SILICON OXIDE NANOIMPRINT STAMP FABRICATION BY EDGE LITHOGRAPHY REINFORCED WITH SILICON NITRITE

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Abstract — The fabrication of silicon oxide nanoimprint stamp employing edge lithography in combination with silicon nitride deposition is presented. The fabrication process is based on conventional photolithography and wet etching methods. Nanoridges with width dimension of sub-20 nm were fabricated by edge lithography. Additional silicon rich nitride layer was deposited over the original silicon dioxide nano-ridges to improve the ridge stiffness and to achieve a positive tapered shape which is friendly to nanoimprint. The replica of the nano-ridges with silicon rich nitride shield was obtained by imprint in PMMA.

Key Words: nanoimprint, stamp fabrication, edge lithography

I INTRODUCTION

Nanoimprint lithography (NIL) is an emerging lithographic technology that promises high-throughput patterning of nanostructures. There are two major nanoimprint methods available: step and flash imprint lithography (S-FIL) [1] and compression nanoimprint lithography [2]. In S-FIL, a low-viscosity photocurable monomer is dispensed on to a substrate. A transparent template, which can be made from fused silica for example, is brought into contact with monomer. After UV exposure the patterned and hardened polymer is ready for the next steps. The compression NIL was first introduced by the Chou group [2] in the mid 1990s. It is basically comprised of two steps: imprint and pattern transfer. In the imprint step, the stamp with nanostructures is pressed into a substrate coated with resist when it is heated. After cooling down, the stamp is released and the inverse pattern is formed. In the pattern transfer step, reactive ion etching (RIE) is employed to remove the resist residual layer, transferring the stamp pattern entirely into the resist. Although the stamps prepared for compression NIL should be strong enough to stand the high pressure during imprint, transparency is not an issue and basically any hard material can be used. In this report, we concentrates on the stamp fabrication for compression NIL.

The stamp used in nanoimprint lithography has the same functionality and importance as the mask used in conventional photolithography. The critical points need considering choosing a proper material to make the hard stamp including material hardness, material thermal expansion coefficient and compatibility with conventional microfabrication principles [3]. In nanoimprint lithography a widespread choice of stamp material is Si with an oxide layer on top. As to obtain nanostructures in imprint with higher resolution, the primary concern is to fabricate a stamp with high resolution. At present, electron beam lithography (EBL) is the most standard means of fabricating stamps with resolutions down to 100 nm[4-6].

Previously we reported the fabrication of nano-ridges by local oxidation of Si [7]. This is a unique fabrication scheme in which sub-20 nm ridge structures were fabricated using conventional photolithography. To further develop the technology, this report concentrates on the extension and analysis of the fabrication method. The mechanical strength and shape of nano-ridges are improved by depositing a layer of silicon rich nitride over the original SiOx nano-ridges. An example of using this reinforced stamp for nanoimprint is also demonstrated.

II EXPERIMENTAL

Figure 1 illustrates the SiO2 nano-ridges stamp fabrication process. For detailed experimental descriptions readers could refer to [7]. Here we concisely present the experimental data for easy understanding:

(a) Start with a Si <110> wafer, a 15 nm thick silicon rich nitride (SiNx) layer was deposited (LPCVD), which was then followed by a 40 nm thick TEOS deposition.
(b) After conventional photolithography, the line and spacing patterns were transferred to TEOS in 1%HF using photoresist as mask.

(c) After stripping the photoresist, 85% H$_3$PO$_4$ acid heated up to 180°C was used to pattern SiN$_x$ by using the TEOS as the mask layer.

(d) First TEOS is stripped in 1% HF. Then the nitride pattern is transferred to Si<110> using OPD 4262 as the etchant.

(e) The wafer was dry oxidized at 950°C using SiN$_x$ as the mask to protect the area where should not be oxidized. This is also referred as LOCOS (local oxidation of silicon) [8, 9].

(f) Then hot phosphoric acid was used again to strip SiN$_x$ mask. The fabrication of SiO$_2$ nano-ridges is completed by etching back into Si<110> using OPD 4262.

