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Rimjhim Chaudhary
University of Pennsylvania, rimjhim@seas.upenn.edu

Hiromichi Yamamoto
Singh Center, hyam@seas.upenn.edu

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Abstract

This report describes fabrication of 100 to 200 nm diameter silicon nanopillars with ~140:1 aspect ratio using Metal Assisted Chemical Etching (MacEtch) process giving a high etch rate of ~930 nm/min, and also discusses an area dependence of the etch uniformity and rate, using 0.5 and 1 μm diameter, and 2 mm x 2 mm Au films. It is found that the etching using the Au film with the area of 0.2 μm^2 is uniform, but that with the area of more than 0.8 μm^2 is not, suggesting that the diffusion length of the species in MacEtch reaction underneath the Au film is ~300 nm.

Keywords

Nanopillar, Metal Assisted Chemical Etching, High Aspect Ratio

Disciplines

Engineering | Life Sciences | Physical Sciences and Mathematics

Fabrication of High Aspect Ratio Nanopillars using Metal Assisted Chemical Etching

Rimjhim Chaudhary[1] and Hiromichi Yamamoto[1, a)]
[1]*Singh Center for Nanotechnology, University of Pennsylvania*
3205 Walnut St. Philadelphia, PA 19104

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This report describes fabrication of 100 to 200 nm diameter silicon nanopillars with ~140:1 aspect ratio using Metal Assisted Chemical Etching (MacEtch) process giving a high etch rate of ~930 nm/min, and also discusses an area dependence of the etch uniformity and rate, using 0.5 and 1 μm diameter, and 2 mm x 2 mm Au films. It is found that the etching using the Au film with the area of 0.2 μm^2 is uniform, but that with the area of more than 0.8 μm^2 is not, suggesting that the diffusion length of the species in MacEtch reaction underneath the Au film is ~300 nm.

Key Words: Nanopillar, Metal Assisted Chemical Etching, High Aspect Ratio

I. Introduction

It is well known that silicon (Si) has some properties specific to the nanostructure, but not to the bulk planar Si,[1] such as enhanced performance in Lithium-ion batteries,[2] improved light trapping for high efficient photovoltaics,[3,4] light emission of nanowires,[5] and amplified sensitivity of chemical sensors.[6,7] A high aspect ratio nanostructure is expected to further enhance those unique properties.[8] The most common technique to obtain the high aspect ratio nanostructure is the Bosch process, where etching is carried out using a sequence of alternating steps of nearly isotropic silicon etching using SF_6 plasma and passivation of already etched silicon to prevent further lateral etching using a chemically inert polymer (typically, C_4F_8).[9] Although the Bosch process provides fast etch rates, it only allows one-directional vertical etching and the etch rate decreases as the aspect ratio reaches the point where SF_6 and C_4F_8 gases are not effectively switched.

Metal Assisted Chemical Etching (MacEtch) has attracted much attention in the above applications, owing to the controlled formation of porosity, nanocrystal, and nanowire in Si.[1,10] Furthermore, MacEtch offers a simple and low-cost way of fabricating extremely high aspect ratio nanostructure with a controllability of structural parameters such as orientation, length, and morphology.[10] The goal of this project is to perform the on-site inspection of MacEtch to make this technique available at Quattrone Nanofabrication Facility (QNF).

MacEtch is a wet etching process which uses the catalytic activity of noble metals (*e.g.* Au, Ag, or Pt) to etch semiconductor (Si) beneath the noble metal, in a mixed solution of an oxidant (*e.g.* H_2O_2) and an acid (*e.g.* HF). Figures 1 and 2 depict a schematic diagram of MacEtch process and the MacEtch process flow, respectively. As can be seen in Fig. 1, the electron holes are generated on the Au layer by the reduction of H_2O_2 and are injected into the Si substrate at the interface between the Si and Au layer. HF will dissolve away the oxidized Si atom by forming silicon hexafluoride ion (SiF_6^{2-}). The etch rate underneath the noble metal is much higher than that without the metal, due to the catalytic properties of noble metal, so that the metal layer descends into the semiconductor as the semiconductor is being etched directly underneath.[10–12]

