A comparative study of different thick photoresists for MEMS applications

E. KOUKHARENKO[1], M. KRAFT[1], G. J. ENSELL[1], N. HOLLINSHEAD[2]
[1] *University of Southampton, School of Electronics and Computer Science, Highfield, Southampton, SO17 1BJ, UK*
E-mail: ak@ecs.soton.ac.uk
[2] *Tecan Components Ltd., Tecan Way, Granby Industrial Estate, Weymouth, Dorset, DT4 9TU, UK*
E-mail: nickh@tecan.co.uk

This work reports on recent advances in microfabrication process technology for medium to high-aspect ratio structures realised by UV photolithography using different kinds of photoresists. The resulting structures were used as moulds and will be translated into metallic structures by electroplating. We used four types of photoresists: SPR 220-7 novalak based (positive), SU8 epoxy based (negative), Ordyl P-50100 acrylate based (negative) dry film photoresist, and Diaplate 132 acrylate based wet photoresist (negative). The motivation for this work was to find an alternative to SU-8 photoresist, which is difficult to process and remove after electroplating. Depending on the application, we found that Ordyl P-50100 dry film photoresist is the best alternative to SU8 for realization of approximately 100 μm deep moulds for electroplating in acidic electroplating solution. SPR 220-7 is a good alternative to SU8 for fabrication of 50 μm deep moulds and electroplating in alkaline solutions. The results presented in this paper will open up new possibilities for low-cost processes using electroplating for MEMS applications.
© *2005 Springer Science + Business Media, Inc.*

1. Introduction

High-aspect-ratio structures are commonly used for many MEMS applications such as sensors, actuators and micro-machines. The specific aim of this work is the realisation of 3D structures using micro moulds for/and electroplating.

There is a range of fabrication techniques for realising 3D structures: X-Ray and UV-LIGA techniques, Deep Reactive Ion Etching (DRIE), wet Si bulk micromachining and excimer laser ablation [1].

Originally the X-ray LIGA (Lithografie Galvanoformung Abformung) process was extensively used to realise very high aspect ratio microstructures. However, this technique involves considerable process complexity, high-contrast X-ray masks, difficulties in structuring PMMA (polymethylmethacrylate) photoresist thicker than 200 μm, and high cost, since a synchrotron radiation source is required. The DRIE (Deep Reactive Ion Etching) technique has became very popular nowadays because of its high etching speed, good profile control, and the capability to realise microstructures with good uniformity and high-aspect-ratio. However this process causes a sidewall roughness (scalloping), with amplitudes of up to 1 μm [2]. Moreover, for many applications micro structures with submicron resolution are not required and medium to high aspect ratios at micron resolution would be sufficient. This motivated the search for a cheaper and simpler method to realize micro-moulds for electroplating.

The most promising alternative technique is based on UV LIGA (thick photoresist photolithography). Very thick photoresist lithography requires photoresists with layer thicknesses that are orders-of-magnitude thicker than those used for the fabrication of ICs [3]. This paper reports on the development of very thick photoresist lithography techniques using four different kinds of photoresist with different formulations.

Up till now SU8 negative tone photoresist has been extensively used for many applications and is the most well known because of its outstanding characteristics for high aspect-ratio structures, its use as an etch mask, its excellent chemical resistance, and its interesting mechanical and optical properties [4–7].

SU8 is an epoxy based photopolymer. Its structure is depicted in Fig. 1.

Other negative thick photoresists suitable for very thick structures are Diaplate and Ordyl P-50100. These are wet and dry film photoresists respectively, which are acrylate-based photopolymers. Fig. 2 shows their structures. The structure of the dry film resist has to have a chemical resist formulation that is a very viscous, in order to sandwich it between a polyolefin sheet and a polyester base, and to be rolled up on a support core, and to enable it to be cut or finished to various widths and

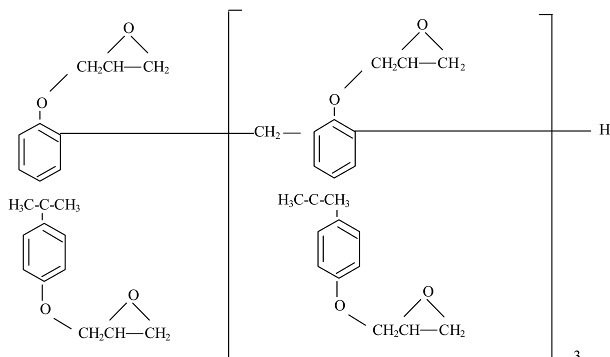

Figure 1 Molecular structure of SU8.