III RESULTS AND DISCUSSIONS

III.1 TEOS PATTERNING

In Figure 1 step (b), 1% HF was used as the etchant to pattern TEOS. The etch rate of TEOS in 1%HF is about 30 nm/min [10]. Visual inspection of etching step is not possible in this step since the underlying SiN$_x$ shows also hydrophilic surface characteristics as TEOS layer does. Therefore, 3 min etch, almost 100% over etch, was carried out to make sure complete pattern transfer.

III.2 SiN$_x$ PATTERNING

Hot phosphoric acid was used twice to etch SiN$_x$: step (c) and step (f) in Figure 1. It is known that the etch rate of SiN$_x$ in 85% H$_3$PO$_4$ at 180°C is 4.2 nm/min [10]. According to this etch rate, in step (c), the 15 nm thick SiN$_x$ should be finished patterning in 4 min. However, 6 min was needed at least to see water running following the line and spacing patterns. This can be explained by the fact that a thin native oxide layer could be formed during LPCVD SiN$_x$. Though 1%HF dip was done before SiN$_x$ deposition, a thin native oxide layer can also be formed when the wafer carriers were pushed into the center of the deposition system in which the standby temperature was around 700°C and air could go into the system during wafer loading. The etch rate of TEOS in 85% H$_3$PO$_4$ is 2.1 nm/min [10]. The thickness of TEOS layer of 40 nm is thick enough serving as SiN$_x$ patterning mask in this process, after which 12.6 nm of TEOS was consumed.

Concerning SiN$_x$ stripping in step f, 9 min etching time of SiN$_x$ was observed if the previous LOCOS step was set around 30 min. This longer etching time can be explained by that fact that SiN$_x$ can also be oxidized during LOCOS [11]. Furthermore, it was also found that the etching time of SiN$_x$ after LOCOS also depended on the oxidation time. For example, when the oxidation time was increased from 30 min to 3 hours, experiments showed that the etching time increased from 9 min to 15 min accordingly. Moreover, as the etch rate of SiO$_2$ in 85% H$_3$PO$_4$ is acid 0.3 nm/min [10], few nanometers of SiO$_2$ were also consumed during SiN$_x$ stripping.

III.3 SILICON DIOXIDE NANO-RIDGES

As mentioned in the experimental section, the SiO$_2$ nano-ridges were made by dry oxidation at 950°C, Figure 1(e). Dry oxidation was selected considering oxidation uniform over the whole wafer. Oxidation temperature can not go beyond 1100°C otherwise the protective SiN$_x$ can go through compositional change and consequently influence the subsequent etching process [10]. The height of the SiO$_2$ nano-ridges is mainly determined by the Si etching time in Olin OPD 4262, Figure 1(d), and the thickness can be tuned by oxidation time, Figure 1(e). Figure 3 is an electron scanning microscopy (SEM) picture showing a SiO$_2$ nano-ridge of 20 nm in maximum width by LOCOS of 25 min. Figure 4 illustrates a SiO$_2$ nano-ridge of 80 nm in maximum width by LOCOS of 3 hours.
layer of SiN, after step (f) in Figure 1. SiN was chosen because it has a lower compression strength compared with stoichiometric silicon nitride and it is a stronger material compared with SiO₂. Figure 4 illustrates a SiN shield nano-ridge of 120 nm in maximum width. The SiN was deposited over a sample of SiO₂ nano-ridges of 20 nm in maximum width. In Figure 3, there is an over etch in Si according to Figure 1 step (f). The over etch, which went beneath the bottom SiO₂ layer, together with the thinning at SiO₂ corner were filled by SiN, and finally came to an angle slightly larger than 90°. Deposition also lead to a rounded top surface[13].

The shape of the SiO₂ nano-ridges is inherent in the oxidation process [12]. After oxidation the corner where <110> and <111> intersects showed rounding and sharpening effects, as indicated by points A and B in Figure 3 respectively. Moreover we can also observe SiO₂ thickness difference in Figure 3: W₂ is thinner than both W₁ and W₃.

