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A preliminary study on chemical micro-machining of complex three-dimensional patterns on silicon substrates

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Abstract Chemical micro-machining of complex 3-dimensional (3-D) patterns of silicon substrates was preliminarily explored by the confined etchant layer technique (CELT). Through systematic investigation, we demonstrated that cysteine as a scavenger and Br₂ as an etchant can be used to etch silicon substrates. The CELT has the potential to develop into a new means of micro-machining complex 3-D patterns on silicon substrates. However, due to the highly corrosive property of the chemicals used for the silicon etched system, great effort must be made to overcome these problems including the mold electrode with high chemical stability.

Keywords Micro-machining · Confined etchant layer technique · Cysteine · Silicon · Etching

Introduction

Silicon is the most important material used in micro-electromechanical systems (MEMS) in terms of its electronic and mechanical properties [1]. Microstructuring of silicon substrates is therefore the key issue in the MEMS technology. In order to extend and strengthen the working functions of the MEMS to more

applications, it is essential to develop new methods to fabricate 3-D complex structures [2–11].

The electrochemical fabrication method has the potential to micromachine silicon. The major advantages over other methods are its simplicity and low cost. A single electrochemical step can usually complete the whole fabrication [12–34]. Based on its working principle, this method can be divided into two categories: direct and indirect electrochemical processing [12–34]. Direct electrochemical etching technology has been frequently used. Anisotropic etching of silicon substrates in basic solution can fabricate essentially 3-D structures on the basis of various properties of different crystal faces, but is limited by the intrinsic crystal structure [12]. Several electrochemical methods have been developed along this line [13–17]. For instance, the anodic method, based on special characteristics of the depletion layer, can fabricate certain structures such as trenches or pores of micrometer size on silicon substrates [13–15]. The anodic dissolution method has also been used to selectively etch the epitaxially grown thin silicon films [16, 17]. These methods based on the selectivity of doping dependent or depletion layer are insufficient to fabricate various complex 3-D structures. Many attempts using the electrical scanning probe-based lithography (SPL) have been made [18–26]. By applying proper bias, the scanning tips can locally etch the silicon surface or write a pattern on the substrate [26]. In spite of the fact that this approach has very good spatial resolution at the nanometer level, this method of fabrication using a tip point by point is not suitable for mass production of the MEMS. Recently, Schuster and coworkers developed a new 3-D microfabrication method [27, 28]. They used a shaped tool electrode as a milling cutter to engrave the workpiece electrode by applying ultrashort voltage pulses. However, direct electrochemical processing method has its own limitations. It cannot fabricate nonconductive materials. Moreover, the micro-machining precision achieved on the silicon substrate is not satisfactory [27]. This is mainly because of the complex oxidation processes of the semiconductive silicon [29].

Dedicated to Professor Gygy Horyi on the occasion of his 70th birthday

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Indirect electrochemical processing may overcome, at least partially, the problems presented by direct electrochemical processing. When the electrode approaches the workpiece substrate, the electrode surface generates an etchant that can chemically react with the substrate. A typical application is to use the scanning electrochemical microscope (SECM) [30–35]. For instance, Br_2 as an etchant is electrochemically generated on the ultramicroelectrode surface which then chemically etches the silicon substrate, resulting in the formation of etched patterns on the silicon surface [35]. The essential chemical reaction between Br_2 and the silicon surface in acidic HF solution results in isotropic etching and shows slight variation with the doped levels and type of the silicon substrate [36–38]. The indirect electrochemical etching makes fabricated silicon materials more flexible. However, the free diffusion of the Br_2 -etchant in solution significantly decreases the extent of local etching. The machining precision achieved in the lateral direction parallel to silicon wafer surface was usually larger than $20\ \mu\text{m}$ [35]. Therefore, how to improve the machining precision is a crucial issue for micro-machining of complex 3-D microstructures on silicon substrates.

