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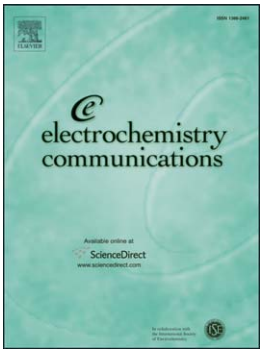

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3D patterning of silicon by contact etching with anodically biased nanoporous gold electrodes

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ABSTRACT

A novel strategy to achieve 3D pattern transfer into silicon in a single step without using lithography is presented. Etching is performed electrochemically in HF media by contacting silicon with a positively biased, patterned, metal electrode. Dissolution is localized at the Si/metal contacts and patterning is obtained as the electrode digs into the substrate. Previous attempts at imprinting Si using bulk metal electrodes have been limited by electrolyte blockage. Here, the problem is solved by using, for the first time, a nanoporous metal electrode that allows the electrolyte to access the entire Si/metal interface, irrespective of the electrode dimensions. As a proof of concept, imprinting of well-defined arrays of inverted pyramids has been performed with sub-micrometer spatial resolution over 1 mm^2 using a nanoporous gold electrode of the complementary shape. Under a polarization of +0.3 V/SME in 5M HF, the etch rate is ~0.5 µm/min. The pyramidal pattern is imprinted independently of the Si crystallographic orientation. This maskless imprinting technique opens new opportunities in the fabrication of Si microstructures.

Keywords: silicon; nanoporous gold; imprinting; microstructure; MACE

INTRODUCTION

Silicon (Si) etching is a key process in the fabrication of Si microstructures essential for many devices used in microelectronics, photonics, photovoltaics or labs-on-chips. Efficient Si microstructuring technologies already exist (e.g. wet/dry etching, photo/electron beam lithography) but their remarkable efficacy comes at the cost of a series of lithography and etching steps – this is not ideal for industries where reduced cost and manufacturing time are key (e.g. manufacture of solar cells). Eliminating the use of masks would dramatically simplify the fabrication of microstructures but is extremely challenging and implies movement towards micromachining techniques.

Only three maskless wet etching processes have been proposed so far, to the best of our knowledge. In 2000, electrochemical (EC) micromachining of Si was first demonstrated by Schuster *et al*. [1]. They used nanosecond pulses to confine the EC reactions to electrode regions in close proximity. This technique allowed holes and trenches to be etched with the tip of a tungsten wire (2 µm) in HF under anodic bias of Si vs. tungsten [2]. The machining precision (~10 µm) and process speed were, however, not suitable for the design of sub-micrometer structures in low doped Si.

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A second innovative approach, essentially an electrochemical version of Metal Assisted Chemical Etching (MACE) of Si in HF, was proposed in 2009 by the group of Matsumura [3]. A noble metal wire is polarized against a counter-electrode in solution and put in contact with a Si sample, playing the role of an etching tool by oxidizing Si atoms close to its areas of contact. Hence, the Si sample is no longer part of the EC cell. Grooves and through-holes could be etched in wafers using these "catalytic" metal wires [3–7]. With a 200 µm Pt wire polarized at 2.25 V vs. Ag/AgCl, the dissolution rate was 2.4 µm min^{-1} for an etched area of 0.03 mm^2 [6]. The major problem encountered with EC contact etching using macroscopic tools is that electrolyte diffusion becomes negligible over a few hundreds of micrometers. Hence, surface structuring at the macroscopic scale (e.g. 1 cm^2) cannot be expected under these conditions.

The third approach, developed by the group of Kobayashi, corresponds to traditional MACE in HF-H_2O_2, the positive bias of the metal tool being replaced by the oxidizing power of H_2O_2 [8–10]. Pattern transfer in (100) and (111) oriented Si was performed with Si/SiNx/Pt etching tools with random pyramidal structures [8]. Their flatness at the macroscopic level undermined contact etching for the reason described above. Similarly, cone-shaped pores were etched in Si with a Pt/Ir needle [10] and metal meshes (10 µm wires and 50 µm openings) on sponge-like stamps have been used, but only the largest features were transferred (50 µm pillars). Very recently, pattern transfer by contact etching in HF-H_2O_2 has been successfully achieved by Azeredo *et al.* in porous Si by using macroscopic Au metallized pre-patterned stamps with a sinusoidal shape [11]. The process was shown to be capable of centimeter-scale parallel 3D patterning with sub-20 nm resolution. Shape transfer was impossible in Si but easily obtained in porous Si since the electrolyte could reach the metal interface through the porous Si network. A similar nanoimprint lithography approach using platinized PDMS molds has recently been reported for n-type Si and GaAs [12-13].

