

Single Batch Process for Area-Selective Formation of Si Micropore Array and Metal Filling

H. Sato^a, K. Mori^a, T. Homma^a, T. Osaka^a, S. Shoji^b
^aDept. of Applied Chemistry and ^bDept. of Electrical Engineering and Bioscience, Waseda University
 3-4-1, Okubo, Shinjuku-Ku, Tokyo 169-8555, Japan

Electrochemical reaction enables to perform alternative processes, such as deposition (reduction) and etching (oxidation), within the identical apparatus by controlling the electrode potential. Such a feature could be advantageous to develop simple processes to fabricate various micro and nanostructures. In this study, we attempted to develop simple single-batch process consisting of area-selective micropore array formation by Si electrochemical etching and metal filling by electrodeposition using single electrolyte, which contains HF for etching and metal ion for the deposition.

Figure 1 shows experimental procedure of the present work. In order to initiate the micropore formation, inversed pyramid shaped pit array was formed by anisotropic alkaline etching prior to the Si electrochemical etching. We designed a test pattern of the pit array on the foreside of Si substrate and formed Au/Cr micropatterned shade mask on the backside. Si electrochemical etching was carried out in the electrolyte containing 1.5 wt% HF, 350 g/l of Ni(OSO₂NH₂)₂·4H₂O and 8.15 wt% C₂H₅OH. During the etching, halogen lamp illuminated the backside of Si substrate to generate holes which act as Si dissolution agent. The holes were generated area-selectively by the shade mask and were focused at the edge of the each pit. Following the etching, electrode potential was switched to cathodic potential to deposit Ni into the micropores using the same electrolyte. Then Si substrate was removed using alkaline etchant to release the Ni microstructures formed in micropores. The fabricated microstructures were observed by a scanning electron microscope (SEM, Hitachi S-4700).

First, the Si electrochemical etching was carried out in the electrolyte and the formation condition of the micropores was observed. It was revealed that high aspect ratio etching were performed in the electrolyte containing Ni(OSO₂NH₂)₂·4H₂O, suggesting that Ni²⁺ did not affect the micropore formation at the Si surface. Following the electrochemical etching, the electrode potential was switched to cathodic potential for the electrodeposition of Ni.

Figure 2 shows cross-sectional SEM image of the specimen after the Ni deposition. It is confirmed that the Ni is filled into the micropores successfully without damages of the pore wall during the Ni electrodeposition.

After dipping the Ni filled specimen into alkaline etchant to remove metallic Si region, Ni pillar structures were observed. Since they were prepared using the micropore arrays formed at Si surface as molds, the length and diameter of the Ni pillars can be controlled precisely by the micropore formation conditions, such as the size of initiation pit, current density, and reaction time.

From these results, it was confirmed that single batch process consisting Si etching and metal filling was achieved, which could be useful to form various micro and nanostructures, such as the high aspect ratio pillar array.

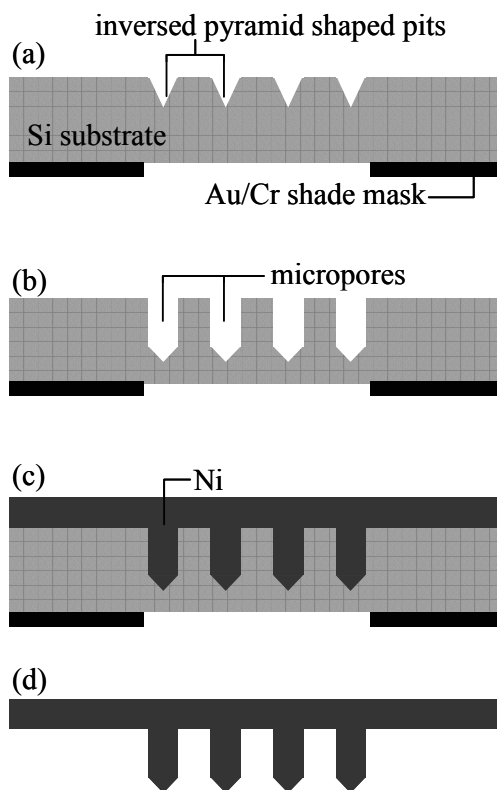


Fig. 1 Experimental procedure; (a) alkaline etching and Au/Cr patterning, (b) Si electrochemical etching, (c) Ni electrodeposition, (d) alkaline etching to remove metallic Si region.

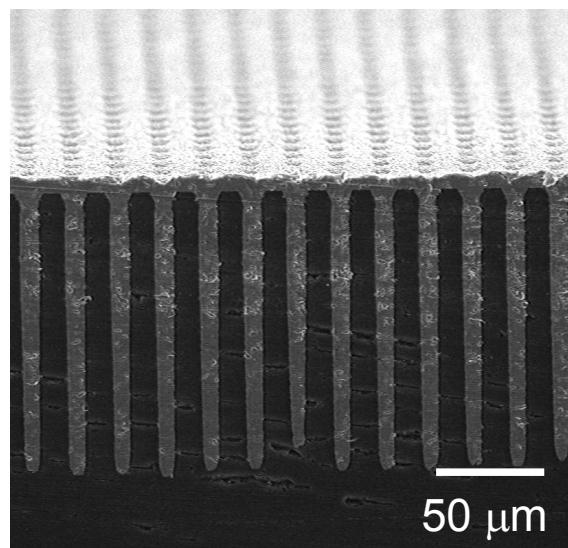


Fig. 2 Cross-sectional SEM image of Ni filled specimen.

Acknowledgements

This work was financially supported in part by the Grant-in-Aid for Scientific Research (C), MEXT, Japan and by the Research Grant from the Shorai-Foundation, and performed at the 21st Century Center of Excellence (COE) Program “Practical Nano-Chemistry”, MEXT, Japan.