NiColoy: A versatile electroforming process for bio-sensor fabrication by embossing

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Abstract

High strength, hard, electroformed stampers are formed from a silicon master using Nickel-Cobalt electrodeposited alloy. They are found to replicate structures from submicron dimensions like optical gratings and to hundreds of microns like micro-fluidic channels without distortion. The channels and optical elements constitute building blocks of many bio-sensors. The electroform is a negative replica of the silicon master and a low cost reproduction of the master is obtained by embossing it onto plastic substrates. We find that damage free reproduction in the plastic substrate is achieved when the aspect ratio of the structures is less than 3.

Keywords
Electroplating, electroforming, NiColoy, hot embossing, micro-fabrication, micro-fluidics, SAM coating, DRIE.

1. INTRODUCTION
Low cost biosensors need cost effective fabrication processes for micro-fluidic channels and optical elements like gratings. A common approach is embossing replication on a plastic substrate using silicon or nickel masters. Silicon is a brittle material and tends to fail if a wafer containing the pattern is subjected to large forces. Electroformed nickel stampers are usually too soft and may exhibit internal stresses that can lead to geometric distortions [1]. A production oriented stamper should be rigid and durable, distortion free, chemically resistant and capable of replicating sub-micron features. NiColoy electroforms meet these practical requirements.

2. SILICON MASTER FABRICATION

Two silicon wafers were fabricated to test the embossing process. One wafer (wafer 1) had larger features: T shaped micro-fluidic channels, lines and grids. Shipley 1813 resist was spun on a 4-inch silicon wafer and the mask pattern was exposed in Karl Suss MA6 contact aligner. After resist development, exposed silicon was deep etched in Plasmatherm PT 770 etcher using Bosch Deep Reactive Ion Etching (DRIE) process [2]. The etch depth was about 65 μm and the minimum feature size was 10 μm. The fluid channels were 300-400 microns wide.

The second wafer (wafer 2) had finer features: dots, dot arrays, and gratings. 4-inch plasma enhanced chemical vapor deposited (PEVCD) oxide coated wafers (570 nm thick), covered with OiR 620-7i (Shipley) resist were exposed in Autostep 200 5X reduction stepper. After development, the resist pattern was transferred into oxide by performing reactive ion etching of the exposed oxide on a custom built etcher (at Cornell Nanofabrication Facility). The resist was subsequently stripped by exposing the wafers in oxygen plasma (Branson/IPC P2000 barrel etcher). Silicon etch was performed using chlorine dry etch chemistry in an inductively coupled plasma (ICP) chamber etcher. The silicon etch depth was 2μm. Height of the features including the oxide mask remaining after Si etch is about 2.3μm. Chlorine etch chemistry being an ion assisted process, was chosen for etching small features since it does not exhibit the loading effect that would occur in the Bosch DRIE process or other purely chemical etch process [3]. It ensures that the etch depth is uniform across the wafer, both in dense structures like gratings and in open structures like dots.

The wafer with micro-fluidic channels was then sputtered with a 50nm thin layer of gold to act as electroplating seed layer. The wafer with smaller features was sputtered with nickel-cobalt alloy of similar thickness. The wafers are then ready to be electroplated as described in the following section.

3. STAMPER ELECTROFORMING

The electroforming process is carried out in a tank filled with plating solution containing nickel and cobalt anodes, a thermostatically controlled heater, circulation and filtration systems and a DC power supply. An electronic controller maintains the composition of the alloy. A sulfamate based plating chemistry is used. The electrolyte contains nickel and cobalt ions, boric acid, surfactants and other ingredients. At the operating temperature of 45 - 50 °C, pH 4 and current density of 10-20 mA/cm^2, a 0.5 mm thick electroform can be produced in about 24 hours at the average deposition rate of 20-25 µm/hr. The alloy consists of approximately 98% nickel and 2% cobalt.

