Evaluation of Heat Durability of Fluorinated Antisticking Layers

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1. Introduction

The nanoimprint lithography (NIL) [1-5] is attracting considerable from many industrial field because it is a promising method to fabricate various nanostructure applications with a low cost and a high throughput. In NIL, the mold must be in direct contact with resin during NIL. Therefore, the mold is usually coated with an antisticking layer to avoid resist adhesion and fluorinated self-assemble monolayer (F-SAM) is known as a good antisticking layer. In thermal NIL, the temperature of the antisticking layer coated on the mold increases around the glass transition temperature of thermoplastic resin. Therefore, it is important to investigate the heat durability of antisticking layers. And, in recent years, the thickness of the antisticking layer is becoming a key issue as size of the nanostructure fabricated by NIL close to nanometer-level.

In this study, we investigated the heat durability of three kinds of F-SAMs with different chain length. We evaluated the macro- and nano-scale releasing effect of F-SAMs with and without annealing by measurement of contact angle and adhesion forces obtained by scanning probe microscopy (SPM). And we analyzed chemical compositions by X-ray photoelectron spectroscopy (XPS).

2. Experiment

2.1 Coating fluorinated antisticking layers

In this study, we used F₃-SAM, F₁₃-SAM and F₁₇-SAM formed by using (3,3,3-Trifluoropropyl)trichlorosilane (F₃-TCS), (Tri-decafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (F₁₃-TCS) and (Heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane (F₁₇-TCS) respectively, as antisticking layers. These F-SAMs have different chain lengths, F₃-SAM has the shortest and F₁₇-SAM has the longest chain length of three monolayers. We diluted commercially available F₃-TCS, F₁₃-TCS and F₁₇-TCS (Gelest Inc.) by 0.1 weight % busing a thinner (HD-TH, HARVES Co., Ltd) and used those as the antisticking agents. The method of forming antisticking layers is as follows. First, each antisticking agents was spin-coated onto a Si substrate. Second, the coated Si substrates were taken into the high humid environment to make chemical bonding between the antisticking layer and the surface of the Si substrate. Finally, the excess antisticking agent on the Si substrates was washed-off by using HD-TH as a rinse agent.

2.2 Releasing Effect of F-SAMs without and with annealing

We annealed Si substrates coated with F₃-SAM,
F_{13}-SAM and F_{17}-SAM at 300, 400, 500, 600 and 700 °C at a vacuum pressure of $1 \times 10^{-3}$ Pa. Figure 1(a) shows the annealing process. A uniform-temperature heat-treatment system (Thermo Riko: GFA430VN) was used in this study. To evaluate the macro-scale releasing effect of F_{3}-SAM, F_{13}-SAM and F_{17}-SAM without and with 300, 400, 500, 600 and 700 °C annealing, we measured the contact angles of these F-SAMs with a commercially available contact angle meter (Kyouwa Interface Co: Drop Master 500). And the nano-scale releasing effect was evaluated by measuring adhesion forces obtained from force curves[6-8]. A SPM system (SII NanoTechnology: E-sweep/NanoNavi Station) using a Si cantilever with a spring constant of 0.33 N/m was used for measuring force curves. The contact force was 5 nN.

We next examined the dependence of F_{3}-SAM, F_{13}-SAM and F_{17}-SAM durability on annealing time at 400 and 500 °C by using another annealing process shown in Fig 1(b). The temperature was kept at 400 °C for 1, 2, 3 hours and at 500 °C for 30, 60, 90, 120 min.

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(b)

2.3 Surface state of F_{3}-SAM, F_{13}-SAM and F_{17}-SAM with and without annealing

We analyzed the surface states of F_{3}-SAM, F_{13}-SAM and F_{17}-SAM before and after annealing with the process shown in Fig. 1(a) by XPS. XPS measurement was carried out using the conventional photoelectron spectroscopy apparatus, which was mounted with a hemispherical electron energy analyzer (VSWCL150). The Mg Kα line ($\lambda v = 1253.6$ eV), used as X-ray source, was incident at 45° with respect to the surface normal, and XPS spectra were recorded at the emission angle of 45° to the surface normal. The total energy resolution was approximately 1.0 eV. The base pressure in the photoelectron analysis chamber was $2 \times 10^{-8}$ Pa.

