

# Microstructuring of *p*-Si(100) by localized electrochemical polishing using patterned agarose as a stamp

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## Abstract

Localization of electrochemical polishing using patterned agarose has been employed to fabricate microstructures on *p*-Si(100). The patterns were first transferred from a master to an agarose stamp, and then the microstructures were fabricated by limiting electrochemical polishing in the small contact area between the stamp and the workpiece. The gel stamp acts as the current flow channel between the working electrode and the counter electrode, simultaneously directing the electrolyte to the preferential parts of the Si workpiece. Microstructures fabricated by partial anodic dissolution on *p*-Si are approximately the same as those on the master. Lateral deviation of the fabricated microstructures from those on the master is approximately 2.6% and the electrochemical etching rate in HF is around several micrometers in an hour. This newly developed technique can be used as a low-cost and simple approach to fabricate microstructures on *p*-Si with high fidelity at a fast rate.

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## 1. Introduction

Silicon is an important semiconductor material used for producing solid-state electronic devices and is extensively applied in many micromechanical fields owing to its excellent engineering properties [1]. Recently, techniques using electrochemical etching have been employed to fabricate microstructures on Si [2–6]. The Si surface is first prepatterned with an oxide or nitride using a standard photolithographic process. To localize the electrochemical etching, factors such as the local electric field, surface passivation and mass transport are very complex. Very often, initial pore nucleation is an important and a pattern of pits is introduced onto the front side of the Si surface by photolithography and anisotropic chemical etching. This type of process requires relatively high initial and running costs, and hence there is great interest in developing novel tech-

niques to confine the electrochemical process and then fabricate desired microstructures on Si. For example, scanning probe lithography (SPL) [7,8] and electrochemical micromachining (EMM) using nanosecond pulses [9] have been applied to produce structures down to micrometer or even nanometer scale. However, these techniques work mainly on a “point by point” direct basis, and hence are very time-consuming for fabrication of large-area microstructures. Recently, a new technique termed reactive wet stamping (r-WETS) was developed by Grzybowski et al. [10–12], which involves patterning of an agarose gel in bas relief for fabrication of microstructures on many materials. However, the best resolution of fabrication on Si by r-WETS was still around hundreds of nanometers, which was limited by the lateral diffusion of HF on the surface due to its very slow etch rate (2 nm/h) [13]. Hence the stamp and the substrate were often placed in a Petri dish containing light mineral oil, which could prevent lateral spreading of the etchant and limit the chemical etching to the contact area. Even though, the longer application time

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still makes the agarose gel denaturalize and prevent its future application on Si.

In this letter, the application of agarose stamp was extended to the electrochemical fabrication of microstructures for the first time. Many more applications that are related with the electrochemical process such as electrodeposition, electroadsorption etc. are expected to be developed. For instance, when it combines with the electrochemical etching, it provides more flexibility than chemical etching and it also overcomes the difficulty of erraticism and non-reproducibility in the chemical etching process. The agarose that has been soaked in a desired electrolyte before the microfabrication is employed as a patterned stamp. It can direct and supply the electrolyte to preferential parts of the Si wafer. Anodic dissolution progressively removes the Si substrate from the small contact area with the stamp. Then, using nominal pressure to maintain the contact, the stamp etches into the Si and approximately the same microstructure as on the master can be fabricated on the Si with high efficiency. This approach achieves two goals. First, it provides a good copy of the microstructures on the gel stamp at high efficiency, because of the fast rate of electrochemical etching. Second, the process requires no expensive instruments for the pre-experimental procedures and is suitable for fabricating large-scale microstructures at a low-cost. In preliminary experiments, *p*-type was preferred to *n*-type Si, since the apparatus for *p*-Si electrochemistry without an illumination apparatus is much simpler and its electrochemical etching is usually isotropic.