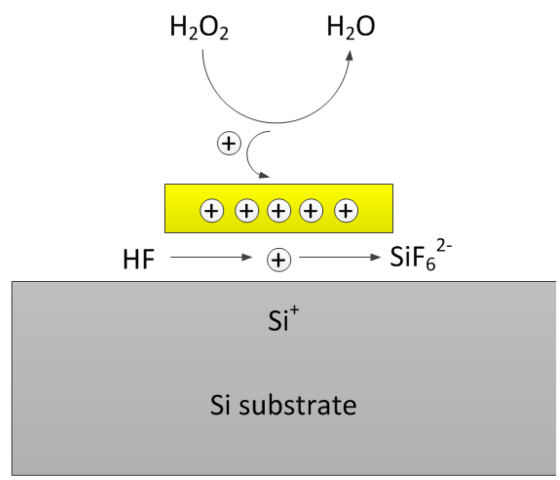

FIG. 1. A schematic diagram of Metal Assisted Chemical Etching

Thus, the etch rate of Si should be strongly affected by the generation of electron holes and the mass transfer of

a) Electronic mail: hyam@seas.upenn.edu

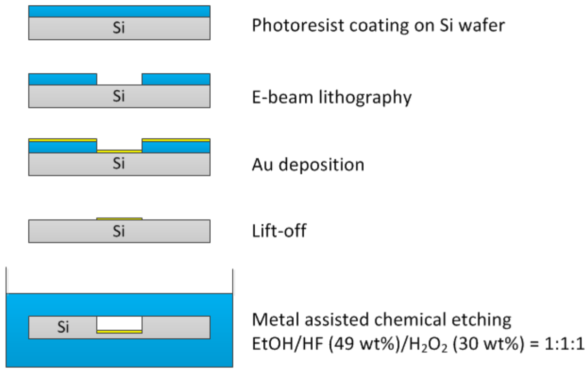

FIG. 2. Process flow for Metal Assisted Chemical Etching

reagents and by-products beneath the metal layer during the electrochemical reaction,[10] depending on some parameters of the solution, such as the concentration, the fraction, the temperature, adhesion between a metal film and Si substrate, and the area of the patterned metal film. The number of electron holes increases with increase in the area of the metal film. However, the previous report[13] confirmed that the etch rate decreases with increase in the Au coated area, suggesting that the diffusion of the species underneath the metal layer should have a strong impact on the etch rate. This report describes fabrication of 100 to 200 nm diameter Si nanopillars with ~140:1 aspect ratio using MacEtch process, and discusses an area dependence of the etch uniformity and rate, using 0.5 and 1 μm diameter, and 2 mm x 2 mm Au films.

II. Kinetics for Metal Assisted Chemical Etching

MacEtch essentially operates like an electrochemical cell with the metal coating acting like a cathode and the semiconductor acting like an anode, and the acid and oxidant solution acting like an electrolyte. In this report, Si is etched using a Au metal layer in a solution of HF and H_2O_2.[11] H_2O_2 is catalytically reduced by Au and the resultant electron hole current is injected into the Si layer beneath the Au layer, resulting in removal of Si underneath it. The cathodic and anodic reaction can be written as:[11]

Cathode:

$$H_2O_2 + 2H^+ \rightarrow 2H_2O + 2h^+ \tag{1}$$

Anode:

$$2Si + 12HF + 6h^+ \rightarrow 2H_2SiF_6 + 6H^+ + H_2\uparrow \tag{2}$$

The related current at the cathode, I_c and anode, I_a, can be written as:

$$I_\mathrm{c} = A_\mathrm{Au} N_\mathrm{c} F k_\mathrm{c} [H_2O_2]^\mathrm{m} [HF]^\mathrm{n} \tag{3}$$

$$I_\mathrm{a} = A_\mathrm{Si} N_\mathrm{a} F k_\mathrm{a} [HF]^\mathrm{p} \tag{4}$$

where m, n, and p are constants, A refers to the electrode area of the material indicated in the subscript, F refers to Faradays constant, [ ] refers to the concentration of the species (in mol/m^3) enclosed within the brackets that is in the etching solution, k_c and k_a refer to the rate constant for the cathode and anode reactions, and N_c and N_a refer to the number of holes produced/consumed per molecule of H_2O_2 and HF in the cathodic and anodic reactions. The rate limiting reaction is assumed to be the generation of electron holes *i.e.* the anodic reaction. Using these cathodic and anodic current value, the etch rate is given in the following equation:[11]