3. Results and Discussion

3.1 Releasing effect of F_{3}-SAM, F_{13}-SAM and F_{17}-SAM without and with annealing

To evaluate the macro-scale releasing effect of F_{3}-SAM, F_{13}-SAM and F_{17}-SAM without and with 300, 400, 500, 600 and 700 °C annealing, we measured contact angles of those. Figure 2 shows the annealing temperature dependence of contact angles of F_{3}-SAM, F_{13}-SAM and F_{17}-SAM.

![Fig. 2. Annealing temperature dependence of contact angle of F_{3}-SAM, F_{13}-SAM and F_{17}-SAM.](image)

The contact angles of F_{3}-SAM, F_{13}-SAM and F_{17}-SAM clearly decreased around 500-600 °C annealing. We next evaluated nano-scale releasing effect by measuring adhesion forces. Figures 3. (a), (b) and (c) show the adhesion forces of F_{3}-SAM, F_{13}-SAM and F_{17}-SAM before and after 400, 500 and 600 °C annealing, respectively. The adhesion forces of F_{3}-SAM, F_{13}-SAM and F_{17}-SAM rapidly increased at 500 °C annealing. This result indicates that F_{3}-SAM, F_{13}-SAM and F_{17}-SAM were decomposed by 500 °C annealing.
To investigate heat durability at 400 and 500 °C, the annealing time dependence at 400 and 500 °C of the contact angles for F\textsubscript{3}-SAM, F\textsubscript{13}-SAM and F\textsubscript{17}-SAM was measured by using annealing process shown in Fig. 1(b). Figure 4(a) shows the annealing time dependence at 400 °C of the contact angles for F\textsubscript{3}-SAM, F\textsubscript{13}-SAM and F\textsubscript{17}-SAM. The contact angles of F\textsubscript{3}-SAM, F\textsubscript{13}-SAM and F\textsubscript{17}-SAM decreased as annealing time increased. This result indicates that three kinds of F-SAMS decompose at 500 °C annealing.

3.2 Surfaces state of F\textsubscript{3}-SAM, F\textsubscript{13}-SAM and F\textsubscript{17}-SAM before and after annealing.

We analyzed the chemical compositions of F\textsubscript{3}-SAM, F\textsubscript{13}-SAM and F\textsubscript{17}-SAM without and with annealing at 400, 500 and 600 °C annealing by XPS. The F-SAMS were annealed with the process shown in Fig. 1(a). Figures 5(a), (b) and (c) show C 1s spectra of F\textsubscript{3}-SAM and F\textsubscript{13}-SAM and F\textsubscript{17}-SAM obtained by XPS, respectively. The strong peak at 294 eV in Figs. 5(a) was assigned to the CF\textsubscript{3} groups of the F\textsubscript{3}-SAM. And the two peaks at 292.5 and 294.8 eV in Figs. 5(b) and (c) correspond to CF\textsubscript{3} and CF\textsubscript{2} groups, respectively. The peak center of CF\textsubscript{3} groups of F\textsubscript{3}-SAM is lower than those of F\textsubscript{13}-SAM and F\textsubscript{17}-SAM because the CF\textsubscript{3} groups of 13-SAM and F\textsubscript{17}-SAM bind to CF\textsubscript{2}.
which might have great electronegativity. The two broad peaks centered at binding energy of 287 and 285 eV in Figs 5. (a), (b) and (c) are assigned to C-O and C-C, respectively. The intensity of CF$_3$ groups of F$_3$-SAM, rapidly decreased at 500 °C annealing, as shown in Fig. 5(a). And intensity of CF$_3$ and CF$_2$ of F$_{13}$-SAM and F$_{17}$-SAM also decreased by annealing at 500 °C, as shown in Figs. 5(b) and (c). From these results, it was confirmed that the three kinds of F-SAMs thermal decomposed at 500 °C annealing.

4. Conclusion

We investigated the heat durability of F$_3$-SAM, F$_{13}$-SAM and F$_{17}$-SAM by measuring contact angle, adhesion forces and XPS. These results indicate that F$_3$-SAM, F$_{13}$-SAM and F$_{17}$-SAM have thermally decomposed by 500 °C annealing.

Reference