Journal of Visualized Experiments

Metal-Assisted Electrochemical Nanoimprinting of Porous and Solid Silicon Wafers

--Manuscript Draft--

Article Type:	Invited Methods Article - JoVE Produced Video
Manuscript Number:	JoVE61040R2
Full Title:	Metal-Assisted Electrochemical Nanoimprinting of Porous and Solid Silicon Wafers
Section/Category:	JoVE Engineering
Keywords:	Electrochemical nanoimprinting; metal-assisted chemical etching; metal-assisted chemical imprinting; microfabrication; microengineering; silicon photonics
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Additional Information:	
Question	**Response**
Please indicate whether this article will be Standard Access or Open Access.	Standard Access (US$2,400)
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Cover Letter

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November 18, 2019

Dear Editors,

I am submitting our manuscript entitled “Metal-Assisted Electrochemical Nanoimprinting of Porous and Solid Silicon Wafers” for consideration in this journal. In the past 5 years, our research group has published several key papers that connects these two disjoint fields of research: Nanoimprint Lithography (NIL) and Metal-assisted chemical etching (MACE) and called it Metal-Assisted Electrochemical Nanoimprinting. On one hand, **research on NIL** has gradually expanded its library of patternable materials beyond polymeric materials [1, 2] which receives world-wide attention as a method for patterning that is highly reproducible. In 2002, Stephen Chou et al demonstrated nanoimprinting of silicon [3] using high-temperature nanoimprinting which was subsequently expanded into amorphous metals by Lister et al [4] and Golden Kumar et al [5] and crystalline metals by Gary Cheng et al [6]. However, thermal-based nanoimprinting of silicon produces crystallography defects during recrystallization and, as a result, nanoimprinting of defect-free electronic-grade silicon has never been shown until recently when our group elucidate both experimentally and theoretically the limitations of mass transport of this process [7].

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Research on metal-assisted chemical etching has drawn world-wide attention for its ability to fabricate high-aspect ratio nanostructures in semiconductors and has focused on fundamental understanding of the reaction kinetics [8], diffusion models [9], and mechanical models [10]. While these studies were performed in a thin-film configuration, our research group recently elucidated how the diffusion and reaction kinetics are modified in an imprinting configuration [7] by Mac-imprinting porous silicon and Mac-imprinting silicon with stamps coated with mesoporous catalyst [11].

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Our manuscript introduces the experimental details and variables relevant to reliably perform metal-assisted chemical nanoimprinting (Mac-Imprint) process for 3D nano- and micropatterning of porous and monocrystalline Si wafers. It thoroughly describes stamp manufacturing, substrate pretreatment and system configuration required for Mac-Imprint. In addition, the work points out the process limitation (i.e. mass-transport of the etching solution species) and reports the successful implementation of porous materials to overcome this hindrance. Finally, it proposes future research for the commercialization of the process.

The impact of this work.
We strongly believe this technique will be resourceful to research across multiple disciplines, particularly those in the application domain where the 3D silicon micro and nanostructures are needed such as nanophotonics, silicon photonics, optical-based biosensing, optoelectronics, photovoltaics and much more. This will have a cascade effect similar to the introduction of NIL back in 1995 by Prof. Chou. It is therefore needed to transfer this knowledge to a larger number of scientists around the globe to adopt its use. We have included a high level of details in our protocols that will permit anyone to reproduce this work in a research facility.

Please don’t hesitate to contact me if the committee needs further information from me.



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TITLE:

Metal-Assisted Electrochemical Nanoimprinting of Porous and Solid Silicon Wafers

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KEYWORDS:

nanoimprinting, electrochemical nanoimprinting, MACE, metal-assisted chemical etching, silicon photonics, microfabrication, microengineering

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 that is 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 a Si wafer in the presence of a 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: (1) Porous Si Mac-Imprint with a solid catalyst; and (2) Solid Si Mac-Imprint with a porous catalyst. This process is 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 requires the etching selectivity of a mask pattern during reactive ion etching and thus limits the aspect ratio, and induces shape distortions and surface roughness due to scalloping effects[7,8].

A new method called Mac-Imprint has been achieved 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 that requires contact between substrate and a noble metal-coated stamp possessing 3D features in the presence of an 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]: a cathodic reaction (i.e., the H_2O_2 reduction at the noble metal, during which positive charge carriers [holes] are generated and subsequently injected into Si[17]) and an anodic reaction (i.e., Si dissolution, during which the 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, the method can deliver a sub-20 nm etching resolution that is compatible with contemporary direct writing methods.

The key to attaining high-fidelity imprinting is the diffusion pathway to the etching front (i.e., contact interface between catalyst and substrate). The work of Azeredo et al.[9] first demonstrated that ES diffusion is enabled through a porous Si network. Torralba et al.[18], reported that in order to realize solid Si Mac-Imprint the ES diffusion is enabled through a porous catalyst. Bastide et al.[19] and Sharstniou et al.[20] further investigated the catalyst porosity influence on ES diffusion. Thus, the concept of Mac-Imprint has been tested in three configurations with distinct diffusion pathways.

In the first configuration, the catalyst and substrate are solid, providing no initial diffusion pathway. The lack of reactant diffusion leads to a secondary reaction during imprinting that forms a layer of porous Si on the substrate around the edge of the catalyst-Si interface. The reactants are subsequently depleted, and 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]. A schematic of all three configurations is shown in **Figure 1**.

[Place **Figure 1** here].

In this paper, the Mac-Imprint process is thoroughly discussed, including stamp preparation and substrate pretreatment along with Mac-Imprint itself. The substrate pretreatment section within the protocol includes Si wafer cleaning and Si wafer patterning with dry etching and substrate anodization (optional). Further, a stamp preparation section is subdivided into several

procedures: 1) PDMS replica molding of Si master mold; 2) UV nanoimprinting of a photoresist layer in order to transfer the PDMS pattern; and 3) catalytic layer deposition via magnetron sputtering followed by dealloying (optional). Finally, in the Mac-Imprint section the Mac-Imprint setup along with the Mac-Imprint results (i.e., Si surface 3D hierarchical patterning) is presented.

PROTOCOL:

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

1. Stamp preparation for Mac-imprint

1.1. PDMS mold fabrication

1.1.1. Prepare the RCA-1 solution by mixing deionized pure (DI) water and ammonium hydroxide in the glass beaker in a 5:1 ratio (volume). Place the beaker with the mixture onto a stirring hotplate (see **Table of Materials**) and heat the mixture up to 70 °C. Measure the temperature of the mixture with a calibrated thermocouple and add 1 part of the hydrogen peroxide to the preheated mixture to obtain the RCA-1 solution. Wait until the RCA-1 solution starts to bubble vigorously (**Figure 2**).

[Place **Figure 2** here]

1.1.2. Keep the RCA-1 solution at 70 °C.

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

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

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

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

silicone elastomer kit (PDMS) (see **Table of Materials**) in a 10:1 ratio (mass). Slowly stir the mixture with a 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 the Si master mold to completely cover it with the 2–3 mm layer of PDMS (**Figure 3A**).

1.1.11. Repeat step 1.1.6.

1.1.12. Degas the 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 the PDMS-covered Si master mold and place it onto a hotplate (see **Table of Materials**) preheated to 80 °C (**Figure 3B**).

1.1.14. Cure the PDMS with Si master mold on the hotplate at 80 °C for 120 min (**Figure 3B**).

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

1.1.16. Carefully remove all the PDMS that leaked underneath the Si master mold using a scalpel. Peel off the cured PDMS from the Si master mold using tweezers. Peel it off slowly, parallel to the direction of the Si master stamp pattern.

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

[Place **Figure 3** here]

1.2. Photoresist UV nanoimprinting

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

1.2.2. Repeat steps 1.1.–1.1.4 to clean the Si chip.

1.2.3. Bring SU-8 2015 photoresist out of the refrigerator and let it stay at room temperature (RT) for 10–15 min prior to spin coating.

1.2.4. Open the spin coater lid (see **Table of Materials**). Place the Si chip inside the spin coater onto the vacuum chuck (**Figure 4A**).

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

1.2.6. Select a spin coating procedure with the following parameters: spread at 500 rpm for 10 s with acceleration 100 rpm/s, spin at 2,000 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**" on the spin coater display. Refer to **Supplemental File** (**Figure S1**).

1.2.8. Pour 1.5 mL of SU-8 2015 photoresist onto the center of the Si chip (**Figure 4B**).

1.2.9. Close the spin coater lid. Start spin coating by pressing "**START**". Refer to **Supplemental File** (**Figure S1**).

1.2.10. Open the spin coater lid. Turn off the vacuum by pressing "**VAC OFF**". Refer to **Supplemental File** (**Figure S1**). Take out the Si chip with the spin-coated layer of SU-8 2015 photoresist using tweezers (**Figure 4**).

1.2.11. Carefully place the PDMS mold on the photoresist-coated Si chip with the pattern facing down. Manually flatten the PDMS mold. Put a UV transparent glass plate on the backside of the PDMS resulting in 15 g/cm^2 weight applied to the PDMS mold (**Figure 4B**).

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

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

[Place **Figure 4** here]

1.3. Gold catalyst thin film deposition by magnetron sputtering

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

1.3.2. Open the chamber of the magnetron sputter (see **Table of Materials**). Place the 4 inch Si wafer with attached Si chips onto a rotational plate. Close the plate solid shutter by pressing the "**Solid**" button in the control software. Refer to **Supplemental file** (**Figure S2B**).

NOTE: The "**Solid**" button will turn green when the shutter is closed.

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

1.3.4. Close the chamber of the magnetron sputter and start evacuating the chamber by pressing "**Pump Down**" and "**Turbo Enable**" in the control software. Leave it overnight. Refer to **Supplemental File** (**Figure S2A**).

1.3.5. Turn on the DC and RF power supplies. Open the Cr gun shutter by pressing "**Gun 1 Open**" 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 the "**Thickness Controlled Process**" to 200 Å. Enable the rotation of the rotational plate by pressing the "**Cont**" and "**Rotation**" buttons in the control software. Refer to **Supplemental Files** (**Figure S2B**).

1.3.7. Set the deposition pressure to 3 mTorr. Refer to **Supplemental Files** (**Figure S2B**).

1.3.8. Set the Ar flow rate to 50 sccm in the control software. Enable the DC power supply by pressing "**DC supply**" in the control software. Change the 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 the "**START**" and "**ZERO THICKNESS**" buttons respectively in the control software. Refer to **Supplemental Files** (**Figure S2B**).

1.3.10. Start the thickness-controlled process by pressing "**Thickness Controlled Process**". Open the plate solid shutter by pressing "**Solid**". Tare the thickness monitor one more time by pressing "**ZERO THICKNESS**". Refer to **Supplemental Files** (**Figure S2B**).

1.3.11. After the sputtering ends, close the plate solid shutter by pressing "**Solid**". Stop the thickness monitor by pressing "**STOP**". Refer to **Supplemental Files** (**Figure S2B**).

1.3.12. Open the Au gun shutter by pressing "**Gun 2 Open**". Set the DC power supply to 35 W. Refer to **Supplemental Files** (**Figure S2B**).

1.3.13. Set the "**Thickness Controlled Process**" to 800 Å. Enable the rotation of the rotational plate by pressing the "**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**" in the control software. Refer to **Supplemental Files** (**Figure S2C**). The resulting structure is a solid Au Mac-Imprint stamp

(**Figure 5**).

