Abstract

This paper reviews microscale processes to fabricate three-dimensional structures, in particular, high-aspect-ratio arrayed structures, using precise electrochemical etching process. Array of sharp micropits were pre-formed on the front side surface of Si wafer and the electrochemical etching was carried out using aqueous HF solution, with the back side illumination to generate holes, which diffused to the edge of the micropits to proceed the dissolution of Si with fluoride species. In order to form high-aspect-ratio pores at selected areas, a shade mask pattern was fabricated on the back side surface to align the illumination to the pre-patterned area on the front side surface. The parameters, such as HF concentration, current density and hole diffusion length, were optimized and uniform array of straight pores was formed into the designed area of Si wafer.

Subsequently the surface of the pores was thermally oxidized to form SiO₂ layers, and arrayed glass tubes with picoliter volume were fabricated. On the other hand, the pore filling with metal was attempted using electrodeposition to obtain array of the metal needles. For this, the “single batch” process was developed to form the pore array and metal filling with single electrolyte, and array of metal micro needles was successfully formed. These processes demonstrated capability and possibility of the electrochemical processes for microscale fabrication, and further precise processes can be developed using these approaches.

Keywords: Electrochemical etching; Electrodeposition; Micropore array; Micro needle array; High-aspect-ratio microstructure; Three-dimensional microstructure; MEMS; Micro reactor

Contents

1. Introduction .................................................. 468
2. Area-selective formation of high-aspect-ratio pore array into Si wafer using electrochemical etching ................. 469
3. Fabrication of picoliter-volume glass-tube array into Si wafer using electrochemical etching and wet-thermal oxidation .... 471
4. Fabrication of metal micro-needle array into Si wafer using “single batch” process consisting of Si electrochemical etching and electrodeposition ................................................................. 471
5. Summary .......................................................... 473
Acknowledgements ................................................ 474
References .......................................................... 474

1. Introduction

High-aspect-ratio micro and nano structures are key components for various microscale devices and systems, such as MEMS and μTAS [1–19]. For example, ordered arrays of uniform pores are applicable to micro-channels for micro-fluidic and filtering devices [5–7]. Microscale tube and chamber structures are also required for micro reactors [8–9]. Micro and nanoscale needles can be applied to precise injector for cell [10–14], painless injectors [11–14], and microelectrode for electric measurement of targeted
microscopic area [15–17], etc. The key processes to fabricate these high-aspect-ratio structures are deep etching to form pores and uniform coating or filling to modify the pores. For the deep etching, dry processes such as reactive ion etching (RIE) have been widely used [20–22], which require relatively high initial and running costs and have limitation for fabricating the structure with maximum aspect ratio up to 30–40. On the other hand, electrochemical or wet processes, which are applicable to wide surface area with relatively low cost, have capability for precise etching to fabricate high-aspect-ratio pores. It is well known that electrochemical etching process of Al has been used to form highly ordered array of nanoscale pores [23,24], and such an electrochemical etching can be used for Si wafer: the etching with aqueous HF solution proceeds straightly along Si (1 0 0) facet, forming branched pores [25–29]. In order to utilize such an anisotropic etching to form straight pores into Si wafer, photo-assisted electrochemical etching process was proposed [27–31]. In order to utilize the array of the pores to various devices and systems, their selective formation to designed microscale area was attempted. Furthermore, the modification of the pore arrays was also attempted to form various functional structures, such as picoliter-volume glass-tube arrays, as well as metal micro-needle arrays. The following sections will describe the processes for fabricating these structures.

2. Area-selective formation of high-aspect-ratio pore array into Si wafer using electrochemical etching

Fig. 1 shows basic process steps to fabricate the array of high-aspect-ratio pores into Si wafer. N-type Si (100) wafers were used, whose front and back side surfaces were coated with 140 nm thick Si$_3$N$_4$ layer by low-pressure chemical vapor deposition (LPCVD), which was then micro-patterned using photolithography and RIE. After dipping in 0.5 wt% HF solution to remove the native oxide, the substrate was immersed in 20 wt% KOH solution at 90 °C to form array of inverted-pyramid-shaped micropits at the surface by anisotropic etching. The micro-patterned Si$_3$N$_4$ layer serves as the protective mask for the alkaline etching, and the micropits act as initiation sites for the electrochemical etching to form high-aspect-ratio pores into the Si wafer. The micropit pattern was 100 μm$^2$, and ca. 2000 pits were arranged at interval of 10 μm in a 1000 μm diameter domain on the wafer. After the anisotropic etching, the entire Si$_3$N$_4$ layer on the back side surface was removed by RIE. Following this step, two types of patterned Au/Cr masks, shown in Figs. 2(a) and (b), were formed on the back side surface. For the electrochemical etching process, the wafer was mounted at the bottom of an electrochemical cell and the back side surface of the wafer was illuminated using a halogen lamp (15 V, 150 W) during the etching to generate hole. In the case with the rim type Au/Cr mask (Fig. 2(a)), entire back side surface was illuminated, while only selected areas, corresponds to the patterned areas of the front side surface (Fig. 2(c)), were illuminated with the shade mask type one (Fig. 2(b)). Table 1 shows the bath composition and operating conditions for the electrochemical etching. The current density at the electrochemical etching was estimated by taking the actual surface area of inverted-pyramid-shaped micropits into account.