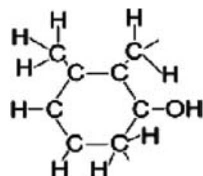

Figure 2 Molecular structure of SPR 220-7.

roll lengths, as illustrated in Fig. 3. There are different types of dry film photoresists widely used and commercially available, such as Riston® [8], Ordyl BF 410 [9], Etertec® 5600 [10], DF 4615 [11], DFR-15 [12]. Dry film resists are commonly used for the fabrication of printed circuit boards, photochemical machining, and some formulations for electroplating applications [13].

Diaplate 133 was used for the electroforming of micro parts for MEMS by Niedermann *et al.* [14]. The processing was developed for thicknesses up to 700 μm. It has been applied to the fabrication of two demonstrators: nickel foils with precise holes and gear wheels. In our work we investigated processing parameters for Diaplate 132.

However, there are positive thick photoresists, which are suitable for 3D-structure fabrication. One of the photoresists is SPR 220-7, which is photopolymer, based on novalak resin, where novalak resin is Cresol+Formaldehyde. Fig. 4 shows the chemical formula of the polymer.

Each of these photoresists has its advantages and disadvantages depending on the application.

In our work we used Ordyl P-50100, commercially available from Elga Europe to fabricate a micromachined disk for inertial sensing applications [15] and SPR 220-7 for fabrication of wires for atom guides [16]. Both processes require electroplating of Ni or Au, respectively, on an Au seed layer into a mould of thick layer photoresist.

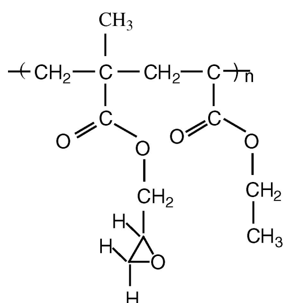

Figure 3 Molecular structure of Ordyl P50100 and Diaplate 132

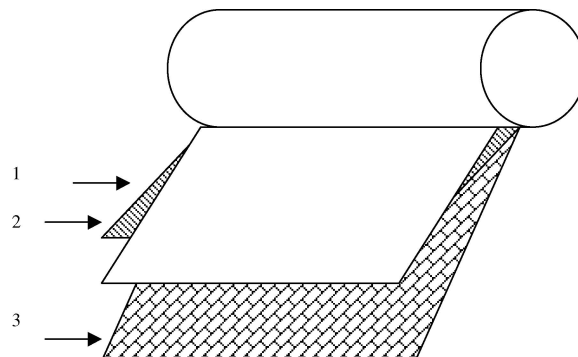

Figure 4 Three-layer structure of dry film photoresist, 1—Polyethylene separation sheet, 2—Photoresist, 3—Polyester Support.

2. Processing techniques

To realize the micro-moulds, we used SPR 220-7 novalak based positive photoresist, SU8, 100 XP with a 73% solvent content, (GBL, γ-butyrolactate) epoxy based negative photoresist, Diaplate 132 acrylate based wet thick negative photoresist, and Ordyl P-50100 acrylate based dry film negative photoresist commercialized by Shipley, Shell Chemical, HTP HiTech Photopolymere AG, and Elga Europe, respectively [17–20].

For all our experiments we used standard 4-inch (100) silicon substrates, p type, 17-33 Ω cm resistivity which were cleaned by immersion in fuming nitric acid (FNA). In the case of SPR 220-7, Diaplate 132, and Ordyl P-50100, after a dehydration bake for 40 min at 140 °C, the wafers were primed using hexamethyldisilazane (HMDS) vapour for 3 minutes. This was followed by several spin-coating steps to deposit these photoresists at low speed using a hand spinner.

The photoresists were exposed using a contact mask with a Hybrid Technology Group (HTG) aligner and a UV light source with 1.6–1.9 mW/cm^2 intensity (350–450 nm spectrum, Mercury lamp). In the case of SPR 220-7, we used a standard developer, Microporosit, MF 322, (Tetramethylammonium, 1-4.99%).

SU8, Diaplate 132 and Ordyl P-50100 were processed in a different way to a standard photolithography processes and used different chemicals.

Depending on the nature of the coating of the silicon substrate, the wafers were treated differently prior to the SU8 spinning. Thin metal film coated silicon wafers were used as substrates, and Titanium and Cromium/Gold layers were evaluated initially for electroplating applications.