In this work, we present a new strategy to achieve pattern transfer into Si by EC contact etching with metal tools of large dimensions. The main novelty lies in the fabrication and use of patterned nanoporous gold (np-Au) electrodes as high-performance imprinting tools. The first results demonstrate the transfer at sub-micrometer resolution of arrays of inverted pyramids over a treated area of around one square mm in a single step, independent of crystallographic orientation.

EXPERIMENTAL

Reagents. AuAg leaves (12 carats, $Au_{35}Ag_{65}$, 170 nm thick, Noris) were used for the synthesis of np-Au electrodes. (100) n-type (phosphorous) c-Si wafers (1-3 Ω cm, 400 µm thick, Sil'tronix) were employed as Si substrates. Analytical grade (VWR chemicals) 30% H_2O_2, 96% H_2SO_4, 40% HF, 65% HNO_3, 60% $HClO_4$ and ultra-pure water (18.2 MΩ cm, Millipore) were used in all the experiments.

Instrumentation. All EC experiments were performed with a PGSTAT20 Metrohm Autolab and Nova software. EC dealloying and contact etching were conducted in a three-electrode PTFE cell. The np-Au electrode, a Pt wire and a Hg/Hg_2SO_4 electrode (SME) were used as working, counter and reference electrodes. The SME included a K_2SO_4 bridge with a glass frit (EC dealloying) or a K_2SO_4 agar-gel tip (etching in HF). Ultrasonication was performed with a Vibracell 75043 (Sonics & Materials). Scanning electron microscopy (SEM) images, Energy Dispersive X-ray Spectroscopy (EDS) and Electron Back Scattered Diffraction (EBSD) images were obtained with a Merlin FEG microscope from Zeiss equipped with AZtec systems (EDS Advanced, HKL Advanced Nordlys Nano, Oxford Instruments). AuAg powders were sintered using a Dr-Sinter 515S-Syntex Spark Plasma Sintering (SPS) machine.

Fabrication of Si molds. E-beam lithography (alkaline etching using a Si nitride mask) was employed to create arrays of square-shaped inverted pyramids of 10×10 or 14×14 $µm^2$ and 7 or 10 µm depth, respectively, in p-type (100) Si wafers (5–10 Ω.cm^2).

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Fabrication of patterned np-Au electrodes. The AuAg leaves were fragmented by ultrasonication in water (10 min, 55 W) and dried at 100°C. The obtained powders (~350 mg) were sintered against the Si mold at 500°C under vacuum, with a uniaxial pressure of 50 MPa for 20 min, in a graphite die (Ø = 10 mm) enclosed between two graphite punches. After dissolution of the mold in HF-HNO_3-H_2O (44:16:40), AuAg disks 10 mm diameter and 0.35 mm thick, with a patterned central surface area measuring 64 mm^2, were obtained.

The AgAu disks were dealloyed electrochemically following the procedure described in [14]. A constant potential was applied in $HClO_4$ 0.77 M at 60°C until the current decayed to almost zero. Various dealloying conditions were tested (potential, time). At 0.6 V/SME, almost complete removal of Ag was obtained after ~50 hours, the resulting nanoporous structure and electrode integrity being suitable for etching experiments.

EC contact etching. n-type Si wafers were cleaved into 2×2 mm^2 pieces, cleaned in H_2SO_4-H_2O_2 (3:1) and rinsed with ultra-pure water. A freshly cleaned Si piece was placed in contact with the np-Au electrode and pressure applied via a Pt wire attached to a micromanipulator. The electrolyte was 5 M HF with 2 vol% ethanol to favor elimination of the H_2 bubbles generated during etching. The EC cell was placed on a balance to quantify the applied pressure. In this configuration, the best etching results were obtained at 18 g cm^{-2}.

RESULTS AND DISCUSSION

Figure 1a illustrates the EC contact-etching process developed in this work. The patterned np-Au electrode is brought into contact with a Si substrate in a HF solution.

Upon application of a positive bias vs. a Pt wire, the electrode drains electrons from Si–Si bonds in the close vicinity of the metal contacts and Si atoms are dissolved (cf. half reaction). The positive bias plays the role of the oxidizing agent in classical MACE, with the additional possibility of controlling the etch rate via the applied potential or current and the extent of etching through the charge passed. As Si is etched away, the electrode moves in (under application of gentle pressure) and eventually imprints its pattern into the Si substrate.

