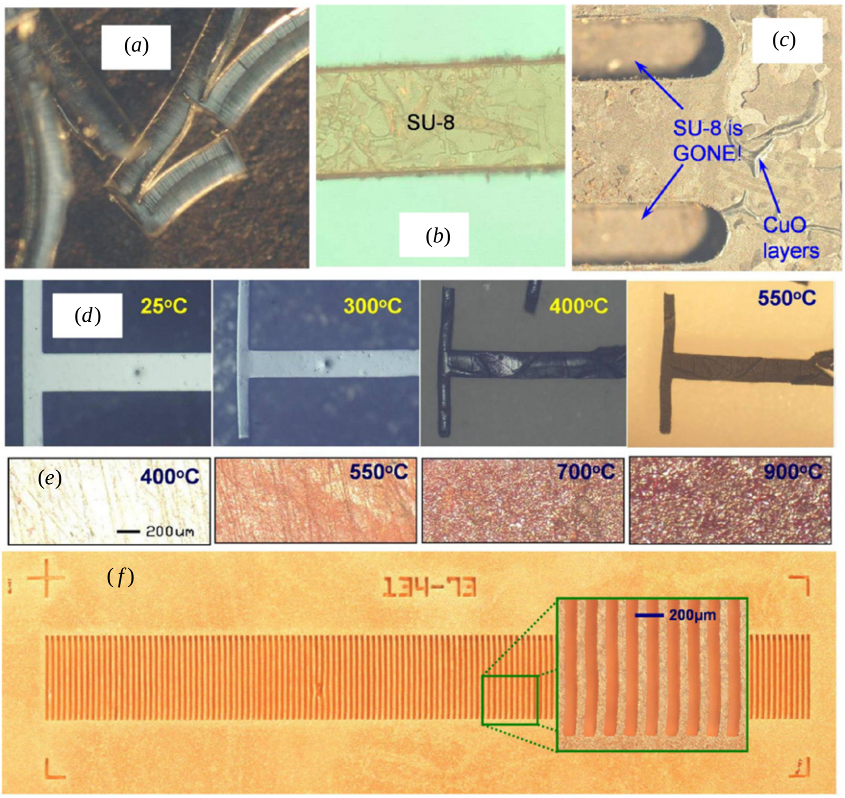

Figure 11. (*a*) Liquid chemical treatment of SU-8 using MicroChem SU-8 Remover PG at 80 °C causes softening and swelling. (*b*) Oxygen plasma treatment of a piece of SU-8 shows heavy crazing of the surface. (*c*) SU-8 has been completely burned out in air at 500 °C, but the copper heavily oxidizes and spalls off. (*d*) Sequence of treatment in an argon furnace, which causes shrinking and carbonization at 400 °C, along with (*e*) the effect of grain growth on copper. (*f*) A finished G-band all-copper amplifier grating with 134 slots after SU-8 removal by a molten salt bath.

3.4. Molten salts

The most effective method found to date in our laboratory for the removal of SU-8 2000- and 3000-series photoresists from copper has been a molten salt bath, which was also found to be effective on nickel and to a lesser extent silicon by Dentinger [33]. Using dry $NaNO_3$ and KOH in 2:1 mixture by weight, the SU-8 effectively decomposes into gases at between 310 °C and 350 °C. The decomposition occurs in a progressive manner from where the surface of the SU-8 contacts the molten salt and gradually works through the SU-8 volume until it has been consumed. A 400 μm deep grating with the dimensions in table 1 can be completely freed of SU-8 in about 5 min, with a concomitant oxidation of the surface of the copper. The copper oxidation is easily removed with a weak sulfuric acid solution in an ultrasonic cleaner followed by a formic acid solution. The copper does not visibly oxidize until about 2 min into the process, so if the process can be sped up by pre-treating the SU-8, even less etching of the copper may result. Suitable pretreatments might include crazing of the surface of the SU-8 to increase surface area by THF, or modest shrinkage of the SU-8 in a hydrogen furnace to allow the molten salts to attack from a multitude of directions simultaneously.

