Template fabrication of 3D metallic microstructures by electrochemical etching and electroplating

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1. Introduction

Metallic microstructures, have become an object of intensive research due to their potential applications in electronics and optics. Although a variety of 1D and 2D metallic microstructures can now be fabricated using a number of advanced lithographic techniques, e.g. electron beam (e-beam) or focused ion beam (FIB) writing, proximal probe patterning, X-ray and deep UV-lithography, further development of new techniques to produce large quantities from a diversified range of materials, rapidly, and at reasonably low costs, is still challenging. A straightforward route is the template-based synthesis of such structures because it enables a simple, high through-put, and cost-effective production and allows also the complex topology of the template to be reproduced in a single step [1]. The most widely used templates are porous alumina or polycarbonate membranes [2], templates based on self-assembly of colloidal spheres [3] or fabricated by using the conventional microelectronic technology, i.e. layer-by-layer stacking [4]. However, porous templates like alumina or polycarbonate membranes suffer from difficulties in controlling pore arrangement and dimensions and limit the fabrications to only two dimensions; the self-assembly of colloidal spheres provides structures with only *fcc* symmetry and stacking disorder or cracks in many cases do not allow large-area fabrication, while layer-by-layer stacking is prone to misalignment errors and requires long-time fabrication processes.

In this work, we show that macroporous silicon [5] consisting of periodic arrays of etched pores is a feasible alternative for the synthesis of 2D and 3D metallic microstructures due to its flexibility in the definition of complex geometries in bulk. In addition, macroporous silicon features full three-dimensionality, well controlled pore distribution and growth, and scalable dimensions (0.5-100 μm). We present here the fabrication of 3D Ni micro-structures by electroplating of macroporous silicon templates. The given approach can be applied for depositions of different metals and in more complicated template-structures.

2. Results and discussion

Macroporous silicon is prepared by photo-assisted electrochemical etching of *n*-type silicon in hydrofluoric acid (HF) solution. The pore arrangement over the surface is defined by lithographic techniques. Except the square arranged pore distribution presented here, the technique allows to pattern any wanted distribution. The diameter of the pores in depth is accurately controlled during the etching process by the photogenerated etching current. In this way, periodicity in the third dimension is introduced by properly modulating the current of the system (that is, the backside illumination). A pore widening of the macroporous templates is performed after the etching in order to obtain fully 3D structures with more complex geometry. This pore widening can be carried out by multiple oxidation/oxide-removal cycles [6] or by alkaline etching in base solutions [7]. Both pore widening processes enable the fabrication of 3D structures, however, with different geometries. While oxidation is an isotropic process which leads to a conformal erosion of pore walls and thus to a smooth 3D lattice with tetragonal symmetry similar to overlapping air spheres embedded in silicon, alkaline etching is strongly anisotropic and provides structures formed of overlapping polyhedra, i.e solid bodies having many sides. Some examples are shown in Fig. 1.

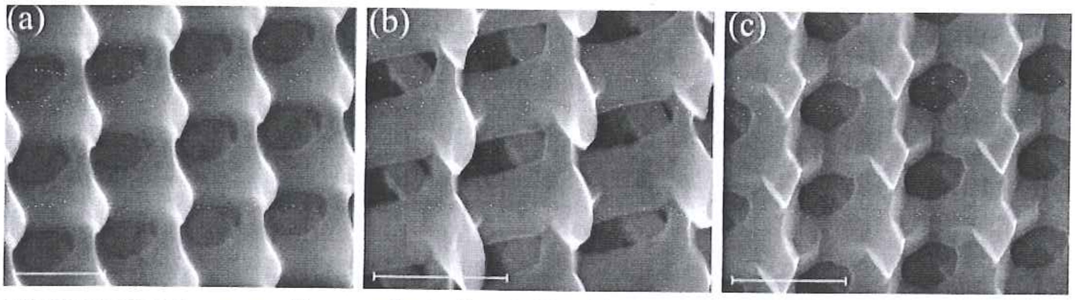

Fig. 1: 3D macroporous silicon prepared by pore widening through: (a) multiple oxidation/oxide removal cycles, (b) alkaline solution at 25wt.% and (c) diluted alkaline solution with an alcohol addition. Pores get connected laterally at the position of diameter maxima, but the pores openings exhibit different shapes. Scale bar is 4 μm.

