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# Removal of SU-8 photoresist for thick film applications

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**Abstract**

SU-8 photoresist has consistently shown excellent resolution in thick film applications, has been utilized as an electroplating mold, and is sensitive to inexpensive UV sources. However, the highly crosslinked epoxy remaining after development is difficult to remove reliably from high aspect ratio structures without damage or alteration to the electroplated metal. A review of physical and chemical removal options is discussed with data on the most promising options shown. Several standard solvent mixtures have proven particularly useful in our laboratory. The solvent systems remove the resist through crazing and peeling rather than dissolution. They are inexpensive, and can be utilized on very low aspect ratio features, or on parts with no included SU-8. Alternatively, a very promising option for reliable removal is downstream chemical etching (DCE; Matrix Integrated Systems, Richmond, CA) which achieved removal rates of approximately 7–10 μm/min at 225 °C for several hundred micron thick molds. At higher temperatures, an inexpensive molten salt bath has shown to be reliable. The K10 (Kolene Corp., Detroit, MI) process salt bath operated at 350 °C is efficient at completely oxidizing the highly crosslinked epoxy. Sputter Auger depth profiling of Ni parts after removal by DCE and molten salt bath indicated only superficial elemental damage to the metal, though deposits of antimony from the photocatalyst are left after DCE. Initial mechanical properties of electroplated Ni tensile specimens subsequent to the salt bath and DCE processing are presented. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* SU-8; Photoresist stripping; LIGA; MEMS

## 1. Introduction

A considerable amount of attention has been focussed recently on a breadth of microfabrication technologies. In many cases, the microfabrication strategy is to borrow toolsets and techniques from the semiconductor industry, but to extend or adapt them to fit the desired feature geometries. Much focus has been on utilizing resists in microfabrication which were developed for different purposes. One such resist that has consistently produced outstanding thick film imaging whether exposed with UV or X-ray exposures is SU-8 [1,2]. SU-8 has considerable photospeed for X-ray lithography and

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outstanding resolution when exposed with cost-effective proximity/contact aligners. However, the highly crosslinked network can be difficult to remove after utilization as an electroplating mold. In particular, reliable removal without damage to the plated metal has been a particularly difficult challenge.

There are a variety of techniques that may be used to remove the intractable polymer. Physical techniques such as water jetting or bead blasting are possible, as is laser ablation and liquid nitrogen freeze/thawing. Presumably, these physical techniques can be fairly selective to the polymer over metal molds, but suffer from the ability to reliably remove small included areas of polymer from high aspect ratio features due to the fundamental size regime of the incident etchant. It may also be possible to include a sacrificial layer as reported by McGall [3], but again, one would suffer from the ability to get the etchant into areas completely surrounded by electroplated metal. In addition, some solvents are reasonably effective at swelling/cracking/crazing the polymer. However, without pure dissolution, the solvent or physical methods remain potentially effective removal techniques for some sample geometries, but not for general application.

On the other extreme, exceedingly oxidative methods have been used to remove and clean a variety of organic materials. Peroxydisulfate radical can be generated electrochemically in good yield and oxidizes effectively all organic matter [4]. Additionally, other highly oxidizing materials have been studied [5]. Unfortunately, these highly oxidizing materials tend to be rather non-specific and oxidize most metals as well [6]. In addition, UV/Ozone cleaning is a popular choice for oxidatively removing trace carbonaceous contaminants. However, practical etch rates as high as 1 μm/min are unlikely with this method, even with heated platens. Other oxidative methods appeared more promising. Since eventual acceptance of the technology is likely to include some high value added applications, damage to the electroplated structures is considered an important parameter. This paper describes techniques explored to remove effectively the highly crosslinked SU-8 material in high aspect ratio geometries with minimal damage to the included Ni electroplated structures.

## 2. Experimental

Processing of SU-8 was done as described elsewhere [7].

