FABRICATION OF SILICON NANOSTRUCTURE BY METAL-ASSISTED ETCHING AND ITS EFFECTS TO MATRIX-FREE LASER DESORPTION/IONIZATION MASS SPECTROMETRY

C.W. Tsao1,*, J.T. Huang1, Y.C. Cheng2, W.Y. Chen1 and C.C. Chien2
1Department of Mechanical Engineering, National Central University, Jhongli, Taiwan
2Cathay Medical Research Institute, Cathay General Hospital, Sijhih, Taiwan
3Department of Chemical & Materials Engineering, National Central University, Jhongli, Taiwan

ABSTRACT

Silicon nanostructure surface fabricated from metal-assisted etching have been demonstrated as high sensitivity matrix-free laser desorption/ionization mass spectrometry chip. The silicon nanostructure morphology was found to have direct effect to the mass spectrometry ionization efficiency. Creation of different silicon nanostructure morphologies by changing the metal thickness, etching time and etchant composition in metal-assisted process was explored and its effects to mass spectrometry ionization efficiency was investigated in this paper.

KEYWORDS: Nanostructured silicon surface, Nanofilament silicon, Metal-assisted etching, Matrix-free laser desorption/ionization mass spectrometry, Desorption/ionization on silicon

INTRODUCTION

Mass spectrometry (MS) is one of the major analytical techniques in biological analysis. Developing a simple, fast and efficient MS chip becomes an intriguing topic for researchers in recent years. A novel high sensitivity, matrix-free MS chip called desorption/ionization on silicon was first proposed by Siuzdak.[1] The MS chip utilizes high surface/area ratio porous silicon surface replacing organic matrix solution to ionize biomolecules. Except porous silicon surfaces, various nanoscale silicon surfaces such as silicon nanowire[2], nanofilament silicon[3] and silicon nanocavity array[4] have been investigated for matrix-free MS chips by using different nanofabrication techniques. In those research demonstrations, it was found that the silicon nanostructure morphologies have direct effect to the MS detection sensitivity with an optimized value of pore size and depth. Information about the nanostructure morphology to ionization efficiency still limited and need further development. This paper study the fabrication of silicon nanostructure morphology and its effect to the MS ionization efficiency.

Fabrication of silicon nanostructure using metal-assisted etching presenting in this paper exhibits as a fast and efficient way to produce MS chips with high MS detection sensitivity. The silicon nanostructures fabricated from the metal-assisted etching process were first proposed by Li and Bohn[5]. Silicon wafers was first sonicated in acetone bath for 30 minutes followed by DI water rinse and nitrogen blow dry to clean the silicon surface. A thin noble metal layer was then deposited onto a bare silicon substrate followed by immersing the metal-coated silicon in hydrofluoric acid (HF), hydrogen peroxide (H₂O₂) and ethyl alcohol (EtOH) mixture etching for couple seconds. The metal-assisted etching process exhibits good process controllability to generate different silicon nanostructures. By changing the noble metal, metal layer thickness, silicon substrate resistivity, etchant composition and etching time, different silicon nanostructures with different pore depths, sizes and densities can be created across silicon substrate to study silicon nanostructure morphology effects to mass spectrometry efficiency.

RESULTS AND DISCUSSION

The metal-assisted etching acts as localized electrochemical etching process. Electrodeless etching occurs at the metal/silicon interface in which each nanometer size metal particles acts as a local cathode and silicon surface acts as an anode. Metal particles promote the H₂O₂ decomposition and cause electron holes injection into the silicon surface and silicon was dissolved by the HF to create pits or nanostructures on the surface. Thus, presence of metal catalyst layer plays an important role in this electrodeless etching process. Effects of metal catalysis layer to silicon nanostructure creation were experimentally investigated. 3nm, 5nm and 10nm thick of Au were deposited onto 10cm diameter P-type (100) silicon substrates by E-beam evaporator to investigate the metal thickness effects to silicon nanostructure generation. The Au-deposited surface morphology shown in Figure 1a–c exhibits differently with the layer thickness. From the top and cross-section silicon nanostructure after metal-assisted etching shown in Figure 1d–f, it can be clearly observed that the silicon nanostructure is highly correlated to the deposited metal surface. In the experimental demonstrations, in 3nm thick Au (Figure 1a) PVD deposition conditions, the metal particles surface coverage rate is usually low. In such condition, the particle interspace area is higher than the metal particle area. During metal-assist etching process, due to the large space between metal particles, the nanopores created by each individual particle will have less chance to connect or combine with neighboring nanopore. As consequence, porous-like nanostructure will be formed across the silicon substrate. On the other hand, in the conditions of high surface coverage rate such as the 5nm (Figure 1b) and 10nm Au (Figure 1c) case, most majority of silicon will be removed leaving individual silicon “posts” to create wire or filament-like nanostructure the silicon substrate as shown in Figure 1e and Figure 1f after metal-assisted etching. Other process controls such as silicon substrate resistivity, etchant composition and etching time were investigated. The results shows that etching time have direct effect to the depth of silicon nanostructure and the higher silicon substrate conductivity promote higher etching rate. In etchant composition study, more lateral etching occurs when hy-
Hydrogen fluorine concentration increases which results an increasing pore size near the silicon surface and when the hydrogen peroxide concentration increases, higher redox reaction occurs at the metal/silicon interface resulting higher etching rate during the etching process.

