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Silicon Dioxide Micropillars for Sieving Fabricated by Macroporous Silicon-Based Micromachining

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In this paper, a new macroporous silicon-based micromachining technique and its application are reported. Macropores are formed on a silicon substrate by electrochemical etching in hydrofluoric acid. This etching technique has been used to fabricate regularly arrayed holes with a high aspect ratio (depth/width). In this work, the etching technique is extended to form not only holes but also silicon structures. The interesting points of this etching technique are that the etched width can be controlled during the etching without affecting the existing silicon structures, and the etched width less than the lithographic resolution can be achieved. Using these features, silicon dioxide pillars mutually separated by the space of 100 nm have been fabricated in a channel formed on a silicon substrate. These structures will be used for deoxyribose nucleic acid (DNA) separation.

1. Introduction

Recently, sensor devices have been required to be made smaller with higher performance. In order to satisfy these requirements, micromachining techniques have been employed to fabricate sensors on a silicon wafer. The micromachining techniques have numerous similarities to the techniques used for fabricating semiconductor devices. However, the silicon etching techniques used are different between sensors and semiconductor devices. When a semiconductor device is fabricated on a silicon wafer, the surface of the wafer is usually processed. However in the case of micromachining, silicon has to be

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etched to a depth of about 10 μm to form silicon structures and in some cases entirely through the wafer to isolate it thermally from the substrate. Thus, several silicon etching techniques have been developed for micromachining.

In order to fabricate devices of smaller size and with higher performance, the silicon etching technique is required to fabricate complicated silicon structures in small number of process steps. Using conventional silicon etching techniques, it is difficult to satisfy these requirements. Electrochemical etching in hydrofluoric acid (HF) is one of the solutions available for fabricating a complicated silicon structure in small number of process steps.

In this paper, the electrochemical etching technique is described and one of the applications, which is achieved by macroporous-silicon-based micromachining, is discussed.

2. Materials and Methods

2.1 *Overview of electrochemical etching*

Electrochemical etching has been studied since the 1950s as an electropolishing technique and much attention has been paid to porous silicon formation since the 1990s.[1,2] Porous silicon is classified based on its diameter into three groups, as shown in Table 1.[3] Micro- and mesoporous silicon are formed isotropically and are highly interconnected, while the macroporous silicon is formed directly on the wafer surface. Lehmann and Föll found that the small pits formed on the surface prior to electrochemical etching work to initiate macropores, in 1990.[4] The location of the macropores can be controlled using the small initial pits. However, this etching technique has been used only to form holes on the silicon wafer. We focus on the macropore formation technique as a silicon wet etching process to fabricate silicon structures.

2.2 *Mechanism of macropore formation*

Some models have been proposed to explain the formation of porous silicon and their reviews can be read in the literature.[5,6] In these studies, much attention has been paid to microporous silicon due to the photo- or electro-luminescence from it.[7] Lehmann and coworkers have focused on macroporous silicon, and proposed its formation mechanism[4,8,9] and its applications have been proposed by Lehmann *et al.*[10] and Ottow *et al.*[11] A brief explanation of macropore formation is given in this section.

Macropores are usually formed on n-type silicon. In electrochemical etching, an electronic hole works as a trigger for a chemical reaction of silicon dissolution. Electronic holes are minority carriers in n-type silicon, and thus have to be supplied during the

