A Highly Reliable Pattern Transfer of Hydrogen Silsequioxane

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ABSTRACT

In this paper, we focus on the effects of process parameters on pattern embossing into HSQ films, and the pattern degradation of HSQ for room temperature aging effects. We used MIBK to dilute HSQ (FOx15, Dow Corning) to control the film thickness. NX-1000 (Nanonex) was used to imprint HSQ embossed with Si grating mold at 25~180^{0}C under 2~2.5MP. The experiment results show the HSQ films diluted with MIBK become more suitable for imprinting. In order to get fidelity replication, the optimum process parameters can be determined. The dilute HSQ is prebaked at 150^o C for 3 min and imprinted at 180^o C for 2 min under the pressure of 2.5 MPa. This sample also shows no degradation in replication patterns after aging at room temperature for 20 days.

Keywords: hydrogen silsesquioxane (HSQ), nanoimprint lithography (NIL)

1. INTRODUCTION

Photolithography has been the patterning technology for manufacturing integrated circuits. However, due to diffraction limit, there are no expectations that sub-100 nm features could be easily patterned by traditional photolithography. Therefore, nanofabrication technologies are indispensable techniques for making sub-100 nm features. Nanoimprint lithography (NIL) is a very useful lithography technique to make nanostructure devices with high resolution and low cost [1] and regarded as one of 10 emerging technologies that likely to change the world [2].

The principle of nanoimprint lithography is quite simple. In this method, a mold with engraved patterns is mechanically pressed onto a substrate coated with a resist material (such as PMMA) at a certain temperature and pressure conditions. This compression leaves the "negative" of the mold patterns in the resist when the pressure is released and the mold is lifted. The resist layer having this thickness contrast, which the photolithography essentially does, thereby realizes the pattern transfer onto the substrate. PMMA is the most used material as NIL replication resist. Recently, some resist materials are proposed to replace PMMA such as hydrogen silsequioxane (HSQ).

In the works of Matsui et al. [3], they proposed room temperature NIL using HSQ as a replicated material. They found the room-temperature imprinting depth decreases suddenly around prebaked at 150^{o}C with pressure set in a range from 2.5 to 4.5 MPa. The replicated nano-scale patterns of holes (90 nm diameter and 600 nm pitch) and lines (50 nm linewidth and 200 nm pitch) were obtained after impressed at 4.0 MPa for 1 min, which was pre-baked at 50^o C for 20 min.

As discussed above, although HSQ has been demonstrated as a useful NIL resist for its superior properties, the fidelity between mold and imprinted HSQ patterns has not yet studied in reasonable pressure range. Also, it is still no research to investigate the effects of room temperature aging on imprinted HSQ patterns. In this paper, we focus on the effects of process parameters on pattern embossing into HSQ films. By comparing the imprinted patterns, we determine optimized process parameters. Another objective of works is placed on the pattern degradation of HSQ films for room temperature aging effects.

2. EXPERIMENTS

Table 1 lists compositions and process parameters of HSQ prepared for the study. HSQ (FOx15, Dow Corning corporation) was mixed with methylisobutylketone (MIBK) in a ratio of 2:1 or 4:5 and stirred for 2 hrs.

Before coating HSQ, 6” silicon wafers were cleaned using RCA process and then dried with N_2. The HSQ solution was spun onto silicon wafers in two steps, 1000 rpm for 10 sec and then 6000 rpm for 20 sec. HSQ films were then prebaked at 50°C or 150°C for 3 min on hot plate.

Table 1. Compositions and process parameters of HSQ.

Sample code	HSQ: MIBK	Prebake T	Imprint P	Imprint T
A150-25-130	2:1	150ºC	2.5 MPa	130ºC
B150-25-130	4:5	150ºC	2.5 MPa	130ºC
B150-25-180	4:5	150ºC	2.5 MPa	180ºC
B150-20-180	4:5	150ºC	2.0 MPa	180ºC
B050-25-025	4:5	50ºC	2.5 MPa	25ºC

A 6” silicon mold, which had pattern of grating lines with 56 nm in width, 72 nm in depth was provided by Nanonex. Imprinting of HSQ was conducted by using NX-1000 (Nanonex). After vacuuming, the pre-press was set as 0.8 MPa by introduced Ar introduced into the chamber during heating-up. Once the defaulted temperature (25º C, 130º C or 180ºC) is reached, the imprint press pressure was rapidly raised to 2.0 or 2.5 MPa within 10 sec and kept for 2 min then cooling to room temperature and releasing the press pressure.