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

[Place **Figure 5** here]

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 the 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**". Set the 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 an Ag/Au alloy with composition 60/40 (volume)

1.4.3. Set the "**Timed Process**" to 16.5 min in the control software. Enable the rotation of the rotational plate by pressing the "**Cont**" and "**Rotation**" buttons. Refer to **Supplemental Files** (**Figure S2B**).

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

1.4.4. Set the air flow rate to 50 sccm. Enable the DC and RF power supplies by pressing "**DC Supply**" and "**RF Supply**" respectively. Change the air flow rate to 5 sccm. Refer to **Supplemental Files** (**Figure S2B**).

1.4.5. Start the crystal thickness monitor and tare the thickness by pressing "**START**" and "**ZERO THICKNESS**" respectively. Refer to **Supplemental Files** (**Figure S2B**).

1.4.6. Start the time-controlled process by pressing "**Timed Process**". Open the plate solid shutter by pressing "**Solid**". Tare the thickness monitor one more time by pressing "**ZERO THICKNESS**". Refer to **Supplemental Files** (**Figure S2B**).

1.4.7. After the sputtering ends, close the plate solid shutter by pressing "**Solid**". Stop the thickness monitor by pressing "**STOP**". Refer to **Supplemental Files** (**Figure S2B**).

1.4.8. Repeat step 1.3.15.

NOTE: The resulting structure is an 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 (volume). Let it cool down to 30 °C.

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

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

1.5.4. After dealloying, quench samples in RT DI water for 1 min.

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

2. Silicon substrate patterning and cleaning

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

2.1.1. Oxidize the 4 inch Si wafer at 1,150 °C for 24 h in an O_2 flow of 4 sccm.

2.1.2. Take SPR 220 7.0 photoresist out of the refrigerator and let it stay at RT for 10–15 min prior to spin coating.

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

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

2.1.5. Select a spin coating procedure with the following parameters: spread at 400 rpm for 30 s with acceleration 200 rpm/s, spin at 2,000 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**" on the spin coater display.

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

2.1.8. Close the spin coater lid. Start spin coating by pressing "**START**".

2.1.9. Open the spin coater lid. Turn off the vacuum by pressing "**VAC OFF**". Take out the 4 in Si wafer with the spin-coated layer of SPR 220 7.0 photoresist using tweezers.

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

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

2.1.12. Develop the exposed photoresist layer in 4:1 (volume) of developer: DI water for 3 min. Rinse the sample with DI water and check the features in microscope.

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

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

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

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

2.1.17. Remove the oxide layer with buffered oxide etch solution.

2.1.18. Thoroughly flush with DI water.

NOTE: Si wafer patterning mask layout and single patterned chip is shown in **Figure 6**.

[Place **Figure 6** here]

2.2. Substrate preparation for porous Si imprinting with solid catalyst

2.2.1. Repeat step 2.1.

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

2.2.3. Cleave 2.5 x 2.5 cm Si chips out of the patterned 4 in Si wafer using a scriber.

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

2.2.5. Set the galvanostatic regime in the potentiostat (see **Table of Materials**) control software. Refer to **Supplemental Files** (**Figure S3**). Connect a working electrode to the Si chip and the counter electrode to the platinum electrode (**Figure 7**).

2.2.6. Carefully fill the EC with HF and insert a cylindrical platinum electrode from the top to 5

mm above the Si chip surface (**Figure 7B**).

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

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

2.2.9. Thoroughly flush with DI water.

NOTE: The Si anodization process and Si chip with a porous Si layer are shown in **Figure 7**.

[Place **Figure 7** here]

3. Mac-Imprinting setup

3.1. Stamp to PTFE rod fixation

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

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

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

3.1.4. Bring the PTFE rod in contact with a SU-8 droplet by setting the "**Move Relative**" command 173,500 steps from the home position and pressing the "**Write**" button in the stage control software. Refer to **Supplemental Files** (**Figure S4A**).

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

3.1.6. Bring the PTFE rod with the attached Mac-Imprint stamp into the home position by setting the "**Home**" command and pressing "**Write**" in the stage control software. Refer to **Supplemental Files** (**Figure S4A**).

3.1.7. Assemble the EC.

3.2. Mac-Imprinting operation

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

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

the Mac-Imprint stamp (**Figure 8**).

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

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

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

3.2.5. Bring the PTFE rod with the attached Mac-Imprint stamp in contact with the patterned Si chip by setting the "**Move Relative**" command 173,500 steps from the home position and pressing the "**Write**" button. Refer to **Supplemental Files** (**Figure S4a**).

3.2.6. Next, set 600–2,000 steps and press "**Write**" to obtain loads in the range of 4–10 lbf. Measure load values through a software-controlled load cell. Refer to **Supplemental Files** (**Figure S4B**).

3.2.7. Hold in contact during Mac-Imprint (**Figure 8C**). The Mac-Imprint time varies from 1–30 min.

3.2.8. Move the PTFE rod with the attached Mac-Imprint stamp into the home position by pressing "**Home**". Refer to **Supplemental Files** (**Figure S4A**). Carefully suck the ES out of the EC with a plastic pipette.

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

3.2.10. Dry the imprinted Si chip with clean, dry air.

[Place **Figure 8** here]

REPRESENTATIVE RESULTS:

Scanning electron microscope (SEM) images, optical microscope scans (

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

Figure *9*A (left).

[Place **Figure 9** here]

[Place **Figure 10** here]

FIGURE AND TABLE LEGENDS:

Figure 1: Schematics of Mac-Imprint configurations. This figure highlights the role of porous materials in enabling the 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. (**B**) Photographs of the process steps.

Figure 4: Photoresist UV nanoimprinting process. (**A**) Photographs of photoresist spin coating. (**B**) Schematics and photographs of UV nanoimprinting.

Figure 5: Catalytic stamp preparation process. (**A**) Schematics of the thin film deposition. (**B**) Photographs of the magnetron sputtering system. (**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. (**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). (**C**) SEM images of various patterns produced by Mac-Imprint. This figure is reprinted with permission[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[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. (**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. The Mac-Imprint of prepatterned Si chip with stamps containing 3D hierarchical patterns was performed according to section 3 of the protocol (**Figure 9**). As shown in **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 nonlocalized 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), high pattern transfer fidelity was observed, which leads to the conclusion that Mac-Imprint is a mass transport dependent process. Also, the imprinted Si surface was roughened after imprinting with porous Au (**Figure 9A**, right).

It was proposed that surface roughening originates from the porosity of the porous Au used. In order to test the hypothesis, a series of porous Au layers with various controlled pore volume fractions (PVF) was created according to sections 1.4 and 1.5 of the protocol and subsequently implemented for Mac-Imprint (**Figure 9B**)[20]. A direct relation between the 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 undeveloped porous Au structure, resulting in delocalization of the etching front[20]. Thus, a developed and interconnected porous structure is critical for high pattern transfer fidelity during Mac-Imprint. Moreover, imprinted Si porosification was observed at medium PVF when a porous Au layer already had an 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 control of the HF and H_2O_2 ratios in the ES.

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

Further investigations of porous Au/Si interface chemistry, in particular PVF-dependent etch rate and localization, along with imprinting system improvement, will make the Mac-Imprint process

suitable for industrial scale applications in the future.

ACKNOWLEDGMENTS:

We acknowledge Dr. Keng Hsu (University of Louisville) for insights regarding this work; University of Illinois's Frederick Seitz Laboratory and, in memoriam, staff member Scott Maclaren; Arizona State University's LeRoy Eyring Center for Solid State Science; and the Science Foundation Arizona under the Bis grove Scholars Award.

DISCLOSURES:

We do not have anything to disclose.

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Figure 1

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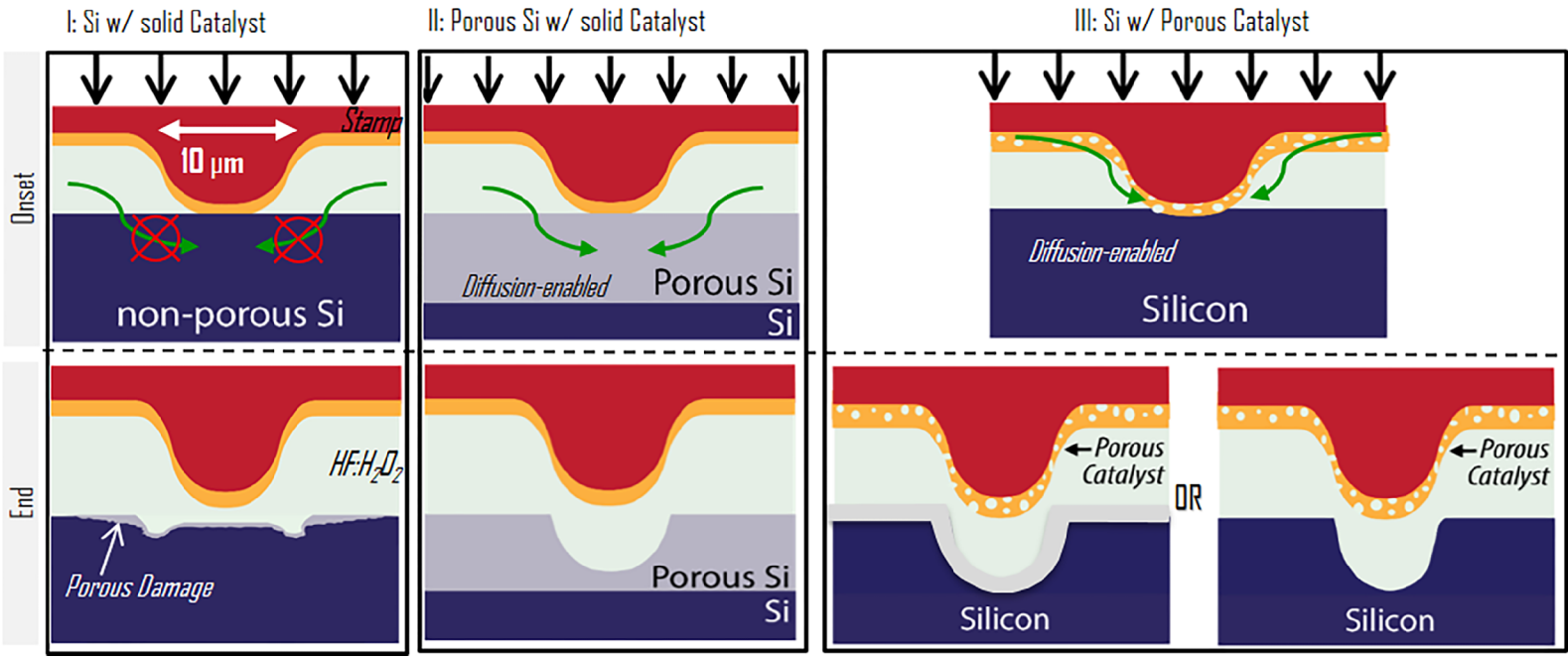

