The fabrication of patterned metallic master by photolithography and electroplating technique for making PDMS-stamp as a tool for drug delivery system preparation

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Abstract. In this work, the micropatterned (Ni micropillars) masters were fabricated by combination of photolithography and electroplating technique. The polydimethylsiloxane (PDMS) stamps were successfully made by casting technique on micropatterned masters and used for further preparation of polymeric microchamber arrays film considered to be a drug delivery system. Micropatterned master fabrication is more precise technique, which is necessary for defects elimination.

1. Introduction

Preparation of biodegradable microchamber arrays film which is considered to be a drug delivery system requires using a special polymeric micropatterned stamp as it was demonstrated in previous work [1]. Such stamp is a reverse replica of a master, thus, it is necessary to fabricate patterned master for it. Since the stamp and microchamber patterns directly depending on the master, the technique of master fabrication should be appropriate to provide the desired pattern.

Photolithography is a standard well-spread technique for the pattern fabrication on a metallic substrate by a top-down approach. This technique consists of covering substrate with photoresist; transferring patterns from a photomask to a photoresist by using UV light exposure and its development; etching unwanted parts of the substrate [2]. However, despite the simplicity of standard photolithography technique, it has a limitation in shapes of patterns [3].

Combination of photolithography and electroplating technique named as LIGA (lithography, electroforming and molding) is down to top approach which includes plating of metal instead of etching substrate [4]. Such combination allows getting more precise structures with variety of shapes and dimensions from micro- to nano- sizes. Furthermore, due to low roughness of plated metallic pattern polymeric reverse replica has a high quality [5].

Polydimethylsiloxane (PMDS) is the most common elastic polymer used for stamp making because it ensures a conformal covering over a large area including micro- and nano-nonuniform surfaces, has a quick curing time and has a low cost. Moreover, prepared PDMS-stamp is chemically stable, non-toxic and hydrophobic [6,7]. Traditionally, PDMS-stamp made by the casting of PDMS and curing agent mixture onto a master, wherein it is easy to gain necessary PDMS stamp stiffness by the variation of curing agent concentration.

In this work, the micropatterned master fabrication by combination technique of photolithography and electroplating in order to make micropatterned (MP) PDMS-stamp for the future biodegradable microchamber arrays film preparation was described.

2. Materials and methods

2.1. Materials

Aluminum ceramics plates (Policor, Russia) VK-100 were used as a substrate. Positive photoresist AZ 9260 from the AZ Electronic Materials (Luxembourg) and photomask with pattern diameter of 10 µm was used for MP master fabrication. Chemicals as dimethylformamid (EKOS-1), hydrochloric acid (HCl), sodium hydroxide (NaOH) and nickel electrolyte were used for master fabrication without further purification.

Poly(dimethylsiloxane) (PDMS) (ELASTOSIL RT 601) from Wacker AG, Germany was used for stamp making. Poly(L-lactic) acid (PURASORB PL38) from Purac, Netherlands and chloroform from Fisher Scientific, UK were used for microchamber arrays film preparation.

2.2. Micropatterned master fabrication

The scheme of MP Masters fabricating by photolithography and electroplating of nickel combination technique is shown in figure1.

Ceramic plates were taken as a substrate. A copper (Cu) layer with a thickness of 0.5 µm was deposited on ceramic plates by magnetron sputtering as a conductor for electroplating. For better adhesion between Cu-layer and plates, a tantalum (Ta) layer with thickness of 200 nm was deposited on plates.

For the photolithography process, a positive photoresist AZ 9260 was spin coated on a substrate by a centrifuge at 2000 rpm for 60 s. The photoresist layer having a thickness of 10 µm on the plate was exposed by UV light lamp (380 – 410 nm) through the photomask for 30 seconds. After developing in 1.5% NaOH (m/m) solution for 8 s, the pattern in a photoresist was formed and clean from contaminants in 10% HCl (v/v) solution.

Electroplating was carried out in a bath with Ni electrolyte (table 1) under the current density of $0.1 A\cdot mm^2$, a direct current of 0.5×10^{-1}A. Such direct current and current density were used to avoid detachment of the photoresistive mask. The different electroplating time was chosen: 20 minutes (Master 1) and 10 minutes (Master 2).