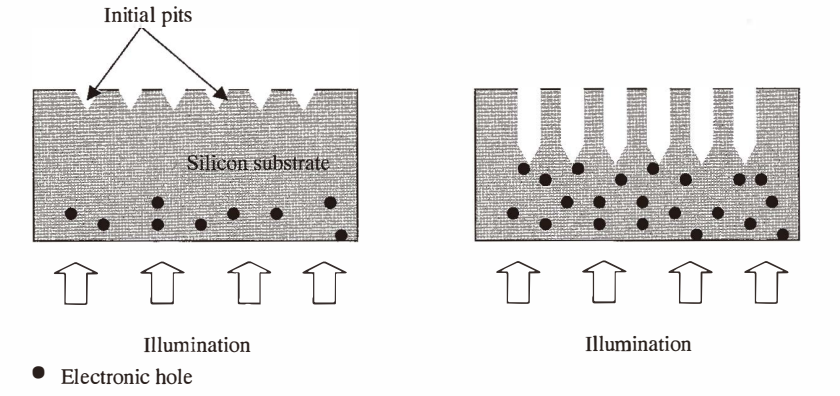
Table 1
Classification of porous silicon.

	Pore diameter
Microporous silicon	<2 nm
Mesoporous silicon	2 nm–20 nm
Macroporous silicon	>20 nm

etching. Several techniques have been proposed to supply electronic holes during the etching.[2,12–14] Among these techniques, illumination has been conventionally used in the etching due to its simplicity.[12] Considering the band-gap of silicon, 1.1 eV, the wavelength should be less than 1.1 μm to generate electron-hole pairs. The sample is illuminated from the back surface and the electronic holes are generated there, as shown in Fig. 1(a). Initial pits are formed on the sample surface prior to electrochemical etching. The electronic holes diffuse to the surface and reach the pore tip. The chemical reactions of silicon dissolution take place only at the pore tip. Most of the electronic holes are captured by the pore tips due to the higher electric field there, as shown in Fig. 1(b). In this manner, straight etched holes can be achieved on the sample.

2.3 *Electrochemical etching setup and process sequence*

A schematic of the electrochemical etching setup is given in Fig. 2. A wafer is fixed on a copper wafer holder, which is screwed into the etch bath containing 5% HF.[15] The wafer



(a) Electronic holes generated by illumination (b) Electronic holes captured by pore tips

Fig. 1. Schematic diagram of the mechanism for electrochemical etching.

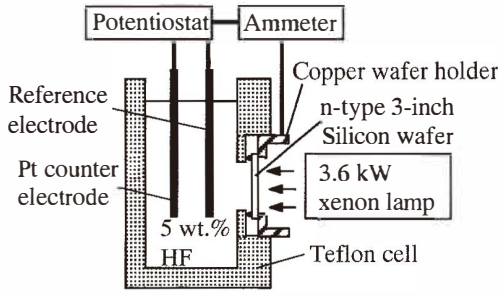


Fig. 2. A schematic diagram of the electrochemical etching setup.

holder has an opening to illuminate the back surface of the wafer with a xenon lamp of which the intensity can be varied. A positive voltage is applied to the wafer with respect to the platinum counter electrode. Current is adjusted by the light intensity and monitored by an ammeter. The process sequence for electrochemical etching is given in Fig. 3. The starting material is n-type silicon with 1 to 10 Ω·cm resistivity (a). In order to obtain a good ohmic contact between the backside of the wafer and the copper holder, an n+ layer was formed on the back surface of the wafer by phosphorous ion implantation with a 10^{16} cm^{-2} implantation dose. After the ion implantation, the wafer was annealed at 900°C for 1 h (b). Silicon nitride was deposited on the surface and patterned (c) to define initial pits by tetramethyl ammonium hydroxide (TMAH) (d). Then, vertical holes or trenches were fabricated by electrochemical etching (e) using the setup shown in Fig. 2.

2.4 *Electrochemical etching*

In electrochemical etching, electronic holes generated by illumination are consumed by the chemical reactions of silicon dissolution. Thus, the current density shows the quantity of the chemical reactions and can be controlled by the light intensity. Figure 4 shows the pore diameter and the etch rate as a function of the current density. The initial pit layout used in these experiments is given in Fig. 5. The etch rate is constant with respect to the current density (white circle: solid line) while the pore diameter increases with the increase of the current density (black circle: dotted line).