Figure 2

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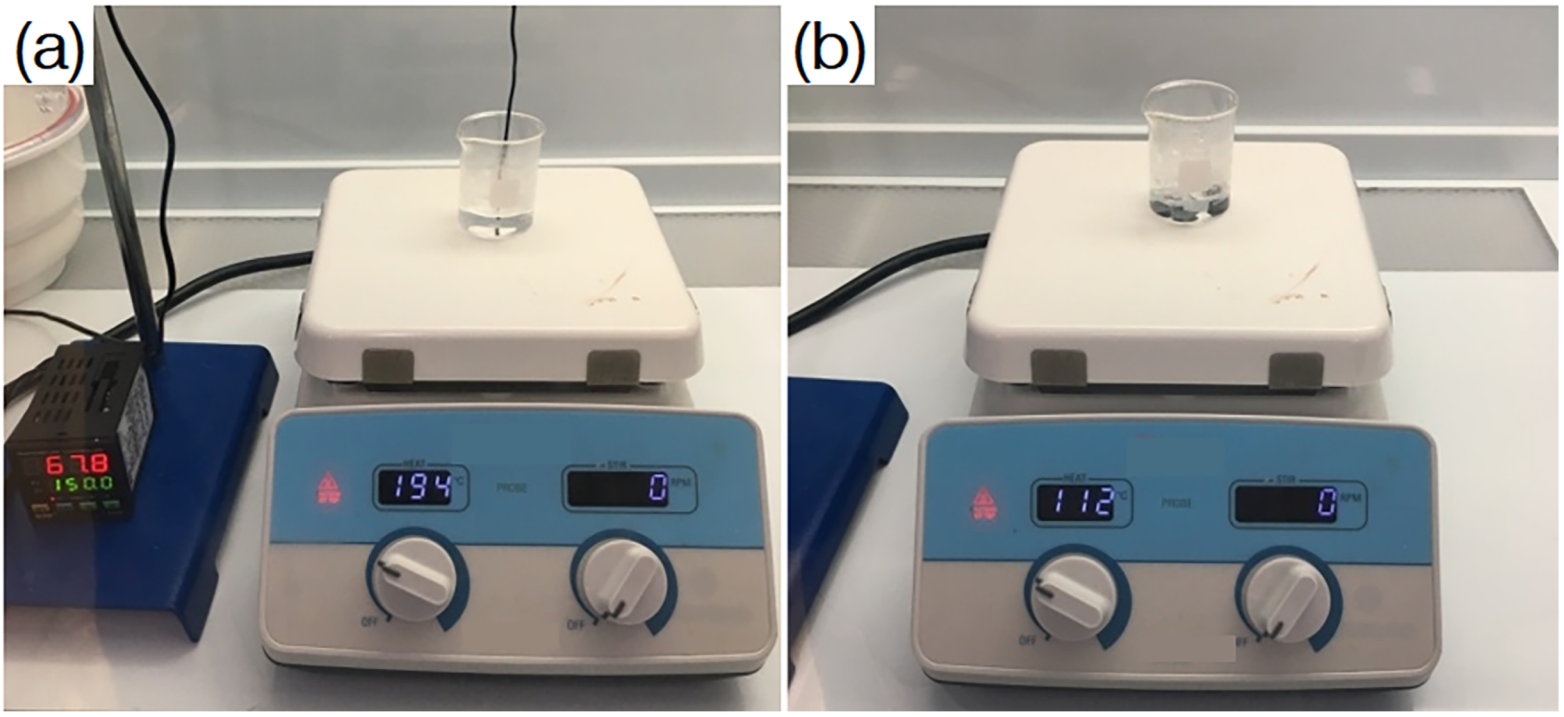

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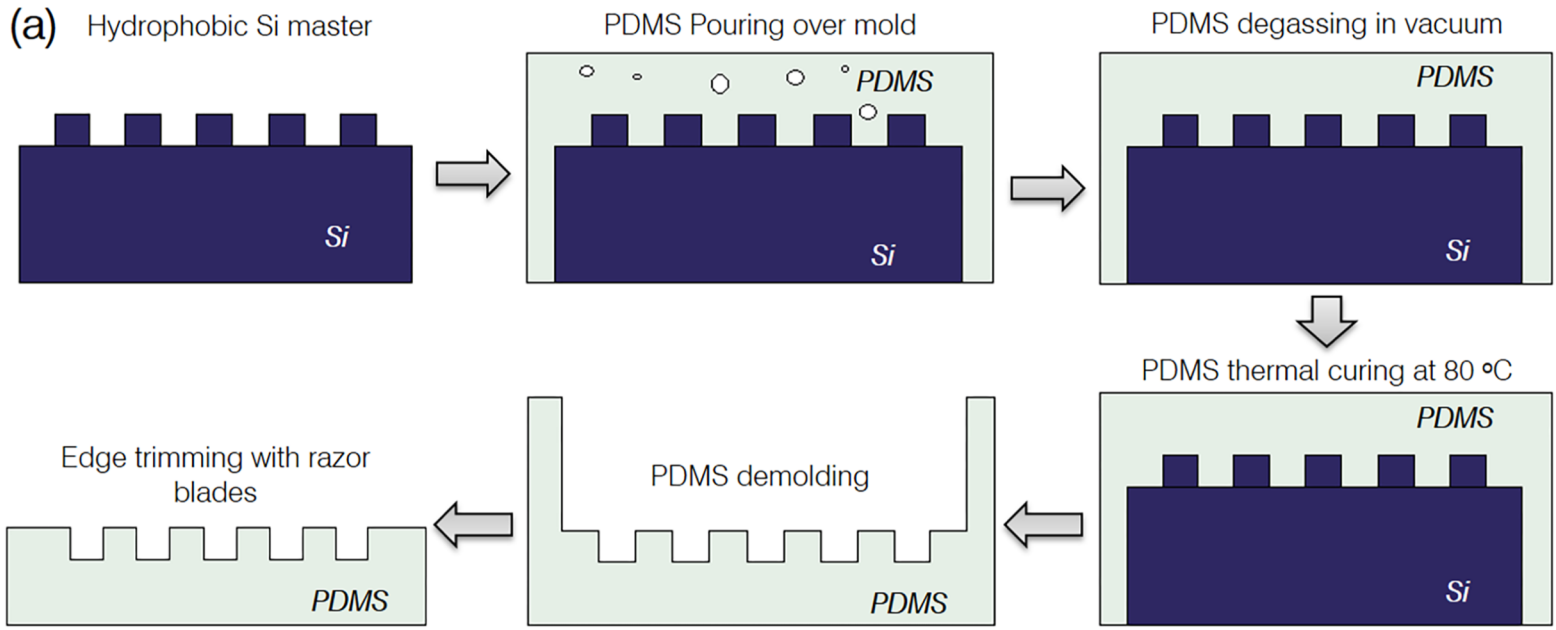

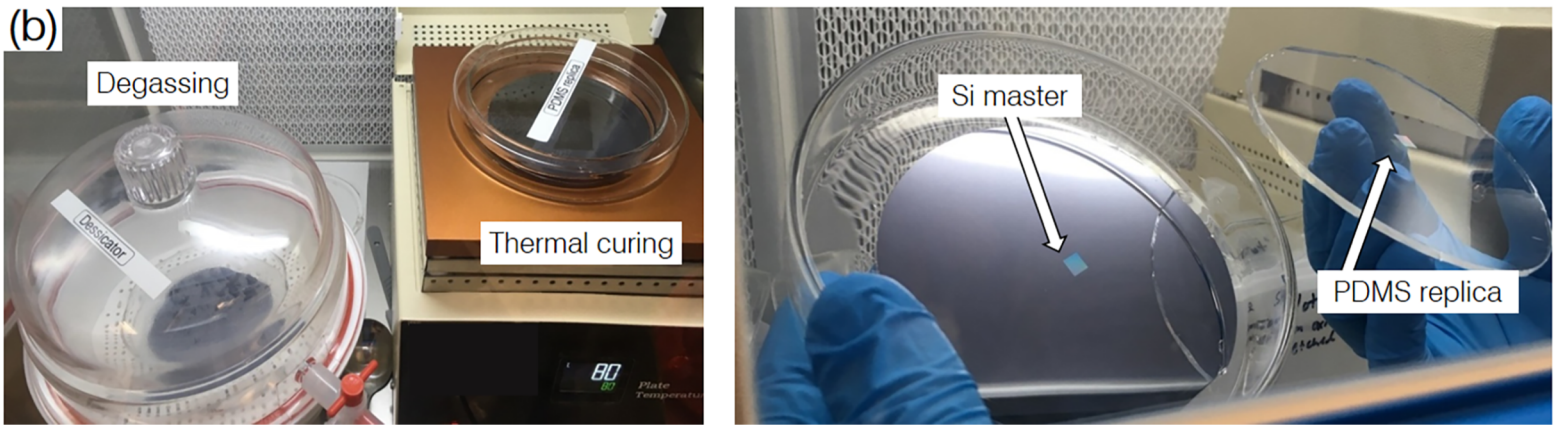

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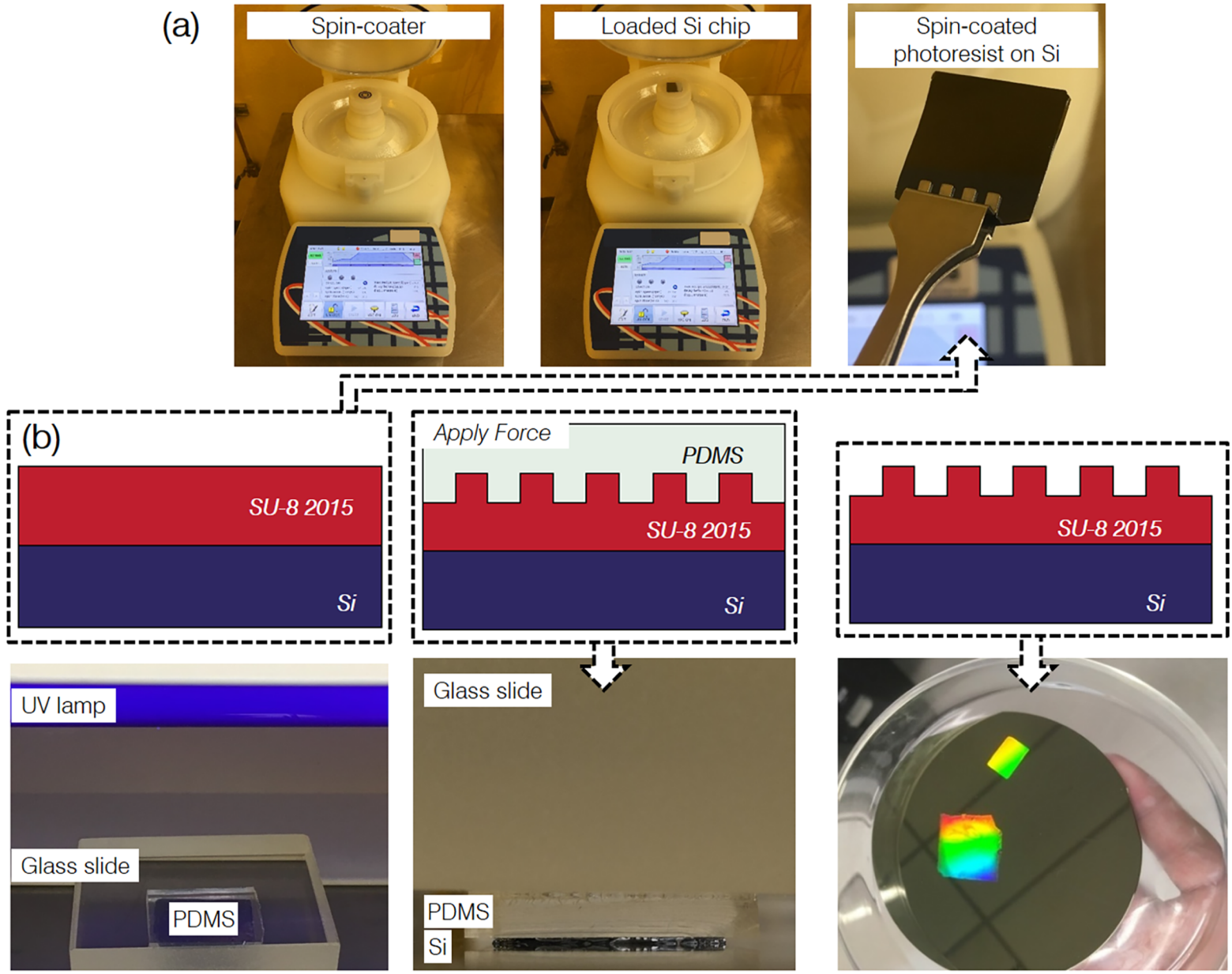

