TITLE:
Metal-Assisted Electrochemical Nanoimprinting of Porous and Solid Silicon Wafers

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SUMMARY:
A protocol for metal-assisted chemical imprinting of 3D microscale features with sub-20 nm shape accuracy into solid and porous silicon wafers is presented.

ABSTRACT:
Metal-assisted electrochemical imprinting (Mac-Imprint) is a combination of metal-assisted chemical etching (MACE) and nanoimprint lithography capable of direct patterning 3D micro- and nanoscale features in monocrystalline group IV (e.g., Si) and III-V (e.g., GaAs) semiconductors without the need of sacrificial templates and lithographical steps. During this process, a reusable stamp coated with a noble metal catalyst is brought in contact with Si wafer in the presence of hydrofluoric acid (HF) and hydrogen peroxide (H_2O_2) mixture which leads to the selective etching of Si at the metal-semiconductor contact interface. In this protocol, we discuss the stamp and substrate preparation methods applied in two Mac-Imprint configurations: (i) porous Si Mac-Imprint with solid catalyst, (ii) solid Si Mac-Imprint with porous catalyst. This process is a high throughput and is capable of centimeter-scale parallel patterning with sub-20 nm resolution. It also provides low defect density and large area patterning in a single operation and bypasses the need for dry etching such as deep reactive-ion etching (DRIE).

INTRODUCTION:
Three-dimensional micro- and nanoscale patterning and texturization of semiconductors enables numerous applications in various areas, such as optoelectronics[1,2], photonics[3], antireflective surfaces[4], super hydrophobic and self-cleaning surfaces[5,6] among others. Prototyping and mass-producing 3D and hierarchical patterns has been successfully accomplished for polymeric films by soft lithography and nanoimprinting lithography with sub-

20 nm resolution. However, transferring such 3D polymeric patterns into Si relies upon etching selectivity of a mask pattern during reactive ion etching and thus limits the aspect ratio, induces shape distortions and surface roughness via scalloping effects[7,8].

A new method (called Mac-Imprint) has been realized for parallel and direct patterning of porous[9] and solid Si wafers[10,11] as well as solid GaAs wafers[12,13,14]. Mac-Imprint is a contact-based wet etching technique which requires contact between substrate and noble metal-coated stamp possessing 3D features in the presence of etching solution (ES), composed of HF and an oxidant (e.g. H_2O_2 in the case of Si Mac-Imprint). During the etching two reactions occur simultaneously[15,16]; (cathodic reaction) H_2O_2 reduction at the noble metal, during which positive charge carriers (holes) are generated and subsequently injected into Si[17] and (anodic reaction) Si dissolution, during which holes are consumed. After sufficient time in contact, the stamp's 3D features are etched into the Si wafer. Mac-Imprint has numerous advantages over conventional lithographical methods, such as high throughput, compatibility with roll-to-plate and roll-to-roll platforms, amorphous, mono- and polycrystalline Si and III-V semiconductors. Mac-Imprint stamps can be reused multiple times. Additionally, it is capable to deliver sub-20 nm etching resolution which is compatible with contemporary direct writing methods.

Key to attaining high-fidelity imprinting is the diffusion pathway to the etching front (i.e., contact interface between catalyst and substrate). It has been firstly demonstrated in the work of Azeredo et al. (2016)[9] were ES diffusion was enabled through porous Si network. In order to realize solid Si Mac-Imprint the ES diffusion enabled through porous catalyst has been reported by Torralba et al. (2017)[18], followed by further investigations of the catalyst porosity influence on ES diffusion in works of Bastide et al. (2019)[19] and Sharstniou et al. (2019)[20]. Thus, the concept of Mac-Imprint was tested in 3 configurations with distinct diffusion pathways.

[Place Figure 1 here].

In the first configuration, the catalyst and substrate are solid providing no initial diffusion pathway. The lack of reactants diffusion leads to a secondary reaction during imprinting which forms a layer of porous Si on the substrate around the edge of the catalyst-Si interface. The reactants are subsequently depleted, the reaction stops resulting in no discernable pattern transfer fidelity between the stamp and substrate. In the second and third configurations, the diffusion pathways are enabled through porous networks introduced either in the substrate (i.e., porous Si) or in the catalyst (i.e., porous gold) and high pattern transfer accuracy is attained. Thus, the mass transport through porous materials plays a critical role in enabling the diffusion of reactants and reaction products to and away from the contact interface[9,18-20].