In order to overcome the above mentioned obstacle, our laboratory has developed a new method called the confined etchant layer technique (CELT); based on SECM technique [39–41]. The important feature is the use of a scavenger to efficiently consume the etchant so as to confine the etchant to an ultrathin layer on the working electrode surface [39]. To test this idea, in the previous study, we used a Pt ultramicroelectrode and demonstrated that the machining precision achieved on the silicon substrate could be improved when the Br_2 -etchant is confined to the AsO_3^{3-} -scavenger [40]. Here, we report a preliminary CELT study on the micro-machining of complex 3-D patterns on the silicon substrate by using cysteine as a new scavenger.

Experimental

The electrochemical experiment was performed in a teflon cell. A saturated calomel electrode (SCE) was used as reference electrode with HF-resistance and a platinum foil as the counter electrode. All potentials are quoted versus the SCE reference. Voltammetric measurements were recorded with a CHI-660a Voltammetric Analyzer (CH Instruments Inc., USA). The most important factor in the present work is the fabrication of conductive mold electrodes. Silicon molds with complex 3-D pattern were first metallized by sputtering metal thin layer of Ti and Pt of 100 nm in sequence. A diamond carbon layer (doped with N, $1 \times 10^{20}\ \text{cm}^{-3}$) of about 150 nm was deposited at Pt surface of the mold. Corresponding molds were immobilized at the end of a steel rod with conductive glue of silver and were insulated by resin except towards the top. The area of mold electrode exposed to solution was about $1 \times 10^{-3}\ \text{cm}^2$. Silicon wafer

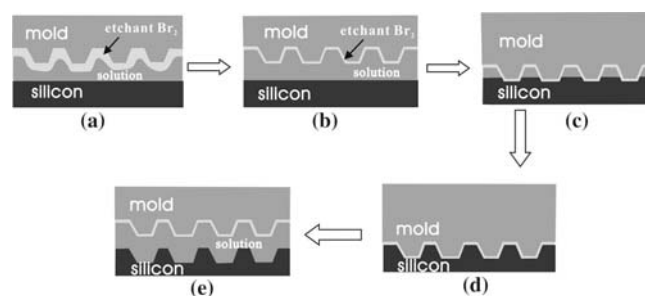
of n-type $\langle 100 \rangle$ ($2.3\text{--}4.3\ \Omega\ \text{cm}$) was obtained from Huajing electronic Corp. (Wuxi, China).

The etching experiment was performed in the same cell. A silicon piece of about $1\ \text{cm}^2$ was immobilized at the bottom of the cell by tapping after washing thoroughly with deionized water. The movement of the mold to the silicon surface was realized through a controlled instrument (Hit Boshi Precision Measure and Control Co. Ltd., Harbin, China) [41]. Each move could be controlled from $50\ \mu\text{m}$ to $50\ \text{nm}$. The distance between the mold and the silicon surface was controlled on the basis of the feedback current values [30–35]. The patterns of the mold and the etched workpiece were characterized respectively with atomic force microscope (Nanoscope IIIa, Digital Instruments).

All chemicals were of reagent grade and were used as received. Deionized water was obtained by purification through Millipore system and was used throughout. Reagent solutions were freshly prepared and were degassed with nitrogen before use.

Results and discussion

The etching procedure and the working principle of the present work is described in Scheme 1. The electrochemical combined chemical system is presented as a side view and the mold used here is like a gear. Br_2 as an etchant can be electrochemically generated from Br^- ion at the mold electrode surface. The diffusion of Br_2 into the solution phase results in a thick etchant layer since its diffusion coefficient (D) is about $10^{-5}\ \text{cm}^2/\text{s}$ [40]. The addition of the scavenger into the solution rapidly destroys the diffusing Br_2 back to Br^- ion. As a consequence, Br_2 is confined within a very thin layer around the mold surface. The thickness of the confined layer can be estimated from the value of $(D/K_s)^{1/2}$ if the scavenger concentration is high enough [39, 40]. When the mold comes into contact with the silicon substrate the con-