Typical solvent removal was done in beakers. Molten salt bath removal performed at Sandia used a Lindberg crucible furnace with a stainless steel liner insert. An alumina heat transfer powder was placed within the insert and then a large alumina crucible (Vesuvius McDanel, Beaver Falls, PA) contained the salt. A monel-sheathed thermocouple was used for temperature measurements. The wafer was placed within a monel mesh and dipped directly without preheating into the molten salt, and a monel cover with insulating material was placed on top. All downstream chemical etching (DCE) experiments were performed at Matrix Integrated Systems (Richmond, CA), using 6000 sccm of flow, 2500 W, and a chuck temperature and $CF_4$ concentration specified. Electroplating of Ni plating was done at 16 $mA/cm^2$ using a Ni sulfamate bath as described elsewhere [8].

Auger analysis was done using a PHI 660 scanning Auger microprobe operated at 5 kV 75 nA and rastered over a $50 \times 50$ μm area at 30° from normal incidence. The ion gun is a PHI Duoplasmatron operated at 2 kV and rastered over an $300 \times 300$ μm area at a 45° angle. Sputter rates are for $SiO_2$ and were not adjusted for the material being sputtered. Mechanical properties of the electroplated Ni subsequent to SU-8 removal were evaluated by testing the ‘dog-bone’ shaped, as-plated tensile

specimens. The gauge section of the specimens measured 5.08 mm in length × 0.762 mm wide × ≈ 0.25 mm thick. Specimens were tested on a SATEC Electromechanical (model 22 EMF) test frame using an Electronic Instruments Inc., non-contacting laser extensometer (model L-01).

## 3. Results and discussion

### 3.1. Solvent removal

In an attempt to completely dissolve the material, a considerable number of solvents and conditions have been tried, and it is clear that simple dissolution of the crosslinked polymer is not feasible. However, it is also clear that some solvents are so effective at cracking/crazing the material, that they may be effective removal techniques for parts with no internal SU-8 components, and should be considered depending on the application. A typical processing sequence has a post-exposure bake (PEB) of only 85–95 °C on a non-vacuum hot plate. Subsequent submersion of the SU-8 mold on a Si wafer in *N*-methyl pyrollidinone (NMP) will produce a precipitate of delaminated, crazed polymer at the bottom of the beaker given sufficient time (≈24 h). Certain processing conditions such as sonication or temperature may speed up or slow down the removal process and lower exposure doses or PEB conditions may help. This result on patterned SU-8 is deceiving, however, as removal of polymer after plating and lapping is significantly more difficult.

We have found, however, that MS-111 (Miller-Stephenson, Danbury, CT) is considerably faster and more effective in this regard when compared directly to NMP, typically on the order of a few hours. MS-111 is a mixture of methylene chloride, phenol, and organic acids, which appeared to work considerably better than the individual chemicals, and worked well at room temperature on molds without electroplated metal. The toxicity of the mixture, however, makes it unappealing for some applications, and NMP-based Magnastrip (Inland Technologies, Tacoma, WA) and sulfolane-based RS-120 (Cyantek, Fremont, CA) are clearly superior choices for these cases. Magnastrip requires warming the wafer to approximately 70 °C for optimal use, while RS-120 requires higher temperatures to be useful at all, such as 100–120 °C, but both can be utilized below their flash point of approximately 90 and 140 °C, respectively.

When metallic parts are electroplated within the mold, the removal time increased. The interfaces between SU-8 and Si are decreased, pre-plating etch steps and long plating times at 50 °C all seem to be factors. Solvent removal with electroplated metal is considerably more difficult than removal of the mold from Si wafers. Processing for metallic parts in our laboratory usually involves a post development bake of the SU 8 mold at 110 °C to harden the material sufficiently for rapid lapping. Once this bake has occurred, solvent techniques have been found to be unsuccessful.

### 3.2. Chemical removal

#### 3.2.1. Reactive ion etching (RIE)

Typical semiconductor laboratories contain RIE equipment for removal of polymers. In our laboratories, 1 μm/min. etch rates have been achieved on the pure SU-8 material using $CF_4/O_2$ mixes approaching 50%. SAMCO International (Sunnyvale, CA) has achieved rates of up to 4 μm/min. on SU-8 samples using a particularly isotropic etcher. However, RIE suffers from several

serious drawbacks. First, the temperature of the metal mold is not controlled. For long process times (h) protruding metal parts may experience significant and uncontrolled temperature profiles. Second, it was found that the etch rates dropped dramatically when the metal was present in the mold so that rates measured on pure resin were not at all representative of rates found on metal parts surrounded by resin. It is also not clear that ionic species will easily remove high aspect ratio included SU-8 from simple geometric and line-of-sight considerations. Finally, the low pressure and lack of coupled plasmas in RIE chambers leaves little etch species in the chambers compared to other oxidative methods. RIE is an excellent alternative for thin films, but has not proved useful to scaling towards several hundred micron thick films.