$$\ln v = m \ln[H_2O_2] + n \ln[HF] + \ln k_\mathrm{c} + \ln \frac{A_\mathrm{Au} N_\mathrm{c} F}{S N_\mathrm{h} Q \chi} \tag{5}$$

where v is the etch rate, N_c is the ratio of the number of holes to the number of H_2O_2 molecules in the cathodic reaction, N_h is the stoichiometric ratio of holes to Si in the anodic reaction, χ is atomic density in Si (5 x 10^{28}/m^3), and Q is the charge carried by a single electron hole (1.6 x 10^{-19} C). This equation relates the etch rate v with the exposed metallic area A_Au, which is the area of the top surface of the Au layer plus the exposed area of the bottom surface of the Au layer during MacEtch reaction. S is the projected area of the surface over which etching is taking place. C. Q. Lai *et al.*[11,14] also gives $A_\mathrm{Au}/S = 13/9$ for a Au film with a square array of square holes of width b and period $2b$, suggesting that the etch rate is independent of Au area.

III. Experimental Section

A. E-beam Lithography

The Si wafer was cleaned with buffered oxide etch (BOE) for 1 min, followed by a de-ionized (DI) water rinse. A 100 nm thick poly(methyl methacrylate) (PMMA) film was spin coated at 1500 rpm for 45 sec, followed by a bake at 180 °C for 5 min on a hot plate. For e-beam lithography, the acceleration voltage was 50 kV, the beam current was 100 pA, and the objective lens aperture was 40 μm. The e-beam dose was 200 μC/cm^2, and the dose time was 2 μsec (for pitch size = 2, using Beamer)[15] in the area of 300 μm x 300 μm with the total dots of 60000 x 60000. The PMMA film exposed was developed in IPA:DI water (3:1) for 60 sec, followed by rinsing in IPA for 60 sec.

B. Au Deposition and Lift-off

A 20 nm thick Au film was deposited onto the developed PMMA film under a base pressure of ~8.0 x

