Metal-assisted chemical etching using sputtered gold: a simple route to black silicon

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Abstract
We report an accessible and simple method of producing ‘black silicon’ with aspect ratios as high as 8 using common laboratory equipment. Gold was sputtered to a thickness of 8 nm using a low-vacuum sputter coater. The structures were etched into silicon substrates using an aqueous H$_2$O$_2$/HF solution, and the gold was then removed using aqua regia. Ultrasonication was necessary to produce columnar structures, and an etch time of 24 min gave a velvety, non-reflective surface. The surface features after 24 min etching were uniformly microstructured over an area of square centimetres.

Keywords: silicon, gold, etching, nanostructure, sputtering

1. Introduction
Silicon porosification has been studied intensely since the early 1990s [1, 2]. The fabrication of silicon wafers with hollow pores ranging from <2 nm to >50 nm in diameter, while preserving the crystalline integrity of the surrounding silicon, has been explored for semiconductor applications [3]. Although the majority of this work has been undertaken using electrochemical methods, metal-assisted chemical etching (MaCE) has also been well studied [4]. Many types of noble metals have been used in MaCE, most commonly Ag, Au, Pt and Pd, and each provide different porous silicon morphologies [5]. On the other hand, gold-assisted etching tends to produce isolated, straight pores, only in regions covered by the metal [6]. Therefore, using gold metal can allow more control over the pore distribution.

In general, the metal acts as a catalytic site to promote the activity of the oxidant. Typically, a solution of HF/H$_2$O$_2$ is used, and the peroxy oxygen undergoes reduction to produce water. An electron-depleted region is formed in the vicinity of the metal, and the silicon is oxidized and dissolved away as SiF$_6^{2-}$.

Black silicon is closely related to porous silicon but consists of high-density vertical pillars or nanowire assemblies. Black silicon characteristically has low reflectivity, as apparent in its matte, black colour and has great potential in photovoltaic applications or antireflective coatings [7]. It has also been investigated as a superhydrophobic surface, assisted by electrowetting [8]. Traditionally reactive ion etching is used, but MaCE has also shown promise for production of black silicon [9, 10].

Some contributing factors to surface morphology include etchant composition, oxidizing agent, time of etch, agitation and others. In recent literature, agitation by ultrasonication has been shown to detach H$_2$ bubbles that accumulate on the substrate surface during normal etching procedures and inhibit uniform etch [12]. Depending on how the metal was deposited, ultrasonication has had very contradictory effects. Reasons for this have not been adequately explained. It has been shown that the time of etch is proportional to the etching rate [10]. The aim of this study is to determine the effect of ultrasonication on the etching of silicon.

2. Experimental details
Si (100) wafers were cleaned using a standard piranha surface treatment. The 18 × 6 mm$^2$ substrates were coated...
with sputtered gold using an Anatech Ltd. HUMMER VII Sputtering System set to deposit 8 nm. Each sample was submerged in a beaker containing 24 ml of aqueous etchant solution, comprised of H$_2$O$_2$ (4.3 M, 15 ml) and HF (2 M, 3 ml), and ultrasonicated in a VWR Model 250D sonicator for a duration of 6–24 min. Scanning electron microscopy (SEM) images were acquired with a Tescan Vega-II XMU VPSEM scanning electron microscope and atomic force microscopy (AFM) data were collected with an NT-MDT ST0505 system.

### 3. Results and discussion

Our approach was to develop a simple, easily accessible and scalable synthesis of black silicon using metal-assisted chemical etching with gold. To this end, we sputtered gold using low-vacuum sputter coater common to SEM facilities, and etched using an ultrasonication bath common to synthesis laboratories. In a typical experiment, an 18 × 6 mm$^2$ silicon (100) wafer was sputtered with a layer of gold using a simple sputtering apparatus. AFM showed this layer to be 4–5 nm thick, with a root mean square (RMS) roughness of 4.7 Å, similar to that of the silicon substrate.

Of the many factors that contribute to the control of uniformity of roughness over the surface area of the etched wafer, ultrasonication has been the least explored in the literature. Recent work suggests that bubbles of H$_2$ created during etch stick to the substrate and shield the silicon surface from the etchant [12]. Therefore, bubble coalescence is a key event in the production of a rough surface. When two bubbles coalesce on the Si surface in an explosive event, a larger daughter bubble is formed and tiny micron-scale droplets of etching solution, formed by the impact, are scattered near the merging site and across the surface of the substrate. These droplets continue etching underneath the daughter bubble and once the bubble grows large enough, it is liberated from the surface. Thus, ultrasonication plays an important role in the formation of deep trenches, and we initially undertook a study of ultrasonication.

The duration of etch was held constant at 6 min, with one sample agitated and the other not (figure 1). The non-agitated sample had a distinct ‘peaked’ pattern with relatively smooth edges and features, while the ultrasonicated sample showed similar topography with features of the order of 500 nm that dimpled the overall pattern (best depicted in figure 1(d)). The round, concave dimples were found consistently across the entire substrate. It appears that ultrasonication caused these finer features. We suspect that H$_2$ bubbles, formed from the etching reaction, were subsequently imploded by ultrasonication and quickly exposed the surface to HF. The pressure and heat generated at the site of an ultrasonication-generated bubble implosion likely accelerates the HF etch.