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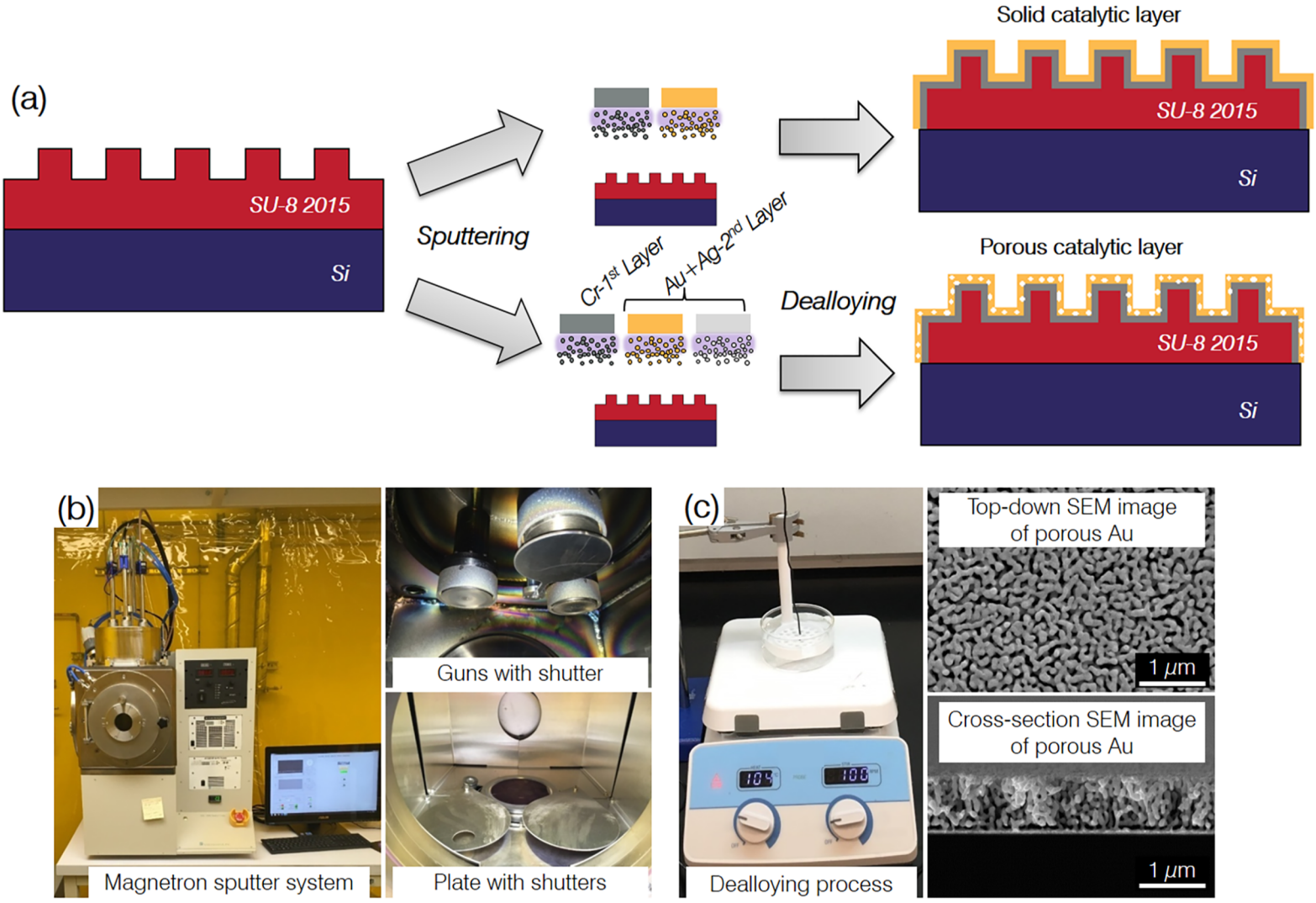

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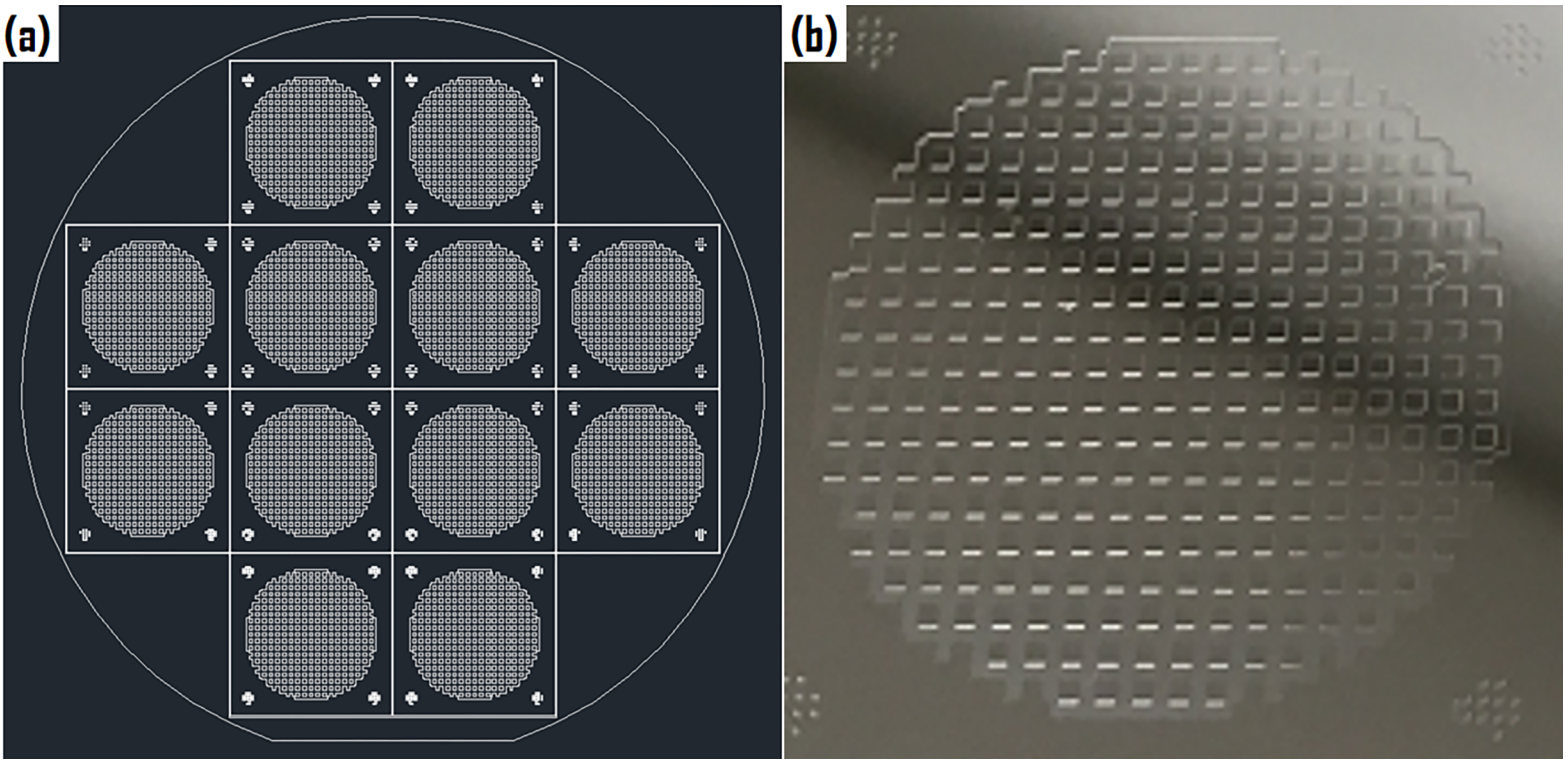

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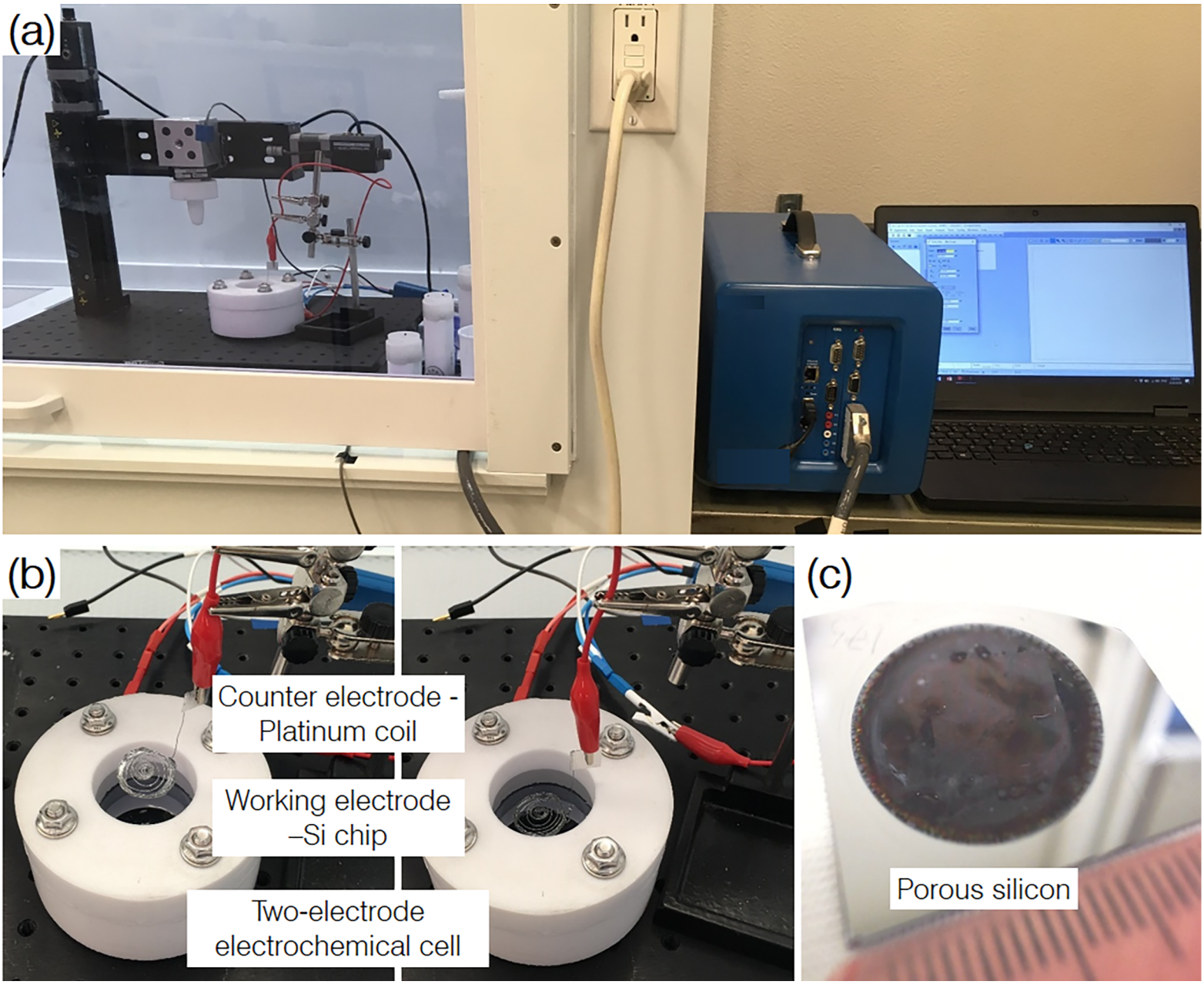