At the end of the electroplating, the photoresistive mask was removed in dimethylformamid, and then the masters were washed and dried.

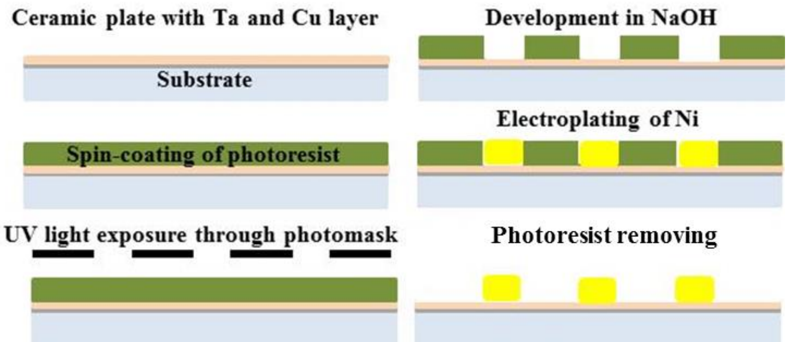

Figure 1. The scheme of the patterned master fabrication.

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Table 1. Ni electrolyte composition.

Composition	Quantity
$NiSO_4 \cdot 7H_2O$	150 $g \cdot l^{-1}$
$Na_2SO_4 \cdot 10H_2O$	60 $g \cdot l^{-1}$
HBO_3	24 $g \cdot l^{-1}$
NaCl	6 $g \cdot l^{-1}$

2.3. Micropatterned PDMS-stamp preparation

The MP PDMS-stamp was prepared according to the following method. A liquid PDMS and curing agent were thoroughly mixed in a standard ratio of 10:1 (w/w). The mixture was poured onto a clean master and vacuum degassed for 10 min to remove air bubbles. The PDMS curing was in a heat chamber at 70ºC for 20 min. The cured PDMS was easily peeled off and was subsequently used for polymeric microchamber arrays film preparation.

2.4. Polymer microchamber array film preparation

The MP PDMS-stamp was dip-coated into 1wt.% PLLA solution in chloroform and then it was dried under an ambient condition to full solvent evaporation for receiving PLLA film on it. The MP PDMS-stamp/PLLA was sealed by micro-contact printing on the pre-coated in PLLA solution flat substrate. After that, the MP PDMS-stamp was lifted off and the PLLA film repeating pattern of the PDMS-stamp left on a flat substrate. The model drug was loaded prior MP PDMS-stamp/PLLA sealing.

2.5. Characterisation

Scanning electron microscopy (SEM) on ESEM Quanta 400 FEG (FEI, USA) was used to investigate the morphology and the quality of the masters, the MP PDMS-stamp and polymeric microchamber arrays film. Preliminary the stamp and microchamber arrays film were coated with a conductive thin gold layer *via* magnetron-sputtering system SC7640 (Quorum Technologies Ltd, UK).
The SEM images was analysed with using ImageJ program. For each parameter 100 measurements were carried out.

3. Results and discussion

3.1. Fabricated micro-patterned master

The fabricated MP masters after photolithography development process and Ni electroplating on a substrate are shown in Fig 2. SEM images shows the repeating structures as ordered Ni micropillars with some defects.

The center-to-center distance of micropillars for the both masters is 20 µm. The micropillars height is nonuniform for the both masters. The micropillars height on the Master 1 is in the range of 4.1 to 6.9 µm; on the master 2 is in the range of 1.8 to 3.2 µm. As the electroplating time for the Master 1 was two times longer, its micropillars are two times higher.

On the Master 1, the micropillars have a trapezoid-shaped profile: the diameter of micropillars at the base of the plate is lower than at the top. However, on the Master 2 fabricated under the same condition, but with a less electroplating time, has regular shaped micropillars. A lack of exposure in the lower layers of the photoresist due to a relatively large thickness of the photomask and not complete photoresist development could cause changing in patterns shape. Since residual photoresist remains near the substrate, the contact area for nickel electroplating is less.