Silicon substrates with non-metallic coatings such as silicon, silicon dioxide and silicon substrates with a thin metallic layer of Ti were not primed prior to spin-coating. After a dehydration bake for 40 min at 200 °C the photoresist SU-8 was spun at different spin-speeds depending on the desired film thicknesses.

Gold coated silicon substrates were treated using different mechanical and chemical techniques in order to modify the inert gold surface to provide good adhesion

between the SU8 photoresist and the substrate across the whole wafer. We used a combination of cleaning processes for substrates by acetone and oxygen plasma ash.

The adhesion promoter 2-mercaptoethanol from Sigma-Aldrich was applied by spinning. In this way good adhesion was achieved between the layer of SU8 and the gold on the silicon substrate.

In all cases the photoresist formed an edge bead during the spin, which tended to reflow and vanish during the softbake. The softbake was done on a very flat levelled horizontal hotplate. Exposure was performed using a soft-contact mask-aligner. Next, a post-exposure bake (PEB) was carried out with no ramping of the temperature of the hotplate in order to accelerate cross-linking of the exposed areas of the photoresist. The development was performed using undiluted MicroChem PGMEA (propylene glycol methyl ether acetate) developer (EC-solvent) from Sigma-Auldrish at room temperature in a beaker on a shaker table. After the development the substrate was rinsed. We used IPA (Isopropanol alcohol) for rinsing instead of water. The stripping of SU8 was done in hot NMP (1-methyl-2 pyrrolidon) solution for 25–30 min at 70 °C followed by cleaning in HNO_3 for 10 min.

In the case of Diaplate 132 and Ordyl P-50100, major differences in processing were the deposition method (lamination for Ordyl P-50100) and the development technique. In order to laminate photoresist, we used a hot roll laminator (Dynachem Manual Laminator/Cleaner 360), which requires manual loading, resist trimming, and unloading. Since the resist is not diluted by a solvent a drying step is not needed. However, to make the dry photoresist layer conform to the substrate surface, heat and pressure were applied in a lamination step. The hot roll temperature was 130 °C for the upper roller and 120 °C for the lower roller. The rollers are heated electrically, each one is independently thermostatically controlled. The hot roll pressure and lamination speed were 45 Psi and 52 cm/min, respectively. As developer sodium carbonate 0.8–1.1% w/w was used with a processing temperature of 30 °C (tolerance ± 2 °C).

The same developer was used for Diaplate*132 and Ordyl P-50100* sprayed on the substrate with a pressure of 15–30 Psi. The remover used consisted of sodium carbonate 10–30%, sodium hydroxide 30–60% and disodium metasilicate 10–30%, which is commercially available as 'Emphax Cleaner' from Canning or a solution of concentrated potassium hydroxide prepared in house.

3. Results

3.1. Mould fabrication

In this work we were concerned with the realisation of moulds for electroplating for different applications; one application is for atom guides and a second application is to form a disk to be used as the mass element in an inertial sensor insure the disk is levitated by electrostatic forces. Atom guides allow the manipulation, confinement, and guiding of cold neutral atom clouds and Bose condensates. Atoms levitated above a magnetized surface can be guided electrostatically by wires deposited on the surface. The flow and interaction of atoms in such a structure may form the basis of a new technology "integrated atom optics" with which it might be possible to realise a quantum computer, building a novel microscopic atom interferometer with the potential to be exceedingly sensitive [21, 22].

The micromachined disk has applications for inertial sensors such as accelerometers and gyroscopes [28]. We experimented with the four types of photoresist in order to choose the optimal ones for our applications. Tables I, and II show the optimised results of the spin coating, exposure, and development for the resists. A single layer of SPR 220-7 was deposited by spin-coating up to 18 μm thickness. Thicker layers can be achieved with multi-layer coating/baking. We have experimented with two and three layers of SPR 220-7 resulting in 34 and 54 μm thick structures.

The sidewall verticality was very good, as shown in Fig. 5. There is very good adhesion between the two layers of SPR 220-7 and between the gold seed layer and photoresist. SPR220-7 is easy to work with and can be used as a sacrificial layer if removed after processing. It has medium-to-high aspect ratio of 4:1 [23]. It is easy to remove using acetone. SPR 220-7 was suitable for both acidic and mild alkaline electroplating solutions (pH = 8.5–9.0). It was unstable only in strong alkaline electroplating solutions (pH > 9) without a special hard bake treatment. This photoresist had the following disadvantages: low transparency, time consuming processing and formation of an edge bead. Also, the fumes of SPR 220-7 are very toxic [24].