It is advantageous to use nanoporous metal because its ligaments are only a few tenths of a nanometer in size, thus providing Si/metal contacts as small as in classical MACE with metal nanoparticles (a highly efficient etching system). At the macro scale, the porosity also ensures supply of electrolyte to the entire Si/metal interface, with in theory no limitation regarding the size of the electrode.

The patterned np-Au electrodes are fabricated in a three-step procedure as explained in the Experimental section. Representative SEM images of a typical Si mold and a patterned AuAg alloy are shown in **Figure 1b** and **1c**, respectively. The pyramidal pattern of the latter represents a good replica of the mold with well-defined pyramids, except for some voids probably due to foreign particles present in the AgAu powder or at the mold surface before sintering (non-clean room environment). SEM images of the np-Au electrode obtained after EC dealloying are shown in **Figure 1(d,e)**. EDS analysis along a cross-section of the electrode reveals that the bulk is entirely nanoporous, with Ag < 1 at%. The overall pyramidal morphology is not affected by the removal of Ag. The porosity is therefore close to 65 % (volume of removed Ag atoms). The structure is typical of np-Au, with interconnected ligaments between 25 and 50 nm in size and an active surface area of 9-11 $m^2\,g^{-1}$ [15]. The surface area of the electrodes (175 mg) is ~1.5–1.9 m^2, in agreement with the high capacitive current measured by cyclic voltammetry (cf. inset of **Figure 2a**).

Figure 2a gives the chronoamperometric response in the dark of a np-Au gold electrode biased at +0.3 V/SME in HF media, when it is repeatedly brought into contact with n-type Si. Each contact results in an anodic current that first increases sharply, then decays until a stationary value is attained (60 µA in this case) and eventually drops just after contact removal. This clearly indicates that n-type Si is oxidized despite the lack of photogenerated holes (contrary to conventional photo-EC etching). H_2 evolution during etching suggests a dissolution of the porous Si formation regime, in agreement with a measured current density much lower than

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the critical current density in 5M HF (~6 mA cm^{-2} vs. 121 mA cm^{-2}). The current decay during contact is ascribed to mass transport limitations due to volume confinement and perhaps trapped H_2 bubbles in the nanoporous gold network.

Figure 2(b–e) shows optical and SEM images of the Si surfaces after 10 minutes EC contact-etching with a np-Au electrode biased at +0.2 V (b, c) and +0.3 V/SME (d, e). The images reveal imprinted arrays of square-based inverted pyramids, the size (depth) of which increases from 1.2×1.2 μm^2 (0.9 μm) at +0.2 V/SME to 5.1×5.1 μm^2 (3.6 μm) at +0.3 V/SME. The etching rate is thus ~4 times faster at +0.3 V/SME (0.5 vs. 0.15 μm min^{-1}). At +0.2 V/SME, the pyramid faces are clearly distinguished, indicating a spatial resolution higher than 1 μm. At +0.3 V/SME, however, some etching between pyramids can be observed from the presence of a porous Si layer at the Si surface, and the pyramid faces are rough. By comparing theoretical and experimental charges related to the pyramid volume, a faradaic efficiency of ~10% is estimated for the imprinting process. Note that concomitant etching outside the Si/metal contact area would be much larger with p-type Si. Indeed, due to the ohmic character of the Au/p-type Si contact and the presence of holes as majority carriers, any polarization of the np-Au electrode would result in polarization of the bulk Si and thus delocalized etching (cf. MACE of p-type Si with Pt nanoparticles [16]). By contrast, with n-type semiconductors (in the dark), the lack of holes prevents delocalized etching to some extent. This has been demonstrated by Zhang *et al.* through high resolution nanoimprint lithography of n^+-type Si and n-type GasAs using platinized polymer molds in HF-H_2O_2 [12-13].