In this paper, Mac-Imprint process steps will be thoroughly discussed including stamp preparation and substrate pretreatment (protocol section) along with Mac-Imprint itself. The substrate pretreatment section will include following steps: Si wafer cleaning; Si wafer patterning with dry etching and substrate anodization (*optional*). Further, stamp preparation section will be subdivided into several procedures: PDMS replica molding of Si master mold; UV nanoimprinting of photoresist layer in order to transfer PDMS pattern and catalytic layer deposition via magnetron sputtering followed by dealloying (*optional*). Finally, in the Mac-Imprint section the Mac-Imprint setup along the Mac-Imprint results (i.e., Si surface 3D hierarchical patterning) will be presented.

PROTOCOL:

Caution: Use appropriate safety practices and personal protective equipment (lab coat, gloves, safety glasses, closed-toe shoes). This procedure utilizes HF acid (48% wt.) which is extremely hazardous chemical and requires additional personal protective equipment such as face shield, natural rubber apron and second pair of nitrile gloves that covers hand, wrists and forearms.

1. Stamp Preparation for Mac-imprint

1.1. PDMS mold fabrication

[Place Figure 2 here]

1.1.1. Prepare RCA-1 solution. To do so, mix deionized pure (DI) water and ammonium hydroxide in the glass beaker in 5:1 ratio (by volume). Place the beaker with the mixture onto stirring hotplate (see **Table of Materials**) and heat the mixture up to 70 °C. Measure the temperature of the mixture with calibrated thermocouple.

1.1.2. Add 1 part of the hydrogen peroxide to the preheated mixture to obtain RCA-1 solution. Keep RCA-1 solution at 70 °C. Wait until RCA-1 solution will start to vigorously bubble.

1.1.3. Soak Si master mold into RCA-1 solution for 15 min.

1.1.4. Take the Si master mold out of RCA-1 solution and thoroughly rinse with DI water.

[Place Figure 3 here]

1.1.5. Make a Si master mold hydrophobic. Put Si master mold into plastic Petri dish and place it inside desiccator (see **Table of Materials**). Using plastic pipette drop few droplets of trichloro(1H,1H,2H,2H-perfluorooctyl)silane (PFOCS) onto plastic weighing boat and place it inside the desiccator next to the plastic Petri dish with Si master mold.

1.1.6. Close the desiccator lid. Connect the output of the desiccator to the vacuum pump (see **Table of Materials**) through PVC tube. Start vacuum pump. Set the pressure level to 30 kPa using vacuum pump valve.

1.1.7. Open the desiccator valve and apply vacuum for 30 min.

1.1.8. While vacuum is applied to the desiccators, mix the base and curing agent provided in silicone elastomer kit (PDMS) (see **Table of Materials**) in 10:1 ratio by mass. Slowly stir mixture with glass spatula for 10-15 min.

1.1.9. Turn off the vacuum pump. Open the desiccator and remove the plastic weighing boat with PFOCS.

1.1.10. Carefully pour PDMS over Si master mold to completely cover it with the 2-3 mm layer of PDMS.

1.1.11. Repeat step 1.1.6.

1.1.12. Degas PDMS. Open the desiccator valve and apply vacuum for 20 min or until bubbles disappear.

1.1.13. Turn off the vacuum pump. Open the desiccator. Take out the plastic Petri dish with PDMS covered Si master mold and place it onto the hotplate (see **Table of Materials**) preheated to 80 °C.

1.1.14. Cure PDMS with Si master mold on the hotplate at 80 °C for 120 min.

1.1.15. Remove the plastic Petri dish with cured PDMS from the hotplate. Using scalpel trim the edges of the cured PDMS inside the plastic Petri dish. Carefully take cured PDMS with Si master mold out of the plastic Petri dish using tweezers.

1.1.16. Carefully exscind all PDMS that leaked underneath Si master mold using scalpel. Peel off cured PDMS from Si master mold using tweezers. Perform peeling off slowly in the direction parallel to the direction of Si master stamp pattern.