Tables II and III show the optimised results for the spin coating, exposure, and development process for different types of substrates and thicknesses of SU8. This resist can be coated to a very large thickness and the minimum realisable feature sizes are very small hence very high aspect ratios can be achieved (up to 100) [25]. SU8 resist thicknesses up to 500 μm were realised with very good reproducibility by a single spin coating step. Much greater thicknesses up to 1 mm can be achieved by multiple coating [26]. Fig. 6 show scanning electron microscopy sections through structures in 450 and 497 μm thick SU-8, which were used as moulds to electroform a Ni-disk. However, SU8 has

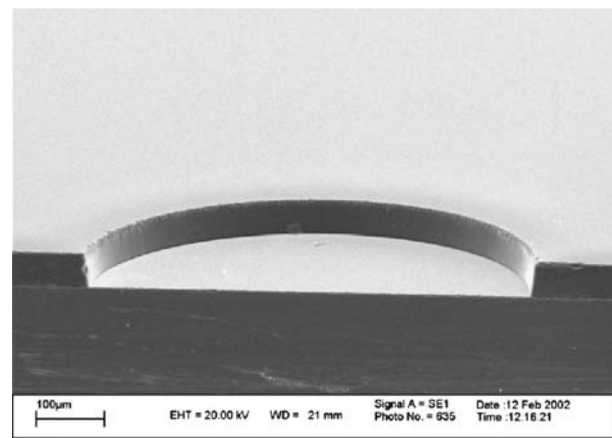

Figure 5 SEM image of 54 μm thick mould in SPR 220-7.

TABLE I Optimized values of spinning, softbake, exposure and development time for SPR 220-7 thick positive, SU8 thick negative, and Diaplate132 thick negative photoresists

		Parameters					
Photoresist	Thickness	up to 18 μm		up to 36 μm		up to 54 μm	
SPR 220-7	Spin	2 min @ 350 rpm, 20 sec @ 1000 rpm		2 min @ 350 rpm, 20 sec @ 1000 rpm		2 min @ 350 rpm, 20 sec @ 1000 rpm	
	Softbake	1 min @ 90 °C, hotplate		1 min @ 90 °C, hotplate; 55 min, oven		1 min @ 90 °C, hotplate; 90 min, oven	
	Exposure	195 sec		230 sec		900 sec	
	Develop time	2 min		5 min		7 min	
		Thickness					
SU8	Substrate	up to 100 μm/Au	up to 100 μm/Ti	up to 100 μm/Si	up to 100 μm/SiO_2	up to 300 μm/SiO_2	up to 500 μm/SiO_2
	Spin	30 sec @ speed 1455 rpm	30 sec @ speed 1455 rpm	30 sec @ speed 1455 rpm	30 sec @ speed 1455 rpm	40 sec @ 320 rpm	17 sec @ 500 rpm
	Softbake	10 min @ 70 °C, 60 min, @ 95 °C hotplate	10 min @ 70 °C, 60 min, @ 95 °C hotplate	10 min @ 70 °C, 60 min, @ 95 °C hotplate	10 min @ 70 °C, 60 min, @ 95 °C hotplate	90 min @ 85 °C, 120 min@ 95 °C, hotplate	140 min @ 95 °C, hotplate
	Exposure	800–1000 sec	1000 sec	370 sec	370 sec	320–340 sec	2060 sec
	Post exp bake	1 min @ 50 °C, 15 min @ 95 °C hotplate	1 min @ 50 °C, 10 min, @ 95 °C hotplate	1 min @ 50 °C, 15 min @ 95 °C hotplate	1 min @ 50 °C, 15 min @ 95 °C hotplate	30 min @ 95 °C, hotplate	30 min @ 95 °C, hotplate
	Develop time	25 min	20 min	25 min	25 min	40 min	80 min
		Parameters					
	Thickness	up to 20 μm		up to 40 μm		up to 50 μm	
Diaplate 132	Spin	40 sec @ speed 2000 rpm		30 sec @ 1000 rpm		60 sec @ 1200 rpm	
	Softbake	3 min @ 80 °C, hotplate		3 min @ 80 °C, hotplate		3 min @ 80 °C, hotplate	
	Exposure	100 sec		120–140 sec		120–140 sec	
	Postexpos urebake	10 min @ 90 °C, oven		10 min @ 90 °C, oven		10 min @ 90 °C, oven	
	Develop time	1 go at 200		2 go at 200		2 go at 200	