Figure 2(f, g) presents SEM images of a Si sample also etched at +0.3V/SME (imprinted area of ~1 mm^2, inverted pyramids of 5×5 μm^2) with an additional post-cleaning step to removed porous Si and impurities. The non-planar surface observed between pyramids in **Figure 2g** confirms some amount of delocalized etching. Rough pyramid faces are still visible after this treatment, the reason for this not yet being clear. The inset of **Figure 2f** shows the pole figure established by EBSD of the (100) Si crystal. The pyramid sides are clearly not aligned with the [001] and [010] directions of the sample (21° off), which is to be expected since the np-Au electrode was randomly positioned on the sample surface. Inverted pyramids obtained by alkaline etching (different rates along {100} and {111} directions) always have their bases aligned on {100} directions. Following the results of Fukushima *et al.* [8], this is the second example of square-based pyramids being produced which are independent of the crystallographic orientation of the Si substrate.

The same np-Au electrode could be used several times before the pyramidal pattern was damaged. The damage consisted mainly in traces from handling instruments (np-Au is fragile) and in the flattening of the pyramid tips due to the applied pressure. The influence of several parameters is currently being investigated using different types of patterns, with the aim of improving the resolution, the etch rate, the imprinted area and the reusability of the electrodes.

CONCLUSION

Direct imprinting of well-defined arrays of inverted pyramids has been achieved for the first time by EC contact etching with electrodes made of a nanoporous metal. The electrodes were designed by sintering AuAg powders into Si molds with a pyramidal pattern and dealloying them electrochemically to form np-Au. Inverted pyramids, 5-6 μm in size, were imprinted after 10 min etching in 5 M HF with np-Au electrodes polarized at +0.3 V/SME (vs. a counter electrode in solution). The faradaic efficiency of the imprinting process is ~10 %, due to some delocalized etching resulting in porous Si formation between pyramids. The surface pattern of the electrodes was transferred to the Si substrate with a sub-micrometer resolution and is independent of crystallographic orientation over a treated area of 1 mm^2. These results constitute a proof of concept for EC contact etching with nanoporous metals and provide the basis to develop a new imprinting technique of great utility in the field of Si surface processing.

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Figure captions

Figure 1. (a) Schematic representation of the Si EC contact-etching process. SEM images of (b) a Si mold; (c) a patterned AuAg electrode after sintering; (d) a pyramid of np-Au after dealloying; (e) the np-Au structure at its tip.

Figure 2. Chronoamperogram of np-Au polarized at +0.3 V/SME in HF (in dark) repeatedly brought into contact with n-type Si. Inset: voltammogram of np-Au in contact with Si at 25 mV s^{-1} (a). Optical and SEM images of Si surfaces after imprinting inverted pyramids with np-Au electrodes biased at +0.2 V (b, c) and +0.3 V (d,e) in HF 5M (2% ethanol), in the dark. (f, g): The sample after cleaning with HF-HNO_3 to remove porous Si and impurities. Inset of (f): pole figure established by EBSD at 70° from (g).

