Microelectronic Engineering 110 (2013) 427-431

Contents lists available at SciVerse ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Ferromagnetic shadow mask for spray coating of polymer patterns

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ARTICLE INFO

Article history: Available online 18 March 2013

Keywords: Spray coating Nickel electroplating Magnetic clamping Eudragit Polymer patterning

ABSTRACT

We present the fabrication of a wafer-scale shadow mask with arrays of circular holes with diameters of 150–400 μ m. Standard UV photolithography is used to define 700 μ m thick SU-8 structures followed by electroplating of nickel and etching of the template. The ferromagnetic properties of the shadow mask allow magnetic clamping to the substrate and spray coating of well defined polymer patterns. © 2013 Elsevier B.V. All rights reserved.

1. Introduction

Spray coating is a versatile technique for the deposition of thin polymer films on both flat and pre-structured substrates [1–3]. Typically, photolithography is used for subsequent patterning of the deposited layer which requires that the polymer is photosensitive. Direct spray coating of polymer patterns could remove considerable limitations on the composition of the processed material. In practice, direct writing of micropatterns by spray coating beam is in the mm-range. Here, we investigate the use of a shadow mask to restrict polymer deposition on the substrate to well-defined areas with dimensions between 150 and 400 μ m.

A large number of materials and methods have been suggested for the fabrication of shadow masks for other applications than spray coating. Si shadow masks have been used for metal evaporation or local plasma polymerization [4–5]. For metal deposition, nanostencils with hole dimensions down to the nanometer range were successfully applied [6]. However, Si stencils are fragile particularly for designs with dense hole arrays and not suitable for repeated deposition of polymers and subsequent cleaning steps. Alternatively, metal patterning was achieved by evaporation through shadow masks made of polymers such as SU-8 [7], Parylene [8], Polydimethylsiloxane (PDMS) [9] or Kapton[®] [10]. Zhao et al. fabricated similar stencils based on SU-8 laminate and used them for the deposition of protein patterns by immersion [11]. Dubourg et al. demonstrated spray coating of Poly(methyl methacrylate) (PMMA) micropatterns through SU-8 shadow masks [12]. Our preliminary attempts to use thin polymer films for spray coating of polymer patterns with sub-mm dimensions were not successful. The experiments showed that a low distance between shadow mask and substrate is crucial to avoid broadening of spray coated patterns. For thin polymer shadow masks non planarity due to intrinsic stress is a major challenge particularly for patterning on wafer scale. Also, repeated use of these stencils is difficult due to the low mechanical stability of the polymer films. Furthermore, exposure to organic solvents during spray coating and cleaning potentially affects the integrity of polymer shadow masks. A metal shadow mask presents a potential solution both in terms of mechanical and chemical stability. Yi and co-workers employed electron discharge milling (EDM) for the fabrication of a stainless steel shadow mask [13]. This approach is very versatile, but the processing of a wafer scale stencil is very time consuming.

Here, we propose the fabrication of a ferromagnetic shadow mask which allows the use of magnetic forces to provide clamping between substrate and stencil. More specifically, we describe a simple process for the fabrication of a Nickel shadow mask by electroplating on a SU-8 template defined by standard UV photolithography. The negative photoresist SU-8 was initially introduced as a thick film resist for the patterning of molds for electroplating [14]. Finally, we demonstrate the potential of magnetic clamping for spray coating of polymer micropatterns on wafer-scale. The first proof-of-concept is done with the commercially available polymer Eudragit. This copolymer of methacrylic acid and methyl methacrylate is used in the pharmaceutical industry for coating of solid dosage form such as tablets and capsules and is interesting for micro- and nanotechnological applications in drug delivery and tissue engineering.