Figure 8

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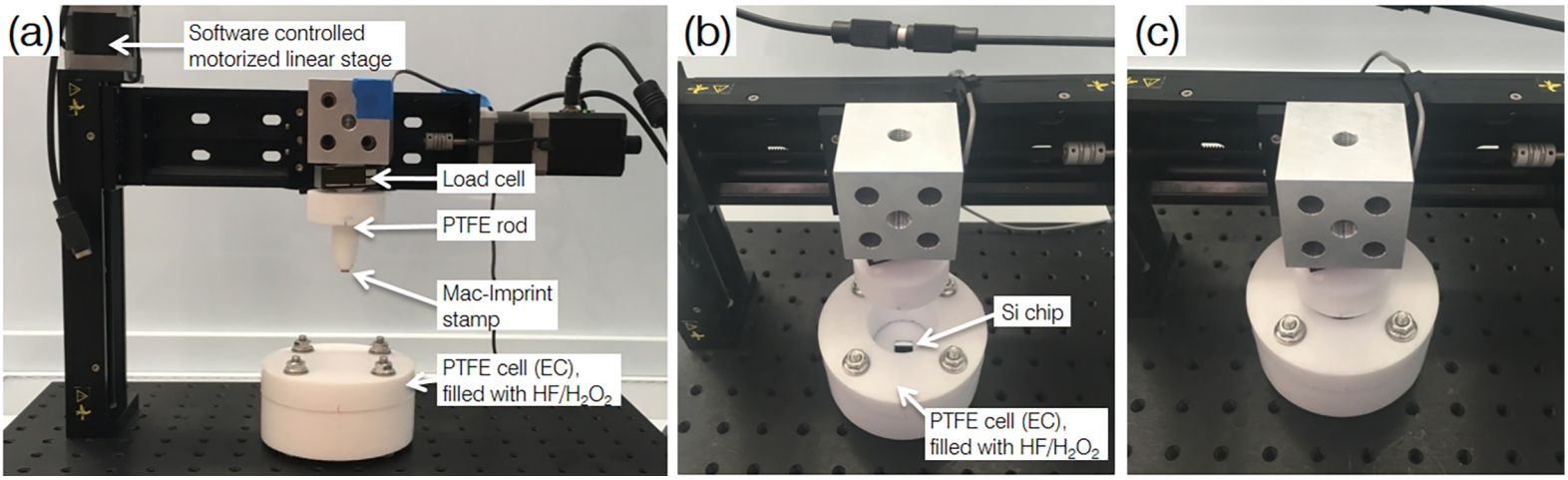

Figure 9

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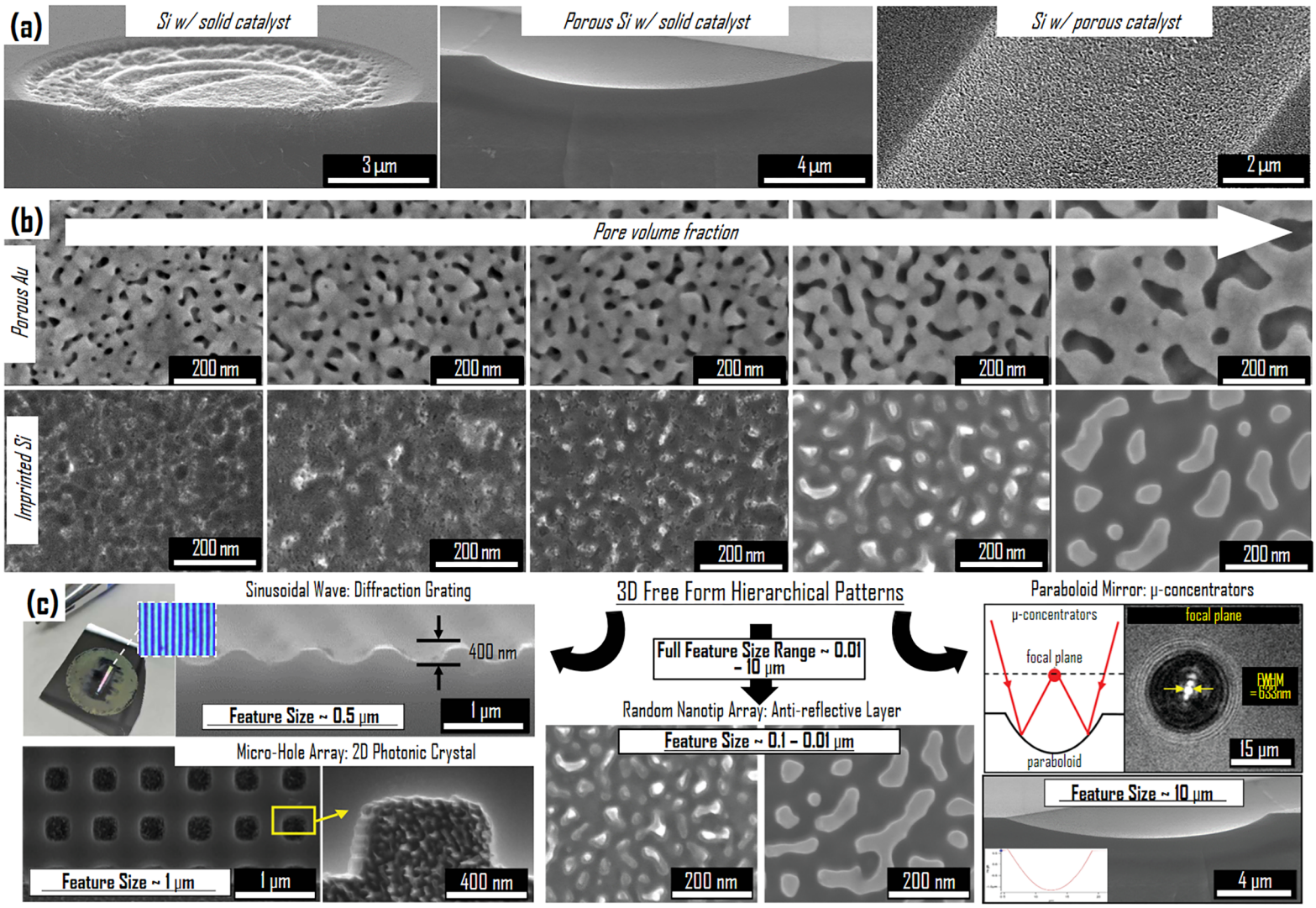

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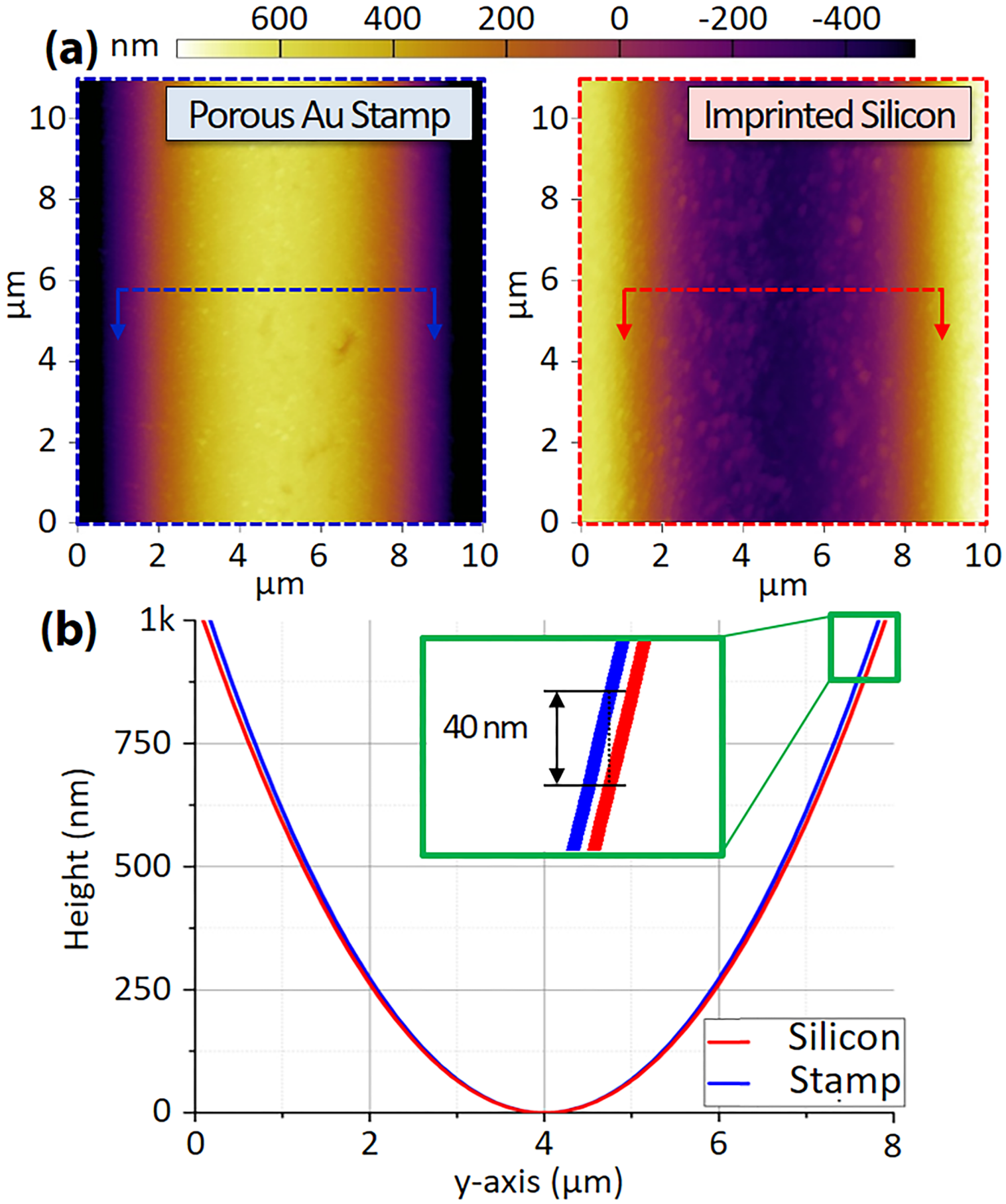

