

Fast electroless fabrication of uniform mesoporous silicon layers

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Abstract

We present a new route for the fabrication of mesoporous silicon using Pt nanoparticle-assisted chemical etching. In contrast to stain etching, the mesoporous silicon films show good uniformity. The porosity and thickness can be tuned well via adjusting the HF and H₂O₂ concentration. Etching rates of more than 1.7 $\mu\text{m}/\text{min}$ have been obtained under optimized conditions. The charge transfer through the Pt-Si nano-Schottky contact was simulated to qualitatively explain the observed phenomenon. Our approach will allow a much simpler and cheaper route to fabricate mesoporous silicon layers compared to electrochemical etching as used in the area of surface micromachining and layer transfer techniques.

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1. Introduction

Porous silicon (PSi) can be classified into three types depending on its pore diameter d : micro-PSi ($d \leq 2\text{nm}$), meso-PSi ($2 < d \leq 50\text{ nm}$) and macro-PSi ($d > 50\text{nm}$) [1]. The morphology of PSi strongly influences its mechanical, optical and electrical properties, thus determines the device performances for application. Here, we mainly concentrate on meso-PSi. At room temperature, micro-PSi emits visible light from its highly porous structures arising from quantum confinement effects [1,2]. However, micro-PSi-based light emitting devices still yield a low quantum efficiency with insufficient environmental stability despite years of research efforts [1,3]. In contrast, meso-PSi has demonstrated considerable potential for bio-medical applications regarding on biocompatibility and biodegradability [4], such as drug delivery [5] and in-vivo monitoring [6] due to its large internal surface area and its mechanical stability. In microsystem technology, meso-PSi is used as a key technology of surface micromachining [7]. In photovoltaics, meso-PSi has been utilized for antireflective layer [8], and as a sacrificial layer for layer-transfer processes [9]. The latter technique is also known to hold the potential to revolutionize the photovoltaic industry by dramatically reducing the Si material use [10].

Until now, two methods have been developed to fabricate meso-PSi, namely, electrochemical etching (ECE) and stain etching. Stain etching [11] has a limited etching depth and lacks controllability of pore size and porosity. As the most commonly used method, ECE [12,13] permits to control the pore size and porosity via simply tuning the applied current as well as the

HF electrolyte concentration. However, ECE is cost-inefficient on a wafer-scale, additionally, its process stability for high-throughput, in-line processes is critical on wafer-scale.

Metal-assisted chemical etching (MaCE) [14-18], is a purely solution-based and high-throughput technique. It consists of two successive steps, nucleation of metal nanoparticles (NPs) and anisotropic etching in a solution containing HF and oxidant agents [15]. Despite the numerous reports focused on the synthesis of silicon nanowires by using Ag as catalysts [15-17], there is no report concerning the formation of uniform and high-throughput mesoporous PSi layers. Here, we present a systematic study of Pt-nanoparticle-assisted chemical etching (PaCE). In contrast to Au or Ag, Pt is a very active catalyst [19] for decomposing H_2O_2 during MaCE. Pt has been shown to have significant higher etching rates compared to Au and Ag, producing highly luminescent microporous structures [14]. An additional question is whether the mesoporous layer can be also produced with improved etching speed. We present a detailed morphological study on PaCE to fabricate micro- or meso-PSi. The discussion on our results is based on a PtNP-Si nano-Schottky contact model.

2. Experimental

Czochralski-grown, single-side polished, p-type single crystal (100) silicon wafers with two different resistivities, i.e. 1-10 $\Omega\text{ cm}$ (p^-) and 0.01-0.02 $\Omega\text{ cm}$ (p^+), were used in the present study. Prior to the etching, the silicon wafers were cleaned in Piranha (98% H_2SO_4 / 30% $\text{H}_2\text{O}_2 = 3:1$, (v/v)) for 15 mins and then rinsed by DI water. Clean Si wafers were then cut into pieces of suitable size and dipped into 5% HF solution for 3 mins to remove the native oxide. Subsequently, the PaCE was carried out by immersing Si samples into 0.5 M HF and 1 mM K_2PtCl_6 solution for 3 mins for deposition of PtNPs (see supporting information at Fig. S1) and then etched in an aqueous etchant containing 5 M HF and 0.3 M H_2O_2 for 3mins. After etching,

the Si samples were rinsed by DI water and dried by N₂ gas blowing. All experiments were performed at room temperature inside a fume hood (~ 15°C).