Figure 11 photographically summarizes the effects of various chemical, plasma, burning and molten salt treatments on SU-8.

4. Conclusions and future work

In summary, great advances have been made in microfabrication capabilities that are important for vacuum electronics at the millimeter and sub-millimeter wavelengths. Using UV-LIGA, we have extended the fabrication capabilities down to tens of microns with high aspect ratios demonstrated to create all-copper circuits capable of low microwave loss. A copper electroplating bath has been experimentally optimized for these kinds of devices, and effective techniques for removal of the SU-8 photoresist have been developed and described. The molten salt bath shows the most promise to date.

Based on the encouraging results from the initial pulsed electroforming experiments, a new custom pulsed transconductance amplifier was built to handle the needs of a large-scale (25 l bath) copper electroforming system presently under construction. Investigations involving more complicated slow-wave structures fabricated using multiple layer lithography will be performed. The work described here, together with the ongoing and future process enhancements, will enable the fabrication and demonstration of new types of millimeter and sub-millimeter wave VEDs.

Table A1. More extensive list of SU-8 removal chemistries.

Chemistry	Condition	Copper damage	Swollen/ soft	Bowed/ shriveled	Discoloration	Crazed	Crumbles	Total effect on SU-8
SU-8 Remover PG (RPG)	3 h, 70 °C		3	1	1	2	2	**3**
N-Methyl-pyrrolidinone (NMP)	2 h, boiling		3	2	1	2	3	**3**
Acetone	1d, boiling		1	1				**1**
NMP + acetone in 1:2 ratio	4 h, boiling		2			2	3	**3**
NMP + acetone in 3:2 ratio	1d, boiling		2			2	3	**3**
Glacial acetic acid + iodine	3d, RT	3			3			**0**[a]
Dimethyl formamide (DMF)	8d, RT		1					**1**
Dimethyl sufoxide (DMSO)	8d, RT			1				**1**
Pyridine (Py)	8d, RT		3		2		3	**3**
Analine	8d, RT							**0**
Acetonitrile	8d, RT							**0**
Iodopropane	6d, RT							**0**
Py + iodine	6d, RT		3		3			**3**
Py + lithium iodide	6d, RT	4	3		3		3	**3**[a]
RPG + Py, 1:1	3d, RT		4	3	3	3	4	**4**
Py + $K_2Cr_2O_7$ + H_2O	3d, RT		3	3	2		3	**3**
1,1-Dimethylpyrrolidinium iodide dissolved in Py	3d, RT		3	3	2		3	**3**
1-Propyl-3-methylimidazolium iodide	3d, RT							**0**
1-Butyl-3-methylimidazolium iodide dissolved in Py	3d, RT		4	3	2	3	4	**4**
Py + anh. $AlCl_3$	3d, RT	2	4	2				**3**
Py + NH_4OH	3d, RT	x	2		2			**2**
Conc. HNO_3	3d, RT	3	4	3	4		4	**4**[a]
Diethyl ether	3d, RT							**0**
Tetrahydrofuran (THF)	3d, RT		1		2	4	3	**3**
Py + pyridinium (Pym) HBr crystals	2d, RT	1	2	3				**2**
Py + Pym HCl crystals	2d, RT	1	1					**1**
Acetone + Pym HBr crystals	2d, RT	1						**0**
Pym dichromate in Py	2d, RT		1		2			**1**
Pym chlorochromate in Py	2d, RT	4	1		2			**1**[a]
Propylamine (PA)	2d, RT	1	2				3	**2**
Py + PA, 3:1	2d, RT	1	4	2	2	3	4	**4**
Py + PA, 2:1	2d, RT	1	4	3	3	4	4	**4**
Butyl amine (BA)	2d, RT		4			2	2	**3**
Py + BA, 2:1	2d, RT		4	3		3	4	**4**
Py + BA, 1:1	2d, RT		4	4		3	2	**4**
Py + BA, 2:1	2d, 75 °C		4	4	3	3	4	**4**
Dichloromethane + formic acid + methanol, 1:1:1	2d, RT	1	2	2			3	**2**
Condensed NO_2/N_2O_4	3 h, 2 °C				4		4	**4**
Py+PA, 2:1 with −325 mesh Cu	2d, RT	x	4	3	2		4	**4**
Py+PA, 3:2 with −325 mesh Cu	2d, RT	x	4	3	2		3	**3**
Py+PA, 2:1 with <5 μm CuO	2d, RT	x	3	2	2		3	**3**
Py+PA, 2:1 with Cu acetate	2d, RT	x	2	2	2		2	**2**
Py+PA, 2:1 with −30 mesh Zn	2d, RT	x	2				2	**2**
Py+PA, 2:1 with –325 mesh Fe	2d, RT	x	4	3			4	**4**
Py+PA, 2:1 (4 ml) + 2 drops 30% H_2O_2	2d, RT	3	4	3	2		4	**4**[a]
Py+PA+acetaldehyde, 4:2:1	2d, RT	3	3	3	2		1	**3**[a]
Py + PA + pyrogallol, 4:2:1	2d, RT	1	3	3			3	**3**
Py+PA + Pym dichromate, 4:2:1	2d, RT	2	3	3			2	**3**
Py + PA, 2:1 with Na_2SO_3 diss.	2d, RT	2	3	2	2		1	**2**
PA + acetaldehyde, 1:1	3d, RT	2		1			1	**1**
Tetramethyl ammonium hydroxide (TMAH) + methanol, 1:3	3d, RT				1			**0**
Py + 1-methyl pyrrolidine, 1:1	3d, RT	1		1				**0**
1-Methyl pyrrolidine	3d, RT							**0**
PA + Remover PG, 1:1	3d, RT	3	4	2			3	**4**[a]
Py + PA, 2:1	2d, 48 °C	3	4	3	3		4	**4**[a]
RPG + PA, 1:1	2d, 48 °C	2	4	3	2		3	**4**
RPG + acetaldehyde, 1:1	2d, RT		1	2			1	**1**
RPG + PA, 1:1 with –325 mesh Fe	2d, RT		3	3			2	**3**