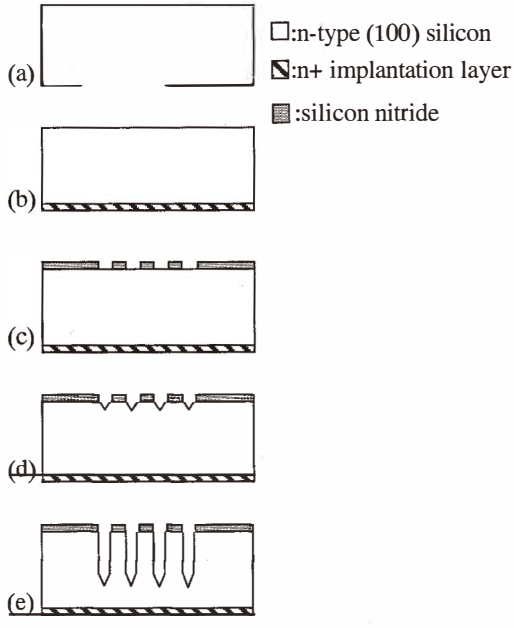


Fig. 3. Process sequence for electrochemical etching.

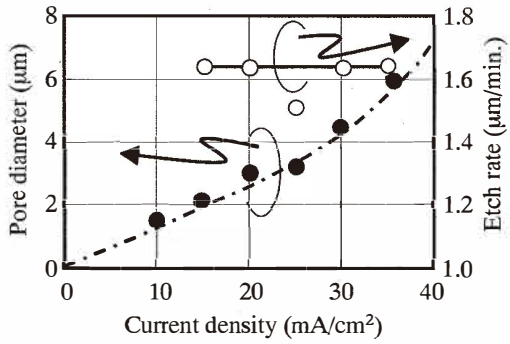


Fig. 4. Pore diameter and etch rate as a function of current density.

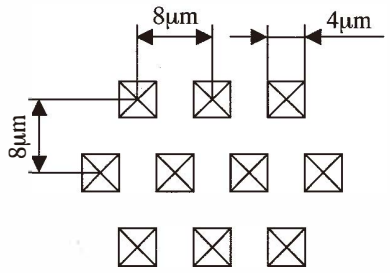


Fig. 5. Initial pit layout.

When the light intensity is increased, more electronic holes are generated. These electronic holes are used to enlarge the pore diameter. In this etching, the chemical reaction occurs only at the pore tip, as shown in Fig. 1(b). Judging from these results, if the light intensity is increased during the etching, the pore diameter is increased from the halfway point. This means the new pore diameter does not affect the existing pore diameter. Figure 6 shows the SEM micrograph of the cross section of the pores. In this experiment, first the current density was 30 mA/cm^2 and then it was raised to 35 mA/cm^2 for 15 min. Uniform pore width can be seen in the upper part of the SEM micrograph and then the pore diameter is seen to increase from the halfway point due to the increase of the light intensity. In this manner, the pore diameter can be controlled during the etching by adjusting the light intensity without affecting the existing pores.

This etching technique can be extended to form free standing structures in a single step.[16,17] After the desired depth was obtained, the light intensity was increased to connect the holes or trenches under the structural parts. Thus, the free standing structure can be obtained in a single step. When using weak light intensity, the etched holes are smaller than the initial pits, as illustrated in Fig. 7. The etched width is defined by the number of electronic holes captured at the pore tip per unit time. In other words, the etched width can be controlled by the light intensity and the pitch of initial pits.

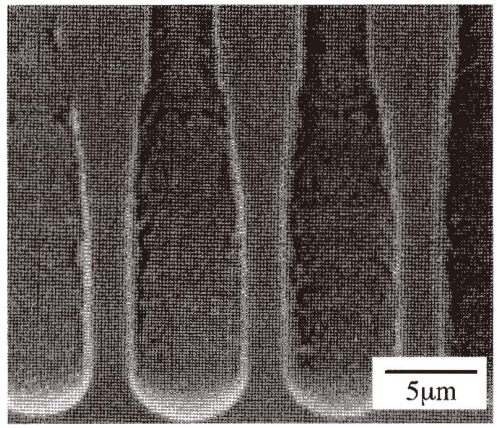


Fig. 6. SEM micrograph of etched holes with increase of light intensity during etching.