The surface morphology of porous Si was observed using a field-emission scanning electron microscope (FE-SEM, FEI Sirion) and transmission electron microscopy (TEM, JEOL 2100F). PSi specimens for TEM were prepared in cross section and thinned using a Focused Ion Beam (FIB). The etching rate was determined by SEM cross-sections. Simulation of the Pt-Si nano-Schottky contact was done by MATLAB.

3. Results and Discussion

Fig. 1(a-d) show the cross-sectional SEM and TEM images of as-generated PSi in p⁺-Si. Silicon beneath the PtNPs was dissolved, drilling macropores of about $d_{macro} = 80$ nm in the <100> direction (see Fig. 1(b)). Meso-PSi was formed in areas without metal coverage as it has already been observed in ref. 14. The porosification of meso-PSi was very uniform, and its etching rate was nearly the same as the macropore etching rate below the PtNPs. Note that for MaCE with AgNPs under the same etching condition, SiNWs were obtained without formation of meso-PSi on the highly doped p⁺-Si (see supporting information at Fig. S2).

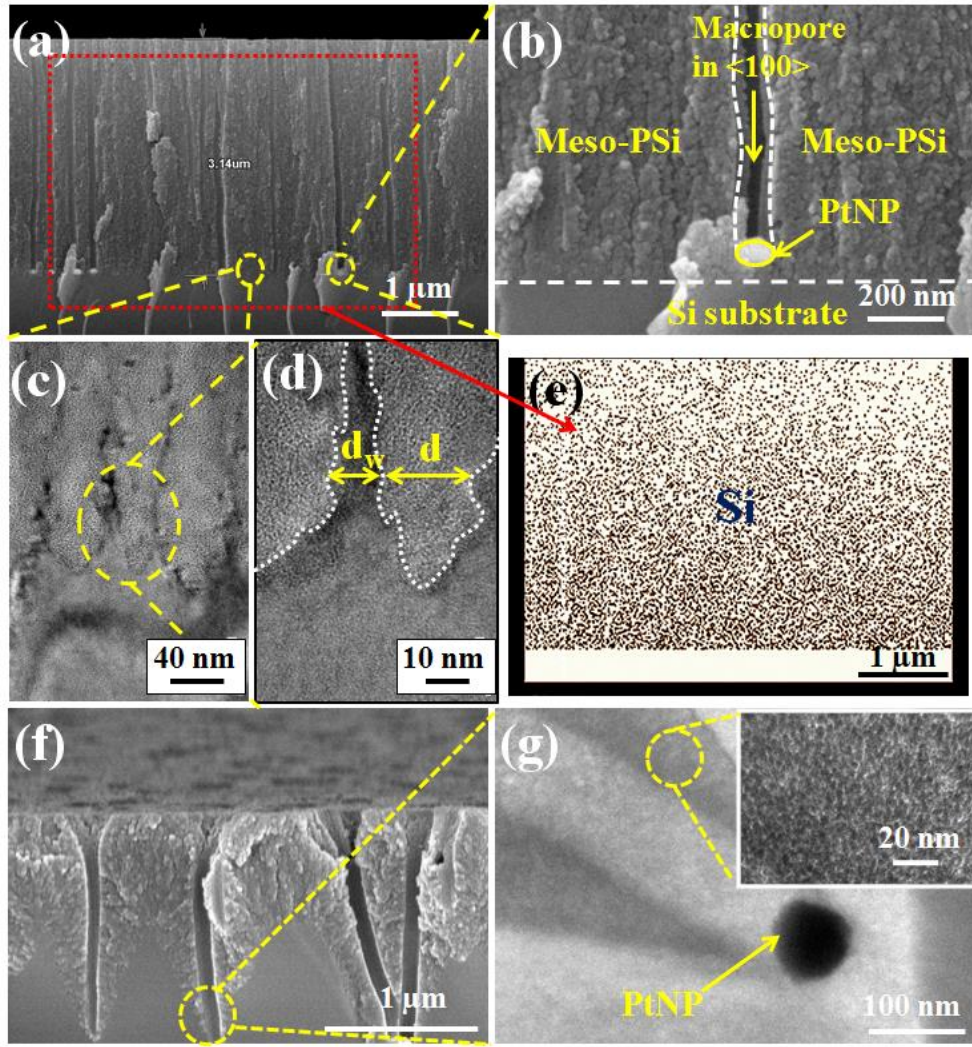
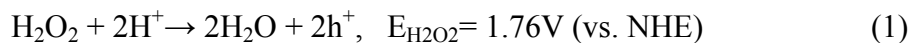