1.1.17. Crop the 2 x 2 cm PDMS mold with the pattern in the center of it using scalpel. Store the PDMS mold in the plastic Petri dish with the pattern facing up.

1.2. Photoresist UV nanoimprinting

[Place Figure 4 here]

1.2.1. Cleave 2.5 x 2.5 cm Si chip out of Si wafer using scriber.

1.2.2. Repeat steps 1.1.1 – 1.1.4 to clean Si chip.

1.2.3. Bring SU-8 2015 photoresist out from the fridge and let it stay at room temperature for 10-15 min prior to spin coating.

1.2.4. Open the spin coater (see **Table of Materials**) lid. Place the Si chip inside the spin coater onto the vacuum chuck.

1.2.5. Connect the output of the spin coater to the vacuum pump through PVC tube. Start vacuum pump. Set the pressure level to 30 kPa using vacuum pump valve.

1.2.6. Select the spin coating procedure with the following parameters: spread at 500 rpm for 10 s with acceleration 100 rpm/s, spin at 2000 rpm for 30 s with acceleration 300 rpm/s.

NOTE: Step 1.2.6 will produce a 20 µm thick SU-8 2015 layer.

1.2.7. Apply vacuum to the vacuum chuck by pressing “VAC ON” button on the spin coater display. Refer to Supplemental file **Figure S1**.

1.2.8. Pour 1.5 mL of SU-8 2015 photoresist at the center of the Si chip.

1.2.9. Close the spin coater lid. Start spin coating by pressing “START” button on the spin coater display. Refer to Supplemental file **Figure S1**.

1.2.10. Open the spin coater lid. Turn off vacuum by pressing “VAC OFF” button on the spin coater display. Refer to Supplemental files **Figure S1**. Take out the Si chip with spin coated layer of SU-8 2015 photoresist using tweezers.

1.2.11. Carefully place PDMS mold on the photoresist coated Si chip with pattern facing down. Flatten PDMS mold using finger press. Put UV transparent glass plate on the backside of PDMS yielding 15 g/cm^2 weight applied to PDMS mold.

1.2.12. Perform constant UV exposure using a 6 W UV bulb (see **Table of Materials**) placed at a distance of 10 cm from Si wafer surface during 2 h.

1.2.13. Peel off PDMS mold from Si chip using tweezers. Perform peeling off slowly in the direction parallel to the direction of cured SU-8 2015 pattern.

1.3. Gold catalyst thin-film deposition by magnetron sputtering

[Place Figure 5 here]

1.3.1. Attach Si chips with patterned SU-8 2015 photoresist layer onto 4” Si wafer using double-sided polyimide tape.

1.3.2. Open the chamber of the magnetron sputter (see **Table of Materials**). Place 4” Si wafer with attached Si chips onto rotational plate. Close the plate solid shutter by pressing “Solid” button in the control software. Refer to Supplemental file **Figure S2b**.

NOTE: “Solid” button will turn green when the shutter is closed.

1.3.3. Place Cr and Au targets (see **Table of Materials**) onto magnetron guns connected to the DC power supply. Place Ag target (see **Table of Materials**) onto magnetron gun connected to RF power supply. Set the distance between targets and rotational plate to 8.5”.

1.3.4. Close the chamber of the magnetron sputter and start evacuating the chamber by pressing “Pump down” and “Turbo enable” buttons in the control software. Leave it overnight. Refer to Supplemental file **Figure S2a**.

1.3.5. Turn on DC and RF power supplies. Open the Cr gun shutter by pressing “Gun 1 open” button in the control software. Set the DC power supply to 100 W in the control software. Refer to Supplemental file **Figure S2b**.

1.3.6. Set “Thickness Controlled Process” thickness to 200 Å. Enable the rotation of the rotational plate by pressing “Cont” and “Rotation” buttons in the control software. Refer to Supplemental files **Figure S2b**.

1.3.7. Set deposition pressure to 3 mTorr. Refer to Supplemental files **Figure S2b**.

1.3.8. Set Ar flow rate to 50 sccm in the control software. Enable DC power supply by pressing “DC supply” in the control software. Change Ar flow rate to 5 sccm. Refer to Supplemental file **Figure S2b**.