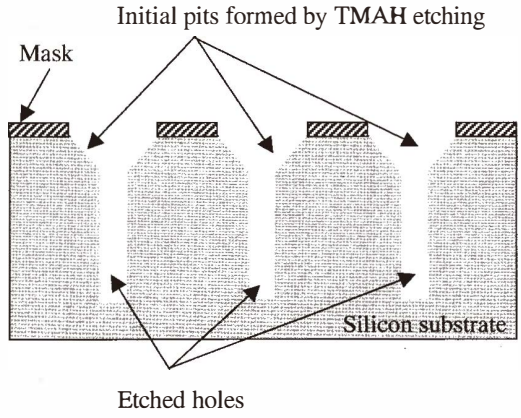


Fig. 7. Small holes fabricated by weak light intensity.

3. Results and Discussions

The features of electrochemical etching have been described in the previous section. There are several interesting points which are not realized by conventional silicon etching techniques. In this section, silicon dioxide pillars fabricated by macroporous silicon based micromachining will be discussed. These structures will be used for the sieving of DNA fragments.

3.1 *DNA analysis*

Recently, DNA analysis has attracted much attention and single nucleotide polymorphism (SNP) analysis become significant. However, it is not the stage to utilize DNA analysis for human disease diagnosis due to the low throughput and high cost. In order to resolve these issues, microchips for a DNA separating device have been proposed.[18,19] In these microchips, artificial sieving structures have to be fabricated into a channel instead of a gel in the capillary electrophoresis. In order to realize the function of the artificial sieving structures as a gel, the distance between the sieving structures should be less than one micrometer. In the case of an artificial sieving structure, the locations of the structures can be controlled by lithography, thus the efficiency for the DNA separation is thought to be improved. Furthermore, the chips can be fabricated on a silicon wafer resulting in mass production at low cost.

3.2 *DNA separating device*

When the DNA fragments pass through a small space in the sieving material, usually gel or polymer, the interactive force between the sieving material and DNA fragment is thought to depend on the DNA fragment's length. Therefore, the time taken for the DNA to reach the outlet differs with the length.

Figure 8 shows the schematic view of the DNA separating device proposed by us. The silicon dioxide (SiO_2) micropillars, which comprise the sieving material, are fabricated in a channel formed on a silicon substrate. An inlet and an outlet are made at both ends of the channel. When DNA fragments pass through the silicon dioxide micropillars with the space less than one micrometer, they are separated from the length. These small spaces work as a gel, and have been used for capillary electrophoresis.

3.3 *Fabrication of SiO_2 pillars*

In the DNA separating device, the key is the fabrication of artificial sieving structures. At the moment, a gel has been used as the sieving material and the spaces are less than 100 nm. To fabricate such a small structure, electron beam lithography has been used.[18]

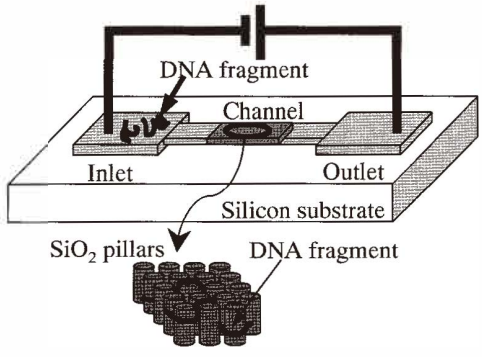


Fig. 8. Schematic view of DNA separating device.

However, the equipment is very expensive and its throughput is low. In order to realize small spaces for DNA separation, a new technique based on macroporous silicon will be presented.