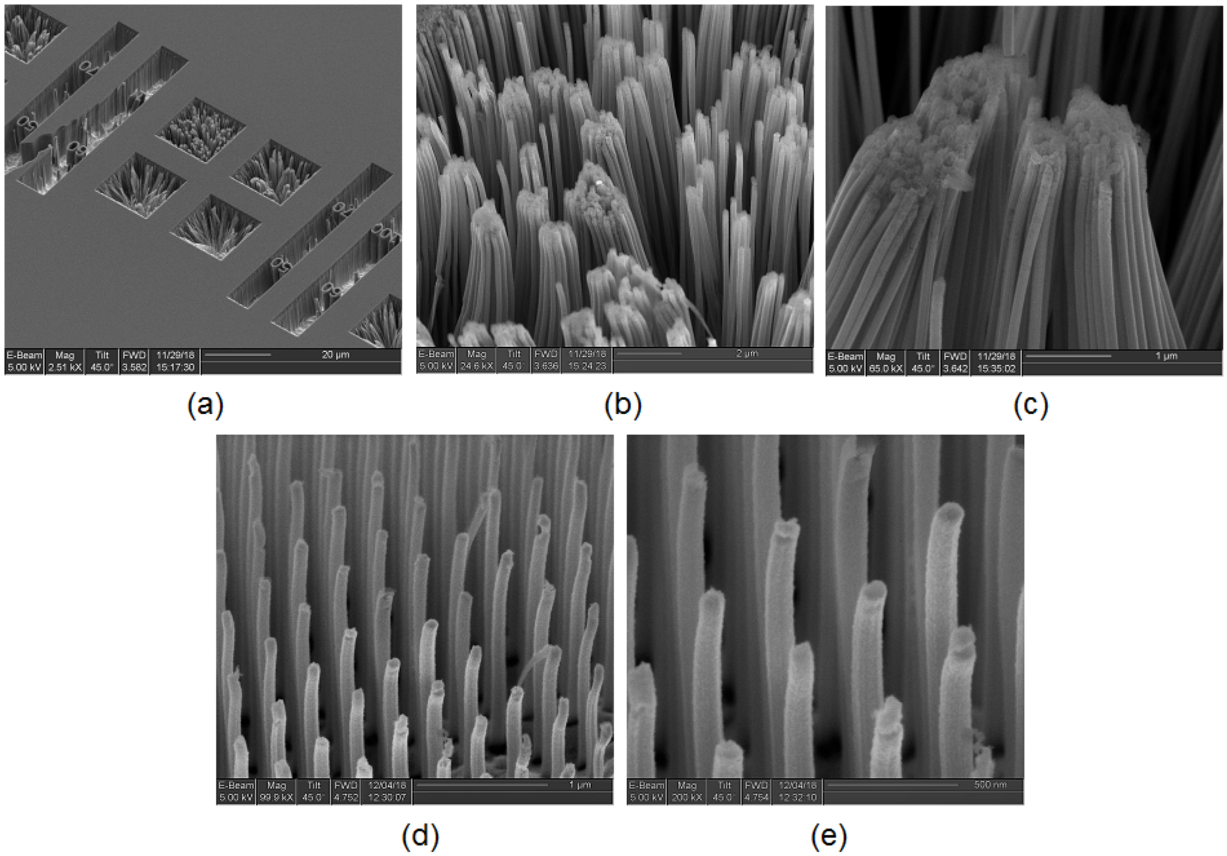

FIG. 3. SEM images of Si nanopillars after MacEtch process; (a) overview of 100 to 200 nm diameter nanopillars without treatment of critical point drying. The patterns of 50, 60, 70, and 100 in (a) show radii of the pillars in nm; (b) 100 nm diameter nanopillars without treatment of critical point drying; (c) zoom-in of (b); (d) 100 nm diameter nanopillars with treatment of critical point drying; (e) zoom-in of (d).

10^{-8} Torr, using a PVD-75 e-beam evaporator (Kurt J. Lesker) with a deposition rate of 0.3 nm/sec. The PMMA film was removed using lift-off by sonicating the sample in acetone for few seconds, followed by drying using a nitrogen gun, leaving behind only the Au film deposited directly on the Si wafer. The pattern lifted-off was 100, 120, 140, and 200 nm diameter through-holes in 20.25 μm x 20.25 μm film regions. The numbers of 100, 120, 140, and 200 nm diameter through-holes were 51 x 51, 48 x 48, 46 x 46, and 40 x 40 circles, respectively. The minimum edge-to-edge distance between through-holes was ~300 nm

C. Metal Assisted Chemical Etching and critical point dry

For performing the MacEtch, the Si wafer with Au pattern was immersed in 2:1:2 (v/v) mixture of ethanol, HF (49 wt%) and H_2O_2 (30 wt%) for 15 min.[12] The sample was then rinsed with DI water, and dried using a nitrogen gun if the sample was not treated with the critical point dryer (Tousimis). If the sample was treated with the critical point dryer, the sample was rinsed with DI water, followed by complete replacement of DI water by anhydrous methanol (diluting the sample into methanol three times consecutively without drying). The sample was placed in the bath filled with anhydrous methanol in the critical point dryer. Then, the sample was processed by the critical point dryer where the methanol was replaced by low surface tension CO_2 liquid, and was dried in the tool.

IV. Results and Discussion

A. High aspect ratio Si nanopillars

Figure 3 shows SEM images of Si nanopillars after MacEtch process; (a) overview of 100 and 200 nm diameter Si nanopillars without treatment of critical point drying; (b) 100 nm diameter nanopillars without treatment of critical point drying; (c) same region, higher magnification (b); (d) 100 nm diameter nanopillars with treatment of critical point drying; (e) same region, higher magnification (d). As seen in Figs. 3(a) to 3(c), the nanopillars are susceptible to collapse due to the surface tension of the DI water. To avoid this collapse and bundling of nanopillars, critical point drying was performed to dry the wafer in a low surface tension CO_2 liquid, thus avoiding the collapse. Figures 3(d) and 3(e) clearly indicate equally