Scheme 1 The schematic illustration of CELT to fabricate complex 3-D pattern on silicon wafer. **a** The etchant is electrochemically generated at the 3-D mold electrode surface; **b** Etchant Br_2 is confined in a very thin layer around the 3-D mold after added the scavenger of cysteine; **c** the confined etched layer of Br_2 touches and starts to chemically etch the silicon substrate; **d** The etched pattern is formed and by repeating the approaching and etching process; **e** a complete negative copy of 3-D mold is fabricated

fined Br_2 layer contacts and begins to etch the substrate. The thickness of the confined Br_2 layer will decide the machining precision achieved. The distance between the mold and the silicon wafer can be monitored by the feedback current of Br^- that is regenerated by the etching reaction [36–38]. Meanwhile, this cyclic process of bromine species during fabrication becomes a source of supply of the etchant. Otherwise, the etchant will be depleted within a narrow slot formed between the mold and the silicon surface. For a certain 3-D pattern, it may be required to repeat the etching process several times in order to remove the products existing at the etched surface. Finally, a complementary fine pattern with the profile of the mold is obtained.

As shown in the scheme, the use of a scavenger is a key step towards realizing the CELT. The use of a scavenger can significantly reduce the thickness of diffusion layer of Br_2 when the rate of reaction between etchant and scavenger is sufficiently high. In our previous studies, AsO_3^{3-} was found to be a good scavenger [40, 41]. However, its low solubility in acidic solutions and the pollution caused to the environment can limit its industrial application. It is therefore desirable to seek a more suitable scavenger. We used cysteine as a candidate [42, 43] to investigate its capability as a scavenger.

Figure 1a and b show the respective voltammetric responses of Pt electrode in $1.0 \text{ mol dm}^{-3} \text{ NH}_4\text{ClO}_4/0.2 \text{ mol dm}^{-3} \text{ NH}_4\text{F}$ solution (pH 1.7) containing $10 \text{ mmol dm}^{-3} \text{ NH}_4\text{Br}$ and 50 mmol dm^{-3} cysteine, respectively. A sharp increase in current was observed at the potential around 0.85 V for curve a, indicating that Br_2 was generated. The net current values corresponding to Br_2 generated were $10.3 \mu\text{A}$ at 1.0 V. Curve b shows that cysteine begins to be oxidized at the potential of 0.43 V. The oxidation current increased considerably with the positive shifting of potential. The oxidation current values was $18.0 \mu\text{A}$ observed at 1.0 V. Curve c represents the voltammetric result in the solution containing both NH_4Br and cysteine. The oxidation current observed at +0.43 V and beyond was dramatically

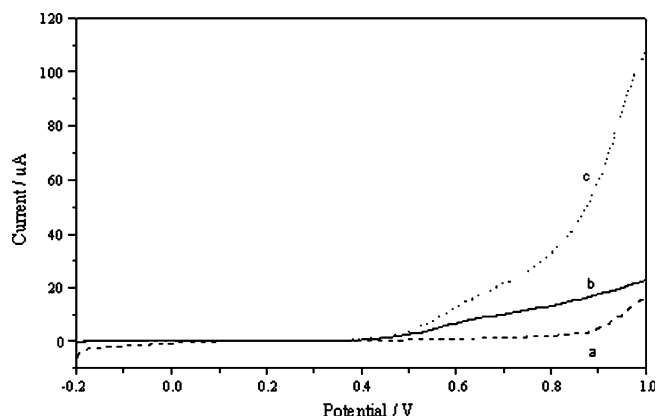


Fig. 1 Voltammetric responses of Pt electrode in $1.0 \text{ mol dm}^{-3} \text{ NH}_4\text{ClO}_4/0.2 \text{ mol dm}^{-3} \text{ NH}_4\text{F}$ solution (pH 1.7) containing **a** $10 \text{ mmol dm}^{-3} \text{ NH}_4\text{Br}$ only; **b** 0.1 mol dm^{-3} cysteine only; and **c** both species. Scan rate: 50 mV/s