TABLE II Optimized values of spinning, softbake, exposure and development time for Ordy1 P-50100 dry film negative photoresists

Parameters	1 layer up to 20 μm	1 layer up to 100 μm	2 layer up to 200 μm
Exposure	40 sec	60–80 sec	300–350 sec under optimisation
Develop time	130 sec	320 sec	640 sec

several disadvantages; difficult to remove, very time consuming to process, difficult to achieve high planarity across a wafer and an edge bead is formed [27]. SU8 is predisposed to mechanical stress introduced by the difference between the thermal expansion coefficients of the wafer and SU8 and to stress due to resist polymerization. These factors lead to adhesion problems between the layer of the SU8 and the wafer and to bowing of the wafer, which is a key issue for many applications [28].

Additionally, adhesion problems to the silicon substrate were found with thin layer Au coating. This is due to the inert nature of this metal. In order to solve the adhesion problem between the gold coating on the silicon substrate and the photoresist, we used different adhe-

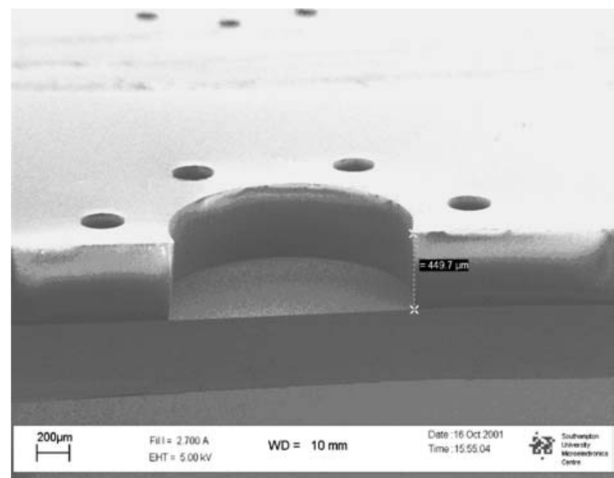

Figure 6 SEM image 450 μm thick mould in SU8.

sion promoters. There are special groups of materials which are suitable for coupling photoresist to gold substrates through chelative and chemisorptive chemistry. These coupling functional groups can include carbonyl,

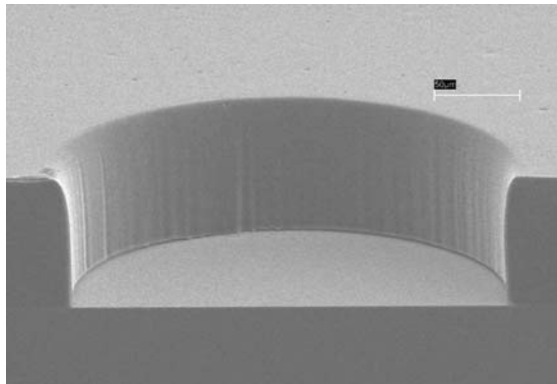

Figure 7 SEM image of 90 μm thick mould in Ordyl P-50100.

sulfur, or hydroxide groups [29]. Gold and other noble metal surfaces are essentially oxide and hydroxyl free due to their highly inert nature. The adhesion is accomplished through formation of a chemisorptive layer through chelative interaction of the promoter layer and gold surface atoms. The adhesion promoter provides a single molecular layer of the chemisorbed adhesion promoter on gold.

We used 2-mercaptoethanol where the interaction between the gold surface and the adhesion promoter occurs through the following mechanism:

$$HS-CH_2-CH_2-OH \text{ forms } Au\,|\,S-CH_2-CH_2-OH$$

Ordyl P-50100 dry film resist is a multipurpose photoresist. It can be used for plating in acid solutions. Dry film resist has numerous other advantages; good conformability, excellent adhesion on any substrate, no liquid handling and absence of solvents, high process speed, excellent thickness uniformity over the whole wafer, simple handling, no edge bead formation, low exposure energy, short processing time, and near-vertical sidewalls. This is also easy to strip. Fig. 7 shows typical resist structures of 90 μm height. The sidewall profiles indicate very good dimensional control over the entire resist thickness. The surface roughness is about 20 nm; this indicates the absence of pinholes. Consequently, this resist is very suitable for stacking multiple layers, and opens possibilities for a multi-level electroplating process [30].

