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Abstract

Engineered Porous Metal Structures via Electroplating in Two-Photon Polymerized Molds †

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Abstract: We report the realization of metallic 3D microstructures, electroplated in two-photon polymerized molds. These molds are typically 150 × 150 × 30 μm^3 in size and the smallest feature size is about 1 µm. After the electroplating process, the mold is removed by means of CF4/O2 etching (1 h). The vertical electroplating growth is about two times higher than the horizontal growth, which creates voids. A new design to prevent voids was tested where the pores were arranged at a 35° angle to the chip surface. The remaining structures consisted of a copper base with a palladium finish, or of pure palladium. They were analyzed through SEM and were shown to be a good reproduction of the mold design, resulting in metallic porous structures with a specific surface area of about 6 mm^2/mm^2.

Keywords: two-photon polymerization; 2PP; electroplating; porous structure; catalyst support

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1. Introduction

Recently, the first trials to create small metallic structures by means of electroplating in two-photon polymerized (2PP) molds were conducted [1]. The mold is etched after the completion of the electroplating process and a final metallic porous structure is obtained. Possible applications include catalytic reactions and energy storage devices [2]. The 2PP process allows the design of very fine structures (~200 nm) resulting in materials with a pore size in the nano/micro scale [1,2].

We investigate the use of polymeric molds for the realization of void-free 3D metallic structures that are covered with, or based on, active metals (Pd). In addition, we apply a fast process to remove the mold after the electroplating process.

2. Materials and Methods

For the realization of the porous metal structures, different pore shapes (squares, circles, and honeycombs) were considered. We calculated that when placing the pores in all directions perpendicular to the surfaces of a rectangle block (150 µm × 150 µm × 30 µm), the square-shaped pores with the smallest size possible (2 to 10 µm) show the highest resulting surface area (up to six times larger compared to the plane surface, about 6 mm^2/mm^2). As the mold material we used IP-Dip, as we observed that compared to IP-S, it can be more easily removed after electroplating. The chip was based on a borosilicate glass wafer (Figure 1). A layer of gold (100 nm) was used for contact leads and the seed material for the electroplating process. A passivation layer of OrmoComp was used in areas where plating was not intended. For the electroplating process, the chips were cleaned in oxygen plasma and then immersed in a metallic electrolyte solution (NB Semiplate Cu 100 and NB Semiplate Pd 200) and the contacts pads were connected to the current source (Cu—20 mA/cm^2 for 60 min, Pd—5 mA/cm^2 for 10 min to obtain a finish layer over Cu, and 90 min for complete Pd structure). The horizontal plating rate was observed to be lower than the vertical rate, creating voids. To prevent voids, the width of the pore to be filled with the metal was increased (the pore resulting after the polymer etch was 50% of the distance between the pores) (Figure 2a). In addition, we designed a new structure where the pores were arranged at a 35° angle to the chip so the plating rate was equal in all directions. Figure 2c shows that this idea provides the desired structures. To etch away the polymer mold, oxygen plasma and CF_4/O_2 plasma were tested and yielded removal times of 10 h and 1 h, respectively.

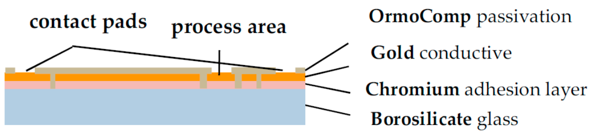

Figure 1. Borosilicate glass chip: Cr/Au metallic layers, and OrmoComp as a passivation layer.

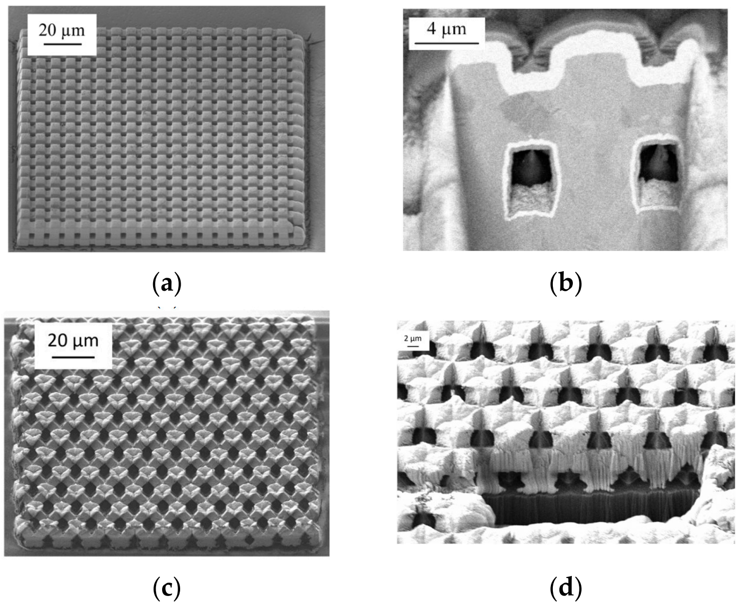

Figure 2. The SEM images (**a**,**c**) show Cu/Pd and Pd-electroplated structures, respectively, after the removal of the polymer mold. (**b**) A FIB cut realized in the structure in (**a**) after the electroplating process with Pd (white layer). (**d**) A FIB cut realized in (**c**).

3. Discussion

We investigated two methods to realize Pd structures. In the first, Cu structures were realized, and after the removal of the polymer, a second electroplating step was performed to obtain a Pd finish (330 nm) (Figure 2a,b). In the second, pure Pd structures were realized (Figure 2c). In Figure 2d, it can be seen through the FIB cut that one hour with CF_4/O_2 reactive ion etching was enough to remove all of the polymer. As a conclusion, we successfully integrated engineered microstructures with a highly active material (Pd) on glass chips.

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