

Metal-assisted chemical etching in HF/H₂O₂ produces porous silicon

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(Received 30 May 2000; accepted for publication 25 August 2000)

A simple and effective method is presented for producing light-emitting porous silicon (PSi). A thin ($d < 10$ nm) layer of Au, Pt, or Au/Pd is deposited on the (100) Si surface prior to immersion in a solution of HF and H₂O₂. Depending on the type of metal deposited and Si doping type and doping level, PSi with different morphologies and light-emitting properties is produced. PSi production occurs on the time scale of seconds, without electrical current, in the dark, on both p - and n -type Si. Thin metal coatings facilitate the etching in HF and H₂O₂, and of the metals investigated, Pt yields the fastest etch rates and produces PSi with the most intense luminescence. A reaction scheme involving local coupling of redox reactions with the metal is proposed to explain the metal-assisted etching process. The observation that some metal remains on the PSi surface after etching raises the possibility of fabricating *in situ* PSi contacts. © 2000 American Institute of Physics. [S0003-6951(00)05542-X]

Porous semiconductors, especially porous silicon (PSi), have received a great deal of attention in the past decade due to applications in silicon-based optoelectronics,^{1–3} in chemical and biochemical sensing,^{4–7} and for direct introduction of high mass biomacromolecules in mass spectrometry.⁸ Finally, porous semiconductors are of interest, because they can potentially serve as compliant substrates for epitaxial growth.⁹

PSi is normally produced by anodic etching, with (n -type) or without (p -type) illumination.² PSi has also been made by chemical etching in HNO₃/HF solutions (stain etching), and by photochemical etching,¹⁰ both of which take place without external bias. Stain etching is usually slow (characterized by an induction period), irreproducible, unreliable in producing light-emitting porous silicon, and is mainly used for making very thin layers. Recently, it was shown that evaporating and annealing 150–200 nm of aluminum (Al) on Si results in rapid stain etching.¹¹ However, the PSi produced was ~10 times weaker in luminescence than anodically etched PSi of similar thickness.

This letter reports that introducing nanometer-size metal particles to the Si surface prior to immersion in an oxidizing HF solution results in a simple and effective way of producing PSi, a method termed H₂O₂ metal-HF (HOME-HF) etching. PSi with different morphologies and luminescence properties can be produced by varying: (a) the type of metal deposited, (b) the dopant type, and (c) the dopant level. Finally, the simplicity of this method should allow it to be scaled for mass production.

Silicon(100) wafers with different doping levels were used, including: p^+ (0.01–0.03 Ω cm), p^- (1–10 Ω cm), and n^+ (0.005–0.02 Ω cm) Si. 30–80 Å of metal (Au, Pt, or Au/Pd) was sputtered onto Si(100). Removing the native oxide from the silicon wafers before sputter coating is not necessary. Aqueous H₂O₂ was added to aqueous HF/EtOH solution in a Teflon beaker to produce a solution of 1:1:1 EtOH:HF(49%):H₂O₂(30%) immediately prior to immersing the metal-coated wafers. Etching time was varied from 2 to

30 s. A mask with rows of 3-mm-diam holes spaced by 6 mm was used to pattern the metal deposition for comparison of etching and luminescence properties in the presence and absence of deposited metal. The development of the pattern deposited using this mask was observed visually upon immersion in the etching solution, with a color change in the metal-coated region from gray to brown then to yellow, depending on the elapsed etching time. Gas evolution from the metal-coated area was clearly observed, especially for Pt and Au/Pd. In no case was any metal dissolution observed, in contrast to the behavior using thicker evaporated Al.¹¹ A high-resolution field-emission scanning electron microscope (SEM) (Hitachi S4700) was used to characterize the surface morphology, both in plane and in cross section. A SPEX fluorimeter equipped with a 500 W Xe lamp excitation source, two monochromators, and a Hamamatsu RT220P photomultiplier tube (PMT), was used to examine the photoluminescence (PL) spectral behavior. Luminescence images were acquired on an inverted microscope (Zeiss Axiovert 100) equipped with a 150 W Hg lamp and a color camera.