The imprinted HSQ was cut into pieces for following tests: SEM observations, FTIR and nano-indentation tests. A Hitachi S-4000 scanning electron microscope (SEM) was used to examine the pattern replication of as imprinted HSQ. After aged in room temperature for several days, the imprinted HSQ was observed again by SEM to check the pattern degradation. The chemical structures of HSQ films were investigated by reflected mode of Fourier transform infrared (FTIR). “XP CSM Standard Hardness, Modulus, and Tip Cal” mode is adapted to measure the mechanical properties of HSQ films by using nanoindenter (Nano Indenter XP System, MTS, America). The defaulted depth is set as 50 nm. The strain rate target is set as 0.05 1/s, surface approach velocity is set as 10 nm/s.

3. RESULTS AND DISCUSSIONS

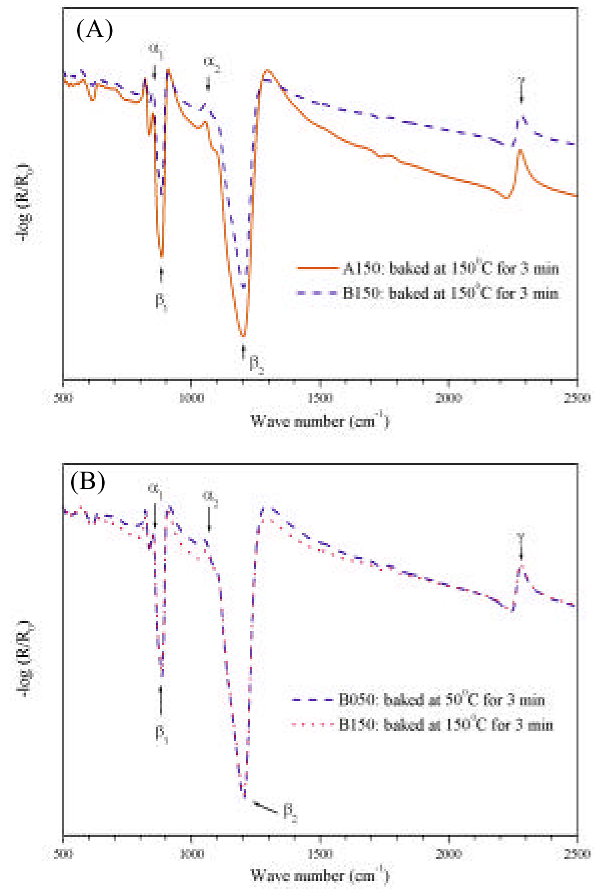

Figure 1. The reflectance FTIR for process parameters effects on HSQ films.

Figure 1 shows the chemical structure of HSQ films measured by reflectance FTIR. Figure 1(A) describes the effects of dilution, and Figure 1(B) shows the effects of heat treatments. Table 2 lists the characteristic structure for HSQ film as shown in Figure 1. α_1 and α_2 presents the network bonding, β_1 and β_2 is the cage-like bonding.

Table 2. The characteristics of chemical bonding in HSQ.

Symbol	Bonding structure	Wave number (cm^{-1})
α_1	Network Si-O bending	822
β_1	Cage-like Si-O bending	881
α_2	Network Si-O stretching	1064
β_2	Cage-like Si-O stretching	1175
γ	Si-H	2250

As shown in Figure 1(A), the network characteristic Si-O peaks (α_1 and α_2) of A150 and B150 show not obviously difference in areas, but the cage-like characteristic Si-O peaks (β_1 and β_2) of A150 is significant larger than B150. This result suggests that the samples A are more cage-like than samples B. In the Figure 1(B), B150 and B050 also differs in the two characteristic bond peaks of αs. Although the peak intensities of βs seem to be almost the same for B050 and B150, the αs of B150 shows higher peak intensity than B050. This result presents that the network type bonding is promoted as increasing prebaking temperatures from 50º C to 150º C. This difference in structure is responsible for the imprinting result.