The drawbacks of this resist are its lower resolution, aspect ratio and transparency compared with SU8. This limits its application for multi-layer structure fabrication. Table I shows the optimised results for the spin coating, exposure, and development process for different thicknesses of DiaPlate 132. This wet negative photoresist withstands acidic plating solutions. It is possible to achieve thickhesses up to 70 μm with a single coating and it is easy to remove. Fig. 8 shows a scanning electron microscopy (SEM) cross section of a DiaPlate 132. We achieved 40, 50 and 70 μm with a single coating. The scanning electron microscopy (SEM) picture shows highly vertical walls across all thickness. The disadvantage of using this material is that there is a poor adhesion between the substrate and the photoresist which needs to be investigated in a future work. It had a lower resolution compared with SU8 and SPR 220-7 and is not suitable for alkaline plating solutions.

3.2. Electroplating

The resulting high-aspect-ratio PR moulds of three resists SU8, SPR 220-7 and ORDYL P50100 were translated into metallic structures by electroplating. Nickel was electroplated into one-level of SU8 and SPR 220-7 moulds. This was also electroplated into one- and two-level ORDYL P50100 photoresist moulds. A nickel sulphamate electrolyte solution was used for electroplating with a current density of 18 A dm^{-2}, and a deposition rate of 4 μm h^{-1} for single-level electroplated

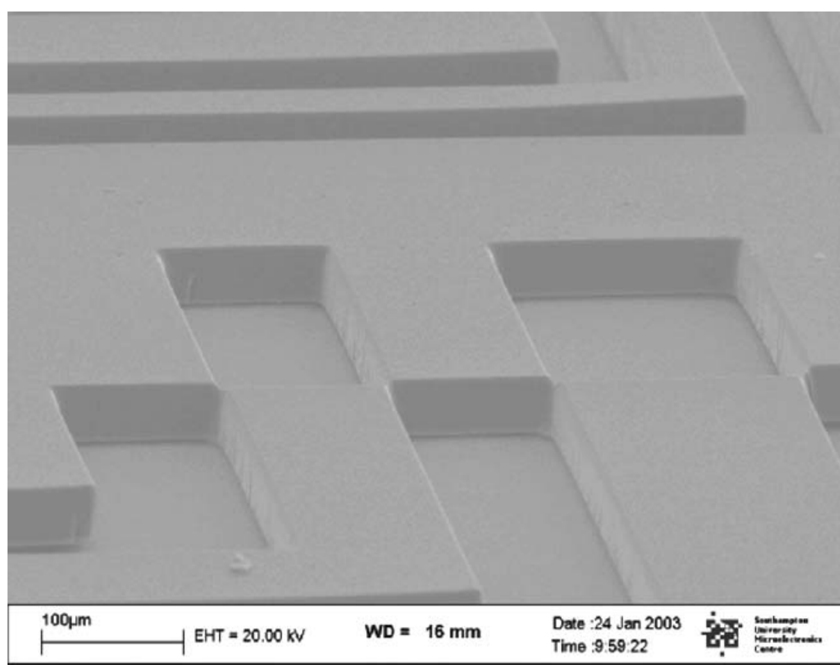

Figure 8 SEM image of 50 μm thick mould in Diaplate132.

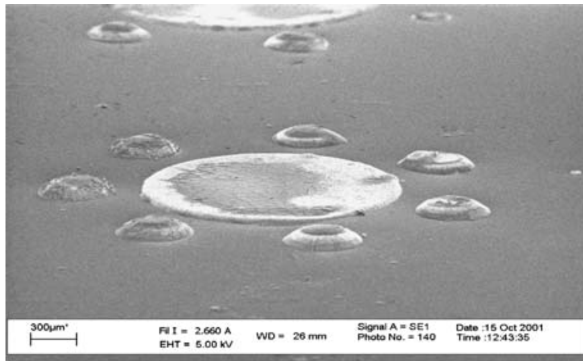

Figure 9 Ni structure plated into SU8 and Ordyl P50100 moulds showing overgrowth.

structures. Fig. 9 shows a scanning electron microscopy (SEM) picture of a Ni-electroplated structure into 100 μm of SU8 for a Ni-disk. The same result was obtained for ORDYL P50100. The dimensions of the disk varied from 1900 to 2800–4000 μm with surrounding pillars between 200 and 400 μm. An overgrowth structure was observed.