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Figure 1

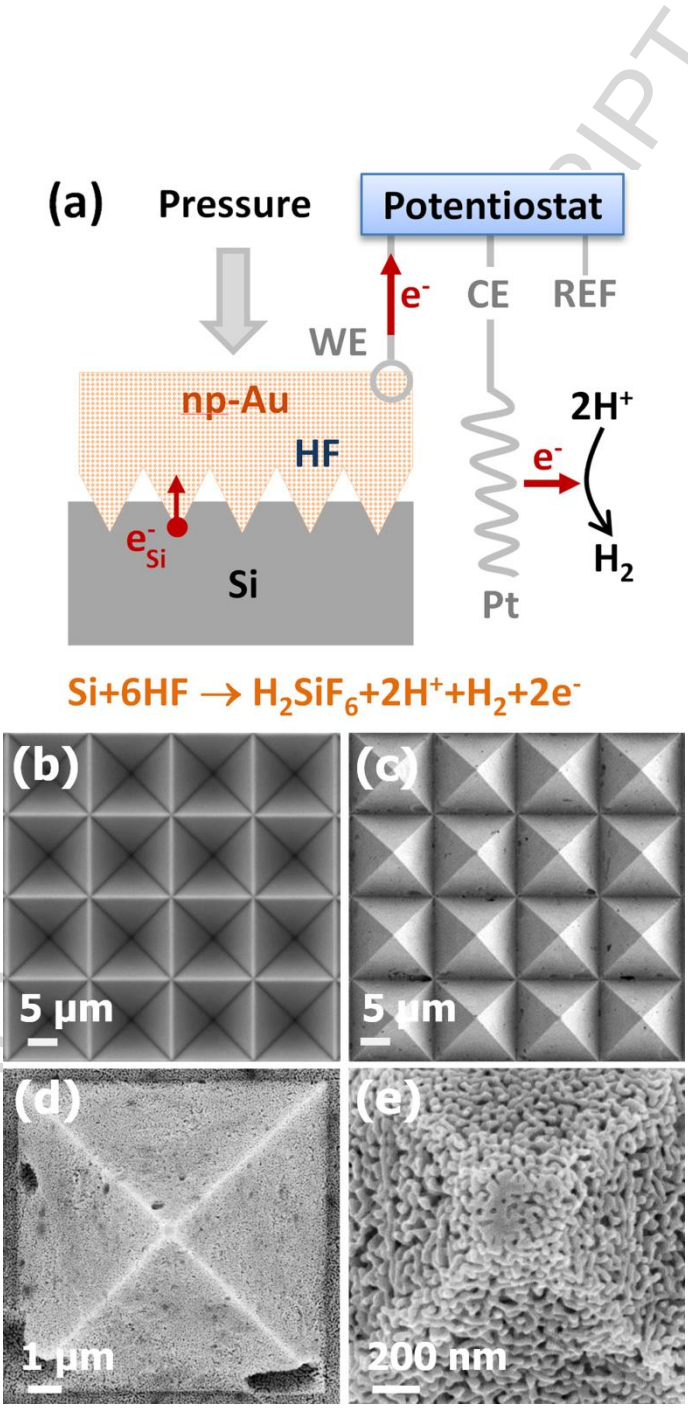

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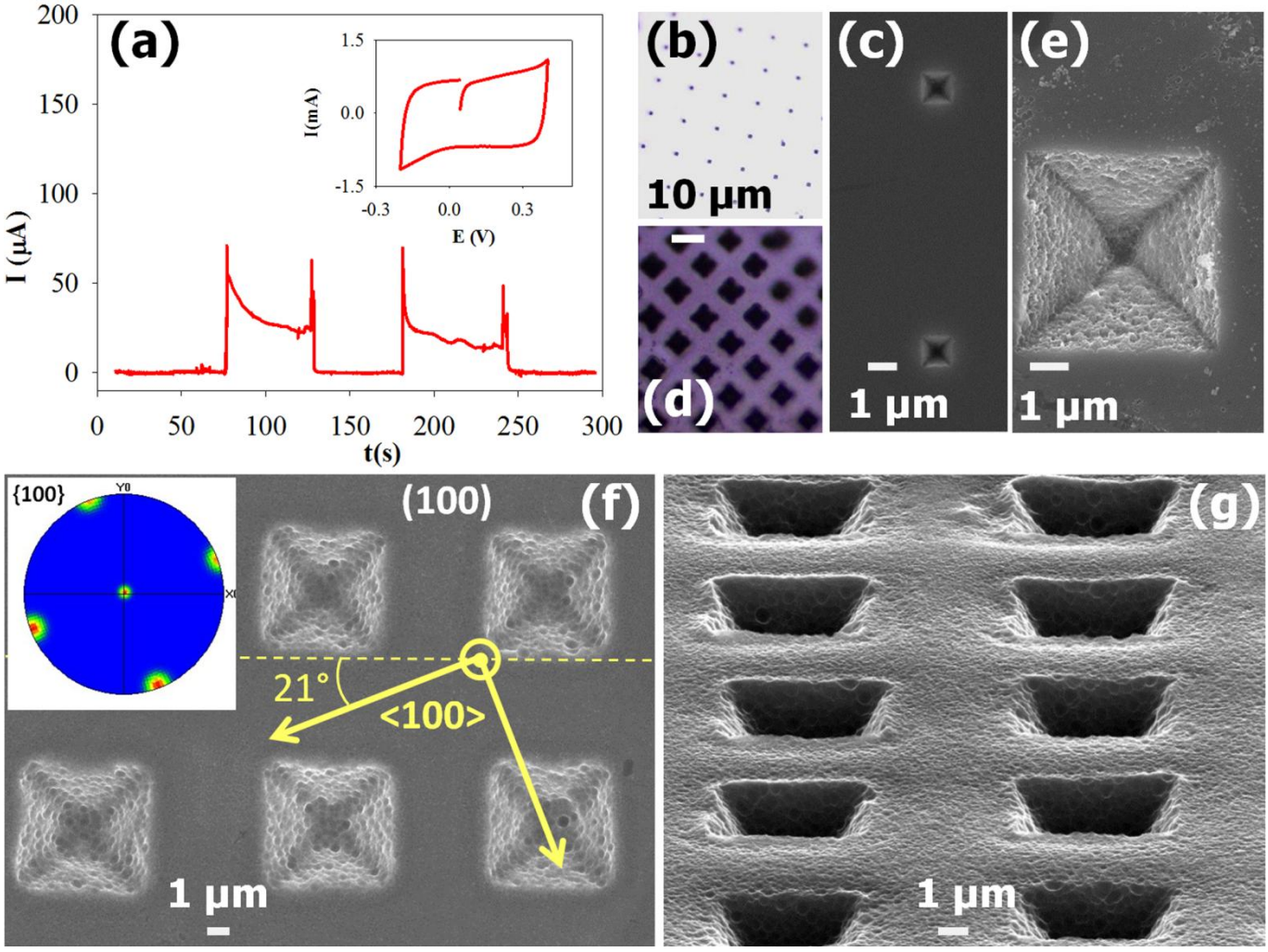
Figure 2