Table of materials

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Name of Material/ Equipment	Company	Catalog Number	Comments/Description
Acetone, >99.5%, ACS reagent	Sigma-Aldrich	67-64-1	CAUTION, chemical
Ammonium fluoride, >98%, ACS grade	Sigma-Aldrich	12125-01-8	CAUTION, hazardous
Ammonium hydroxide solution, 28-30%, ACS reagent	Sigma-Aldrich	1336-21-6	CAUTION, hazardous
AZ 400K developer	Microchemicals	AZ 400K	CAUTION, chemical
BenchMark 800 Etch	Axic	BenchMark 800	Reactive ion etching
Chromium target, 2" x 0.125", 99.95% purity	ACI alloys	ADM0913	Magnetron sputter chromium target
CTF 12	Carbolite Gero	C12075-700-208SN	Tube furnace
Desiccator	Chemglass life	CG122611	Desiccator
F6T5/BLB	Eiko	F6T5/BLB 6W	UV bulb
Gold target, 2" x 0.125", 99.99% purity	ACI alloys	N/A	Magnetron sputter gold target
Hotplate KW-4AH	Chemat tecnologie	KW-4AH	Leveled hotplate with uniform temperature profil
Hydrofluoric acid, 48%, ACS reagent	Sigma-Aldrich	7664-39-3	CAUTION, extremly hazardous
Hydrogen peroxide, 30%, ACS reagent	Fisher Chemical	7722-84-1	CAUTION, hazardous
Isopropyl alcohol, >99.5%, ACS reagent	LabChem	67-63-0	CAUTION, chemical
MLP-50	Transducer Techniques	MLP-50	Load cell
Nitric acid, 70%, ACS grade	SAFC	7697-37-2	CAUTION, hazardous
NSC-3000	Nano-master	NSC-3000	Magnetron sputter
Potassium hydroxide, 45%, Certified	Fisher Chemical	1310-58-3	CAUTION, chemical
Rocker 800 vacuum pump, 110V/60Hz	Rocker	1240043	Oil-free vacuum pump
Silicon master mold	NILT	SMLA_V1	Silicon chip with pattern
Silicon wafers, prime grade	University wafer	783	Si wafer
Silver target, 2" x 0.125", 99.99% purity	ACI alloys	HER2318	Magnetron sputter silver target
SP-300	BioLogic	SP-300	Potentiostat
SPIN 150i	Spincoating	SPIN 150i	Spin coater
SPR 200-7.0 positive photoresist	Microchem	SPR 220-7.0	CAUTION, chemical

Stirring hotplate	Thermo scientific Cimarec+	SP88857100	General purpose hotplate
SU-8 2015 negative photoresist	Microchem	SU-8 2015	CAUTION, chemical
SYLGARD 184 Silicone elastomere kit	DOW	4019862	CAUTION, chemical
T-LSR150B	Zaber Technologies	T-LSR150B-KT04U	Motorized linear stage
Trichloro(1H,1H,2H,2H-perfluorooctyl)silane (PFOCS), 97%	Sigma-Aldrich	78560-45-9	CAUTION, hazardous

le

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Editorial comments:

Thank you for the comments. Please, find responses to each comment written with red font color.

1. The editor has formatted the manuscript to match the journal's style. Please retain the formatting.

The manuscript formatting has been retained.

2. Please address minor specific comments marked in the manuscript.

Specific comments in the manuscript has been addressed.

3. The highlighted section is around 4 pages. Please adjust the highlight to fit 2.75 pages including headings and spacings. Some of the shorter steps can be combined to fit 2-3 actions per step.

The yellow highlight has been adjusted to fit 2.75 pages.

4. Please do not use commercial terms in the manuscript text and figures. All commercial terms must be sufficiently referenced in the Table of materials.

All commercial terms have been excluded from manuscript and figures.

Rebuttal Letter

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Editorial comments:

Thank you for the comments. Please, find responses to each comment written with red font color.

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues. The JoVE editor will not copy-edit your manuscript and any errors in the submitted revision may be present in the published version.

Manuscript has been proofread.

2. Please format the manuscript as: paragraph Indentation: 0 for both left and right and special: none, Line spacings: single. Please include a single line space between each step, substep and note in the protocol section. Please use Calibri 12 points

Manuscript has been formated.

3. Please rephrase the Short Abstract/Summary to clearly describe the protocol and its applications in complete sentences between 10-50 words: “Here, we present a protocol to …”

The Summary has been rephrased.

4. Please do not use in text citation in the Abstract section. Please ensure that the long Abstract is within 150-300-word limit and clearly states the goal of the protocol.

Citations have been excluded.

5. Please ensure that all text in the protocol section is written in the imperative tense as if telling someone how to do the technique (e.g., “Do this,” “Ensure that,” etc.). The actions should be described in the imperative tense in complete sentences wherever possible. Avoid usage of phrases such as “could be,” “should be,” and “would be” throughout the Protocol. Any text that cannot be written in the imperative tense may be added as a “Note.”

Protocol section has been rewritten in imperative tense. Anything, that was not possible to be written in imperative tense was added as “Note”

6. Please revise the protocol text to avoid the use of any personal pronouns in the protocol (e.g., "we", "you", "our" etc.).

Protocol has been revised. All personalization (if any) was excluded

7. The Protocol should contain only action items that direct the reader to do something. Please ensure that individual steps of the protocol should only contain 2-3 actions per step.

Protocol contains only action items.

8. Please define all abbreviations during the first-time use.

All abbreviations are defined during first time use.

9. Please use complete sentences throughout describing the actions in a stepwise manner. Please ensure that there is cohesive story from the beginning to the end.

Cohesiveness of the protocol is maintained. All actions are described in complete sentences in stepwise manner.

10. Please add more details to your protocol steps. Please ensure you answer the “how” question, i.e., how is the step performed? Please include button clicks, knob turns, discrete actions etc.

Protocol has been rewritten in more details. Supporting figures were added to help understand the protocol steps

11. 1.1.7, 1.1.8 how is this done? What is the desired dimension in your experiment?

Details of the steps have been specified in the protocol. The PDMS mold has 2x2 cm dimension.

12. 1.2: Please bring out the difference between silicon substrate and silicon wafers. What is the desired thickness for spin coating? How do you flatten the PDMS mold? How do you perform 1.2.6?

Thank you for observation – there is no difference between Si substrate and Si wafer. In order to avoid misleading It has been changed to Si wafer. The details of the process have been specified in the protocol.

13. 1.3: How do you perform individual steps?

Individual steps have been rewritten in more details in protocol section.

14. There is a 10-page limit for the Protocol, but there is a 2.75-page limit for filmable content. Please highlight 2.75 pages or less of the Protocol (including headings and spacing) that identifies the essential steps of the protocol for the video, i.e., the steps that should be visualized to tell the most cohesive story of the Protocol.

Filmable content has been highlighted with yellow color.

15. Please include a figure or a table in the Representative Results showing the effectiveness of your technique backed up with data.

Figure 10 has been added.

16. Please ensure that the Representative Results in the context of the technique you have described, e.g., how do these results show the technique, suggestions about how to analyze the outcome, etc. The paragraph text should refer to all of the figures. Data from both successful and sub-optimal experiments can be included.

Representative results section has been modified and now contains suggestions on the analysis of the technique effectiveness as well as figures with successful and sub-optimal results.

17. Each Figure Legend should include a title and a short description of the data presented in the Figure and relevant symbols.

Each figure legend contains title and short description of the content.

18. As we are a methods journal, please revise the Discussion to explicitly cover the following in detail in 3-6 paragraphs with citations:

a) Critical steps within the protocol
b) Any modifications and troubleshooting of the technique
c) Any limitations of the technique
d) The significance with respect to existing methods
e) Any future applications of the technique

Discussion section has been revised. All process critical steps, modifications and limitations has been described throughout protocol and discussion section.

19. Please ensure that the references appear as the following: [Lastname, F.I., LastName, F.I., LastName, F.I. Article Title. Source. Volume (Issue), FirstPage – LastPage, (YEAR).] For more than 6 authors, list only the first author then et al.

All references has been formatted according to JoVE requirements

20. Please sort the materials table in alphabetical order.

Materials table has been sorted in alphabetic order.

Reviewer #1 comments:

The introduction and discussion are not very developed. They may be enough to follow the protocol and in this sense are probably adapted to the Jove format, but the basics of MACE should nevertheless be

indicated: half reactions occurring on the metal, on the semiconductor (pointing H2 as a gas product) and their electronic coupling. These are important facts for the rationale of the work presented and the discussion on the limitations of mass transport. The terms "excessive charge carriers" and "delocalization of the etching front" mentioned in the discussion also require additional explanations and/or an additional scheme to be really appreciated.

Thank you for the comments

Indeed, the introduction and discussion sections were written not very developed because of the visualization-focused format of the JoVE journal. However, authors agree that understanding of the reaction involved into metal-assisted chemical etching (MACE) process is important for the technique limitation discussion. With regards to this a short description of the anodic and cathodic reactions has been added as well as a several references onto MACE, including:

15. Li, X., Bohn, P.W. Metal-assisted chemical etching in HF / H2O2 produces porous silicon. Applied Physics Letters. 77 (16), 2572–2574 (2000).

16. Chartier, C., Bastide, S., Levy-Clement, C. Metal-assisted chemical etching of silicon in HF – H2O2. Electrochimica Acta. 53, 5509–5516 (2008).

17. Chattopadhyay, S., Li, X., Bohn, P.W. In-plane control of morphology and tunable photoluminescence in porous silicon produced by metal-assisted electroless chemical etching. Journal of Applied Physics. 91 (9), 6134–6140 (2002).

Major Concerns:

In accordance with the above comment (limited information), readers/viewers will need to read the references provided to further deepen their understanding/knowledge. Since the most significant results concerns bulk silicon imprinting and are obtained by MACE thanks to the use of nanoporous gold as metal catalyst, it is worth mentioning the first report on this system and its application by Torralba et al. [1] and its complementary work by Bastide et al., especially the introduction that provides an overview on MACE applications for silicon imprinting [2]. This will be necessary in particular with regard to (i) the elaboration of the catalyst by AuAg dealloying, (ii) the diffusion of electrolyte into nanoporous gold (e. g. to complete references [15, 16] in the introduction, page 2) and (iii) the imprinting of nanoporous gold ligaments (modelling of this process in [2]).

The following works have been added and cited as the first report on bulk Si imprinting [18] and in-depth investigation of the porous Au influence on the Mac-Imprint [19]:

18. Torralba, E. et al. 3D patterning of silicon by contact etching with anodically biased nanoporous gold electrodes. Electrochemistry Communications. 76, 79–82 (2017).

19. Bastide, S. et al. 3D Patterning of Si by Contact Etching With Nanoporous Metals. Frontiers in Chemistry. 7, 1–13 (2019).

Another helpful review article, with a broader scope on "Electrochemical micro/nano-machining: principle and practices" by Zhan et al. in Chemical Society Reviews, 2017 could be cited as well [3].