### *3.2.2. Aryl ether cleavage*

One possibility for the removal of SU-8 is to chemically disrupt the network by cleaving the aryl ether bonds. We investigated this briefly using LiI and collidine under reflux conditions [9] with little success over NMP alone. NaS with NMP was also attempted, and crazed the SU-8 into pieces smaller than typically seen with NMP alone. However, when the treatment was attempted with Ni interplated, the NaS dissolved the Ni leaving the SU-8 chunks still available. There are other chemistries possible, and certainly more detailed work may prove fruitful. However, it was thought that a fundamental problem of getting the reactants to the chemicals was difficult in the network polymer and this was likely to be a slow, if not cumbersome process for implementation into microfabrication laboratories.

### *3.2.3. Downstream chemical etching (DCE)*

DCE is another common organic removal technique [10]. Developed for high speed removal of exceedingly crosslinked materials found typically after implant steps in semiconductor processing, this method appeared suited for SU-8 removal. Typically, DCE requires generation of reactive oxygen radicals followed by transport ‘downstream’ and removal of ionics which can damage semiconductor dielectrics. Acceptable removal rates (several μm/min.) typically are found in the temperature range of 200–250 °C. Table 1 shows etch rates achieved at Matrix Integrated Systems on SU-8 molds without included metal and processed as stated in Section 2. There was not a concerted effort to optimize etch gas chemistry or microwave power, so these should be regarded as minimum etch rates, but were sufficient for our purpose. However, with samples sent to several companies, it was clear that inclusion of $CF_4$ was critical to achieving adequate rates. The importance of the $CF_4$ inclusion is that this may require expensive sapphire technology for the gas transfer plumbing over quartz, and may drive up to cost of the tools. Also, the high concentrations of $CF_4$ were helpful in RIE, and a necessity in DCE indicated the importance of fluoride chemistry on the removal. In addition, several

Table 1
Etch rates on patterned SU-8 films without interplated metal at Matrix Integrated Systems

| Chuck temperature (°C) | $CF_4$ concentration (%) | Etch rate (μm/min) |
|---|---|---|
| 185 | 2 | 2.1 |
| 185 | 4 | 2.7 |
| 225 | 2 | 7.1 |
| 225 | 4 | 6.8 |
| 275 | 2 | 10 |

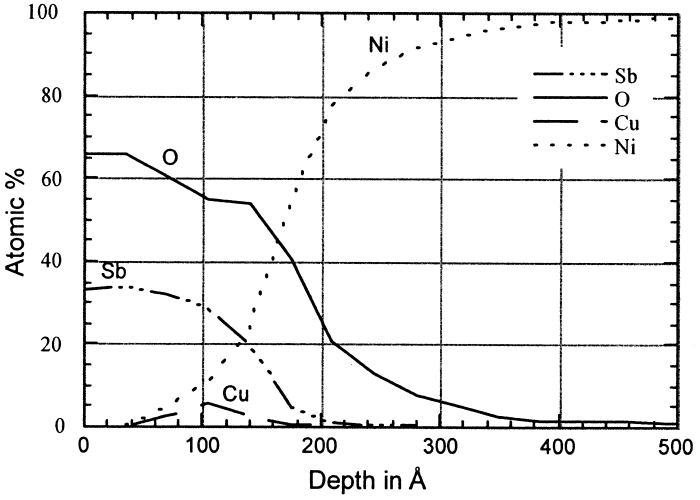


Fig. 1. Sputter Auger results on electroplated Ni removed with DCE at 225 °C for 45 min using 3% $CF_4$.

companies had trouble with leaving their microwave sources on continuously for times up to an hour. Samples run at Matrix were run with a continuously operating source. When run with metal included, etch rates did not appear to decline as in RIE though further work is necessary to determine the degree of anisotropy when the metal is present.

