Fabrication of a Si stencil mask for the X-ray lithography using a dry etching technique

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Abstract. We fabricated a Si stencil X-ray mask only in a dry process without electroplating and chemical etching. An X-ray absorber of thickness 30 µm with vertical sidewalls was able to be fabricated. In addition, we succeeded in demonstration of the X-ray lithography in the beam line BL-4 of the synchrotron radiation facility TERAS of AIST. Line and space patterns of line width 2 – 200 µm were transcribed plainly on the surface of a PMMA sheet. It was confirmed that the edge of PMMA microstructures was sharp. There is a possibility that this Si stencil mask can be applied as an X-ray mask for the deep X-ray lithography.

1. Introduction

In the X-ray lithography that is the first process of the LIGA process [1], the synchrotron radiation (SR) is used as a light source of X-rays. The SR has the high directivity that equals a laser from the characteristic of the generation principle. The processing depth can be rapidly deepened into a resist by selecting X-rays with the photon energy of 1 keV or more from the SR. The development of an X-ray mask is an important technical problem as well as the development of resists and X-ray exposure techniques in the X-ray lithography. The fabrication procedure of an X-ray mask can be divided into four stages of 1) patterning, 2) making of an X-ray absorber, 3) making of a membrane and 4) back side etching. The combination of an X-ray absorber and a membrane in normal LIGA process may be used Au and polyimide. As for this combination, a lot of LIGA research group adopt, and the commercialization has already been done. The thermal expansion coefficient at 20 °C of Au and polyimide are 14.2 × 10⁻⁶ /K and 40 - 55 × 10⁻⁶ /K, respectively. This difference is not too much in the problem when the X-ray exposure time is short. However, In case that the X-ray exposure time becomes long in order to expose a resist of thickness 100 µm or more, there is a possibility that a transcribed pattern on the resist transforms according to heat because that the width of the expansion of the X-ray absorber is different from that of the membrane.

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On the other hand, X-rays are irradiated at very long time in order to expose a resist in the thickness of several mm in the deep X-ray lithography (DXL). Moreover, X-rays with the high photon energy of 5 keV or more might be irradiated. It is difficult to maintain an enough contrast of an X-ray mask under such an exposure condition. Therefore, the development of an X-ray mask corresponding to the DXL is important. However, when a positive type resist that can be removed is used, the patterning of microstructures for depth to exceed 10 \( \mu \text{m} \) using a photolithography and an electron beam drawing is very difficult. Though the negative type resist such as the SU-8 can be used as a membrane without removing, it is difficult to control verticality of the pattern sidewall because the sensitivity of the SU-8 is very high. Then, we decided to fabricate an X-ray mask made of Si for trial purposes. Final target is to make an X-ray absorber and a membrane only with Si. However, we produced a stencil mask without a membrane by only Si because it was the first trial. This X-ray mask was produced neither an electroforming nor a chemical etching only in a dry etching. We also demonstrated the X-ray lithography in the beam line BL-4 [2] of TERAS [3] that was the SR facility of AIST, and confirmed to the enough function as an X-ray mask.