Figure 1. (a, b) Cross sectional SEM pictures of meso-PSi fabricated by etching of PtNPs loaded highly doped p^+ -Si substrate ($0.01\text{-}0.02\ \Omega\ \text{cm}$) in HF and H_2O_2 solution; (c,d) HRTEM images of meso-PSi at different magnification; (e) EDX mapping of Si; (f, g) Cross sectional SEM pictures of micro-PSi by etching of PtNPs loaded moderately doped p^- -Si substrate ($1\text{-}10\ \Omega\ \text{cm}$). (b) and (g) are the magnified view of (a) and (f) respectively. The dashed white lines show the border of PSi structure in (c) and (d).

The HRTEM images in Fig. 1(c-d) revealed more structural details of the meso-PSi region. The dark regions observed in the TEM images are due to the diffraction contrast created by strain fields along the PSi/Si interface. The pore diameter d is around 20 nm, and the pore wall thickness d_w increased with the depth ($d_w \sim 10$ nm at the bottom). The etched morphology has high similarity with electrochemically etched mesoporous layers [13]. The energy-dispersive X-ray (EDX) mapping in Fig. 1(e) reveals the gradually varying porosity of meso-PSi. Very low Pt signals are distributed in the meso-PSi layer, indicating the etching attack of the PSi sidewalls (see supporting information at Fig. S3). A similar behavior was observed for MaCE based on AgNPs [20]. To validate such an attack from the redeposited Pt nuclei, a Pt wire was placed close to the bare wafer. As a result the polished Si surface turned into PSi, verifying the slow dissolution of Pt in the etchant. The etched morphologies of Si were totally different for a lower Si doping level. For moderately doped p⁻-type Si, the macropores induced by PtNPs were surrounded by extremely high porous micro-PSi as shown in the SEM and HRTEM images Fig. 1(f) and (g). Compared with meso-PSi, silicon was less dissolved, resulting in non-uniform micro-PSi film. The micro-PSi films exhibit luminescence properties similar to those reported in ref. 14.

MaCE involves a local coupling of two redox reactions at the metal NPs. The etching process starts with H₂O₂ reduction. The surface area of metal NPs facing the etchant would act as cathodes:

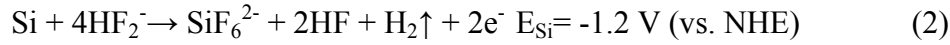
Cathodic reaction [17]:



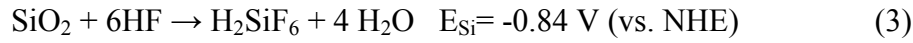
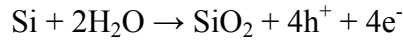
Since the metal-Si interface exhibits a much lower Schottky barrier height as compared to the electrolyte-Si contact, the generated holes are effectively injected through the metal-Si contact [21], leading to a h^+ -rich region of silicon which surrounds metal NPs [22]. Thus, NPs facing the silicon act as anodes for silicon dissolution.

Anodic reaction [17]:

Si dissolution could either be in divalent state (dissolution valence $n=2$)



Or in tetravalent state (electropolishing, $n=4$)



The driving force for anodic dissolution is the electrode potential difference between anode and cathode. As a consequence of the microscopic reactions, silicon beneath the metal NPs would be dissolved and the NPs would drill deep into the Si forming macropores. This mechanism is suitable for Ag induced etching, however, this cannot explain the PSi evolution using Pt as the catalyst.

In the following, we developed a qualitative model to explain the morphological differences between micro- and meso-PSi formed by Pt as a catalyst. In a physical picture, the morphology of porous silicon is determined by the rate limiting step being either the electronic transport over the electronic barriers of electrolyte/Pt and Pt/silicon or the chemical reaction rates involved [23]. Since Pt can decompose H_2O_2 more effectively than Ag [19], more holes would be injected into Si while using PtNPs as the catalysts. This leads to higher etching rates and different porosities

compared to Ag assisted etching. In this model, the doping level of the substrate will influence the hole transport over the Schottky barrier of Pt/silicon interface. For moderately-doped p^- -type Si, the transport will be dominated by thermionic emission whereas for heavily doped p^+ -Si, the transport will be dominated by tunneling [24]. It is expected that tunneling leads to higher local currents and therefore higher dissolution rates than thermionic emission, thus explaining the different porosities and etching rates.