high. The maximum current values was $109.0 \mu\text{A}$ at 1.0 V. Ranwel and Thevenot reported that nascent bromine can chemically oxidize the thiol moiety of cysteine in acidic medium and the products were bromide anion and sulfinic or sulfonic acid [43]. This observation illustrates that cysteine can also react with Br_2 in the etching solution so as to increase the concentration of Br^- near electrode surface, resulting in an increase in the total apparent oxidation current. An increase in apparent oxidation current was observed more than five times demonstrating that cysteine has high capability as the scavenger of Br_2 .

On finding cysteine to be a suitable scavenger, we directly used the mold electrode for the same electrochemical characterization to ensure its availability in the CELT system. The gear mold was first manufactured from the silicon substrate that had a good shape but poor electric conductivity. To improve its conductivity, the mold was first sputtered with metal Ti and Pt in sequence, then with doped diamond carbon layer. The reason behind using the diamond carbon layer is to get high strength to resist strong corrosion as the solution contained both HF and Br_2 [44–46]. Figure 2 shows three curves obtained under conditions the same as those in Fig. 1. As the scale of current for the two figures is different, the small background current can be observed in Fig. 2. It can be seen clearly from curve a that Br^- was oxidized to Br_2 on the mold surface at potential higher than 0.85 V and its net current values was $3.5 \mu\text{A}$ measured at 1.0 V. The mold electrode could also oxidize cysteine at potentials higher than 0.43 V as shown by curve b. The oxidation current value of cysteine was $2.1 \mu\text{A}$ measured at 1.0 V. The comparison of curves a and b indicates that the diamond carbon film coated mold had higher electrochemical activity to Br^- than cysteine, which differs from Fig. 1 where Pt was the working electrode. The characteristic of curve c in Fig. 2 is quite similar to that in Fig. 1, the diamond carbon film coated mold has similar electrochemical behavior as that of the pure Pt electrode.

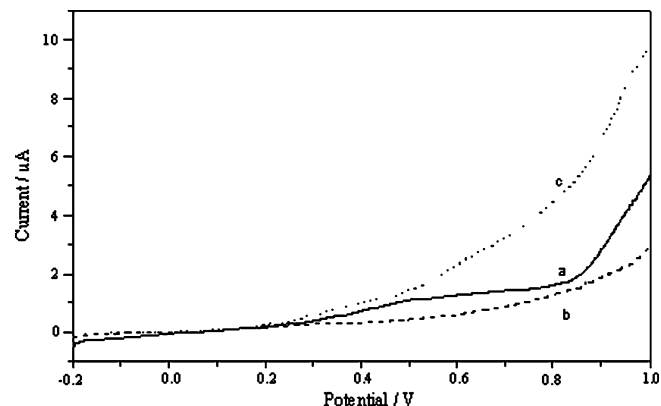


Fig. 2 Voltammetric responses of the mold deposited by the doped diamond carbon of 150 nm in $1.0 \text{ mol dm}^{-3} \text{ NH}_4\text{ClO}_4/0.2 \text{ mol dm}^{-3} \text{ NH}_4\text{F}$ solution (pH 1.7) containing **a** $10 \text{ mmol dm}^{-3} \text{ NH}_4\text{Br}$ only; **b** 0.1 mol dm^{-3} cysteine only; and **c** both species. Scan rate: 50 mV/s