Fig. 3 shows representative cross-sectional scanning electron microscope (SEM) image of the etched specimen prepared with the rim type or shade type masks on the back side surfaces. With the rim type mask, the pore located at the edge grew faster than those at the inner part, as shown in Fig. 3(a). On the other hand, as is clearly seen in Fig. 3(b), the pores grew uniformly with shade mask type pattern. These results suggest that the excess amount of the holes were supplied to the edge in the case with the rim type mask due to nonlinear diffusion of the holes, while such a nonlinear diffusion was inhibited with the shade
mask type pattern aligned with the pattern pre-formed on the front side surface. Thus control of hole-diffusion condition is significant factor for the area-selective formation of the array of uniform pores into Si wafer.

Fig. 4 shows representative cross-sectional SEM images of the etched specimens prepared under various conditions. In the case of the etching with 0.1 wt% HF solution at 2.4 mA/cm², it seems to proceed horizontally, rather than vertically, as is seen in Fig. 4(a). The electrochemical etching of Si (1 0 0) wafer is known to proceed vertically under the hole-transfer-limited condition, i.e., at the lower current density than critical current density $J_{ps}$. $J_{ps}$ is estimated from following equation [27],

$$J_{ps} = C e^{1.5} \exp \left( \frac{-E_a}{kT} \right),$$

where the constant $C$ is 3300 A cm² (wt% HF)$^{-1.5}$, $e$ is HF concentration, the activation energy $E_a$ is 0.345 eV, $k$ is Boltzmann constant, and $T$ is the temperature. At room temperature and 0.1 wt% HF condition, $J_{ps}$ is estimated to be 0.12 mA/cm², which is lower than 2.4 mA/cm². Therefore the rate-limiting factor under this condition is fluoride species, rather than hole, resulting in the side etching. On the other hand, vertical pores were formed with 1.0 wt% HF ($J_{ps}$ is 4.8 mA/cm²), as shown in Figs. 4(b)–(d), while larger diameter pores were formed with an increase in the current density from 0.24 to 24 mA/cm². The smaller diameter pores, shown in Fig. 4(b), were due to reduction of space charge region of Shottky barrier at the bottom edge of the pores, where holes were focused under low-current density. On the other hand, larger diameter pores with rough surfaces were formed, as shown in Fig. 4(d), due to the current density (24 mA/cm²) higher than the $J_{ps}$ of 4.8 mA/cm². From Fig. 4(c), the moderate conditions to form straight pores with identical diameter to that of the micropits are 1.0 wt% HF concentration and 2.4 mA/cm² of current density. At the HF concentration region higher than 1.0 wt%, hydrogen-associated Si fluorides, such as SiH₂(F₂) and SiH₂(SiF), are generated and adsorbed on Si surface [32], resulting in the rough features of the formed pores (Fig. 4(e)).

It should be also noted that the diffusion length of the holes, i.e., the thickness of the wafers, is also one of the key parameters to govern the condition of pore formation. For example, the pore length was not uniform (Figs. 5(a) and (b)) with 625 μm thick wafer, since the nonlinear diffusion of the holes was enhanced with longer diffusion length. In the case of thinner wafer with 200 μm thick, on the contrary, non-uniform formation of the pores were also observed, which could be due to the penetration of light through the Si wafer to generate the holes at near surface region [33]. Therefore, in order to decrease hole diffusion...
length and inhibit the light penetration, 400 μm thick wafer was used, and as a result, uniform pores were formed, as shown in Figs. 5(c) and (d).