Fig. 1 shows the results of sputter Auger depth profile of Ni parts after DCE etching. Residual antimony oxide is left, and is attributable to the photocatalyst used in the resist [2]. The thickness of the oxide deposit varied greatly, and can potentially be intrusive. At approximately 3% by mass of photoacid generator in resist, and with a molecular weight of approximately 600 g/mol, there are $2.9 \times 10^{-5}$ mol of assumed $Sb_2O_5$ available on a 4-inch wafer with 300 μm thick photoresist and 50% surface coverage. For coverage, this could leave as much as 100 nm of oxide, depending on the area of metal and specific geometries. Removal of the antimony oxide from the Ni may be required. Fig. 2a shows a Ni tensile test after the part was subjected to 45 min of DCE at 225 °C. Again, it is clear that the material retains typical ductile behavior up to tens of percent strain. The ultimate tensile strength (UTS) and Young's modulus are degraded somewhat ($\approx$20%) from literature values of

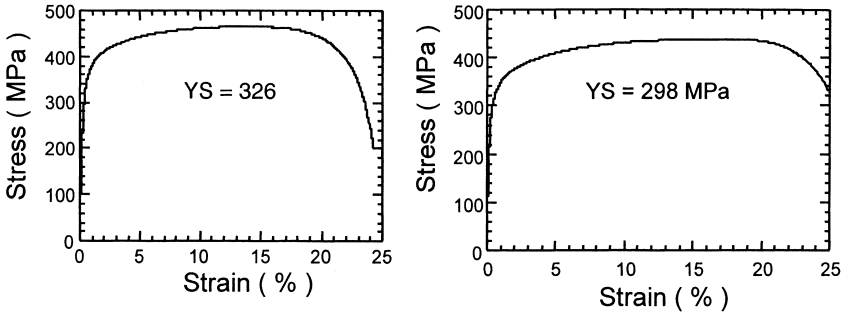


Fig. 2. (a) Left: tensile test results on electroplated Ni after removal with DCE at 225 °C for 45 min. (b) Right: tensile test result on electroplated Ni after removal with K-10 process salt bath at 350 °C and 45 min.

as-plated Ni electrodeposits even though the temperature is less than is suggested as a minimum temperature for annealing effects [8]. While detailed effects of removal on electroplated materials using controlled plating baths and sample handling will be the subject of future work, this preliminary data is promising that no egregious mechanical disruption to the electroplated Ni is expected.

### *3.2.4. Molten salt bath*

Molten salt bath technology has a variety of applications, from heat transfer, cleaning of extruder blades and engine parts, batteries, to sanitizing hazardous waste [11]. Briefly, an oxidizing salt such as sodium nitrate is mixed with a hydroxide salt and potentially other additives. The resulting material typically is used in the range of 300–400 °C, approximately the range where heat treatment damage to electroplated Ni begins to occur [8]. In general, Ni and Ni-based alloys are particularly resistant to the basic, nitrate baths [11]. One distinct advantage of molten salt over other oxidative measures is that the salt is an effective heat transfer medium, so that the exothermic oxidative process of the carbonaceous polymer is less likely to heat the included metal components above the temperature of the bath. In addition, the surface tension behavior of the bath tends to wet most metals well, assisting removal in internal SU-8 components.

Fig. 3 shows a sputter Auger depth profile of parts after two different salt bath treatments at 350 °C. The extremely aggressive bath K-5 resulted in noticeable oxidation of the Ni (Fig. 3a). The Cu plating base looked considerably damaged after this treatment as well as the Si wafer roughened. Complete removal of several hundred micron thick molds was approximately 5 min with this bath. Fig. 3b, however, is a sputter Auger of a Ni part after the milder K10 bath at 330 °C. With visibly less attack on the Cu and on the Si, and the Auger data indicating less attack on the Ni, this bath appears to be more suited for small metallic parts. In other experiments, some deposits from the bath have been found on the Ni parts, so it is imperative that the bath chemistry is chosen properly.