Figures 1(a) and 1(b) show SEM images of a Au-coated p^+ Si subjected to HOME-HF etching for 30 s. Large (~30 nm) interconnected pores propagating anisotropically perpendicular to the surface, similar to the morphology observed on anodically etched PSi from heavily doped Si,¹² are observed on the Au-coated areas [Fig. 1(a)]. In contrast, in areas between the Au on the same wafer [Fig. 1(b)], a much more compact structure with random arrays of small pores (~3 nm spaced by about 3 nm) can be seen, similar to anodically etched porous silicon from moderately doped (p^-) silicon wafers.¹² The etching depth is about 350 and 250 nm on and off the Au-coated areas, respectively. For n^+ and p^- silicon etched under identical conditions, the morphology in the Au-coated areas exhibits columnar structure similar to the p^+ sample [Fig. 1(a)], with small variations in pore size and etching depth. Off the Au-coated areas on both n^+ and p^- silicon the morphology resembles that of p^+ samples, but a dramatically smaller etch depth, merely 10 nm as shown in Fig. 1(c), was obtained for the p^- wafer.

Figure 2 shows the SEM images on and off Pt-coated

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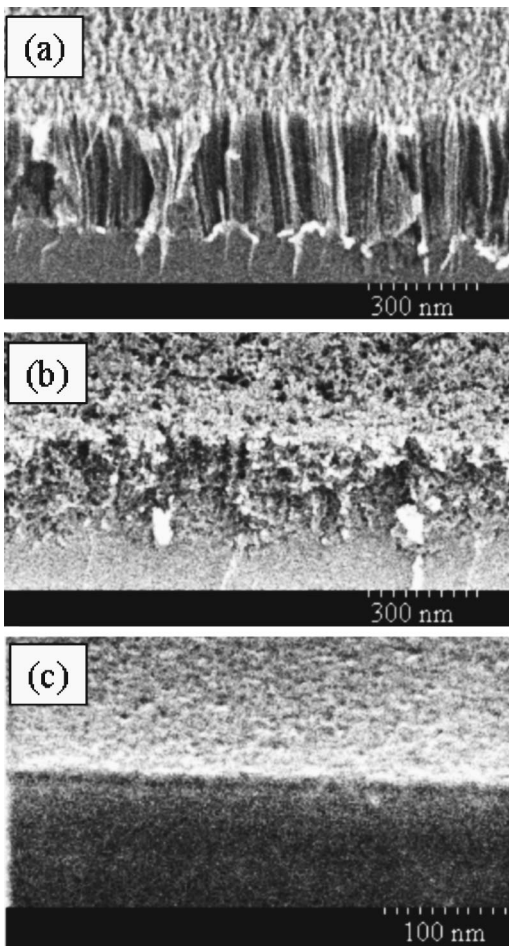


FIG. 1. SEM images of Au-coated Si(100) after etching in HF/H₂O₂ for 30 s. The top surface is tilted 30° from normal to reveal both top surface and the cross section. (a) Au-coated area on p^+ Si, (b) off the Au-coated area on p^+ Si, and (c) off the Au-coated area on p^- Si.

areas of a p^+ silicon subjected to HOME-HF etching for 30 s. A much rougher and deeper structure is produced on the Pt-coated sample than on Au-coated Si. In the Pt-coated area [Fig. 2(a)], columnar structures are clustered together at the tip, and the etch depth exceeds 1 μm . The area without Pt [Fig. 2(b)] is very flat with small ($\sim 5\text{--}20$ nm) but interconnected pores, and the etch depth is ~ 320 nm—small compared to the Pt-coated area but deeper than comparable areas on the Au-coated sample. For p^- wafers, the etch depths on and off Pt-coated areas are about 300 and 35 nm, respectively. The p^- wafers display smoother top morphology on the Pt-coated areas, while the off-Pt areas are rougher in depth than those for p^+ wafers, cf. Fig. 3. HOME-HF etching of Si coated with 1/1 Au/Pd was also studied—the morphology and luminescence properties of the PSi produced being similar to Pt-coated Si. For all doping concentrations examined (p^+ , p^- , and n^+), metal-coated areas always exhibit larger pores with columnar structure, while the off-metal areas always display smaller pores (3–5 nm) and randomly oriented structures. In each case the exact pore sizes and connectivity vary with doping levels, producing large differences in luminescence properties.