Table A1. (Continued.)

Chemistry	Condition	Copper damage	Swollen/ soft	Bowed/ shriveled	Discoloration	Crazed	Crumbles	Total effect on SU-8
RPG + BA, 1:1	2d, RT		2	3			2	**3**
RPG + PA + BA, 1:1:1	2d, RT	1	3	2			1	**2**

1 = weak effect, 4 = severe effect, [blank] = no effect, x = no Cu wire, [a] concurrent moderate to severe damage to copper.

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Appendix A. Liquid chemistries for SU-8 removal

A more extensive table of liquid chemistry experiments to attack SU-8 is presented in table A1. Composition ratios, when given, are for liquids by volume. The tests were mostly performed in test tubes with a chip of post-exposure baked SU-8 and a short piece of OFHC copper wire. A Liebig condenser was used in a reflux configuration where experiments involved boiling. All experiments were performed in an efficient fume hood.

The most effective chemistries center around the use of pyridine (Py), augmented with propylamine (PA) or butyl amine (BA), which result in softening, swelling and spontaneous breakage into small pieces. Refluxing to the boiling points of the mixtures greatly enhances the attack on the SU-8.

A very interesting method involved the generation of brown NO_2 gas by the action of concentrated nitric acid on copper turnings. This gas was then condensed into a green N_2O_4 dimer liquid in a cooled flask at about 2 °C. When the SU-8 was added to this chilled liquid, it broke up spontaneously into tiny pieces. There was no damage to the copper. The strong oxidizing nature of this reagent and its inhalation hazard require caution.

For the processes involving Py and PA, copper and iron were found to have a catalytic effect: the most heavily damaged SU-8 often wrapped itself tightly around the copper, whereas SU-8 without copper was significantly less affected.

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