As a further application of ORDYL P50100 two-level electroplated structures were realised. Fig. 10 shows such a structure demonstrating the feasibility of a multi-level electroplating process using this photoresist. In this case nickel sulphamate electrolyte solution was used with a current density of 3.5 A dm^{-2}, and a deposition rate of 35.8 μm h^{-1}.

ORDYL P50100 and SPR 220-7 photoresist moulds were very easy to remove after electroplating using conventional techniques. SU8 moulds are difficult to remove reliably from high-aspect-ratio structures without damage or alteration to the electroplated metal. We have tried different techniques and materials as an option to remove SU8. We have only recently achieved encouraging results in removing the SU-8 using hot NMP (N-Methyl-2-Pyrrolidone) solution. Even if the solvent systems remove SU8 resist through crazing and peeling rather than dissolution, this technique seems to be convenient for these large structures.

Fig. 11 shows a scanning electron microscopy (SEM) image of a disk realised by Ni-plating disk into a SU8 mould.

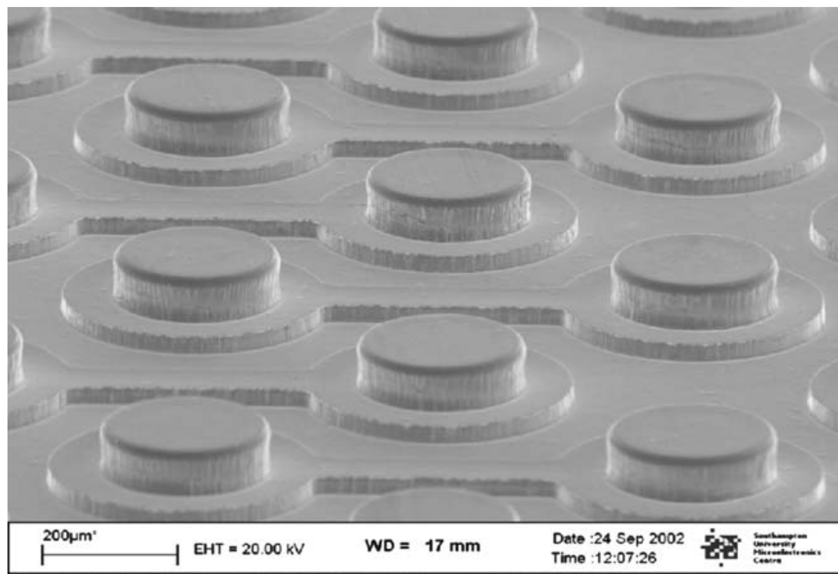

Figure 10 SEM picture of nickel shim double-level electroplated structures fabricated at Tecan LtD. The height of both levels is 37 μm.

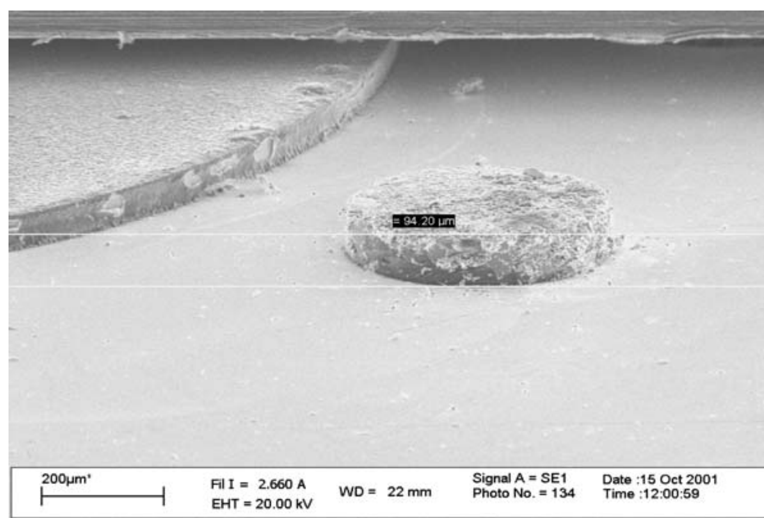

Figure 11 SEM picture of nickel electroplated structure after removing SU8 mould in hot NMP solution.

Electroplating into Diaplate 132 is currently under investigation. Underplating occurred due to the poor adhesion between the metallic seed layer and the photopolymer. We are carrying out additional experiments in order to investigate the aspect ratio value for each photoresist.

4. Conclusion

We demonstrated that the Ordyl P-50100 dry film resist is a promising material for the realisation of high aspect ratio moulds for electroplating to fabricate 100 μm structures using acidic electrolytes. This was suitable for our applications.