After the seed layer metallization, the silicon wafer is mounted in a plating fixture attached to the negative pole of the DC power supply and loaded in the electroforming tank. The electroplating setup is shown schematically in figure 1. The controllers establish proper process current. Nickel and cobalt ions in the solution are attracted to the negatively charged surface of the silicon master. When they approach the charged surface, the ions discharge and crystallize on it forming a metal layer that faithfully replicates the surface of the master. Upon completion of the process, the silicon mandrel (master) is chemically removed in a solution of KOH which does not affect the NiColoy electroform. Post-electroforming planarization of the backside of the stamper may in some cases be necessary. This is usually accomplished by grinding or electron-discharge machining.

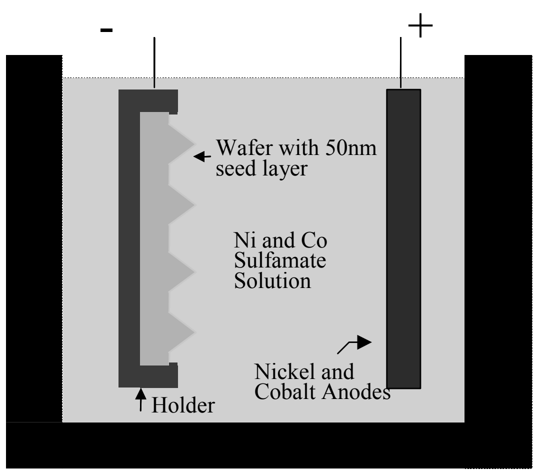


Figure 1: Sketch of the electroplating setup.

Figure 2 shows the features in wafer 1 and corresponding features on the stamp. The replica is an inverted image of the master. The stamper preserves the mirror like finish of the silicon wafer surface. Figure 3 shows features on wafer 2 and corresponding replicas in the electroform. It can be seen that replica is conformal and exhibits negligible distortions. Table 1 compares the properties of Nickel-Cobalt alloy with pure electrodeposited nickel. The alloy exhibits better properties when compared to pure nickel [4].

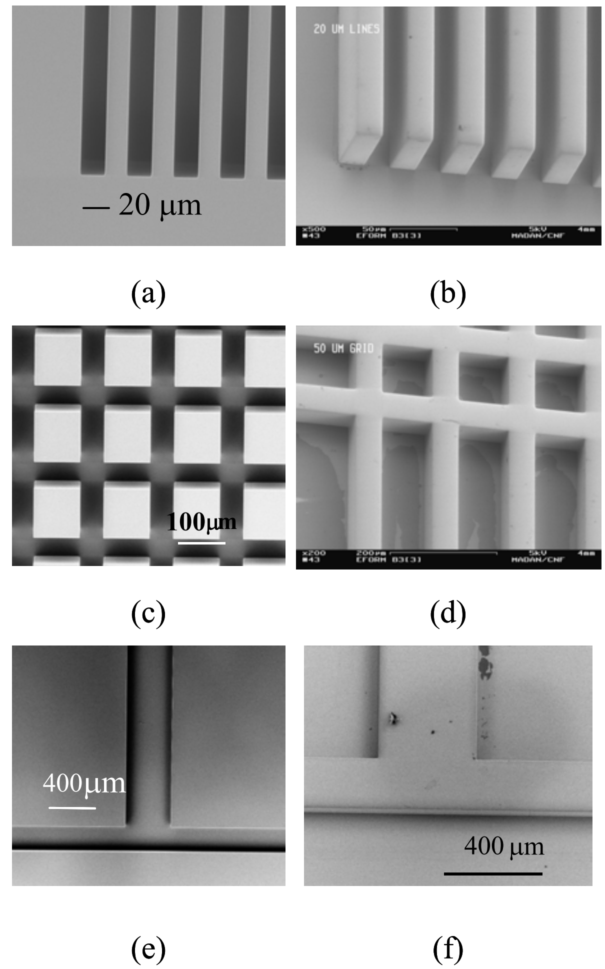


Figure 2: Features on wafer 1 (left) and their replicas in the electroform (right). Note that the edges are sharp and exhibit no distortion.