To understand the difference between meso-PSi and micro-PSi in more detail, we simulated the electric field distribution around the PtNPs for the p^- and p^+ silicon (Fig. 2(a) and (b)) by following the nano-Schottky contact model developed by Tung [25] (simulation details seen in supporting information). Compared to highly-doped Si with a small space charge region (SCR) width ($W \sim 9\text{-}16\text{ nm}$), moderately-doped Si with a SCR width $W > 200\text{ nm}$ shows more twisted electrical field lines at the NP-Si interfacial boundary. The strength of the electric field at the boundary is enhanced and its direction turns back to the solution side. The holes would not only flow into the vertical direction, but also into the side direction, causing extra Si dissolution (see in Fig. 2(d))

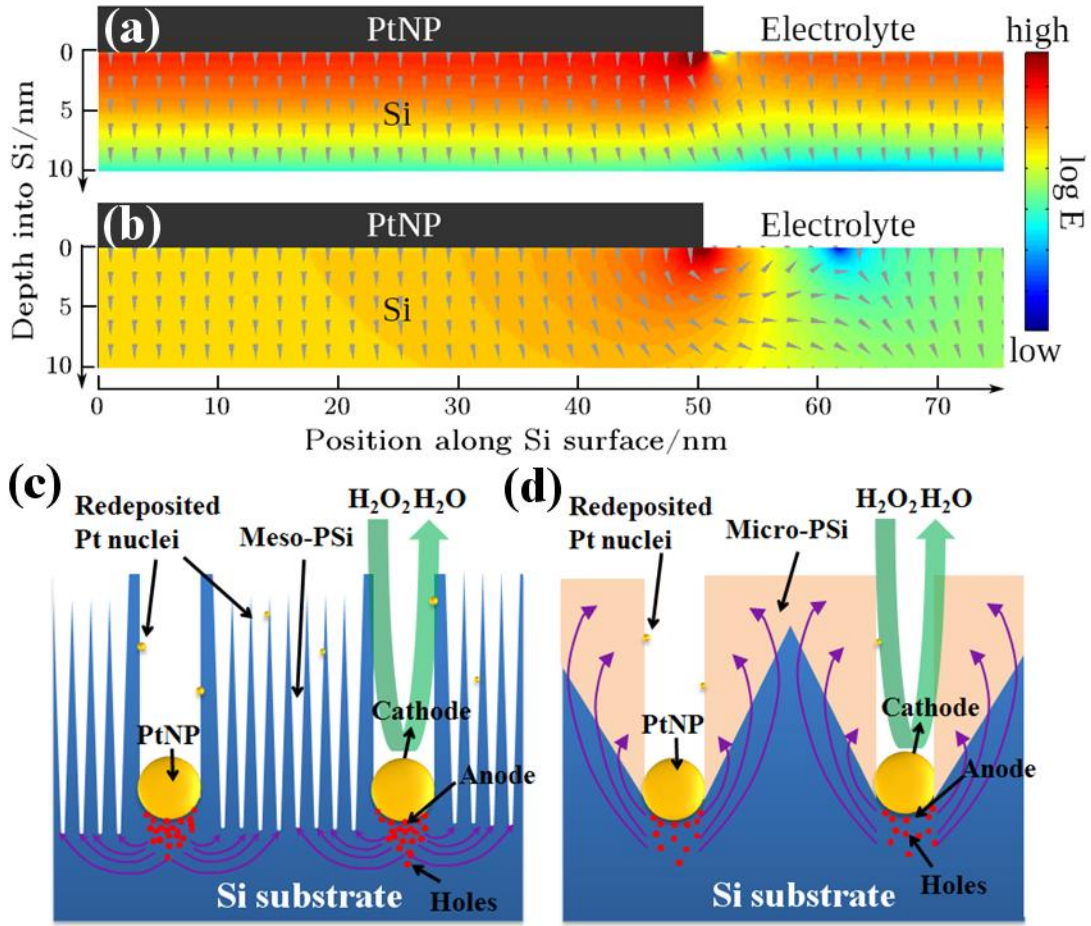


Figure 2. (a-b) Simulation of electrical field distribution of a NP (radius $R=50$ nm) decorated Si substrate with different SCR width: (a) 12 nm, and (b) 200nm. Schematic of the etching process: (c) Meso-PSi formation in highly doped p^+ -type silicon. The purple arrows point the flow direction of holes; (c) micro-PSi formation in moderately doped p^- -type silicon. The yellow circles are PtNPs. The red circles represent holes (Color version is available online).