## 2. Experimental

Micropatterned gels were prepared from an aqueous solution of high-strength agarose (American AMRESCO, Biotechnology grade). First, a solution of agarose in water at weight ratios ranging from 1:8 to 1:12 was prepared by boiling in a beaker. A master with complex microstructures on a Si or Ti wafer was immersed in the solution. Air bubbles were removed by cooling under vacuum for 2 h. The gel can penetrate into the fine features of the master, such as small grooves or concave holes. The micropatterned gel was stripped carefully from the master to yield a stamp. Fabricated stamps were cut into rectangular blocks of 2 cm × 2 cm × 1 cm (height). The masters used here included Ti and Si with the patterns prepared by through mask electrochemical micromachining (EMM) [14,15] and inductively coupled plasma (ICP) [16,17], respectively. After peeling from the master, micropatterned gels were then soaked in HF etching solution (normally 0.6–0.8 mol/L) for 2 h. Prior to use, the gels were dried on filter paper for 10 min, and then under a stream of N<sub>2</sub> for 100 s.

The workpieces to be etched were *p*-Si(100) wafers (Huajing Electronic Corporation, Wuxi, China). Si wafers of 525 μm in thickness were boron-doped and had a resistivity of 10–15 Ω cm. Before mounting in the electrochemical cell, the Si wafer was cleaned with H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> (4:1, w/w) and then covered with a thin Pt film (20 nm

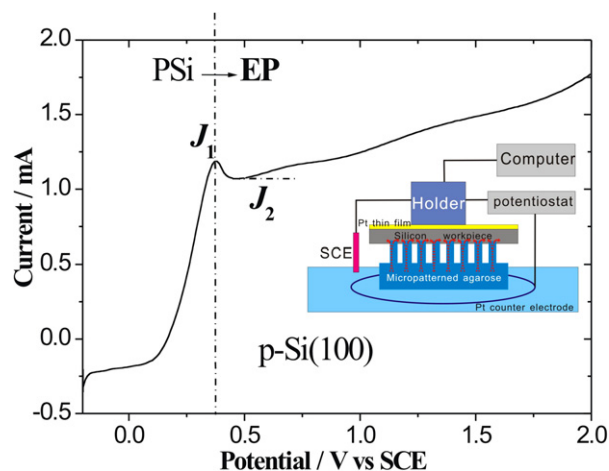


Fig. 1. Typical current–voltage curve for a *p*-Si(100) electrode placed on a micropatterned gel soaked in 0.6 mol/L HF. At potential lower than  $U_{\text{peak}} = 0.39$  V, porous Si (PSi) is formed on the electrode. For  $U_{\text{Si}} > U_{\text{peak}}$ , the Si electrode dissolves in the electropolishing regime (EP). The insert is a schematic drawing of the experimental set-up specially designed for electrochemical polishing.

thick) on the backside to achieve a real ohmic contact. The native oxide layer was removed by dipping in 10% HF solution and then the workpiece was rinsed with ultrapure water. This treatment creates a hydrophobic silicon surface by forming hydrophobic Si–H bonds, which significantly helps to minimize lateral spreading of the etchant in the initial etching process and hence decreases micromachining deviation.

Electrochemical micromachining of *p*-silicon was performed in a specially designed three-electrode electrochemical cell as shown in the insert graph in Fig. 1. The stamp was placed upside down at the bottom of the electrochemical cell filled with a certain concentration of HF. The silicon workpiece is placed on top of the patterned gel as the working electrode. Only the part without patterning was immersed into the HF electrolyte. The polished side of the Si contacts the agarose stamp, which is far from the solution. This ensures that electropolishing is limited to the areas of contact between the stamp and the *p*-Si working electrode. A saturated calomel electrode (SCE) and a Pt circular ring are used as the reference electrode and the counter electrode, respectively. All electrochemical measurements and control of the working potential were performed using a CHI 631B electrochemical workstation. The microstructure of the mold and the etched workpiece were characterized using a confocal microscope (Olympus 2000).

## 3. Results and discussion

We started to apply anodic potential of 1.5 V vs. SCE to *p*-Si in the electrochemical cell shown in the insert graph of Fig. 1. The gel has two other functions here: (1) it removes reaction products from the silicon–gel interface; and (2) it acts as the current flow channel between the working elec-

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