Electrochemical Nanoimprinting of Silicon: A Direct Patterning Approach

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ABSTRACT

Soft-lithography and nanoimprinting lithography have been critical in manufacturing 3D features with sub-20 nm resolution onto polymeric materials which have often been employed for producing micro and nanoscale optical materials and surfaces. However, methods for transferring 3D polymeric patterns (i.e. mask) into silicon have relied upon the etch selectivity of the mask pattern during reactive etching, which in turn limits resolution, aspect-ratio and surface roughness. This paper demonstrates an electrochemical nanoimprinting process for single-crystal semiconductors for directly etching 3D features into silicon wafers. It is shown that stamps made of porous catalysts play a critical role in enabling diffusion of chemical species during imprinting which, in turn, allows for morphology control of imprinted silicon features with sub-20 nm resolution in 3D. This process delivers mirror surface finish (RMS < 5 nm), low-defect density, and large-area patterning (>1 cm^2) in a single imprinting operation. Further, it outperforms the resolution and scalability of leading serial (e.g. FIB, electron beam) and parallel (e.g. gray-scale lithography) methods altogether, allowing for fast replication of patterns onto hard materials from a soft mold. This technique bypasses the need for dry etching and is potentially compatible with roll-to-roll platforms, amorphous and poly silicon and III-V semiconductors. In turn, it may pave the way for mold replication onto hard molds and the manufacturing of complex objects for infrared optics.

Keywords: nanoimprinting, scalable nanomanufacturing, MACE, metal-assisted chemical etching, wet etching, 3D nanostructures

1 INTRODUCTION

While prior work focused on imprinting porous silicon substrates with stamps made of solid catalysts [1], this paper focuses on understanding the role porous catalysts play in enabling diffusion of chemical species during imprinting which, in turn, allows for morphology control of imprinted silicon features with sub-10 nm resolution in 3D. This process delivers low-defect density, and large-area patterning (>1 cm2) in a single imprinting operation. Further, it outperforms the resolution and scalability of leading serial (e.g. FIB, electron beam) and parallel (e.g. gray-scale lithography) methods, allowing for fast replication of patterns from a polymeric mold. This technique bypasses the need for dry etching and is potentially compatible with roll-to-roll platforms, amorphous and poly silicon, and III-V semiconductors. In turn, it may pave the way for the manufacturing of complex objects for infrared optics.

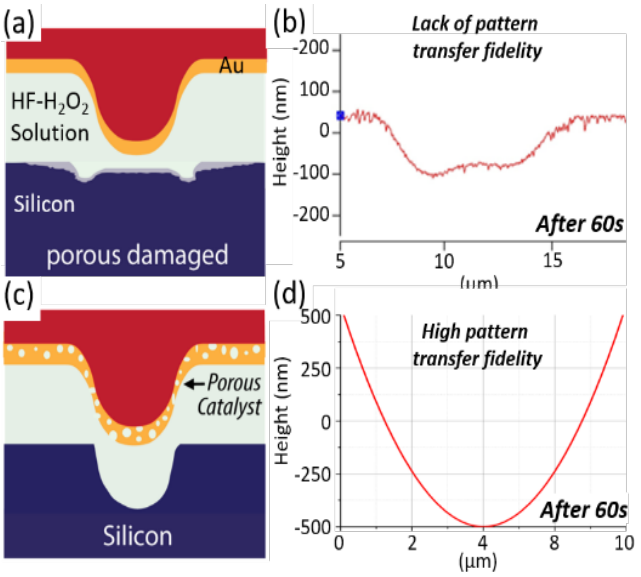

Figure 1: The schematics on the left depict the final stage of Mac-Imprint performed with a thin-film Au catalyst made of (a) solid Au thin film and (c) nanoporous Au. The images (b) and (d) are the corresponding substrate topology measured by AFM imprinted under the identical conditions of pressure, temperature, time and solution composition.