Comparing relative etch rates reveals that Pt-assisted HOME-HF etching proceeds much faster than Au-assisted etching. More importantly, PSi produced with Pt shows more intense PL than those produced by Au-assisted HOME-HF

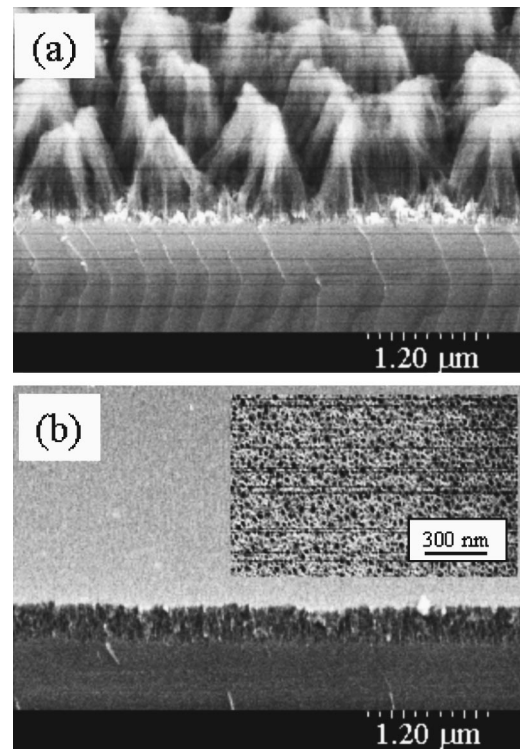


FIG. 2. SEM images of Pt-coated Si(100) after etching in HF/H₂O₂ for 30 s. The top surface is tilted 30° from normal. (a) Pt-coated area on p^+ Si, (b) off the Pt-coated area on p^+ Si with inset showing a high-magnification view of the top surface.

etching. Furthermore, depending on the doping type, doping level, and etching time, luminescence patterns can be formed which are correlated with the Pt deposition pattern. Figure 4 compares luminescence images of HOME-HF etched p^+ and p^- Si patterned with circular Pt areas. Stronger PL can be seen from the Pt-coated area for the p^+ wafer, while the uncoated area provides stronger PL in the p^- sample. Stronger PL is also obtained from the Pt-coated areas on n^+ Si (not shown). PL spectra taken from different areas on differently doped samples are shown in Fig. 5. Remarkably, the thin layer (35 nm) in the off Pt areas of p^- Si produced the strongest PL intensity among all samples, and was much more intense than ten times the thickness of PSi produced by anodic etching. In addition, the PL peaks are centered at 590 nm, which is blueshifted ~ 100 nm from PSi formed by anodic etching.² The intense luminescence is undoubtedly related to the off-Pt structure of HOME-HF etched p^- Si, in which small isolated peaked structures are observed.

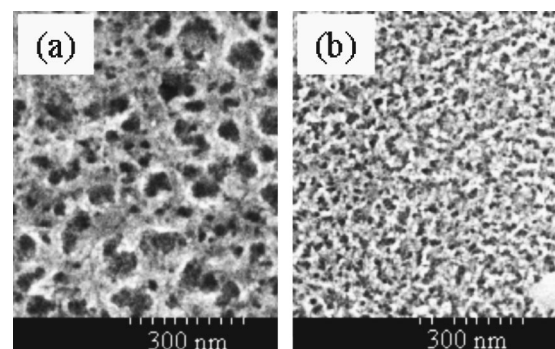


FIG. 3. Top-view SEM images of Pt-coated Si(100) after etching in HF/H₂O₂ for 30 s. (a) Pt-coated area of p^- Si, (b) off the Pt-coated area of p^- Si.

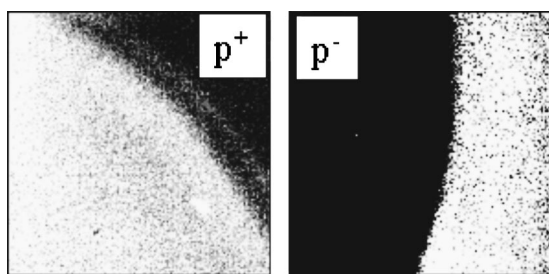


FIG. 4. Luminescence images of p^+ and p^- Si with patterned Pt dots after 30 s HOME-HF etching. The images are produced by exciting at 364 nm and collecting wavelength-integrated luminescence at $\lambda > 400$ nm. Due to the limited field of view only part of the Pt-coated dot is shown in the images—the concave side of the arc corresponding to the Pt-coated area.