Based on the above measurement, the CELT experiment was performed in $0.5 \text{ mol dm}^{-3} \text{ NH}_4\text{ClO}_4/0.2 \text{ mol dm}^{-3} \text{ NH}_4\text{F}$ solution (pH 1.7) containing both $10 \text{ mmol dm}^{-3} \text{ NH}_4\text{Br}$ and 0.1 mol dm^{-3} cysteine. The gear-like mold was controlled in its approach to the silicon wafer and the distance between the mold and the wafer could be monitored by the feedback current while keeping the applied potential of 0.9 V on the mold electrode [40, 41]. After each experiment, the etched silicon wafer was taken for characterization using atomic force microscopy. Usually, only a partial pattern was realized on the wafer as compared to the gear pattern of mold, as sampled in Fig. 3a. The images of cross section analysis were randomly captured from each of the etched patterns for more than five replicate measurements. Figure 3b is a typical picture. The depth of each groove varied greatly, which might result from the fact that none of the conductive ultrathin deposit made the top of each tooth of the mold deviate from the horizon. In order to decrease this effect on the evaluation of the etching results, only the deepest depth was picked from each of the cross section images for statistic analysis. Furthermore, the depth measured in cross section image should correspond to an apparent value

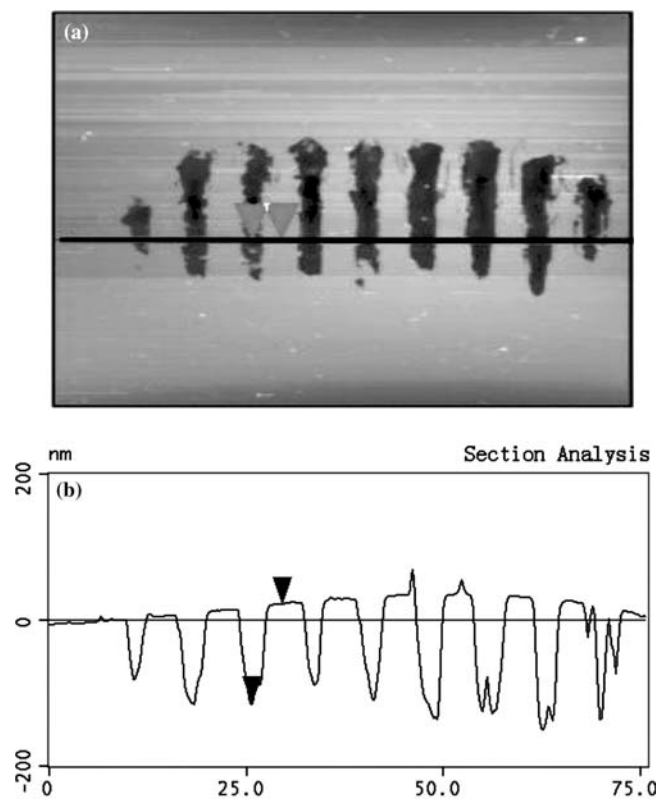


Fig. 3 AFM images of the etched gear-like pattern on silicon wafer of n-type $\langle 100 \rangle$ (a); and the cross section analysis (b). Fabrication conditions were as follows: mold was deposited by the doped diamond carbon of 150 nm; solution was of $1.0 \text{ mol dm}^{-3} \text{ NH}_4\text{ClO}_4/0.2 \text{ mol dm}^{-3} \text{ NH}_4\text{F}$ (pH 1.7) containing $10 \text{ mmol dm}^{-3} \text{ NH}_4\text{Br}$ and 0.1 mol dm^{-3} cysteine; constant potential was kept at 0.9 V and etched for 10 min