SPR 220-7 is a suitable material for electroplating in mild alkaline electroplating solutions (pH=8–9). It was unstable in strong alkaline electroplating solutions without a special hard bake treatment.

SU8 photoresist exhibited excellent resolution in thick film applications. However, not only was it difficult to remove the SU8, but also the electroplated metal was often damaged during this step and there were adhesion problems on the gold substrate.

Diaplate 132 does not give good resolution, adhesion, aspect ratio, and its use for electroplating needs further investigation.

References

1. M.J. MADOU in "Fundamentals of Microfabrication, The science of Miniaturization", 2nd edn (CRC Press LLC, 2002) p. 608.
2. A. A. KUNDIG, M. CUCINELLI, P. J. UGGOWITZER and A. DOMMANN, *Microelectr. Engg.* **67/68** (2003) 405.
3. M. CHATZICHRISTIDI, I. RAPTIS, C. D. DIAKOUMAKOS, N. GLEZOS, P. ARGITIS and M. SANOPOULOU, *ibid* **61–62** (2002) 729.
4. B. EYRE, J. BLOSIU and D. WIBERG, in Proceedings MEMS'98 Heidelberg, (Germany, January 1998) p. 218.
5. V. SEIDEMANN, J. RABE, M. FELDMAN and S. BÜTTGENBACH, *Microsystem Technolog.*, **8** (2002) 348.
6. K.Y. LEE, N. LABIANCA and S.A. RISHTON *J. Vac. Sci. Technol.* **B 13**(6) (1995) 3012.
7. B. BILENBERG, T. NIELSEN, D. NILSSON, B. CLAUSEN and A. KRISTENSEN, *J. Micromech. Microeng.* **14** (2004) 814.
8. http://www.Dupont.com/pcm
9. http://www.tok.co.jp/products/products-e2.htm
10. http://www.insulectro.com/dryfilm.htm
11. http://www.thinktink.com/stack/volumes/voli/store/specs/4615spec.htm
12. http://www.jsits.com/kpr/facility.htm
13. K. H. DIETZ, in "Dry Film Photoresist Processing Technology", (NC, Electrochemical Publications Ltd, USA, 2001) p. 432.
14. PH. NEEDERMANN, H. BERTHOU, S. ZWICKL, U. SCHÖNHOLZER, K. MEIER, CH. GANTNER and D. KAPP-SCHWOERER, *Microelectr. Engng.* **67/68** (2003) 259.
15. M. KRAFT, *Measurement + Control* **33** (2000) 164.
16. E. KUKHARENKA, M. KRAFT (2002) in Proceedings of the 4th International Conference on Material for Microelectronics and Nanoengineering, (ESPOO, Finland, June 2002), p. 165.
17. http://www.shipley.com/
18. http://www.shellchemical.com
19. http://www.htp.ch/
20. http://www.elgaeurope.it/
21. E. A. HINDS, in "Atomic Physics 17" (Arimondo de Natale, and Inguscio, AIP, New York, 2001) p. 405.
22. E. A. HINDS, C. J. VALES and M. G. BOSHIER, *Phys. Rev. Lett.* **86** (2001) 1462.
23. N. ELEJALDE, F. Y. ORGIN and S. L. LEE (2001) in Proceedings of the 12th Micromechanics Europe Workshop (MME'01), Cork, (Ireland, September 2001) p. 11.
24. http://snf.stanford.edu/Process/Lithography/SPR220.html
25. http://www.microchem.com/resources/tok_ebeam_resist.pdf
26. M. DESPONT, H. LORENZ, N. FAHRNI, J. BRUGGER, P. RENAUD and P. VETTIGER in Proceedings MEMS'97, IEEE. (Nagoya, Japan, January 1997), p. 518.
27. H. LORENZ, M. LAUDON and P. RENAUD, *J. Microelectr. Engng.* **41/42** (1998) 371.
28. H. LORENZ, M. DESPONT, N. FAHRNI, J. BRUGGER, P. VETTIGER and P. RENAUD, *Sensors and Actuators* **A64** (1998) 33.
29. http://www.siliconresources.com
30. E. KUKHARENKA, M. M FAROOQUI, L. GRIGORE, M. KRAFT and N. HOLLINSHEAD, *J. Micromechanics and Microeng* **13** (2003) S67.

Received 22 April
and accepted 18 July 2005