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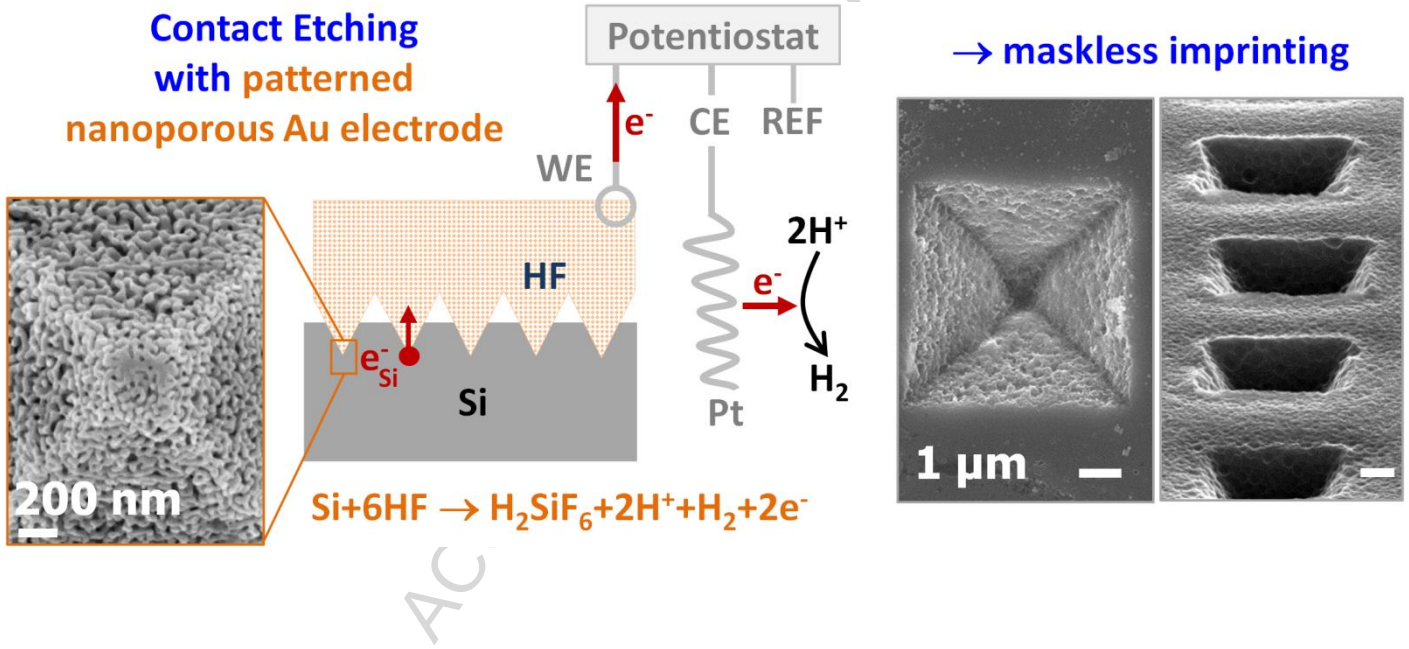
Graphical abstract



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Highlights

- 3D patterning of Si is achieved in a one-step and maskless contact etching process
- A nanoporous metal electrode allows the electrolyte to access the Si/metal interface
- Metal ligament/Si contacts are as small as in classical MACE with metal nanoparticles
- Macroscaled inverted pyramids are imprinted with sub-micrometer spatial resolution
- The imprinting process is independent of the crystallographic orientation of the Si sample

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