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2. Materials and methods

2.1. Shadow mask fabrication

The shadow mask was fabricated with the process illustrated in Fig. 1. First, an electroplating template was fabricated. A seed layer of 100 nm Au with an adhesion layer of 10 nm Ti was deposited on a Si substrate and patterned by lift-off. The patterning of the seed layer was required to ensure adhesion of the SU-8 template to the substrate during further processing and to avoid a final metal etch opening the holes of the shadow mask after template removal. Next, 700 µm high SU-8 structures were defined in one step of standard UV photolithography using the same photomask as for the patterning of the seed layer. The SU-8 structures serve as template for the electroplating process preventing Ni deposition at the locations of the holes of the shadow mask. Two layers of SU-8 2150 (MicroChem, USA) were spin-coated on a RC8 Spin Coater (Karl-Süss. France) for 30 s at 500 rpm and 60 s at 1000 rpm with an acceleration of 100 rpm/s. The two soft-bakes after spin-coating of each layer and the post-exposure bake were performed on a programmable hotplate (Harry Gestigkeit GmbH, Germany) for 10 h at 50 °C with a temperature ramping of 2 °C/min followed by cooldown to room temperature. UV exposure was done on a mask aligner MA6/BA6 (Karl-Süss, Germany) in proximity contact with a dose of $2 \times 250 \text{ mI/cm}^2$. The process parameters were selected to avoid delamination of the SU-8 structures due to thermal stress. Next, 350 µm of Ni were electroplated on a microform.200 Nickel Electroplating machine (Technotrans, Sweden) with a plating bath of aqueous nickel sulphamate, boric acid and sulfamic acid at 51 °C and pH 3.5-3.8. The current was slowly increased to 0.5 A during 15 min followed by ramping to the final value of 1.5 A during additional 15 min. There, the electroplating was continued for approximately 10 h until a final setpoint charge of 15 Ah was reached. The electroplating step was followed by etching of the Si substrate in 28 wt.% KOH at 80 °C for 7.5 h. Finally, the SU-8 template defining the holes of the shadow mask was removed by etching for 4 min in Piranha solution (4:1 H₂SO₄:H₂O₂). As an additional advantage of



Fig. 1. Process flow for fabrication of shadow mask: (a) patterning of Au seed layer on Si substrate; (b) definition of SU-8 template; (c) electroplating of Ni; (d) KOH etching of Si substrate; (e) removal of SU-8 template in Piranha solution.

the pre-patterning of the Au seed layer, SU-8 etching progresses from both sides of the shadow mask, resulting in a shorter etch process.

2.2. Spray coating

A 1 wt.% solution of Eudragit® L100 (Evonik Industries, Germany) in Isopropanol was spray coated using an ExactaCoat spray coating system (Sono-Tek, NY, USA). This system is equipped with an ultrasonic nozzle operating at a frequency of 120 kHz and generating droplets of solution with diameters below 20 µm [16]. The generator power was set to 1.5 W. The polymer solution was pumped through the nozzle by a syringe pump at a flow rate of 100 µL/min. A focusing air shroud is integrated in the nozzle and nitrogen gas at a pressure of 30 mbar was used to direct the beam of droplets onto the substrate. The distance between nozzle and substrate was 40 mm and the beam diameter on the substrate around 4 mm. The lateral movements of the nozzle were controlled by an x-y stage and the nozzle path was defined in the equipment software. The nozzle was moved line-by-line at a speed of 25 mm/s to achieve coating of an area corresponding to a 4 in. wafer. In this study, area coating was repeated 60 times to obtain a coating thickness in the µm range. The thickness of the deposited polymer films was measured with a Dektak profilometer (Veeco, NY, USA).

2.3. Magnetic clamping

Initial spray coating experiments were carried out on microscope glass cover slides. Two glass substrates were arranged in parallel on the Ni shadow mask and disc shaped Neodymium raw magnets (Supermagnete, Webcraft GmbH, Germany) were placed



Fig. 2. Schematic of shadow masked spray coating with magnetic clamping. (a) Patterning of PMMA clamping disc with laser machining; (b) deposition of PDMS layer; (c) magnetic clamping of Ni shadow mask, Si substrate and PMMA disc with rare earth magnets; (d) polymer spray coating; (e) removal of magnets, clamping disc and shadow mask.

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