While the surface chemistry of the K10 bath appeared by Auger depth profiling to be similar to the as-deposited Ni, the temperature of the bath does cause concern. Fig. 2b shows tensile test data on a 250-μm thick Ni part electroplated within SU-8 and subjected to 350 °C K10 for 45 min. The behavior of the Ni has degraded approximately 30% in both yield strength and ultimate tensile

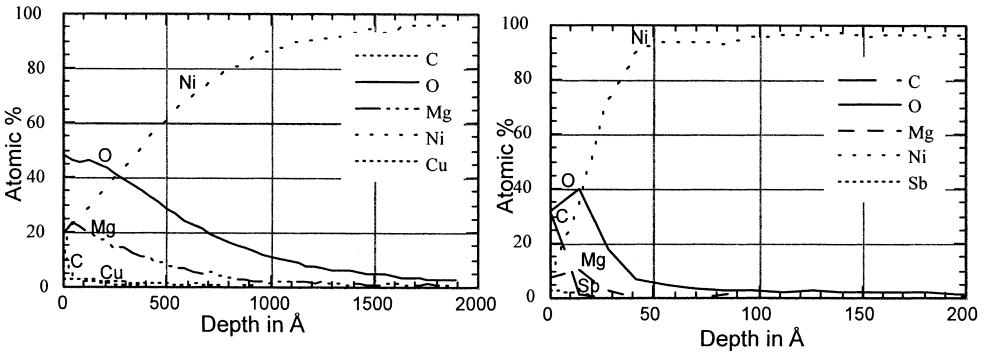


Fig. 3. (a) Left: sputter Auger analysis of K-5 process salt bath after 30 min at 350 °C. Complete removal was at approximately 5 min in the K-5, but roughened the Si and Cu. (b) Right: K-10 process salt bath at 330 °C and 1 h. The Si is less roughened and Cu intact.

strengths from what have been reported in other publications for free standing, electrodeposited Ni films [8]. A more detailed study of the effects of salt bath on the Ni parts is the subject of future work.

One observed problem of the salt bath is that the surface of the metal parts has appeared dull to the eye after treatment. In addition, Si wafers tend to crack when placed into the salt bath. While wafer cracking is not necessarily a problem for large, released parts, thin parts which extend across the cracks may be contorted by this process. The origin of the wafer cracking is not clear. Si wafers typically get thermal shock without fracture in semiconductor process flows, and the surface of the Si appears roughened in the most aggressive baths, it is likely the caustic nature of the bath and the temperature synergistically result in cracking. We have found, however, that a $Si_3N_4$ layer on the surface of the Si effectively keeps the surface from roughening, and we expect that two-side coated $Si_3N_4$ and (111) wafers would help in alleviating the cracking problem.

#### *3.2.5. Burning*

Probably the easiest and most overlooked process for removing SU-8 is to simply burn it off. In a simple air furnace at 600 °C, the SU-8 is completely removed from Si substrates. It is likely that very significant damage can be detected in the resultant metal. Burning is quite inexpensive and simple, and the process can be reduced in temperature by adding coreactants. Pollution Control Products (Dallas, TX) efficiently removed SU-8 at 450 °C using their process. Depending on the requirements of the resultant Ni, this is an extremely easy and inexpensive technique.

### *3.3. Metal parts*

Metallic parts were made from several of the removal techniques discussed above and are shown in a companion article [7]. Several hundred micron thick parts are easily attainable with the most promising techniques, molten salt and DCE. Depending on the mechanical requirements of the resultant metal, burning may be possible as well. While the mechanical properties of the material have still not been characterized completely, and little is known about the surface roughness, it is clear that free standing parts can be produced.

## 4. Conclusions

Several promising techniques for removal of SU-8 have been presented along with initial data of mechanical properties of the resulting Ni parts. Unusually demanding requirements such as high aspect ratio internal SU-8 molds coupled with extreme tolerances on Ni mechanical properties may prevent one of the discussed methods from being practicable. But for many applications it is clear that SU-8 molds of several hundred micron thicknesses can be removed reliably with either burning at 450–600 °C, molten salt bath at 350 °C, DCE at 225 °C, or for lower crosslinking molds solvent cracking at 75–100 °C. DCE in particular offers removal rates of 7–10 μm/min. at temperatures significantly below what is found to rapidly affect electroplated Ni and is compatible with semiconductor and microfabrication process areas and procedures.

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