1.3.9. Start the crystal thickness monitor and tare the thickness by pressing “START” and “ZERO THICKNESS” buttons respectively in the control software. Refer to Supplemental files **Figure S2b**.

1.3.10. Start thickness controlled process by pressing “Thickness Controlled Process” button. Open the plate solid shutter by pressing “Solid” button. Tare the thickness monitor one more time by pressing “ZERO THICKNESS” button. Refer to Supplemental files **Figure S2b**.

1.3.11. After sputtering ends close plate solid shutter by pressing “Solid” button. Stop thickness monitor by pressing “STOP” button. Refer to Supplemental files **Figure S2b**.

1.3.12. Open the Au gun shutter by pressing “Gun 2 open” button. Set the DC power supply to 35 W. Refer to Supplemental files **Figure S2b**.

1.3.13. Set “Thickness Controlled Process” process thickness to 800 Å. Enable the rotation of the rotational plate by pressing “Cont” and “Rotation” buttons. Refer to Supplemental files **Figure S2b**.

1.3.14. Repeat steps 1.3.7 – 1.3.11.

1.3.15. Vent the magnetron sputter chamber by pressing “Press to vent” button in the control software. Refer to Supplemental files **Figure S2c**. The resulting structure is solid Au Mac-Imprint stamp.

NOTE: Perform steps 1.4 and 1.5 only if stamps with porous catalytic films are required.

1.4. Silver/Gold catalyst thin-film deposition by magnetron sputtering

1.4.1. Repeat steps 1.3.1 – 1.3.14. In step 1.3.13 set thickness controlled process to 500 Å instead of 800 Å.

1.4.2. Open the Au and Ag guns shutter by pressing "Gun 3 open" button. Set DC and RF power supplies to 35 W and 150 W respectively. Refer to Supplemental files **Figure S2b.**

NOTE: Step 1.4.2 will provide Ag/Au alloy with composition 60/40 (by vol.)

1.4.3. Set "Timed process" process time to 16.5 min in the control software. Enable the rotation of the rotational plate by pressing "Cont" and "Rotation" buttons. Refer to Supplemental files **Figure S2b**.

NOTE: Steps 1.4.3 to 1.4.8 of the protocol will produce 250 nm thick Ag/Au alloy layer.

1.4.4. Set Ar flow rate to 50 sccm. Enable DC and RF power supplies by pressing "DC supply" and "RF supply" respectively. Change Ar flow rate to 5 sccm. Refer to Supplemental files **Figure S2b**.

1.4.5. Start crystal thickness monitor and tare the thickness by pressing "START" and "ZERO THICKNESS" buttons respectively. Refer to Supplemental files **Figure S2b**.

1.4.6. Start time controlled process by pressing "Timed Process" button. Open the plate solid shutter by pressing "Solid" button. Tare the thickness monitor one more time by pressing "ZERO THICKNESS" button. Refer to Supplemental files **Figure S2b**.

1.4.7. After sputtering ends close plate solid shutter by pressing "Solid" button. Stop thickness monitor by pressing "STOP" button. Refer to Supplemental files **Figure S2b**.

1.4.8. Repeat step 1.3.15.

NOTE: Resulting structure is Ag/Au alloy sputtered Mac-Imprint stamp.

1.5. Silver/Gold catalyst thin-film dealloying

1.5.1. Mix DI water and nitric acid in the glass beaker in 1:1 ratio (by volume). Let it cool down to 30 °C.

1.5.2. Place the beaker with the mixture onto stirring hotplate and submerge perforated polytetrafluoroethylene (PTFE) sample holder into mixture. Heat the mixture up to 65 °C with constant stirring of 100 rpm. Constantly measure the temperature of the mixture with calibrated thermocouple.

1.5.3. Place Si chips with patterned SU-8 2015 layer sputtered with Ag/Au alloy into the mixture and dealloy for 2-20 min[21].