This model can also explain why in the case of meso-PSi the pore walls are passivated. For highly-doped Si, holes easily tunnel through the SCR, and then move to the adjacent backside area as sketched in Fig. 2(c). This is very similar to ECE with applied bias supplying holes from the backside. Here, the numerous NP-Si cells act as microscopic electrodes providing an almost

uniform anodic bias. According to well-known ECE theory, d_w is usually constrained to the SCR width due to hole depletion [12,13], or smaller than 5 nm due to quantum size effects [2,24]. Here, the formed meso-PSi were firstly passivated by the SCR effect ($d_w \sim W$ see Fig. 1(d)), afterwards, due to the redeposited Pt nuclei at the sidewalls, pore walls were laterally etched until the quantum size effect constrains etching.

In order to demonstrate the flexibility of PaCE for controlling the porosity and etching rate, the influence of HF and H₂O₂ during etching of meso-PSi was studied as shown in Fig. 3. According to the ECE theory [24,26,27], there is a critical current density j_{PS} , which roughly defines the transition point from the PSi region ($j_A < j_{PS}$, charge-supply limited) to electropolishing ($j_A > j_{PS}$, chemical-reaction limited). The porosity is proportional to the j_A/j_{PS} . This theory can also be applied to MaCE [17]. Since $j_{PS} \propto C_{HF}^{3/2}$, decreasing the HF concentration would increase the porosity while keeping the j_A unchanged [24]. In other words, the Si dissolution shifts more to the tetravalent electropolishing regime (see Eq. (3)) and the etching becomes more isotropic leading to higher porosity as shown in Fig. 3(a). Meanwhile, the etching rate is lowered due to increased dissolution valence. The etching enters electropolishing region when the HF concentration is smaller than 3 M (Region I in Fig. 3(e), constant H₂O₂ concentration 0.3 M).

The second way to tune the porosity is changing concentration of the oxidizing agent. Because $j_C \propto C_{H_2O_2}$, increasing the H₂O₂ concentration would lead to an increased amount of holes available for injecting into Si [28]. Thus, j_A is enhanced, and the porosity would be increased. However, we found a slight increase of H₂O₂ concentration above 0.5 M (constant HF concentration 5 M) would significantly enhance j_A , causing strong etching non-uniformity and significant cracking of meso-PSi films. Stable mesoporous Si growth is only shown in the region II in Fig. 3(f). At high H₂O₂ concentration, lots of H₂ bubbles were observed due to fast etching. These bubbles would

cause inhomogeneous etchant diffusion, and meanwhile impose strong capillary forces to crack the highly porous PSi film of low mechanical strength [24]. More significant cracking would be created during N₂ drying of samples. High H₂O₂ concentration also led to the dissolution of the top of meso-PSi. Thus, the etching rate increase was lowered when the H₂O₂ concentration was higher than 0.75 M see in Fig. 3(f).

The porosity and the thickness of meso-PSi layer could be well controlled by changing HF or H₂O₂ concentration, and etching time within Region II. A meso-PSi membrane could be fabricated by using two step etching process consisting of low (0.3 M) and high (2 M) H₂O₂ concentrations shown in Fig. 3(c) and (d). The second step was applied for a very short time, and ethanol was added to reduce the capillary forces to reduce cracking.