The process sequence for SiO_2 micropillar formation is given in Fig. 9. First, a silicon nitride (SiN) masking layer was deposited and patterned to form initial pits by TMAH etching for the initiation of macropores (a). Then, macropores were fabricated by electrochemical etching (b) followed by thermal oxidation along the macropore (c). The space between the SiO_2 pillars forms a pass for DNA separation. Thus, the thickness of the oxidation layer has to be precisely controlled. Then, the SiN masking layer was removed by mechanical polishing (d). Finally, the silicon between the SiO_2 pillars was etched by TMAH (e). In this manner, SiO_2 pillars with spaces less than the lithographic resolution were fabricated by the combination of electrochemical etching and thermal oxidation.

The SiO_2 pillars fabricated by macroporous silicon based micromachining are shown in Fig. 10(a). Some of the SiO_2 pillars were broken when the sample was cleaved for the SEM observation. The top view of the SiO_2 pillars is given in Fig. 10(b). The black square part is the macropore formed by electrochemical etching. The black area around the white circle represents the space for DNA separation formed by TMAH etching. The reason that circular SiO_2 pillars are formed around a square pore is the compressive stress concentration at the corner of the pore that leads to the decrease of the oxidation reaction rate. The

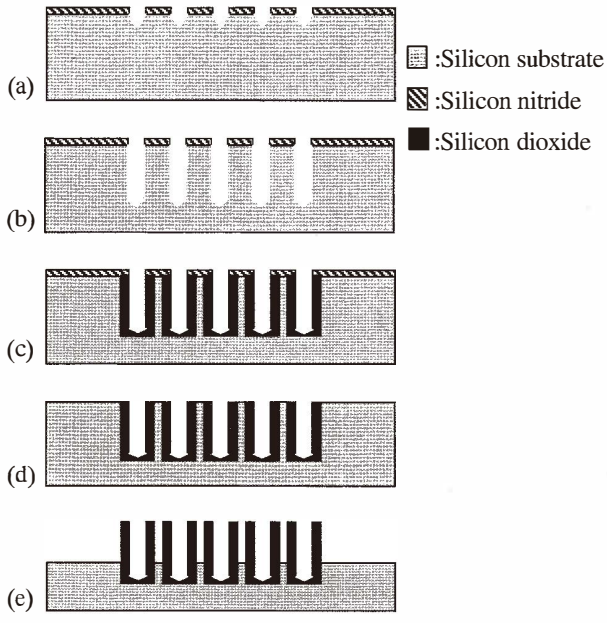
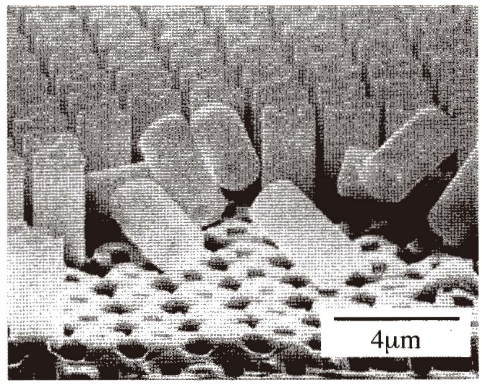
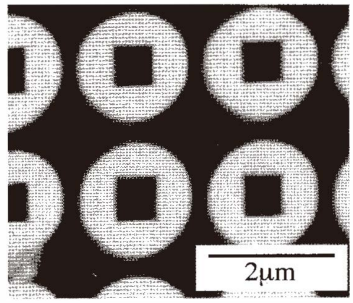


Fig. 9. Process sequence for SiO_2 pillars.



(a) SiO_2 pillars



(b) Top view of SiO_2 pillars

Fig. 10. SEM micrographs of SiO_2 pillars fabricated on a silicon wafer.

space between the pillars is 200 nm, which is defined by the pitch and diameter of the macropore and the thickness of the thermal oxide. Using this technique, SiO_2 pillars with submicron spaces can be easily fabricated.