The reference onto suggested article has been added:

14. Zhan, D., Han, L., Zhang, J., He, Q., Tian, Z., Tian, Z. Electrochemical micro/nano-machining: principles and practices. Chemical Society Reviews. 46 (5), 1526–1544 (2017).

Minor Concerns:

1) Figure 7. The legend could indicate that it is a two-electrodes EC set-up". In the photo, silicon should be identified as one of the electrodes.

Both legend and figure has indication “Two-electrode” in order to avoid misleading

2) Figure 8. The same electrochemical cell is used for the formation of porous silicon and for the imprinting process by MACE. In figure 8a, the label "EC cell" (electrochemical cell) could be misleading since MACE with HF-H2O2 is an electroless process (without electrodes). In addition, an indication like "filled with HF-H2O2" (either in the legend or in the photo) would be helpful for readers/viewers.

Both figure has indication “filled with HF-H2O2” in order to avoid misleading

3) Page 3, line 102 and 116 + Page 5, line 201: composition of the RCA-1 bath could be given (related chemicals are listed at the end). And page 5, line 179: is the Si sample before imprinting also RCA-1 cleaned?

Composition and mixing procedure are given. And yes, Si chip is also RCA-1 cleaned prior Mac-Imprint (related information has been added to protocol)

4) Page 5 line 179: In this section, the use of "EC" can be misleading as well.

This is the same cell, however it is not indicated, that external bias should be applied in this configuration

5) Nanoporous gold (often abbreviated as NPG), rather than "porous gold", is the common expression for this material obtained by dealloying.

Since pore size of the used porous gold catalyst has been varied authors thought it would not be accurate to address “nanoporous gold” to the porous gold with average pore size of 100 nm (the largest used)

6) In the list of materials, Au and Ag sputter targets characteristics could be mentioned, e.g. purity, supplier (thickness, diameter).

Target characteristics has been added to materials list.

Reviewer #3 comments:

Minor Concerns

The reviewer think it is a good chance to give a comprehensive review of electrochemical nanoimprint in the Introduction Section, which will be good for the reader know the state-of-art of this domain. Thus, the authors are suggested to check and reference the publications listed as followed (some are of the authors' own work):

Thank you for your comments.

The introduction section has been slightly developed and now includes more information regarding current state of the electrochemical nanoimprinting including following references:

11. Li, H., Niu, J., Wang, G., Wang, E., Xie, C. Direct Production of Silicon Nanostructures with Electrochemical Nanoimprinting. ACS Applied Electronic Materials. 1 (7), 1070–1075 (2019).

12. Kim, K., Ki, B., Choi, K., Lee, S., Oh, J. Resist-Free Direct Stamp Imprinting of GaAs via Metal-Assisted Chemical Etching. ACS Applied Materials & Interfaces. 11 (14), 13574–13580 (2019).

13. Zhang, J. et al. Contact electrification induced interfacial reactions and direct electrochemical nanoimprint lithography in n-type gallium arsenate wafer. Chemical Science. 8, 2407–2412 (2017).

14. Zhan, D., Han, L., Zhang, J., He, Q., Tian, Z., Tian, Z. Electrochemical micro/nano-machining: principles and practices. Chemical Society Reviews. 46 (5), 1526–1544 (2017).

18. Torralba, E. et al. 3D patterning of silicon by contact etching with anodically biased nanoporous gold electrodes. Electrochemistry Communications. 76, 79–82 (2017).

19. Bastide, S. et al. 3D Patterning of Si by Contact Etching With Nanoporous Metals. Frontiers in Chemistry. 7, 1–13 (2019).

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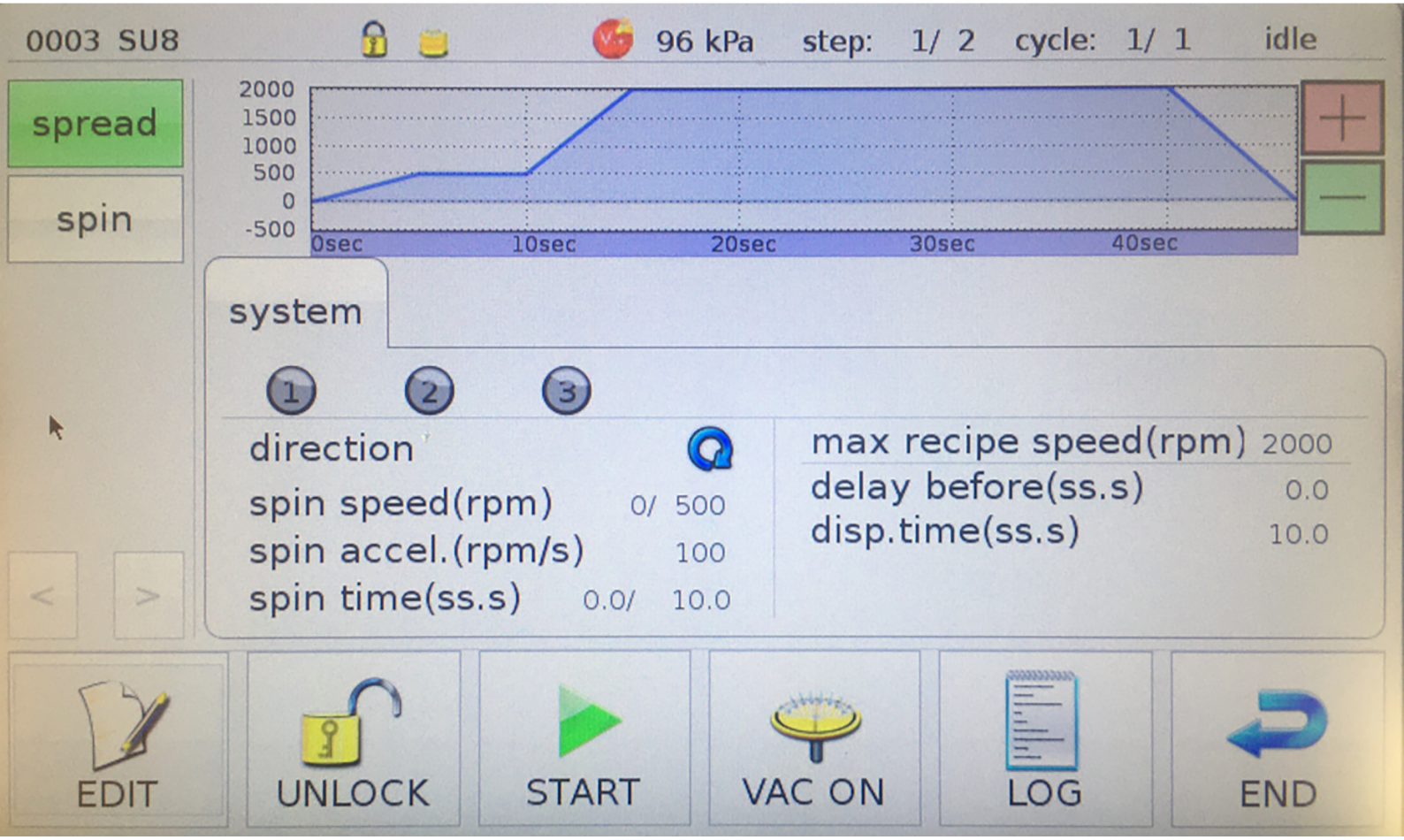

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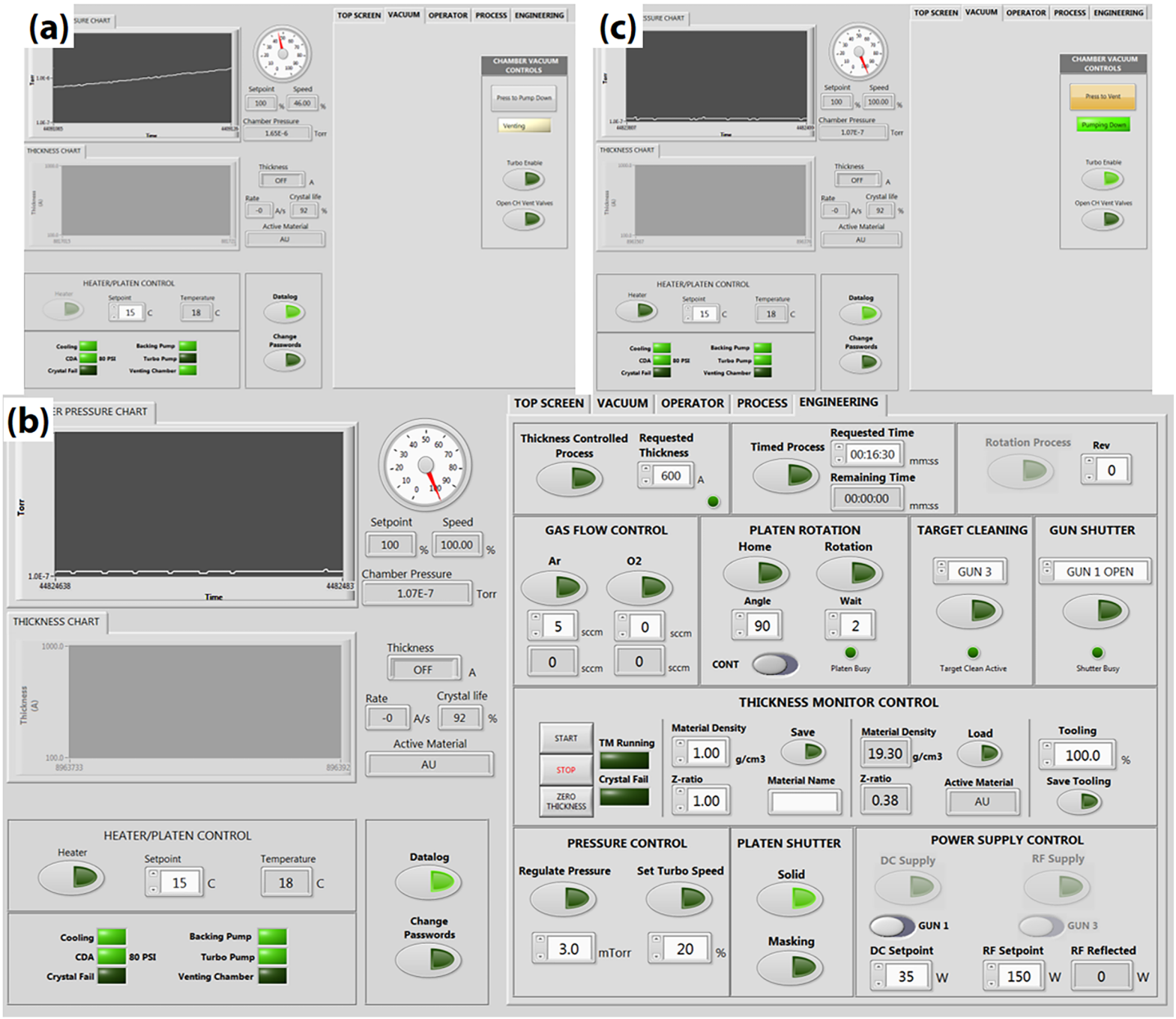