2. Design of the process flow to fabricate an X-ray mask

The photon energy spectrum of TERAS has a peak in 1.9 keV. When the transmission intensity of Si was calculated, the enough contrast was obtained by the thickness of 10 \( \mu \text{m} \). However, to give mechanical strength to an X-ray absorber, we designed by 30 \( \mu \text{m} \) in thickness. Figure 1 shows the process flow to fabricate a Si stencil X-ray mask. First of all, a silicon on insulator (SOI) wafer which the SiO\(_2\) film in the thickness of 1 \( \mu \text{m} \) is placed between Si of thickness 30 \( \mu \text{m} \) and 525 \( \mu \text{m} \) is prepared. Next, the positive-type photoresist (MICROPOSIT\textsuperscript{TM} S1830, ROHM and HAAS electronic materials) of thickness 3 \( \mu \text{m} \) was spin-coated on the surface of the Si layer in the thickness of 30 \( \mu \text{m} \). After the wafer was baked for 20 min at 120\(^\circ\text{C}\) with an oven, it cooled naturally to the room temperature. It was exposed with a contact aligner for 13 sec and developed by the developer for 3 min. The MUC-21 (Sumitomo Precision Products Co.,Ltd.) etching system was used in reactive ion etching (RIE). This system adopts inductively a coupled plasma (ICP) source as a plasma generation method. Si was etched in SF\(_6\)/C\(_4\)F\(_8\) cycle etching (Bosch process) at the pressure in rang from 3 to 6 Pa for 8.5 min. Next, a window was patterned by the photolithography on the back side of the wafer, and the back side Si in the thickness of 525 \( \mu \text{m} \) was etched for about two hours using same etcher. The SiO\(_2\) layer was etched from the back side for 50 min with the RIE equipment (RIE-10NRS, SAMCO, Inc.) because that the SiO\(_2\) layer had been distorted by the internal stress. The CHF\(_3\) gas was used for SiO\(_2\) etching. At the last, the photoresist was removed by a developer.

*Figure 1. Process flow to fabricate a Si stencil X-ray mask.*
removed by the remover.

3. Fabrication of an X-ray absorber by the Bosch process
In an X-ray mask for the DXL, the thickness of tens of μm or more is needed as an X-ray absorber, and the technology that can process deeply and vertically is needed. The anisotropy Si etching method that was called the "Bosch process" by F. Lärmer and A. Schilp of Robert Bosch GmbH was proposed in 1992 [4]. This process uses SF₆ as an etching gas, and uses C₄F₈ as a passivation gas. These gases are switched alternately and etch Si. These two kinds of gases are sent into a vacuum chamber, and generated plasma by using the high RF frequency power supply. A SF₆ molecule is excited by electrons with high energy and it becomes an ion and a radical. Si is etched by these particles' reacting with the Si substrate. The sputtering (ion reaction), the chemical reaction (radical reaction) and the ion assistance mechanism (complex reaction of the ion and the radical) combine to the reactive process.

3.1.1. Decrease of mask undercut
The feature requested as the structure for an X-ray absorber is that the sidewall of a pattern is vertical and the surface is smooth. The SF₆ gas becomes F* in plasma, and F* unites with Si and becomes SiF₄. Only the isotropic etching progresses when only SF₆ is used. As a result, the mask undercut is caused being greatly etched under the mask. Then, two kinds of gases of SF₆ and C₄F₈ are used in the Bosch process. As compared with C₄F₈, the flowing quantity of SF₆ is 1.5 - 3 times, and the etching cycle time is 2 - 3 times. In case that the pressure in the process chamber is high, the ion and the radical stay in the chamber for a long time. Therefore, the ion and the radical react for a long time with the Si wafer. Moreover, the effect of passivation appears strongly from the etching process when the pressure is increased. The processing sidewall cannot maintain vertical, and it leads to the deterioration of shape when the effect of passivation becomes remarkable. Table 1 is cross-sectional SEM images of Si structures when the pressure in the process chamber was changed from 3 to 8 Pa. The pattern was lines and spaces. SEM images of the whole trench, the line width 10 μm, 5 μm, and 2 μm are shown from