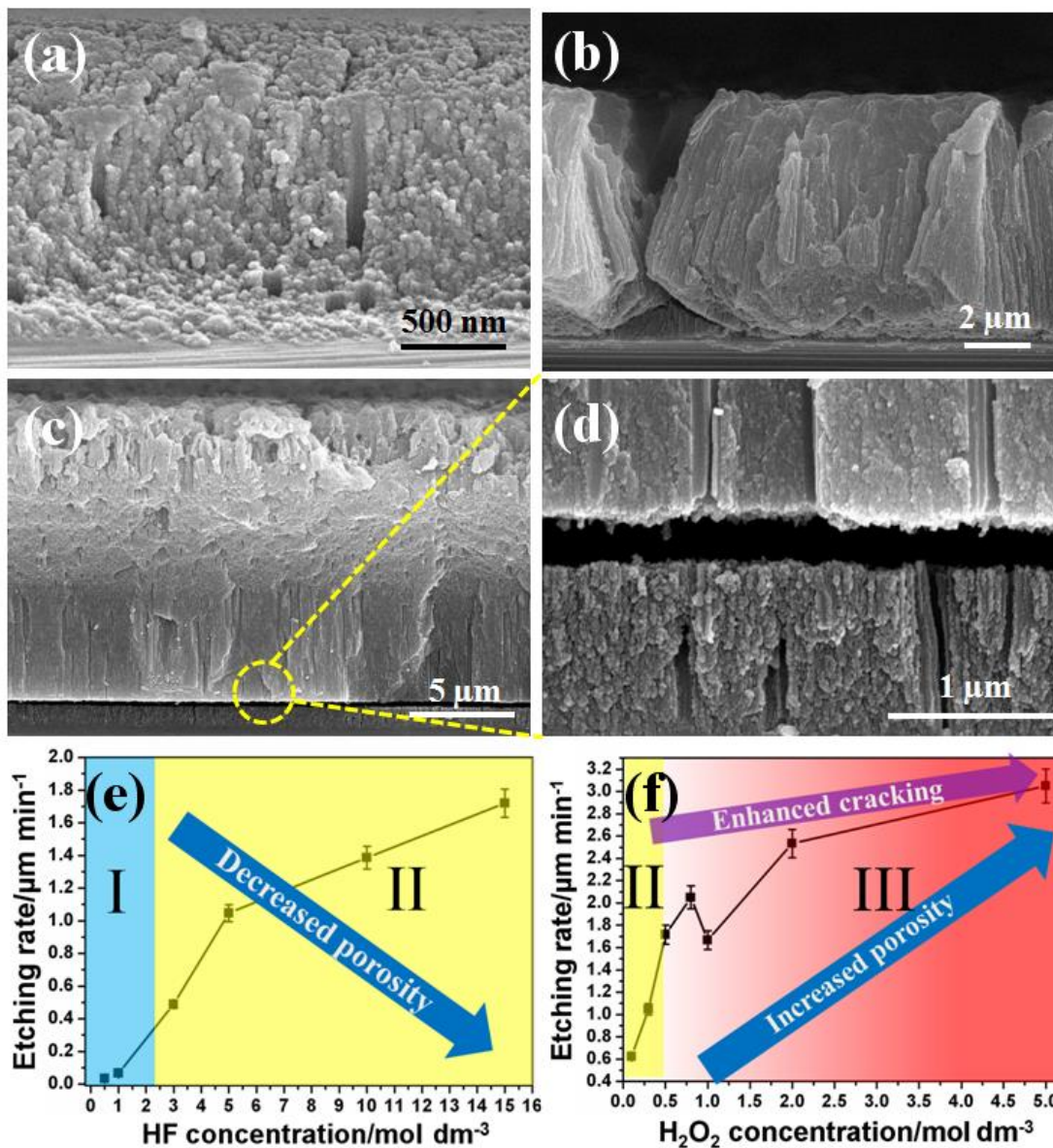


Figure 3. SEM images of meso-PSi formed at (a) 3 M HF and 0.3 M H₂O₂ (b) 5 M HF and 0.6 M H₂O₂; (c, d) A meso-PSi memberane fabricated using two etching steps (first step 5M + 0.3 M H₂O₂, second step 5M + 2 M H₂O₂); (e-f) Dependence of etching rate on the HF concentration while keeping H₂O₂ concentration constant 0.3 M (f) Dependence of etching rate on the H₂O₂ concentration while keeping HF concentration constant 5 M. I is the electropolishing regime, II is the stable meso-PSi growth regime, and III is the meso-PSi cracking regime.

4. Conclusions

In summary, we reported that PaCE is capable of fabricating uniform and meso-PSi. Etching rates of more than 1.7 $\mu\text{m}/\text{min}$ have been obtained under optimized conditions. The obtained meso-PSi shows superior uniformity over the micro-PSi. Electrostatic simulation based on the metal-Si nano-Schottky contact can qualitatively explain the morphological difference of PSi in moderately and highly doped Si. Our work provides a facile, cost-effective route to fabricate various PSi structures, which can be easily scaled to wafer size. Since the etching area would be no longer constrained by electrochemical cell size, this technique can be directly applied to layer transfer technologies in photovoltaics or surface micromachining in microsystem technologies reducing process complexities and improving the yield. The Pt can be recycled after the process and in principle be reused.

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