Table 1: Properties of Ni compared to Ni-Co alloy.

Parameter	Ni	Ni-Co alloy
Tensile Strength	550-600 Mpa	900-1000 Mpa
Knoop Hardness	< 250	350-550
Young's Modulus	115 Gpa	150 Gpa
Internal Stress	10-30 Mpa	~0 Mpa

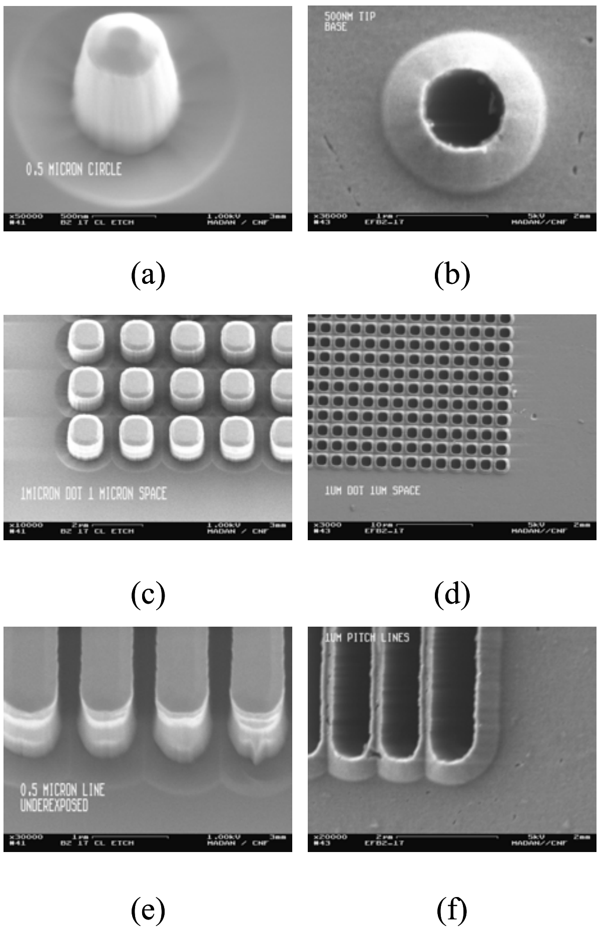


Figure 3: Features on wafer 2 (left) and their corresponding replicas (right) in the electroform. The metal deposition is conformal and is able to replicate features smaller than 300nm easily.

4. Embossing Process

The embossing process was performed on EV520 embosser. Zeonor® 1020R (Zeon chemicals) plastic was chosen for experiments. Zeonor® exhibits high optical transmission (greater than 90% in 400nm-1100nm range), low moisture absorption (<0.01 wt. %), low mold shrinkage (0.1-0.3%) after processing [5]. Other suitable substrates include polycarbonate, polystyrene etc.

The stamper is placed face down on the plastic substrate in an evacuated chamber (chamber pressure: 100Pa). The plastic rests on a rigid metal chuck and constant force of 20KN is applied on top of the stamper by a metallic lid. Both the lid and chuck are heated above the glass transition temperature (105° C) of the plastic. We have used 120°C and 130°C in our experiments. The plastic flows and fills the surface features of the stamper. Pressure is held constant for 10 minutes and then the substrate is allowed to cool down to about 80°C under vacuum before being taken out of the chamber. The substrate and stamper are then separated by gently lifting the edge of the stamper.