| Table 1. Relationship between the pressure in the process chamber and the mask undercut. |
| --- |
| **Chamber pressure** | **Whole Image** | **Line width = 10 μm** | **Line width = 5 μm** | **Line width = 2 μm** |
| 3 Pa | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) | ![Image](image4.png) |
| 4 Pa | ![Image](image5.png) | ![Image](image6.png) | ![Image](image7.png) | ![Image](image8.png) |
| 5 Pa | ![Image](image9.png) | ![Image](image10.png) | ![Image](image11.png) | ![Image](image12.png) |
| 6 Pa | ![Image](image13.png) | ![Image](image14.png) | ![Image](image15.png) | ![Image](image16.png) |
| 8 Pa | ![Image](image17.png) | ![Image](image18.png) | ![Image](image19.png) | ![Image](image20.png) |
the left. From the SEM observation of the whole trench pattern, the etching depth is deep in all line widths when the pressure in the process chamber increased. The effect of etching of the SF₆ gas became remarkable when the pressure in the process chamber was high, and the mask undercut can be observed by each line width. On the other hand, when the pressure in the process chamber was adjusted to 6 Pa or more, the effect of deposition of the C₄F₈ gas became predominant. As a result, etching with the SF₆ gas was suppressed, and the bottom part of trenches was thin. The mask undercut decreased when the pressure in the process chamber was 5 Pa at the line width 2 µm, and vertical Si structures is formed. In the line width 5 µm and 10 µm, the optimum conditions of the pressure in the process chamber was 4 or 5 Pa. When an X-ray mask was actually fabricated based on these results, the pressure in the process chamber was adjusted to about 5 Pa.

3.1.2. Decrease of notch

Another feature problem is the decrease of notches. In the Bosch process, the number of the ion and radical that enters in a trench decreases when the width of the trench becomes thin. Therefore, the etching time of a thin-width trench becomes long compared with a wide-width trench. The wide-width trench is excessively etched while the thin-width trench is etched until the SiO₂ layer of the SOI substrate. The Si etching does not progress because the SiO₂ layer of the SOI substrate works as an etching stop layer in this experiment. However, the over-etching actually progresses horizontally along the oxide layer by the micro loading. The local abnormal shape that generated by such a reason is called a notch like the part marked in Table 2. If the surface of the oxide layer does the charge improvement, a notch is generated by scattering ions.[5] For solving this problem, there is a technique for the control of the charge improvement with the pulse control of the RF power supply. When the negative bias is impressed to the bottom electrode, an ion and a radical are attracted from the plasma source to a Si wafer. In addition, ions can be desorbed from the oxide layer by multiplying high frequency by the bottom electrode during over-etching. The high frequency of 13.56 MHz is a standard specification in a general RIE system. In the RIE system used by this experiment, the low frequency of 380 kHz can be impressed to the bottom electrode besides the high frequency.[6] The etching result of the SOI wafer of the difference when the high frequency is impressed to the bottom electrode and when the low frequency is impressed is settled in Table 2. Impressing the low frequency compared with the high frequency seems to be desorbed more ions on the oxide layer, and decreased notches dramatically. However, it was insufficient only to impress the low frequency to the bottom electrode when an X-ray absorber was actually fabricated, the pulse control to repeat a switch on and off with several µsec was necessary to exclude the notch completely.

Table 2. Relationship between the RF frequency impressed to the bottom electrode and the notch.

| RF frequency impressed to the bottom electrode | Whole image | Line width = 10 µm | Line width = 5 µm | Line width = 2 µm |
|-----------------------------------------------|------------|--------------------|--------------------|--------------------|
| High frequency (13.56 MHz)                   | ![Image](image1) | ![Image](image2) | ![Image](image3) | ![Image](image4) |
| Low frequency (380 kHz)                      | ![Image](image5) | ![Image](image6) | ![Image](image7) | ![Image](image8) |