3. Fabrication of picoliter-volume glass-tube array into Si wafer using electrochemical etching and wet-thermal oxidation

As described, array of high-aspect-ratio pores were formed into Si wafer, which are applicable to microchannels for fluidic devices, filtering devices, etc. Moreover, they can be utilized as templates for fabricating various functional microstructures. From this viewpoint, we attempted to fabricate the array of picoliter volume glass tubes using this structure [34,35].

Fig. 6 shows representative process steps. After formation of the pore array, the specimen was treated with wet-thermal oxidation at 1100 °C for 180 min to form the 1.0 μm thick glass (SiO2) layers on the pore surface, as shown in Fig. 6(b). The SiO2 layer on the back side surface and Si3N4 layer on the front side surface were removed by precise mechanical polishing (Fig. 6(c)), and the specimen was immersed in 25 wt% of aqueous tetramethylammonium hydroxide (TMAH) solution at 90 °C to expose the glass layers, as shown in Fig. 6(d).

Fig. 7 shows representative SEM images for the fabricated glass-tube array. Well-ordered, uniform array of the glass tubes, which exactly follow the uniformity of the shape of the macropore array, is formed. The glass-tube array could be applied to various micro-reactors, and as a preliminary experiment, aqueous rhodamine B solution was injected to monitor a fluorescence reaction using these tubes. Irradiation of excitation light through the wall of the glass tube, red fluorescence was clearly monitored, confirming the validity of the tubes for the application of microreactors for aqueous solutions.

4. Fabrication of metal micro-needle array into Si wafer using “single batch” process consisting of Si electrochemical etching and electrodeposition

Another application of the arrayed micropores is to use them as a template to form the micro-needle array. An important feature of the electrochemical process is that, it
can perform oxidation (etching) and reduction (deposition) in the same apparatus simply by alternating the applied potential. Therefore, we attempted to utilize this feature to develop “single batch” process, consisting of the area-selective formation of arrayed pores by the Si electrochemical etching followed by metal electrodeposition into the pores [36].

In the following section, the value of cathodic current density is expediently expressed with minus number. The electrolyte composition and operating conditions for the single batch process are listed in Table 2. Fig. 8 shows the fabrication process. After the pore formation, the applied bias was switched to negative direction to carry out the electrodeposition of Ni, which was added to the “etchant” for the pore formation. Then the specimen was immersed into 25 wt% of aqueous TMAH solution at 90°C to remove Si wafer part to release the Ni deposits, as shown in Fig. 8(d).

Initially, influence of metal salt addition on the pore formation was investigated and it was confirmed that it did not affect the pore formation condition during the anodic etching process. Next, the single batch process was investigated. Following the electrochemical etching of the Si wafer, Ni was electrodeposited into the arrayed high-aspect-ratio pores by applying cathodic potential at constant current density, i.e., switching the applied potential from anodic to cathodic after the Si electrochemical etching.

Fig. 9 shows representative cross-sectional SEM image of the specimen after the Ni electrodeposition. This Ni electrodeposition was carried out by applying cathodic current density of $-16 \text{ mA cm}^{-2}$ for 600 min. Apparently, Ni was successfully filled into ca. 200-μm-depth pore without void-like defects. This result confirms that the electrochemical single batch process consisting of the electrochemical etching of Si wafer and the metal
electrodeposition using single bath can be successfully achieved. Then the Ni filled specimen was immersed in the 25 wt% of TMAH aqueous solution at 90 °C to remove the Si wafer.

Fig. 10 is the representative SEM image of the obtained Ni micro-needle array. In this figure, it is confirmed that every Ni micro-needle possessed sharp tip with smooth surface. As described, electrochemical single batch process developed in this study is a quite simple fabrication process for high-aspect-ratio structures, such as array of micro-needles, which is applicable to form various microdevices and systems.

5. Summary

In this paper, microfabrication processes using electrochemical etching of Si wafer for various kinds of high-aspect-ratio structures were reviewed. First, area-selective pore formation process with photo-assisted Si
electrochemical etching was described. For this process, the shade mask pattern on the back side surface, aligned with the area selectively formed pattern on the front side surface, was applied to control the illumination condition, i.e., that of the hole generation to form the array of uniform pores into the Si wafer at selected areas. By applying additional treatment including wet-thermal oxidation to form glass (SiO₂) layers on the surface of these pores, arrayed glass tubes with picoliter volume can be obtained. On the other hand, the “single batch” process to form array of metal micro-needles was developed to form the array of pores and metal filling with single electrolyte. As described, the electrochemical processes have capability and possibility for precise microscale fabrication, and using these processes, various micro and nanoscale fabrication could be possible.

Acknowledgements

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