To separate the embossed substrate from the stamper non-destructively, a thin low surface energy self-assembled release layer coating is applied onto the stamper. In our experiments, a long alkyl chain self-assembled monolayer was chosen. The interfacial interaction between the embossed substrate and the stamper is minimized since only weak Van der Waal interactions exist at the interface. The coating layer was chosen according to the sputtered electroforming seed layer. For a gold seed layer, we have used a SAM coating of 1-hexadecanethiol. This coating is applied by covering the stamper with 1mM solution of 1-hexadecanethiol (HDT) in ethanol for 24 hours followed by blow drying. Thiols can bind with nickel surfaces and hence are suitable for use in case of nickel seed layers also. Detailed description of SAM formation is available in literature [6]. Another important self-assembled monolayered system is the silanes on hydroxylated surface system. A Si-O covalent bond is formed in this system, making it very stable at high temperature. Organopolysiloxanes bonding to native nickel oxide surface of the electroform is an alternative choice to provide the surface with a single molecule layer release coating, which is stable at our processing temperature [7]. Thus this coating can be applied in case of nickel-cobalt seed layer, which has native oxide on surface. We have used Sigmacote ® (Sigma-Aldrich) (a cholorinated organopolysiloxane in heptane) for our experiments. Sigmacote® is dispensed on the electroform using a pipette. The electroform is then washed with DI water to remove any hydrochloric acid (HCl) formed on the surface by hydrolysis. A rinse in ethanol or iso-propyl alcohol removes any organic residue on the surface. To toughen the coating, the stamper is baked at 100°C for 30 minutes. The silane coating is then stable at the temperatures used for the embossing process and does not require frequent recoating of the release layer. Our experiments showed silane release coatings are preferred to thiol release coatings both due to its robustness and short application time. Thus a nickel cobalt alloy seed layer is preferred to gold seed layer.

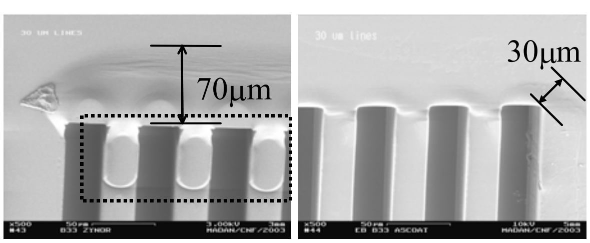
5. Results and Discussion

5.1 Stresses in electroforms

Most electrodeposits are formed in a stressed state causing distortions after the master wafer is dissolved away. A film under tensile stress tends to contract and that under compressive stress tends to expand. The reproduced structure thus would not be a true replica of the master. Distortions would manifest especially in edges of pillars. They can be rounded (compressive stress) or sharpened (tensile stress) when compared to the master. Stress is a function of temperature, electrolyte density, solution pH, current density etc. When all the other parameters in the plating system are fixed, the stress in the deposited film is a function of current density [8]. At low current densities the stress is compressive and at high current densities the stress is tensile. By choosing suitable current density values, the stress of the deposited film can be tuned to be zero. This has to be done by trial and error and thus, it is a good engineering practice to maintain constant plating conditions. From figures 2(a, c, e) and 3(a, c, e) one can observe that the electroform edges are sharp and undistorted when compared to the master, pointing out to negligible residual stresses in the electroform.

5.2 Embossing

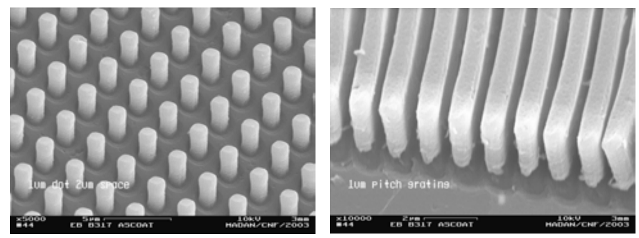
Our initial experiments were carried out without the release layer at 120°C. We observed insufficient material flow at this temperature and hence the embossing temperature was increased to 130°C in subsequent experiments. The anti-stiction coating reduces the metal stamp-plastic interface energy and hence the shearing forces on the plastic substrate when it is separated from the stamp after embossing. This is evident from figure 4 that shows the edges 30μm lines before and after anti-stiction coating. Without the release coating, the shearing forces are large enough to break the lines at the edges, where maximum stresses occur. The use of higher embossing temperature has also reduced the extent of distorted region around an embossed feature. These distortions are caused when the material is forced out of the embossed region by the stamp. This causes compressive stress buildup in the material around the embossed regions and causes wrinkles (local buckling) on the surface. A higher temperature enables stress relaxation by plastic flow and smoothens distortions. This is borne out by reduced distortion extent in figure 4 (b). For features larger than 100μm, stamps with and without release coating perform comparably.