In the electrochemical nanoimprint set-up, a large-area catalytic stamp possessing 3D features and a silicon wafer are brought in contact while immersed in a mixture of HF, water and hydrogen peroxide as in the well-known metal-assisted chemical etching process (MACE) [2-5]. After sufficient time in contact, the stamp's 3D shape and nanoscale features are carved into the silicon substrate. Unlike previous unsuccessful attempts to pattern silicon (i.e. non porous) with solid thin-film catalysts [1] (Figure 1a-b), this paper specifically investigates the effect that porous thin-film catalysts have on improving the morphology of imprinted features, including at its surface.

First, it was necessary to synthesize porous noble metal thin-film catalysts using a well-known method called dealloying [6]. Secondly, porous catalysts used during

imprinting yielded dramatic improvements to etching selectivity and pattern fidelity. Experimental trends are discussed in the context of existing literature on MACE, and diffusion through pore-networks.

2 EXPERIMENTAL RESULTS

2.1 Porous Gold Preparation

The method starts by spinning a 3 µm thick layer of AZ1518 photoresist (PR) supplied by MicroChemicals onto a 4 inch (100) Silicon wafer. This first layer was hard baked at 170 C for 20 min and serves to protect the underlying silicon substrate. Next, a second layer was spun and patterned by lithography and also cured at 170 C for 20 min, leading to dewetting of the second layer. The geometry of the patterns defined on the mask was fixed to an array of lines with 10 µm width and 128 µm spacing. After dewetting, the lines dewet into parabolic cylinders. Next, stamps were co-sputtered with Ag and Au in an AJA Sputtering System calibrated with a crystal monitor. The deposition pressure was set to 3mTorr; the argon flow rate set to 4.5 sccm; the power in the Ag and Au targets were set to 95 W and 16 W, respectively, and its corresponding sputtering rates measured to be 3.5 Å/s and 1.2 Å/s. It is estimated from the relative sputtering rates that (a) volume fraction of silver is 0.75 (Vo) and (b) the film thickness is 400 nm. Finally, the films were dealloyed in a solution of nitric acid (70% diluted in water) and DI water mixed at 1:2 ratio, and kept at 60 ˚C ± 1 ˚C with a temperature controlled hot plate and stirring.

2.2 Silicon Imprinting

In order to establish a direct comparison, silicon substrates (p-type and with resistivity in the range of 1-10 ohm.cm) were imprinted with porous and solid stamps under identical experimental conditions (i.e. ρ = 96%, force = 4 lbf, and time = 3 min). In previous unsuccessful attempts (shown in Figure 1a-b), solid catalysts produce features in silicon without any discernible pattern fidelity (i.e. shapes of stamp and substrate do not match) and etching is delocalized from the catalyst-silicon interface. In contrast, pattern fidelity is restored with the use of highly porous stamps (Figure 1c-d) and etching is localized, leading to patterning resolution in 3D as small as 10 nm. Figure 1d highlights the increase in patterning fidelity obtained in Mac-Imprint with porous stamps. Further, Figure 2 shows the profile of stamp and substrate at complementary locations highlighting the minimal differences in curvature between them.

3 DISCUSSIONS

It is hypothesized that utilizing nanoporous catalysts in Mac-Imprint is a way to increase the effective diffusion coefficient of the catalyst thin-film and reduce the diffusion pathway. That is because, when a contiguous pore network is formed in a porous polycrystalline metal thin-film, molecules and ions diffuse not only through its grain boundaries and bulk grains, but also through the void phase [7]. Although highly tortuous, this void phase possesses a diffusion constant that is orders of magnitude higher than that of grain boundaries.