As Figure 2 shows some defects on the masters could be observed. The substrates cracks associated with a low-quality of aluminum ceramics plates. The defective pillars on the Master 1 (figure 2a) is a result of over electroplating. Defects can be eliminated by more precise selection of parameters of the photolithography such as time exposure, developer composition and time of development and electrical conditions such as electroplating time and current density which have the influence on a plating speed.

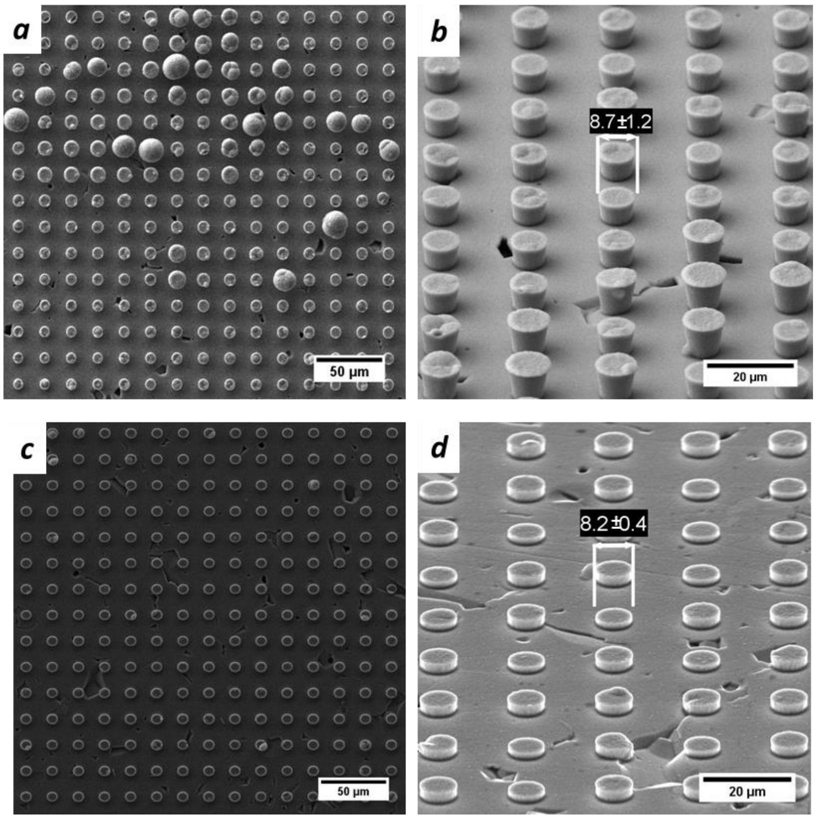

Figure 2. SEM images of the Master 1 (*a, b*) and the Master 2 (*c, d*).

3.2.The PDMS-stamp

The MP PDMS-stamps from the masters are shown in figure 3. The MP stamps from the Master 1 and the Master 2 are named as PDMS-stamp 1 and PDMS-stamp 2, respectively.

The PDMS-stamps have ordered arrays of microwells completely reverse replicate patterns of masters (figure 3 *b*, *d*).

Microwells of PDMS-stamp 1 keeps a trapezoid-shape profile with expansion to the bottom after lifting off due to the elasticity of stamp. The microwells average depth is 6.4±0.3 μm as the height of a metallic pattern. The upper microwells diameters (d_1=6.4±0.3 μm and d_2= 7.4±0.3 μm) are less than the metallic patterns one.

Microwells of PDMS-stamp 2 has a rectangular-shape profile with an average depth of 2.6±0.4 μm. The microwells diameters are the same as for the master 2.

The microwells of PDMS-stamp 2 are the more identical in depth and have a regular shape, so it was decided in further to use just this stamp for microchamber arrays film preparation.