The fabricated 3D macroporous templates are then filled by Ni electroplating to obtain inverse metallic replicas. The electroplating is conducted in a nickel sulphamate bath, and current density, pulse frequency, deposition time as well as temperature of the solution are controlled to achieve homogeneous filling of the pores. Some examples are shown in Fig. 2 and 3. Figure 2 shows SEM pictures of edges cut inside the Ni-filled macroporous silicon sample using an FIB dual-beam workstation. The cutting was arranged in such a way as to reveal images of both (100) and (110) surfaces of the cubic lattice. As can be seen, adjacent pores are connected along <100> equivalent directions, while in <110> direction which corresponds to the diagonal of the square unit cell no connection between the pores is observed. A closer view also reveals that Ni filling follows tightly the form of the modulated pores; voids (unfilled regions) are not observed. The SiO_2 layer which is present in the images was thermally grown before the Ni deposition to insulate the macroporous sample required for the electroplating process. In addition, the polycrystalline nature of the formed Ni wires is clearly seen due to the "channelling" effect of the incident electrons when imaging by SEM.

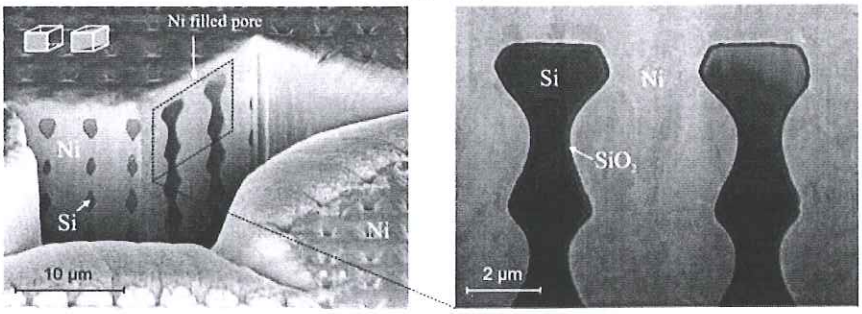

Fig. 3: Bird's eye (left) and closer views (right) of a grove cut inside Ni-filled macroporous sample using FIB system. The images reveal information of the quality of Ni filling and 3D geometry of the structure.

Finally, the removal of the silicon template in diluted alkaline solutions release the 3D Ni structure (shown in Fig. 3) which resembles now a 3D network of overlapping Ni spheres, that is, it is an exact inverse replica of the macroporous template. It should be noted that after releasing, these structures are mechanically stable and can be fabricated on a large scale. In our case, the typical sample dimensions are 2x2 cm but macroporous silicon can be easily formed on full 4- and even 6-inch wafers in one step etching process.

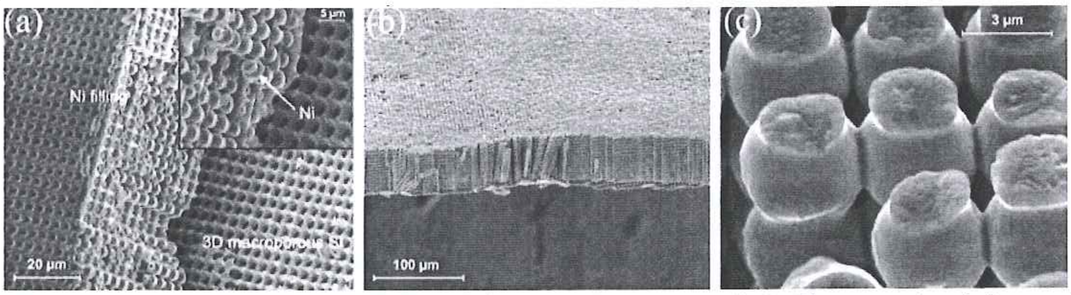

Fig. 3: (a) Bird's eye view of electroplated Ni pillars before removing the silicon template; (b) 3D Ni structure released after complete removal of the template; (c) Closer view of the structure revealing the interconnections between adjacent pillars.

3. Conclusions

Our results show that macroporous silicon is a suitable material for template-based synthesis of 3D periodic Ni structures through electroplating. Macroporous silicon offers the possibility to achieve a variety of pore shapes and lattice geometries. Structures with more than 20 structural periods (with a depth up to the wafer thickness) can be easily fabricated on a wafer scale. In combination with the electroplating technique applicable to a wide range of metals or alloys, macroporous silicon opens the way to large-area fabrication of complex metallic 3D networks.

4. Acknowledgments

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References

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