As the main object of making the nano-ridges is for nanoimprint, the ridges should be strong enough to withstand imprint conditions, saying, high temperature and high pressure. The thinning effect at the corner of SiO₂, referring to points A and B in Figure 3, can be a critical point since it can break when it is completely or partly exposed, comparing Figure 2 and 3. To strengthen the SiO₂ nano-ridges, the Si etching depth in Figure 1(f) can be intentionally tuned to be less deeper than that in Figure 1(d) [7].

III. 4 NANO-RIDGES WITH SiN SHIELD

The thickness at W₂, referring to Figure 3, is increased with longer oxidation time. However, it will still remain as the critical point for imprint. Therefore we came to an idea of depositing another layer of SiN after step (f) in Figure 1. SiN was chosen because it has a lower compression strength compared with stoichiometric silicon nitride and it is a stronger material compared with SiO₂. Figure 4 illustrates a SiN shield nano-ridge of 120 nm in maximum width. The SiN was deposited over a sample of SiO₂ nano-ridges of 20 nm in maximum width. In Figure 3, there is an over etch in Si according to Figure 1 step (f). The over etch, which went beneath the bottom SiO₂ layer, together with the thinning at SiO₂ corner were filled by SiN, and finally came to an angle slightly larger than 90°. Deposition also lead to a rounded top surface[13].

The nano-ridge with a SiN shield has its merits in stronger ridge stiffness and slightly positive taper compared with original SiO₂ nano-ridge. The improved stiffness enables the stamp to be reused more in nanoimprint; while the positive taper shape is an advantage for easy demoulding. However the SiN shield can lead to the loss of sub-20 nm scale. Since the SiO₂ is the basis for further SiN deposition, the width of SiO₂ should be strong enough as to survive in the following fabrication handling after step (f) in Figure 1.

III. 5 NANOIMPRINT LITHOGRAPHY BY USING STAMPS OF SiN REINFORCED RIDGES

The samples with nano-ridges fabricated as described in the previous sections were used as stamps for nanoimprint. Imprint was made by using Poly(methylmethacrylate) (PMMA), which has a glass transition temperature Tg of 105°C. After cleaning the 2cm by 2cm sample of nano-ridges in Piranha, a monolayer of 1H, 1H, 2H, 2H-perfluorodecytrichlorosilane (PFDS) was coated in the gas phase under vacuum condition in a desiccator. The imprint was carried out at a
temperature of 200°C and pressure of 40 bars. The stamp and polymer substrate were separated when the temperature was cooled down lower than \( T_g \).

Figure 6 shows the imprint replica of \( \text{SiN}_x \) nano-ridges, which is shown in Figure 5. As to obtain a clear imprint cross-section view, the imprint sample was broken manually after frozen in liquid nitrogen. Since the polymer and Si substrate have different compression coefficient, the cross-section of PMMA showed a different rapture. However, we can still see the nice replication of the structures on the stamp in PMMA.

![Figure 5 SEM picture of a nano-ridge with \( \text{SiN}_x \) shield of 500nm in maximum width](image)

![Figure 6 SEM picture of imprint replica of \( \text{SiN}_x \) nano-ridges of 500 nm in maximum width](image)

### IV CONCLUSION

We reported the fabrication of \( \text{SiO}_2 \) and \( \text{SiN}_x \) nano-ridges which can act as the stamp for nanoimprint. The maximum width of the \( \text{SiO}_2 \) nano-ridges can be tuned from 20 nm to hundreds of nanometer depending on oxidation time. The shape of the \( \text{SiO}_2 \) nano-ridge is an intrinsic characteristic in oxidation. The strength of the \( \text{SiO}_2 \) nano-ridges can be improved by tuning Si etching time in step f to be less than that in step d in Figure 1. Another option is to deposit another layer of \( \text{SiN}_x \) over the original \( \text{SiO}_2 \) nano-ridges. Though the strength and shape of the nano-ridges are improved by this additional \( \text{SiN}_x \) deposition, it may lead to the lost of sub-20 nm nano scale compared with that of the original \( \text{SiO}_2 \) nano-ridges. The stamp replication in PMMA using \( \text{SiN}_x \) nano-ridges was successfully carried out.

### REFERENCES