3.4 *Fabrication of DNA separating device*

When the SiO_2 pillars were applied to the sieving structures for the DNA separating device, as shown in Fig. 8, side branches formed on the SiO_2 pillars block the DNA flow. These side branches were observed at the edge of the sieving area, as shown in Fig. 11. Considering the fabrication sequence for SiO_2 pillars, SiO_2 was formed around the macropores. Thus, the origin of the side branch is the electrochemical etching. The schematic diagram of the side branch etching is given in Fig. 12(a). In the electrochemical etching, electronic holes are used for the chemical reaction of silicon dissolution. The edge

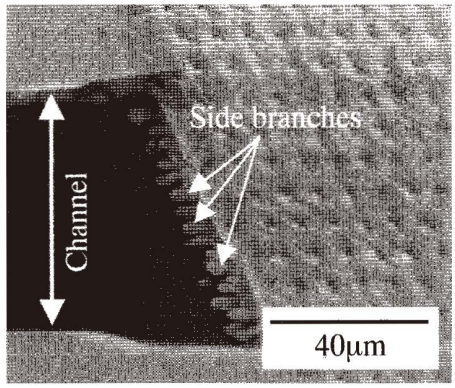
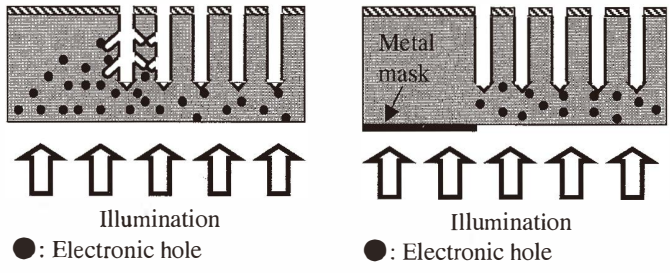


Fig. 11. Edge of sieving area formed in a channel.



(a) Side branch formation at the end of etched area

(b) Effect of the metal mask

Fig. 12. Schematic diagram of the etching at the end of the etched area.

of the structural area is over etched due to the excess electronic holes generated by the illumination. To prevent the excess supply of electric holes to the edge of the structure, a metal mask was formed on the backside of the wafer. This metal prevents the generation of excess electronic holes. This enables macropore formation without side branches, as illustrated in Fig. 12(b). Figure 13 shows the SiO_2 pillars at the edge of the sieving area using the metal mask on the backside of the wafer. The SiO_2 pillars were fabricated with a low density, so the pass for the DNA fragments was not blocked.

The process sequence for fabricating the DNA separating device is given in Fig. 14. After forming the SiO_2 along the macropore (a), the SiN masking layer was removed. In this step, mechanical polishing was used not only to remove the SiN masking layer but also to make the wafer flat due to the large compressive stress induced in the thermal SiO_2.

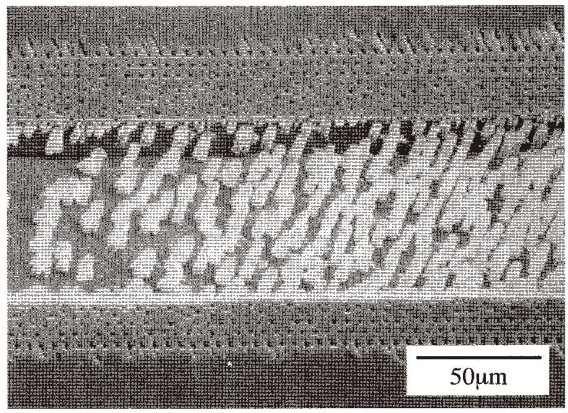


Fig. 13. SiO_2 pillars fabricated in a channel at the end of the sieving area.