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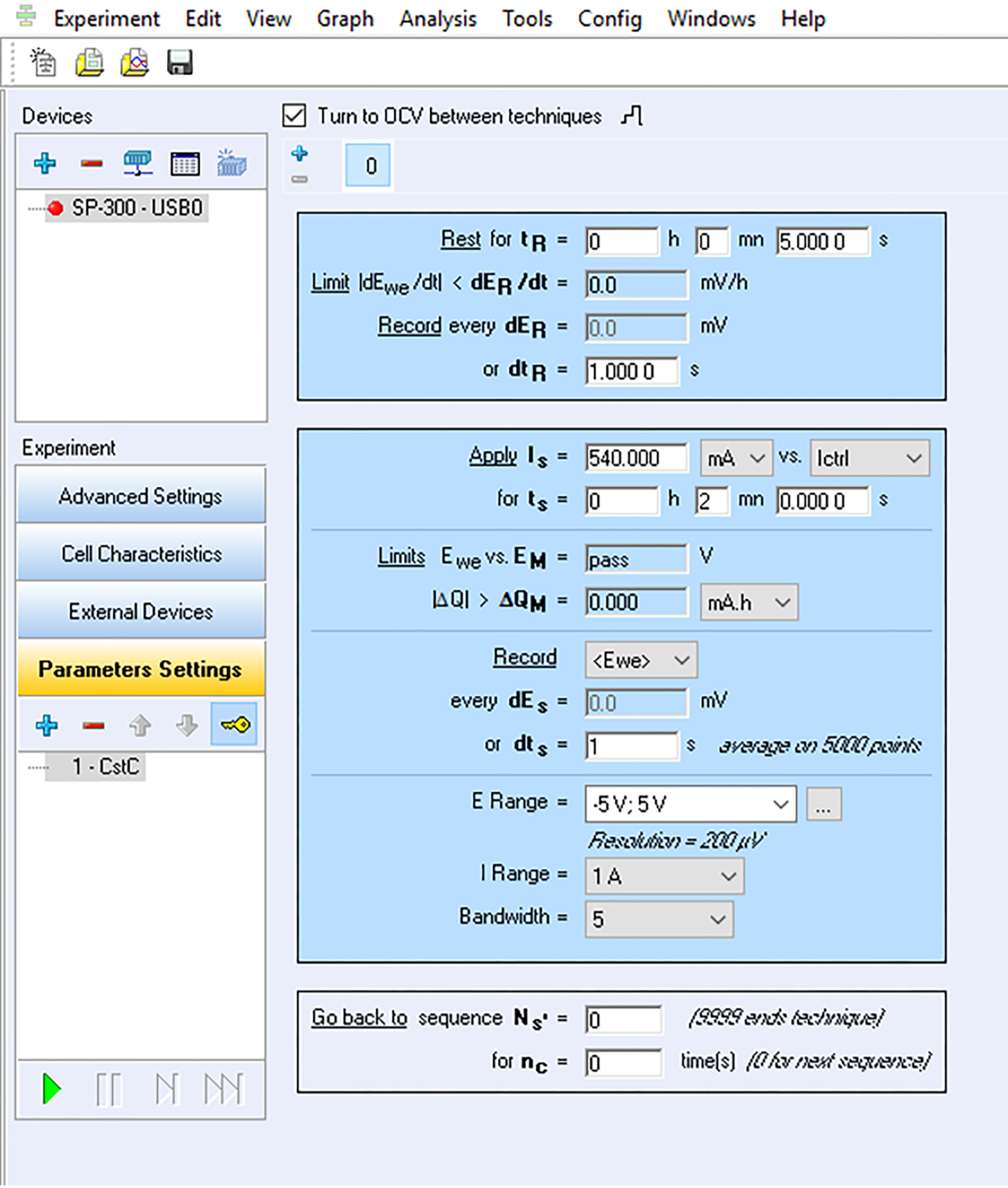

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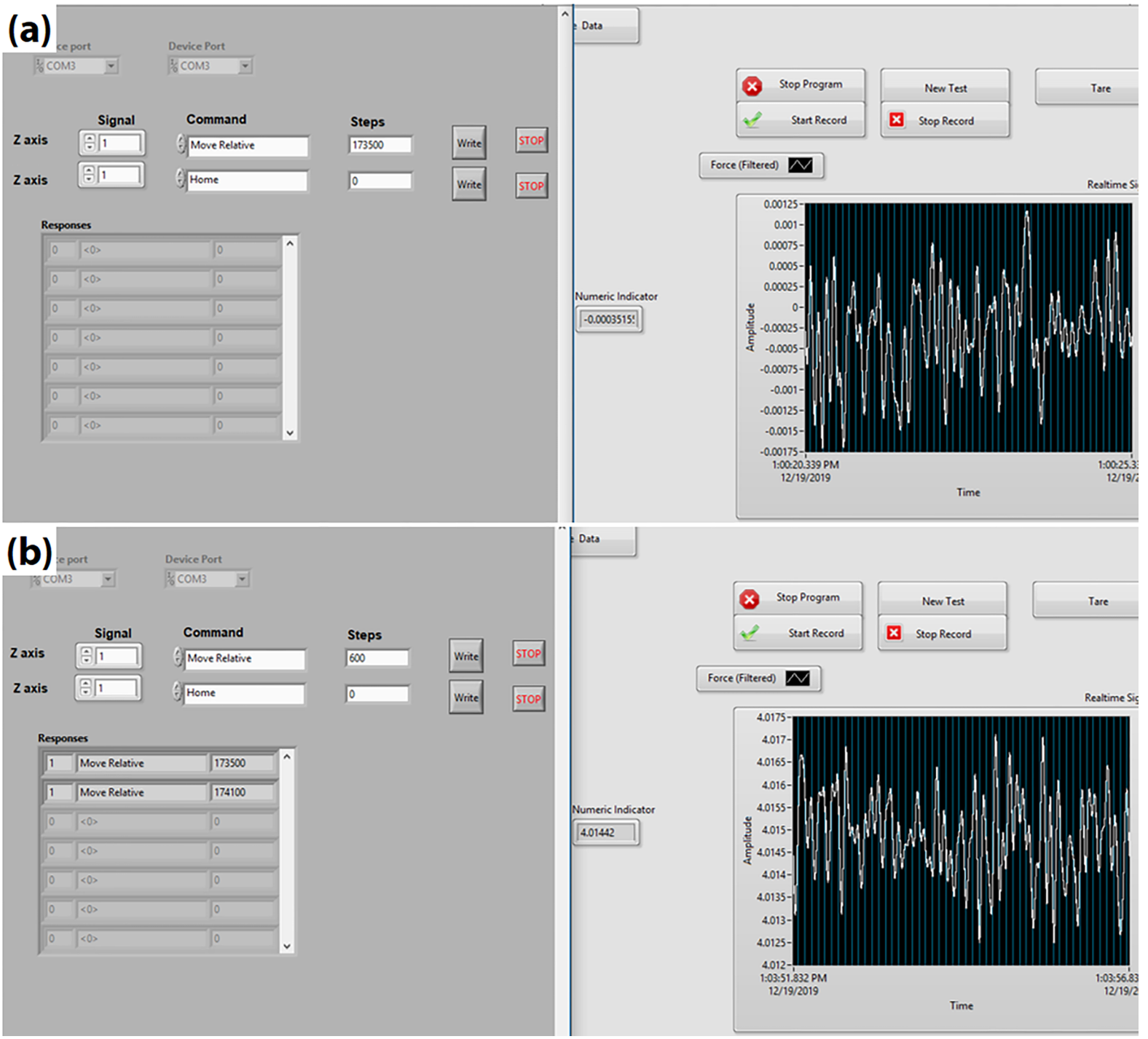

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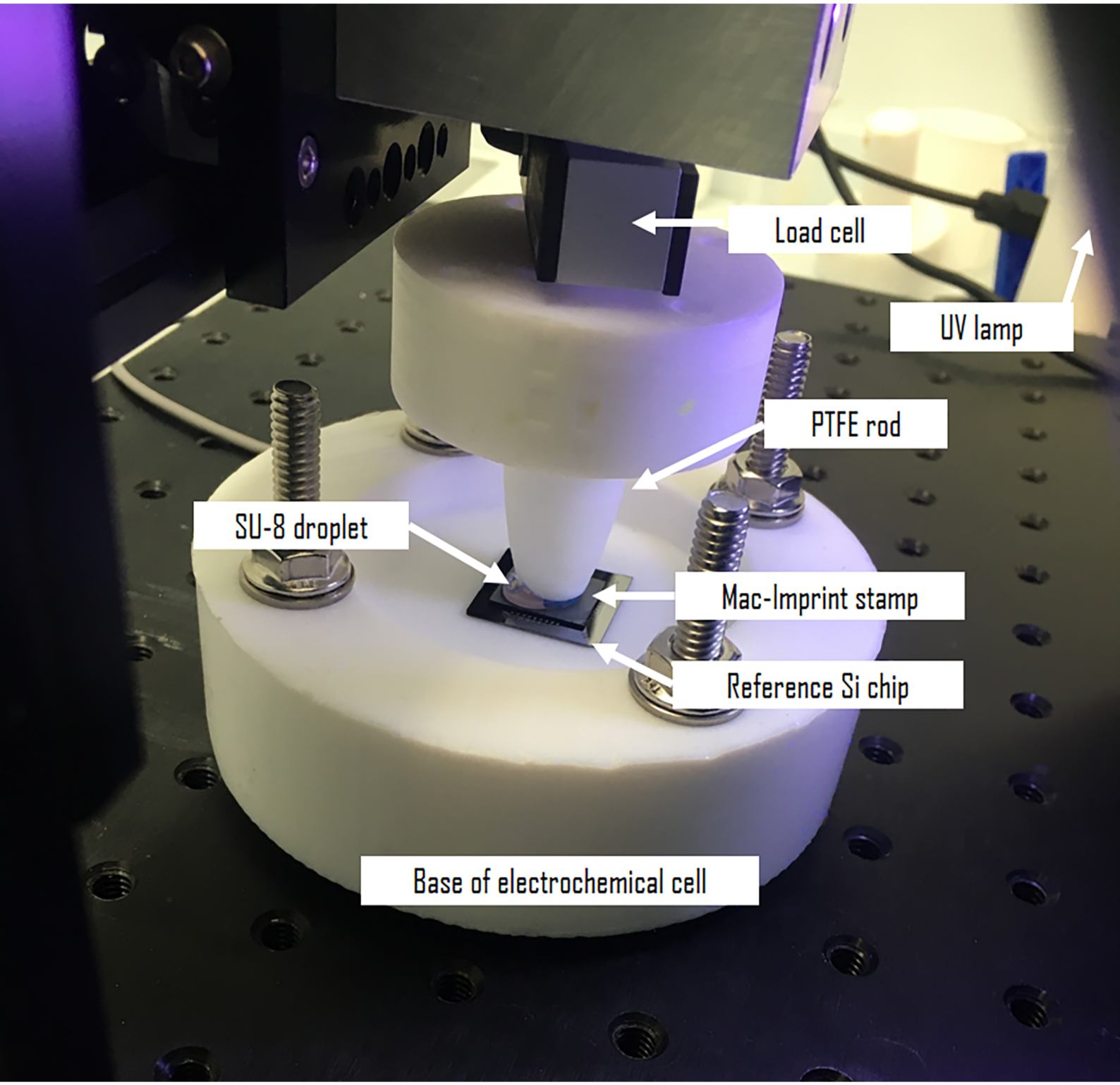

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