1.5.4. Quench samples in room temperature DI water for 1 min after dealloying.

1.5.5. Take Si chips out of DI water and thoroughly rinse with DI water.

2. Silicon substrate patterning and cleaning

[Place Figure 6 here]

2.1. Substrate preparation for solid Si imprinting with porous catalyst.

2.1.1. Oxidize 4” Si wafer at 1150 °C for 24 h in a O_2 flow of 4 sccm.

2.1.2. Take SPR 220 7.0 photoresist outside the fridge and let it stay at room temperature for 10-15 min prior spin coating.

2.1.3. Open the spin coater lid. Place 4” Si wafer inside the spin coater onto vacuum chuck.

2.1.4. Connect the output of the spin coater to the vacuum pump through PVC tube. Start vacuum pump. Set the pressure level to 30 kPa using vacuum pump valve.

2.1.5. Select spin coating procedure with the following parameters: spread at 400 rpm for 30 sec with acceleration 200 rpm/s, spin at 2000 rpm for 80 s with acceleration 500 rpm/s.

NOTE: Step 2.1.5 will produce a 9 µm thick SPR 220 7.0 layer.

2.1.6. Apply vacuum to the vacuum chuck by pressing “VAC ON” button on the spin coater display.

2.1.7. Pour 5 mL of SPR 220 7.0 photoresist at the center of the 4” Si wafer.

2.1.8. Close the spin coater lid. Start spin coating by pressing “START” button on the spin coater display.

2.1.9. Open the spin coater lid. Turn off vacuum by pressing “VAC OFF” button on SPIN 150i spin coater display. Take out the 4” Si wafer with spin coated layer of SPR 220 7.0 photoresist using tweezers.

2.1.10. Place the 4” Si wafer with spin coated layer of SPR 220 7.0 photoresist onto hotplate preheated to 110 °C and perform prebake for 2 min. Let cool for 1 min.

2.1.11. Expose photoresist layer through the mask with square mesas pattern that has following parameters: width 500 µm and spacing 900 µm. Flood exposure for 10 s to achieve 150 mJ/cm^2 dosage.

2.1.12. Develop exposed photoresist layer in 4:1 (by vol.) ratio of Developer : DI water for 3 min. Rinse sample with DI water and check features in microscope.

2.1.13. Place the 4” Si wafer with developed SPR 220 7.0 photoresist onto hotplate preheated to 120 °C and perform hard bake for 5 min. Let cool for 1 min.

2.1.14. Etch oxide layer in reactive ion etching equipment during 20 min using following parameters: pressure of 100 mT, O_2 flow of 3 sccm, CF_4 flow of 24 sccm, power of 250 W.

2.1.15. Remove SPR 220 7.0 layer using acetone, rinse with isopropyl alcohol (IPA) and DI water.

2.1.16. Perform etching in a 30 % KOH bath (by weight) at 80 °C for 100 min with constant stirring of 175 rpm to create mesas on the Si wafer.

2.1.17. Remove oxide layer in buffered oxide etch solution.

2.1.18. Thoroughly flush with DI water.

2.2. Substrate preparation for porous Si imprinting with solid catalyst.

[Place Figure 7 here]

2.2.1. Repeat step 2.1.

2.2.2. Coat the back of the patterned 4” Si wafer with nickel and anneal at 320 ºC in a rapid thermal annealing chamber in N_2 environment for 3 min.

2.2.3. Cleave 2.5 x 2.5 cm Si chips out of patterned 4” Si wafer using scriber.

2.2.4. Place Si chip inside bottom part of electrochemical cell (EC). Place o-ring on the top of Si chip. Place the top part of EC and tight the screws.

2.2.5. Set galvanostatic regime in potentiostat (see **Table of Materials**) control software. Refer to Supplemental files **Figure S3**. Connect working electrode to the Si chip and counter electrode to the platinum electrode.

2.2.6. Carefully fill the EC with HF and insert a cylindrical platinum electrode from the top to the distance of 5 mm above the the Si chip surface.

2.2.7. Apply current density of 135 mA/cm^2 for 120 s by pressing green start button in the potentiostat software. Refer to Supplemental files **Figure S3**.

2.2.8. Carefully suck the HF out of EC with the plastic pipette.

2.2.9. Thoroughly flush with DI water.

3. Mac-Imprinting set-up

3.1. Stamp to PTFE rod fixation

3.1.1. Place reference Si chip inside bottom part of EC. Place Mac-Imprint stamp on top of reference Si chip with pattern facing down.