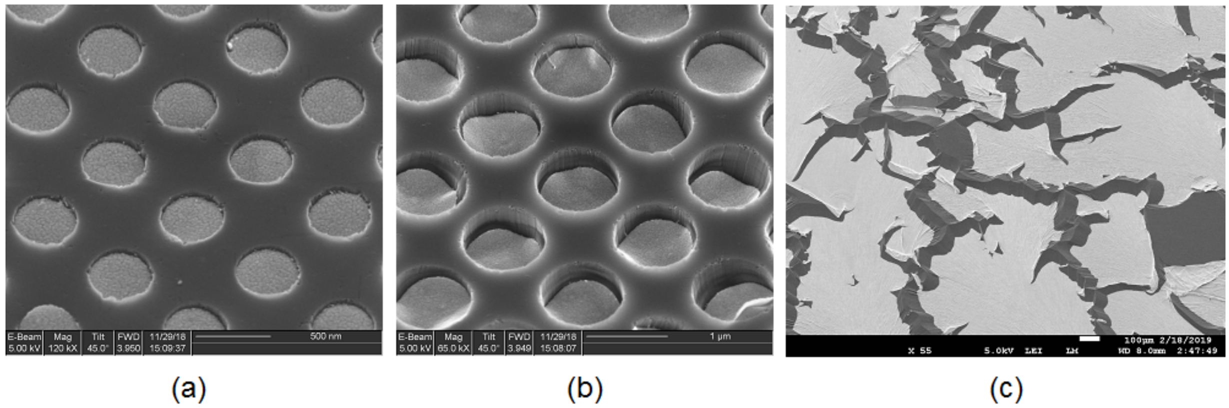

FIG. 4. SEM images of (a) 500 nm diameter (area = 0.2 μm^2), (b) 1 μm diameter (area = 0.8 μm^2), and (c) 2 mm x 2 mm (area = 4 x 10^6 μm^2) Au films without through-holes in their films after MacEtch process with the same condition as the 100 to 200 nm diameter nanopillars.

spaced, vertical, and free-standing Si nanopillars. The height of the Si nanopillars obtained is roughly estimated to be ~14 μm, thus giving an etch rate of ~930 nm/min, which can be estimated from Fig. 3(a). Furthermore, the aspect ratio of 100 nm diameter Si nanopillar is seen to be ~140:1, which is not achievable with Bosch process (50:1 to 60:1).[8]

B. Comparison between Au films with and without through-holes

MacEtch process of the Au film with through-holes is compared with that of the Au film without through-holes in its film, to discuss the mass transfer effect underneath the Au film. The total areas of 20 nm thick Au films with the 100, 120, 140, and 200 nm diameter through-holes are 389.6, 384.0, 377.5, and 359.8 μm^2, respectively, as described above. Those areas give an averaged area of 378 μm^2. Figure 4 shows SEM images of (a) 500 nm diameter (area = 0.2 μm^2), (b) 1 μm diameter (area = 0.8 μm^2), and (c) 2 mm x 2 mm (area = 4 x 10^6 μm^2) 20 nm thick Au films without through-holes, after MacEtch process with the same condition as the nanopillars. Figure 4(a) shows that the etching underneath 500 nm diameter Au film is uniform, whereas Figure 4(b) indicates that the etching underneath 1 μm diameter Au film is not uniform (the aspect ratio of the hole is ~5:1). For 2 mm x 2 mm Au film, the Au film is torn apart during MacEtch process,[13,16] as seen in Fig. 4(c).

The etch rates for 0.2 μm^2 (500 nm diameter), 0.8 μm^2 (1 μm diameter), and 4 x 10^6 μm^2 (2 mm x 2 mm) area Au films without the through-holes were ~1, ~13, and ~1800 (maximum) nm/min, respectively, whereas the etch rate for 378 μm^2 area Au film with the through-holes was ~930 nm/min. It is obvious that the etch rate is not proportional to the area of the Au film without through-holes, which should be ascribed to non-uniform etching underneath the Au film with the area of more than 0.8 μm^2, due to the lack of through-holes for the mass transfer during the MacEtch process. In other words, through-holes must be created in the large Au film for uniform etching. This study also shows that the 300 nm edge-to-edge distance between 100 nm diameter through-holes works well for the uniform etching underneath the 20.25 μm x 20.25 μm area Au film, suggesting the diffusion length of the species in MacEtch reaction is ~300 nm.

V. Summary

This study presented fabrication of Si nanopillars using MacEtch process. The etch rate and the aspect ratio achieved for 100 nm diameter nanopillars were ~930 nm/min and ~140:1. However, the nanopillars collapsed during the standard drying process, due to the surface tension of DI water. This difficulty was overcome by critical point drying. The MacEtch process using the Au film with through-holes was compared with that without through-holes. The etching using the Au film with the area of 0.2 μm^2 was uniform, but that with the area of more than 0.8 μm^2 was not, suggesting that the diffusion length of the species in MacEtch reaction underneath the Au film is ~300 nm.

VI. Acknowledgements

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