because of the limit of the AFM tip diameter. Therefore, the groove width value of the micrometer should more closely reflect the etching results with less effect of the conductive deposit of nanometer. The statistical results show the groove width varies from $3.0 \mu\text{m}$ to $4.5 \mu\text{m}$, and the apparent value of the deepest depth is about 160 nm. The etched surface, especially at the edge of each groove, looks very rough and has low straight extent. To improve the surface smoothness, we added $1 \text{ mmol dm}^{-3} (\text{C}_2\text{H}_5)_4\text{NClO}_4$ into the etchant solution. A relatively better pattern was usually obtained, as sampled in Fig. 4a. The statistical results of cross section analysis (Fig. 4b as one of images) illustrate that the width of each groove varied narrowly between $3.9 \mu\text{m}$ and $4.2 \mu\text{m}$, and the apparent value of the deepest depth was around 170 nm. The reason for improving the surface smoothness might be due to the decrease in the bubble size and the easy removal of hydrogen bubble [47]. Comparable experiments were carried out using the solution without cysteine. We were not able to obtain any regular gear-like pattern on the silicon substrate. This demonstrates that cysteine plays an important role as the scavenger in the CELT experiment.

It must be pointed out that the micro-machining of silicon is one of the most difficult tasks in the CELT, which is mainly due to the fact that a very corrosive

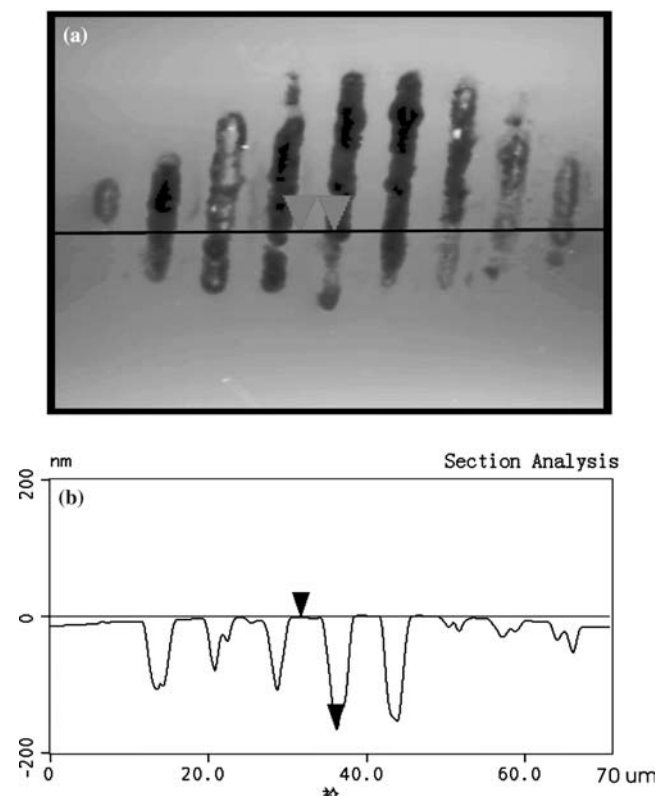


Fig. 4 AFM images of etched gear-like pattern on silicon wafer of n-type $\langle 100 \rangle$ (a); and the cross section analysis (b). $1 \text{ mmol dm}^{-3} (\text{C}_2\text{H}_5)_4\text{NClO}_4$ was added into etchant solution. Other conditions were same as Fig. 3

etchant (chemicals) has to be used. After intensive research, we found that severe corrosion of the mold metalized by Ti and Pt always led to failed and frustrated fabrication. In spite of sealing the mold surface by the diamond carbon film in the present study, we still could not preserve the chemical stability of the mold. The body of silicon was found to be partly exposed after the etching experiment. The corrosion of the mold might be the main reason for the unsatisfactory result in terms of low etching rate and depth, as shown in Figs. 3 and 4. Therefore, the most important factor in improving the CELT in micro-machining of silicon is to solve the corrosion problem of mold, which is underway in our laboratory.

Conclusion

The preliminary experimental results show that Br₂ as an etchant and cysteine as scavenger can be used to etch silicon substrate. The CELT has the potential to lead to means of micro-machining complex 3-D patterns on silicon substrates. However, due to the very corrosive property of the chemicals used for this system, much effort must be made to develop the mold electrode with high chemical stability.

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