The samples looked different when the etch time was extended up to 24 min. With sonication, they took on a velvety, black appearance, reflecting little light compared to the parent silicon. Without sonication, there was an obvious ‘rainbow’ hue of interference colour, and the samples exhibited a strong iridescence. Attempts to measure the reflectance of the non-sonicated samples were hampered by this, and the data were not reportable. However, reflectance experiments could be carried out on the sonicated samples.

When the etching time was increased with ultrasonication, these dimples deepened and became meso- and macro-pores (figure 2). The pore diameters were polydisperse, and the structure was made more complicated as the overall peak pattern of the silicon surface became more extreme. Indeed, the structures seen after a 24 min etch appeared to be more uniform. The SEM images showed that the microstructure adopted an ever-increasing columnar appearance (figure 2). The structure has a random distribution of features, but the aspect ratio and columnar nature are most apparent when viewed at 45° to the plan view. When the substrates were cleaved and SEM images taken of the cross sections, the depth of the pores became apparent.

It was notable that etching up to 6 min produced a significantly different structure than etching up to 12 min or longer. We suspect the initial period of sonication etches slowly because there is a uniform film of gold. As the etching continues, the gold coalesces into assemblies of nanoparticles and then the etching can proceed faster, and can form deeper structures.

The aspect ratios of the features developed were relatively disperse, and there appeared to be a levelling off of this aspect ratio as the etch time was increased (figure 3). As the etch time increased, the porous features also became relatively more uniform in depth. This was an advantageous outcome because the goal was to produce deeply etched, thin, pillar-like structures by etching a high density of pores.

The roughened silicon surface was quite uniform, but extended inspection by SEM showed the occasional occurrence of a plateau with a different, dimpled texture (figure 4). This ‘upper layer’ of etched silicon appeared to become so significantly etched as time was increased that it lifted off from the lower layer. Indeed, black fragments were
Figure 2. The aspect ratio of surface features as a function of etch time. Panels (a)–(d) show a 45°-inclined view and panels (e)–(h) show a cross-sectional view.

Figure 3. The aspect ratio of surface features as a function of etch time. The etch rate fits a logarithmic trend (shown as a dashed line) with a coefficient of determination ($R^2$) of 0.9909.

observed visually in the solution at 18 and 24 min of etching. This phenomenon was repeatable, and the upper layer could be seen by SEM to have a thickness of the order of 10–25 µm, depending on the duration of the etch.

The reflectivity was measured for the samples etched for different lengths of time with sonication, where the radiance factor is the normalized radiance at that angle, compared to the illuminant (figure 4). The samples were illuminated normal to the surface, and the reflectivity was measured at 45° to normal. Because the samples were very matte, this non-specular reflection was similar at all angles of observation. It should be noted that the silicon was measured with an illumination angle at −45° to normal, in plane with the observation angle. This is necessary since the reflectance is highly specular for unetched silicon.

While the sample etched and sonicated for 6 min showed intermediate radiance, the radiance of the samples etched
Figure 6. SEM images of the same pore on two complementary edges of a cleaved substrate. The sample shown was etched for 24 min and gold catalyst has been removed by aqua regia.

for 12 min and longer was very low, around 10% across the visible spectrum. This corroborates our observation by SEM that the 6 min sample had a different surface structure likely due to the slow etch through the initial gold film, while the subsequent samples adopted a more uniform and deeply etched nanostucture. It is also striking that these samples differ very little (only at low wavelength for the 18 min etch), and so the larger aspect ratios at longer etch times seem to have little effect.

By comparing SEM images of samples etched for different lengths of time, it was observed that longer etch time produced thinner top layers that covered a decreasing fraction of the substrate. Figures 5(a) and (b) show a relatively complete top layer, with only a small amount of delamination to reveal the lower layer. As the etch time is increased, the upper layer is reduced to isolated plateaus (figures 5(c) and (d)). The etching continued through these plateaus and into the lower layer (figures 5(e) and (f)) as the etching continued. It was interesting to see that some pores etched in a ‘bent’ manner (figure 5(f)), a phenomenon that has been previously described [13].

In several panels in figure 5 there appear to be wider pores located around the outline of the upper layer. Cross-sectional SEM images showed that these were significantly deeper etched features (figure 6). It can be seen that one such pore was of the order of 45 μm in depth when the pore was serendipitously located on a cleaved edge (figures 6(c) and (d)). The pore is nestled in the top layer with roots throughout the lower layer. It seems likely that these pores in the top layer etched deeper than those formed elsewhere where a large gold particle was formed during sputtering. Given the simplicity of the coating technique, these deeper features were surprisingly rare.

4. Conclusions

The reported very simple sputter-etch method produced black silicon of very good quality that covered square centimetres. It can be easily carried out with common laboratory equipment and thus enables small-scale production of low-reflectivity, black silicon.

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