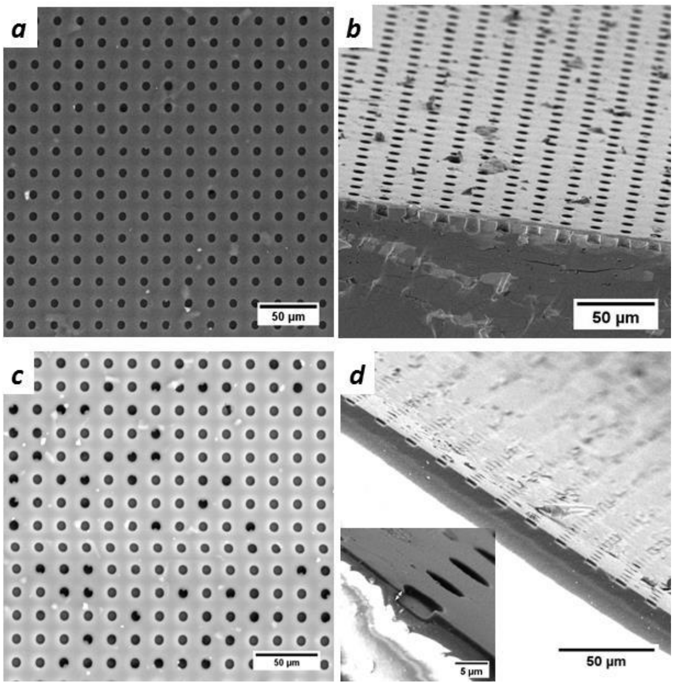

Figure 3. SEM images of the MP PDMS-stamps 1 (*a, b*) and MP PDMS-stamps 2 (*c, d*) on top-view (*a, c*); the tilt-view (*b, d*). The part of image g is magnified in 10 times.

3.3.Polymeric microchamber arrays film

The PDMS-stamp has a low surface energy [6], due to that fact the adhesion of PLLA film to the stamp is a poor that allows easily print it on a flat substrate.

Figure 4 shows the PLLA microchamber arrays film prepared by using the MP PDMS-stamp 2. Microchamber arrays are reverse pattern replica from the PDMS-stamp and a direct replica from the master. The thickness of PLLA film is about 0.5 μm. Microchambers save a free spaces into which drug substance to be loaded. The approximate loading capacity of individual microchamber is 9.12×10^{-8} μl.

It was investigated, that the PDMS-stamp could be swelling in chloroform after being there more than 10 min at 37°C [8]. However, the microchamber arrays film preparation excludes a long contact with the solvent and lasts only 10 s. Thus, the dimensional and shape PDMS-stamp microwells are not changed, so the PDMS-stamp could be used several times.

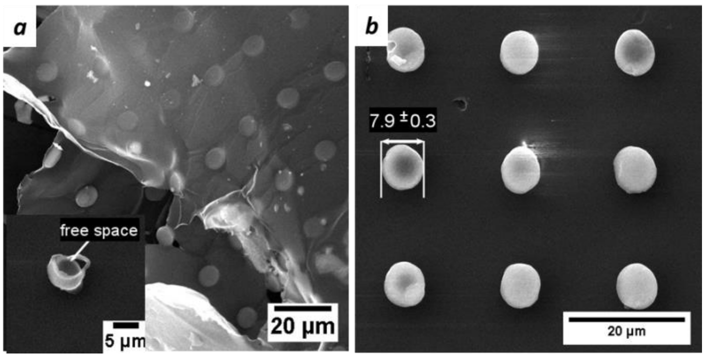

Figure 4. SEM images of PLLA microchamber arrays film prepared with using the PDMS-stamp 2.

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4.Conclusion

In this work, the micropatterned metallic masters were fabricated by combination of photolithography and electroplating technique. The micropattern is an ordered Ni micropillars. The increasing electroplating time in two times allows getting masters with the micropillars two times higher.

The PDMS-stamps were successfully made by casting on fabricated Masters and applied for microchamber arrays film. However, it was observed some defects such as cracks, nonuniform height dismersion on both masters and irregular shapes of micropillars which can influence on a quality of PDMS-stamps and microchamber arrays film. It was considered, that for the elimination of defects, more precise choice of fabrication parameters is necessary.

Acknowledgments

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