3.1.2. Attach PTFE rod to the load cell (see **Table of Materials**) through double side threaded screw. Connect the structure to the software controlled motorized linear stage (see **Table of Materials**) through metal bracket.

3.1.3. Add a small droplet of SU-8 2015 photoresist on the back of Mac-Imprint stamp.

3.1.4. Bring PTFE rod in contact with SU-8 droplet by setting “Move Relative” command, 173500 steps from home position and pressing “Write” button in stage control software. Refer to Supplemental files **Figure S4a.**

3.1.5. Cure the SU-8 2015 photoresist droplet with 6 W UV bulb for 3 h. Refer to Supplemental files **Figure S5**.

3.1.6. Bring PTFE rod with attached Mac-Imprint stamp into home position by setting “Home” command and pressing “Write” button in the stage control software. Refer to Supplemental files **Figure S4a**.

3.1.7. Assemble EC.

3.2. Mac-Imprinting operation

[Place Figure 8 here]

3.2.1. Clean patterned Si chip according to steps 1.1.1 – 1.1.4.

3.2.2. Place patterned Si chip at the center of an EC. Position EC under PTFE rod with Mac-Imprint stamp.

3.2.3. Mix ES of HF and H_2O_2 in the 17:1 ratio (by vol.) inside PTFE beaker. Let the ES stay for 5 min before etching.

NOTE: The suggested ratio lead to solution parameter ρ = 98%[16]. The ratio can be tuned in order to suppress or promote etching rate.

3.2.4. Carefully pour the ES into the EC using plastic pipette.

3.2.5. Bring PTFE rod with attached Mac-Imprint stamp in contact with patterned Si chip by setting "Move Relative" command, 173500 steps from home position and pressing "Write" button. Refer to Supplemental files **Figure S4a**.

3.2.6. Next, set 600-2000 steps and press "Write" button to obtain the loads in the range 4-10 lbf. Measure load values through software controlled load cell. Refer to Supplemental files **Figure S4b**.

3.2.7. Hold in contact for during Mac-Imprint. Mac-Imprint time varies from 1 to 30 min.

3.2.8. Move PTFE rod with attached Mac-Imprint stamp into home position by pressing "Home" button. Refer to Supplemental files **Figure S4a**. Carefully suck the ES out of EC with the plastic pipette.

3.2.9. Rinse imprinted Si chip using IPA and DI water.

3.2.10. Dry imprinted Si chip with clean dry air.

REPRESENTATIVE RESULTS:

Scanning electron microscope (SEM) images, optical microscope scans (**Figure 9**) and atomic force microscopy (AFM) scans (**Figure 10**) are obtained in order to study morphological properties of the Mac-Imprint stamps and imprinted Si surfaces. The cross-sectional profile of the imprinted solid Si is compared to that of the used porous Au stamp (**Figure 10**). Pattern transfer fidelity and porous Si generation during Mac-Imprint are two major criterias to analyze the experiment success. The Mac-Imprint is considered successful if Mac-Imprint stamp's pattern is accurately transferred onto Si and no porous Si is generated during Mac-Imprint. The results of the sub-optimal experiment (i.e., lack of pattern transfer fidelity along with porous Si generation during Mac-Imprint) are presented in **Figure 9a** (left).

FIGURE AND TABLE LEGENDS:

Figure 1: Schematics of Mac-Imprint configurations. This figure highlights the role of porous materials in enabling diffusion of reacting species through the substrate (i.e. case II: porous Si) or in the stamp (i.e. case III: catalyst thin-film made of porous gold)

Figure 2: RCA-1 cleaning process. (**a**) solution heating and (**b**) Si cleaning

Figure 3: PDMS mold fabrication process. (**a**) schematic representation of the process and (**b**)

photographs of the process steps

Figure 4: Photoresist UV nanoimprinting process. (**a**) photographs of photoresist spin-coating and (**b**) schematics and photographs of UV nanoimprinting

Figure 5: Catalytic stamp preparation process. (**a**) schematics of the thin film deposition; (**b**) photographs of magnetron sputtering system and (**c**) photograph of dealloying process with representative porous gold SEM images