3.1.3. Fabrication of an X-ray mask and observation of X-ray absorber's sidewalls
Figure 2 showed the X-ray mask fabricated under the etching condition optimized by the above-mentioned method. The size of the window of an X-ray mask was 30 mm × 20 mm. Figure 3 showed cross-sectional SEM images of Si X-ray absorbers before back etching. The pattern shape was lines and spaces, the minimum line width was 2 μm, and the thickness of the X-ray absorber was 30 μm. As compared with fig. 3(a) and (b), mask undercuts and scallops are observed in the upper part of microstructures in the line width 2 μm, and notches are observed in the bottom part. However, neither a mask undercut nor a scallop is confirmed up in the line width 5 μm, and a notch is hardly observed. If the line width is 5 μm or more, the RIE technique can be used to fabricate absorber structures of the X-ray mask for the DXL. In the Bosch process, the sidewall can be processed vertically in the macro view. However, scallops of the sidewall were observed by the SEM. When the etching rate is made faster, the SF₆ gas has to increase. Then, the reaction proceeds because SF₆ molecules can stay longer in the process chamber. However, a scallop grows so that the etching reaction may occur excessively, and the surface of the sidewall becomes rough. When the flowing quantity and the etching time of SF₆ are reduced oppositely, the etching rate slows though the surface of the sidewall smooths. Making this X-ray mask for trial purposes gave priority to the smoothness of the sidewall roughness more than the etching rate, and set the etching cycle time to the rather short. Maximum roughness of the scallop was about 100 nm as shown in the insertion image of fig. 3(a). There is a possibility that scallops negatively affect the accuracy of the X-ray lithography when the line width of the pattern is thin. However, because the minimum line width to which the contact aligner used for patterning of this X-ray mask can be transcribed is 1 μm, it is difficult to evaluate the influence that scallops give to the X-ray lithography individually. Therefore, the influence of the roughness on the X-ray absorber's sidewall in the X-ray lithography by scallops was disregarded in this experiment.

4. Demonstration of the X-ray lithography in TERAS
Finally, the X-ray lithography was actually demonstrated using the Si stencil X-ray mask. X-rays were irradiated in the beam line BL-4 for the X-ray lithography in TERAS of AIST. TERAS has been operating since 1981, and is the first generation SR facility in Japan. The usual operation energy is 750 MeV and the maximum storage ring current is 270 mA. Figure 4 shows the optical configuration of BL-4. In this beam line, the light source is a bending magnet with the bending radius of 2 m, and the output beam is introduced into the exposure stage through a Be window of thickness 50 μm arranged at the downstream of 10 m from the light source point. The exposure stage is at the downstream of 70 mm from the Be window. The He gas of 1 atm is flowing to replace from air and cool the X-ray mask during X-ray irradiation. The exposure stage can be inclined by a pulse stepping motor and the exposure area is 8 mm × 13 mm. A PMMA sheet of the thickness 1 mm and the Si stencil X-ray mask were piled and fixed on the exposure stage. In this experiment, the X-ray

Figure 4. Optical configuration of the beam line BL-4 in TERAS.
mask was arranged so that front side might touch the surface of the PMMA sheet to lose the gap between the X-ray mask and the PMMA sheet. Therefore, X-rays were irradiated from the back side of the X-ray mask to which the window was opened by the backside dry etching. As a result, the edge of the pattern was able to be prevented from rounding from the X-ray diffraction caused from the gap between the X-ray mask and the PMMA sheet. However, the pattern to which the right and left reversed was transcribed on the PMMA sheet. X-rays irradiated for about 3 h and the total dose energy was 591 mA·h. Development was performed at the room temperature for 18 h using a GG developer (diethylene glycol-mono butylether:60 vol.%, morpholin:20 vol.%, ethanol-amine:5 vol.%, distilled water:15 vol.%). Ultrasonic vibration and churning were omitted during development. The transcription of all patterns of line width 2, 5, 10, 20, and 50, 100, 200 µm was succeeded as shown in fig. 5. The edge part of the pattern was sharp, and X-ray absorbers fabricated by dry etching were achieved an enough contrast. The processing depth of the PMMA pattern was 104 µm.

5. Summary
We succeeded in fabrication of a Si stencil mask that can be used practically to the X-ray lithography using a dry etching technique. It is necessary to make an X-ray absorber of an X-ray mask corresponding to the DXL thick to maintain the contrast even by an X-ray exposure for a long time. Therefore, it is very difficult to maintain verticality of the pattern sidewall. We applied the dry etching technology with SOI wafer that is one of the main technologies for the MEMS device development. As a result, it succeeded in fabrication of a stencil Si X-ray mask that the minimum line width was 10 µm and the thickness of the X-ray absorber was 30 µm. The verticality and smoothness are demanded on the sidewall of the X-ray absorber. However, we think that the Si dry etching technology can satisfy this severe demand enough. We plan to develop a Si X-ray mask that has a membrane structure in the future.

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