AFM imaging indicates that these thin metal coatings on Si appear as nanometer-size (~ 10 nm) islands, with thermal annealing producing larger islands. However, the PSi pore sizes produced have no direct correspondence with the size or spacing of the deposited metal islands, i.e., the metal coating does *not* act as an etch mask. HOME-HF etching works not only for p -type Si but also for n -Si, even in the dark. Control experiments, in which wafers without metal coatings were immersed for the same period of time in $\text{H}_2\text{O}_2/\text{HF}/\text{EtOH}$, produced no morphological features observable by SEM and no detectable PL. The results clearly indicate that Pt, Pd, and Au facilitate Si etching, with Pt producing the fastest etching rate and most intensely luminescent PSi. In fact, these metals are required to obtain chemical etching under the conditions employed here.

Strongly luminescent PSi can also be produced adjacent to, but macroscopic distances away from, the metal-coated areas, in contrast to control experiments in which the absence of a metal coating correlates with the lack of detectable etching. This suggests that lateral transport of charge carriers and chemical species occurs during etching. HOME-HF etching may occur as a localized electrochemical process, with the nanometer-sized metal acting as a local cathode.

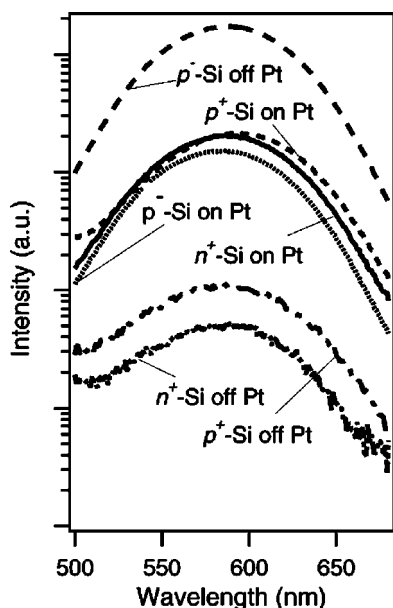
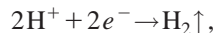
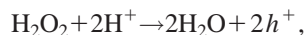


FIG. 5. Photoluminescence spectra taken from Pt-patterned Si after 30 s HOME-HF etching. The doping types and levels, as well as the locations from which the spectra were obtained, are as indicated.

Microscopically local anode (Si) and cathode (metal) sites form on the etched surface with local cell currents flowing between the sites during etching. In analogy with the pioneering studies of Si etching,¹³ the following mechanism is proposed:

Cathode reaction (at metal):



Anode reaction:



Overall reaction:



A critical feature of this reaction scheme is the generation of h^+ from H_2O_2 and the reduction of H^+ to form H_2 , both of which are facilitated by the metal particles. Since h^+ derives from H_2O_2 , this mechanism indicates that PSi can be generated in the same way regardless of doping type and level, as is observed. However, the difference in doping level is reflected in the etch depth away from metal-coated areas. In the uncoated areas higher doping correlates with faster etching and deeper etch depths at fixed times. The observation of much higher etch rates for Pt and Pd than Au suggest a catalytic role. Finally, it is well to note that H_2O_2 is but one possible oxidant, and others may work as well or better—the key feature being the ability to generate mobile holes at the metal-solution interface.

Rutherford backscattering analysis and x-ray photoelectron spectroscopy show that some metal remains on the metal-coated areas of the silicon surface after etching and rigorous rinsing, raising the possibility that HOME-HF etching can be used to make *in situ* metal contacts for PSi. Detailed characterization of the metal distribution in the porous structure and its relationship to transport properties of the PSi so produced illuminate the feasibility of preparing *in situ* contacts to PSi and will be reported separately.

This work was supported by the Department of Energy under Grant No. FG02 91ER45439. The Center for Microanalysis of Materials at the University of Illinois Materials Research Laboratory is supported under the same grant.

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