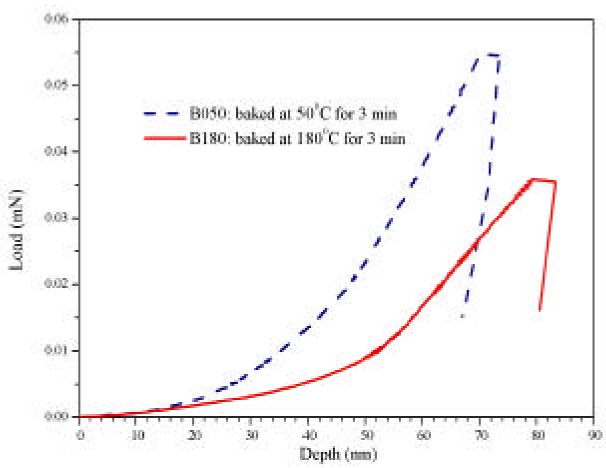

Figure 2. The load-displacement behaviors of HSQ films.

In further analysis of the effects of process parameters on HSQ properties, we test the mechanical property of HSQ by using nanoindenter. Figure 2 shows the typical load-displacement curves of HSQ films. They could be correlated to the hardness of HSQ films. With the same strain rate target and surface approach velocity, it needs about 0.055 mN to indent B050 into 70 nm, but it is only about 0.035 mN to penetrate B180 into 80 nm. In other words, it is easier to imprint into B180 than B050. It might be due to the different degree of residue of MIBK. We can expect that baked at 180º C makes HSQ more suitable for imprinting.

Table 3 summarizes the average width and depth of imprinted HSQ films observed by SEM. A150-25-130 shows 40.2 nm in width and 31.4 in depth. B150-25-130 is 40.2 nm in width, 58.5 nm in depth. Both patterns have shallower depth than mode. It means the in situ temperature of imprint is too low. Then we increase the temperature up to 180º C. The replication of B150-25-180 is 58.1 nm in width and 74.1 in depth. It has almost the same pattern with mold. Decreasing imprint pressure to 2.0 MPa, B150-20-180 only shows 22.9 nm in depth with 42.9 nm in width. It implies 2 MPa is not enough for imprint process. For room temperature imp rint, we find the line width is 41.5 nm for B050-25-025. Except of B150-25-180, all imprinted patterns are deviated from the grating lines of mold. The fidelity pattern replication between B150-25-180 and mold is due to the plastic deformation of B150-25-180 during imprinting process.

Table 3. The characteristics of mold pattern and imprinted HSQ films.

Sample code	Thickness (Å)	Width (nm)	Depth (nm)
Mold		56	72
A150-25-130	4000	40.2	31.4
B150-25-130	2380	40.2	58.5
B150-25-180	2380	58.1	74.1
B150-20-180	2380	42.9	22.9
B050-25-025	2380	41.5	N.A.

Comparing the imprint results of A150-25-130 and B150-25-130, the imprint depth of B150-25-130 is deeper than A150-25-130. As mentioned above, the dilution of HSQ with MIBK results in different chemical structure. It is why B150-25-130 has deeper imprinted depth than A150-25-130. This result suggests that the dilution of HSQ affects not only the film thickness but also pattern transfer.

The sidewall of B150-25-130 (Figure 3(A)) tapers in tips, but B150-25-180 (Figure 3(B)) shows steeper profile. According to the discussions, raising temperature to 180º C makes HSQ easier to imprint. The applying force helps the HSQ to adjust its configuration to conform the mold pattern. And the fidelity replication is kept as shown in Figure 3(B) after cooling to room temperature and removing the applied force. When imprinting HSQ, the energy is either used to deform the molecules or to compact the free volume spaces between molecules. Because of the dense packing nature of cage type structure for baking at low temperature, there is little free volume space between molecules. In contrast, the porous network structure has larger free space. As results, it should be easier to compact network type HSQ than cage type HSQ.