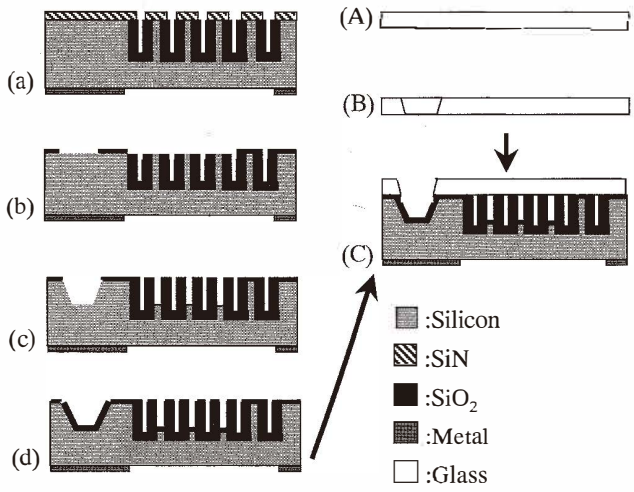
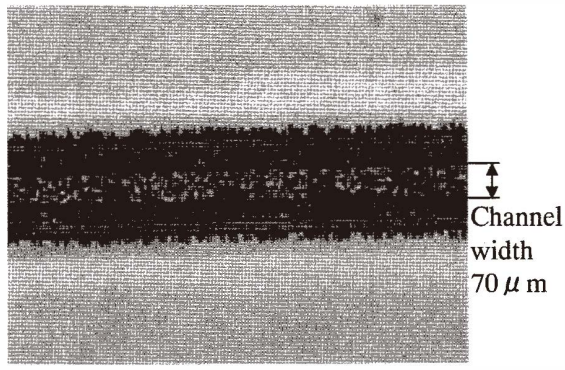


Fig. 14. Process sequence for DNA separating device.

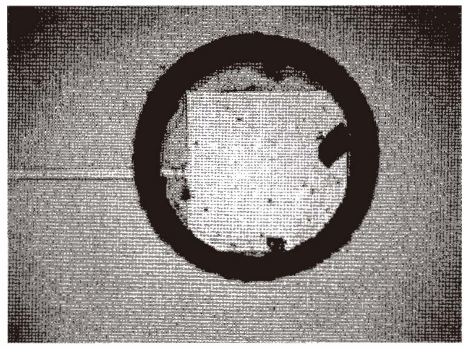
Then, SiO_2 was thermally formed again and patterned to define a channel, an inlet and an outlet (b). Silicon was etched to reveal sieving structures and to form a channel, an inlet and an outlet (c). In the next step, SiO_2 was formed thermally on the silicon surface to form the device surface hydrophilic (d). Through holes were formed in parallel in a glass

substrate for the inlet and outlet by sand blasting (B). Finally, the silicon and the glass were stuck by anodic bonding (C). Figure 15(a) and (b) show the channel filled with the SiO_2 pillars and the inlet after anodic bonding of the final step, respectively. Six devices were fabricated on a 3-inch wafer. We have verified that the DNA can be made to flow into the sieving area by electro-osmotic flow.

Using macroporous-based micromachining, a DNA separating device which has small structures can be realized easily. In this device, SiO_2 pillars were regularly located in the channel. At the moment, the location of the SiO_2 pillars which can separate the DNA fragments effectively has not yet been clarified. The device will be improved in the near future.



(a) Sieving area with SiO_2 pillars



(b) Inlet

Fig. 15. Complete device fabricated on a 3-inch wafer.

4. Conclusions

Macroporous-silicon-based micromachining has been developed as a silicon etching technique to form structures. The etching has several interesting features which cannot be realized by conventional etching techniques. One is that the etched width can be controlled by the light intensity during the etching. This enables a free standing structure to be achieved in a single step. The other is that the etched width is defined by the pitch of initial pits and the light intensity. This leads to a small etched width which is less than lithographic resolution.

Using this new technique, a DNA separating device has been proposed. In this device, SiO_2 pillars mutually separated by submicrons have been fabricated using the macropores and thermal oxidation as sieving structures for DNA separation.

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