(a) (b)

Figure 4: Yield improvement upon anti-stiction coating of the electroform. 30μm lines crack at the edges without release layer (figure 4 (a)) while the lines come out undamaged in presence of the release layer (figure 4 (b)). The extent of the distorted region is also reduced at 130°C, ~30μm (figure 4(b)) when compared to 120°C embossing ~ 70μm (figure 4 (a)).

Significant improvements are observed when embossing smaller features. When replicating gratings and pillars, sharp edges are obtained when release layers are used (figure 5). Features with aspect ratios up to 3 are easily replicated. The edges are rounded by shear if anti-stiction coating is not applied. Without release layers, many pillars and gratings can be severed from the substrate during the separation process. For features with higher aspect ratios, higher embossing temperatures and pressures are necessary to ensure complete filling of the plastic material into stamp features. This is not desirable since at higher temperatures, the plastic would flow laterally without any increase in filling and also a thicker stamp would be needed to withstand higher bending forces.



(a) (b)

Figure 5: Embossed features: 1μm dots (figure 5 (a)) and 1 μm pitch gratings (figure 5 (b)) with release layer applied to the electroform. The embossing temperature is 130°C. Sharp unsheared edges are reproduced when the release layer is applied. The features are about 2.3μm deep. Without the release layer, the pillars and gratings are sheared off the surface during separation of the electroform from the plastic substrate.

The metal electroform allows the use of a large force (20KN) for embossing. This is especially useful when working with plastics with higher T_g. Silicon masters crack when used at these force (20KN) levels. The metal stamper can be reused many times, providing a very cost effective approach when large numbers of replicated devices are needed. The stamper can be periodically cleaned by immersing it in an organic solvent like cyclo-hexane or ethylene glycol.

6.Conclusion

A high fidelity embossing process using Nickel-Cobalt alloy stampers has been demonstrated. An anti-stiction coating, specific to the surface material of the stamper, to ensure smooth separation of the stamp from the replica has also been developed. This increases the yields and produces low distortion replicas. This work provides a cost-effective way to produce micro-optical components like gratings and micro-fluidic devices, with feature sizes from hundreds of microns to sub-micron dimensions. Incorporating these features on a single master will enable low cost production of micro-fluidics devices based biosensors with integrated optical elements.

7. Acknowledgements

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8. References

[1] S. Ballandras, et.al., "Microgrippers fabricated by the LIGA technique". *Sensors and Actuators A,* 58:265-272, 1997.

[2] F.Laermer and A.Schilp, "Method of Anisotropically Etching Silicon", Robert Bosch GmbH, US patent 5,501,893.

[3] H. Jansen, et.al., "A survey on the Reactive Ion Etching of Silicon in Microtechnology". *J.Micromech. Microeng.*, 6:14-28, 1996.

[4] Berl Stein, "Mechanical Properties of Electroformed Nickel Cobalt Alloys", to be presented at ASM international surface engineering congress and exposition, Indianapolis, Indiana, USA, September 15-17, 2003.

[5] http://www.zeonchemicals.com.

[6] Younan Xia and George M. Whitesides, "Soft Lithography". *Angew. Chem. Int. Ed.,* 37: 550–575, 1998.

[7] http://www.gelest.com, literature on silane coupling agents.

[8] Berl Stein, "A Practical Guide to Understanding, Measuring and Controlling Stress in Electroformed Metals", *Proceedings of AESF Electroforming Symposium*, Las Vegas, Nevada, USA, March 1996, pages 49-53.