Figure 1: FE-SEM image of (a) 3nm Au (b) 5nm Au and (c) 10nm Au deposited on P-type (100) 0.01~0.02 Ω • cm silicon substrate. The 3nm, 5nm and 10nm Au coated silicon substrates were immersed into 1:1:1 volume ratio HF/H2O2/EtOH mixture for 60 seconds to create nanostructures. (d-f) show cross-section and top view (on the bottom right corner) image fabricated from 3nm (d), 5nm (e) and 10nm (f) thick of Au-coated silicon substrate.

The nanostructure silicon surface was used as matrix-free mass spectrometry chip and the performance was characterized by recording the MS signal intensity of des-Arg9-Bradykinin (MW:904) model peptide using a SELDI-TOF mass spectrometer. The effect of nanostructure depth to the MS chip performance was shown in Figure 2a. 10^-7 M, 10^-8 M and 10^-9 M sample loading was used. In all cases, the MS signal intensity increasing with metal-assisted etching time from 30 to 300 seconds and decade when etching time increases. This shows that a higher pore depth doesn’t promote higher MS detection sensitivity and an optimized value of 5.2 μm depth (300 seconds etching time) was found. Similar tendency was also observed with the pore size to the MS signal intensity. Figure 2b shows that the rough silicon surface present strongest MS detection sensitivity followed by filament and porous silicon surface. Wire-like silicon nanostructure exhibit lowest detection sensitivity among all. Those findings indicate that silicon nanostructure geometry have more effects to the MS signal intensity than the silicon nanostructure pore depth or size.

Figure 2: (a) MS signal intensity correspond to the metal-assisted etching time. Red, green and blue bars show 10^-7 M, 10^-8 M and 10^-9 M des-Arg9-Bradykinin sample loading respectively and the purple solid line indicates depth of silicon nanostructure. (b) MS signal intensity correspond to the silicon nanostructure geometry fabricated from metal-assisted process.

To investigate the effects, atomic force microscope (AFM) was used to measure the silicon nanostructure surface roughness (Rq). As shown in Figure 3a, the resulting silicon surface roughness increases with etching time from 30 to 300 seconds then decrease to 600 seconds. This tendency is analogous to the MS detection intensity. It was presume that
a rougher surface enhance stronger analyte absorption to the nanostructured surfaces resulting higher MS signal intensity. To further prove this postulation, the des-Arg⁹-Bradykinin model peptide was labeled with FITC fluorescence dye and measure the fluorescence intensity using fluorescent microscope. Figure 3b shows the fluorescence intensity increases with etching from 30 to 300 seconds then decrease to 600 seconds which contest with the MS signal intensity measurements.

![Figure 3: (a) MS signal intensity correspond to surface roughness measured from 30x30µm (red solid line) and 1x1µm (green solid line) AFM scan with various metal-assisted etching time. (b) Fluorescence microscope image (top right corner) and the light intensity profile correspond to metal-assisted etching time](image)

**CONCLUSION**

Effects of metal-assisted etching process parameters creating silicon nanostructure have been reported. The metal thickness have significant influence to the silicon nanostructure morphology while other process parameters such as etching time, etching composition have more effects to the silicon nanostructure pore size and depth. Silicon nanostructure morphologies effects to MS ionization efficiency was also investigated. It was found that higher surface roughness can significant enhance the ionization efficiency due to better analyte absorption to the silicon nanostructure surfaces.

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**CONTACT**

*C.W. Tsao, tel: +886-3-4267343; cwtsao@nec.edu.tw*