The room temperature aging effects on pattern degradation of imprinted HSQ is shown in Figure 4. After aging in room temperature for 4 days, the line shape of B050-25-025 is heavily distorted. The line width marked by an arrow in Figure 4(A) varies from 51.2 to 36.2 nm. However, the line shape of B150-25-180 is still straight, after 20 days aging. Figure 4(B) shows the individual line varying from 57.0 to 59.8 nm in width.

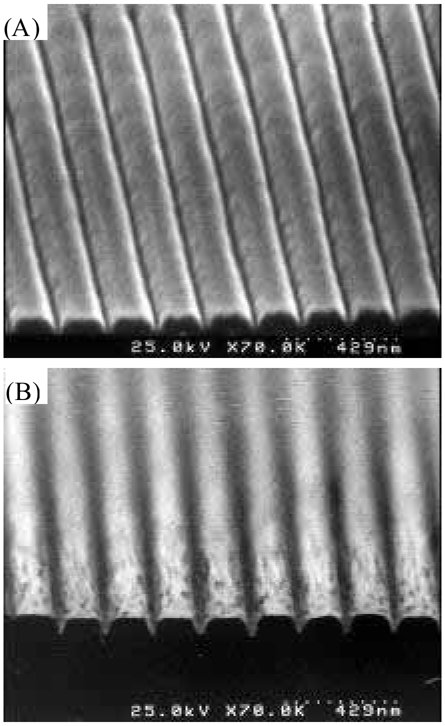

Figure 3. 45^0-tilted SEM pictures of (A) B150-25-130 (B) B150-25-180

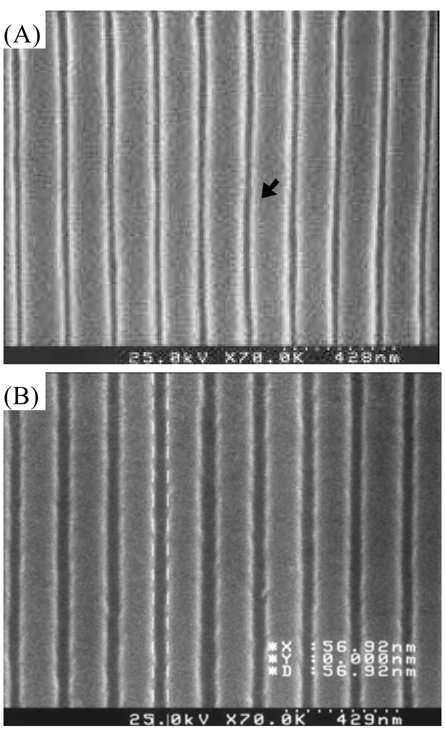

Figure 4. SEM pictures of samples. (A) B050-25-025 after 4 days aging, (B) B150-25-180 after 20 days.

Forming network bonds can unit individual HSQ molecules to form a stable 3-dimension structure. For cage-like HSQ, the movements of molecules are determined by the oligomer itself only. Once forming the network bonding, the movements of atoms are constrained by neighbor molecules and become more difficult. In another word, forming the network connections fasten HSQ atoms on their own sites. In this mechanism, the formation of network bonding makes HSQ more stable than cage-like type HSQ, and become uneasy affected by room temperature age. So, the shape and line width of network type HSQ is not easy to change. It is why the line width and line shape both are the same of B150-25-180 without or with aging at room temperature for 20 days.

Because of lacking 3 dimensional interlocking bonding, the imprint deformation is not permanent for B050-25-025. After 4 days aging at room temperature, some portion of HSQ relaxes from imprint compaction. This stress relaxation is random and causes the inhomogeneous dilation or shrinkage of lines. Finally, the line shape becomes heavily distorted and contributes to the variation of line width as shown in Figure 4(A).

4. CONCLUSION

In this study, we focus on the effects of process parameters on pattern embossing into HSQ films, and the pattern degradation of HSQ for room temperature aging effects. It can be concluded that after dilution with MIBK, the HSQ films with network bonding become more suitable for imprinting. The plastic deformation of B150-25-180 during imprinting process gives fidelity pattern replication. Meanwhile, the formation of network bonding makes HSQ more stable than cage-like type HSQ. As a result, the B150-25-180 shows no degradation in replication patterns after aging at room temperature for 20 days.

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