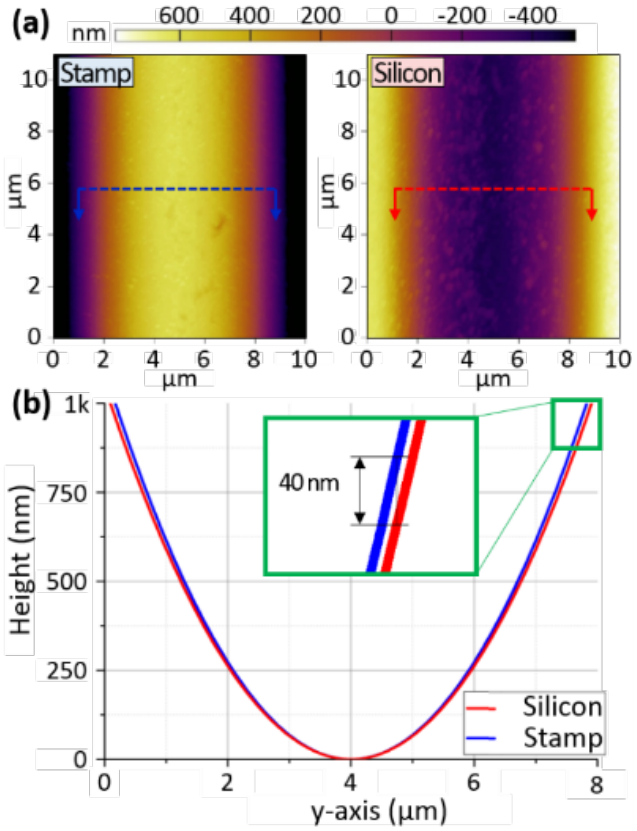

Figure 2: In part (a), the topology of stamp (left) and substrate (right) are measured via AFM at complimentary locations. Porous stamp with high pore volume fraction (>50%) were used during imprinting in this case. In part (b), the cross-section profiles of stamp and substrate (marked by color in part (a)) are superimposed to highlight accurate transfer of shape during imprinting.

4 CONCLUSION

In summary, Mac-imprint has been extended to silicon wafers (i.e. non porous) with the use of porous catalysts. It has been shown that catalyst geometry and porosity are relevant factors in nanoimprinting with MACE-based solutions to reduce the diffusion pathway, increase the effective diffusion constant of the porous metal catalyst, and regulate reaction kinetics. Combined, these factors capture the unique considerations one must have when using the Mac-imprint technique for generating pristine features into silicon and, potentially, other semiconductors.

5 ACKNOWLEDGEMENTS

The authors acknowledge collaborators Dr. Placid Ferreira at University of Illinois at Urbana-Champaign and Dr. Keng Hsu at University of Louisville for general comments regarding the direction of this work.

REFERENCES

[1] B. Azeredo, Y. Lin, A. Avagyan, M. Sivaguru, K. Hsu, P. Ferreira, Direct Imprinting of Porous Silicon via Metal-Assisted Chemical Etching » Advanced Functional Materials, vol 26, p.2929-2939, 2016.

[2] X. Li and P.W. Bohn, "Metal-assisted chemical etching in HF/H2O2 produces porous silicon," Appl. Phys. Lett., 2000.

[3] Z. Huang, N. Geyer, P. Werner, J. Boor and U. Gosele, "Metal-Assisted Chemical Etching of Silicon: A Review," Advanced Materials, vol. 23, pp. 285-308, 2010.

[4] C. Chartier, S. Bastide and C. Levy-Clement, "Metal-assisted chemical etching of silicon in HF–H2O2," Electrochimica Acta, 2008.

[5] N. Geyer, B. Fuhrmann, Z. Huang, J. de Boor, H. S. Leipner, and P. Werner, "Model for the Mass Transport during Metal-Assisted Chemical Etching with Contiguous Metal Films As Catalysts," Physical Chemistry C, vol. 116, no. 24, pp. 13446-13451, 2012.

[6] J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov & K. Sieradzki, "Evolution of nanoporosity in dealloying," Nature, 2001.

[7] J. Zhu, L. Chen, J. Shen, V. Tikare, "Microstructure dependence of diffusional transport," Computational Material Science, vol. 20, pp. 37-47, 2001.