Figure 6: Si wafer patterning mask layout (a) and single patterned chip (b)

Figure 7: Photographs of substrate porosification procedure (Si anodization). (**a**) PC controlled potentiostat connected to two-electrode electrochemical cell; (**b**) electrochemical cell with platinum electrode and (**c**) Si chip with a porous Si layer

Figure 8: Photographs of Mac-Imprint setup (a), stamp before (b) and after (c) contact with Si chip

Figure 9: Representative results: (**a**) Mac-Imprint of solid Si and porous Si with solid Au film (left and middle respectively) and solid Si with porous Au film (right); (**b**) top-down SEM images of porous Au films with different pore volume fraction (top) and corresponding imprinted Si morphology (bottom); and (**c**) SEM-images of various patterns produced by Mac-Imprint. This figure is reprinted with permission from[9,20]

Figure 10: Representative results of solid Si Mac-Imprint with porous Au stamp: (**a**) AFM scans of porous Au stamp (left) and imprinted solid Si (right) and (**b**) overlaid cross-sectional profiles of porous Au stamp (blue) and imprinted solid Si (red). This figure is reprinted with permission from[20].

Supplemental Figure 1: Photograph of spin coater control display

Supplemental Figure 2: Magnetron sputter control software screenshots. (**a**) evacuation of magnetron sputter chamber; (**b**) sputtering control parameters and (**c**) ventilation of magnetron sputter chamber

Supplemental Figure 3: Potentiostat control software screenshot

Supplemental Figure 4: Linear motorized stage and load cell control software screenshots. (**a**) before Mac-Imprint and (**b**) during Mac-Imprint

Supplemental Figure 5: Photograph of Mac-Imprint stamp to PTFE rod attachment process

DISCUSSION:

Mac-Imprint stamps and prepatterned Si chips (p-type, (100) orientation, 1-10 Ohm·cm) were prepared according to sections 1 and 2 of the protocol respectively. Mac-Imprint of prepatterned Si chip with stamps containing 3D hierarchical patterns was performed according to the section 3 of the protocol (**Figure 9**). According to **Figure 9a** different configurations of Mac-Imprint were applied - solid Si with solid Au (left); porous Si with solid Au (middle)[9] and solid Si with porous Au (right)[20]. The diffusion of the reactants was blocked in the first case leading to non-localized etching and partial porosification of the imprinted Si which correlates with the same issue in the conventional MACE process[22,23]. However, when the diffusion was enabled through porous networks (either embedded in Si or Au) the high pattern transfer fidelity was observed, which leads to the conclusion that Mac-Imprint is mass-transport dependent process. Moreover, imprinted Si surface was roughened after imprinting with porous Au (**Figure 9a**, right).

The hypothesis was proposed that surface roughening originates from the porosity of the used porous Au. In order to test the hypothesis series of porous Au layers with various controlled pore volume fractions (PVF) was created according to the sections 1.4 and 1.5 of the protocol and subsequently implemented for Mac-Imprint (**Figure 9b**)[20]. The direct relation between stamp's PVF and imprinted Si surface roughness was observed supporting the hypothesis. Additionally, after Mac-Imprint with low PVF stamps Si was porosified which was explained by hindered ES diffusion through not developed porous Au structure resulting in delocalization of the etching front[20]. Thus, developed and interconnected porous structure is critical for high pattern transfer fidelity during Mac-Imprint. Moreover, imprinted Si porosification was also observed at medium PVF when porous Au layer already had interconnected porous network. This can be attributed to the high ratio between Au and Si surface areas and subsequent injection of the excessive holes into Si which also leads to the etching front delocalization and, as a result, porous Si formation[20]. This process can be controlled through careful consideration of HF and H_2O_2 ratios in the ES.

Implementation of the porous Au stamps along with ES composition variations allows to manufacture various 3D hierarchical patterns via Mac-Imprint that were previously published in the works of Azeredo et al. (2016)[9] and Sharstniou et al. (2019)[20] (**Figure 9c**).

Further investigations of porous Au/Si interface chemistry, in particular PVF dependent etch rate and localization, along with imprinting system improvement allows Mac-Imprint process to be considered for the industrial scale applications.

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DISCLOSURES:
We do not have anything to disclose.

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