

Reduction in Viscosity of Quasi-2D-Confined Nanoimprint Resin through the Addition of Fluorine-Containing Monomers: Shear Resonance Study

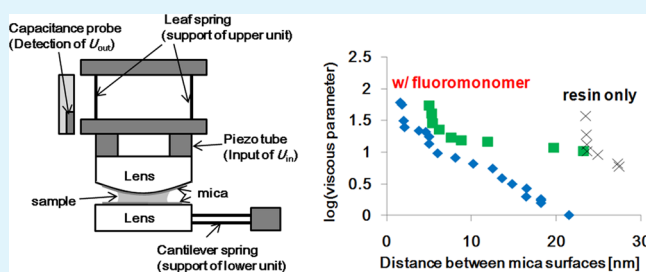
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ABSTRACT: The fluidity of the resin for the nanoimprint lithography was investigated in a quasi-2D space by the shear resonance measurement, which enables us to measure the viscous property of the resin confined in a nanometer gap between mica surfaces. With this technique, we could observe that the resin fluidity was enhanced by the addition of the fluorine-containing monomer. The fluidity of the resin with the fluorine-containing monomer was maintained until the distance between mica surfaces became smaller than 15 nm, whereas the resin without the fluorine-containing monomer started losing its fluidity when the distance became 30 nm. Two reasons possibly explain the result; (i) the interaction between the resin and mica was reduced by the existence of the fluorine-containing segregated layer at the interface, and (ii) the reduction in viscosity took place by the addition of the fluorine-containing monomer that reduced the degree of chain entanglement in the resin because of its small intermolecular interaction force. The effect of the length of the perfluoroalkyl chain in the fluorine-containing monomer is also discussed.

KEYWORDS: shear resonance measurement, resin fluidity, nanoimprint, fluorine-containing monomer



INTRODUCTION

Nanoimprint lithography (NIL) is one of the promising techniques to fabricate fine structures in the length scale ranging from several micrometers down to 5 nm.^{1,2} The advantage of using NIL lies in that it consists of very simple operations; (i) pressing a mold onto a resin surface and (ii) releasing the mold to give the structures. UV-NIL,^{3,4} where the resin is cured by the irradiation of UV light before the mold release, has been developed with a great pace due to the expectation for its fast-production ability and high cost performance. The application of this NIL technology enables us to create the fine resist patterns with the length scale below 100 nm. However, several problems have been impeding the UV-NIL to be applied to the device production. One of the problems is regarding the residual layers.⁵ Because of the interaction between the resin and the substrate that supports the resin, the fluidity of the resin on the substrate is restricted when the resin is pressed by the mold. Therefore, the residual layer is unavoidably formed on the substrate, and a thicker residual layer results from the resin with low fluidity in the small gap between the mold and the substrate. The influence of the thick residual layer is huge because the complementary etching of the thick residual layer often results in the destruction of the original shape of the resist patterns, especially when the length scale of the structure is smaller than 100 nm.

Therefore, the methodology for the reduction of the thickness of the residual layer should be developed to obtain resist patterns that function properly as an etch mask for the fabrication of fine patterns in the device.

In this study, the fluidity of the resin for the UV-NIL is investigated in a quasi-2D space by the shear resonance measurement to obtain a resin with high fluidity in the gap between the mold and the substrate. The shear resonance measurement enables us to measure the viscoelastic property of the resin through the analysis of the resonance vibration behavior of the measuring system.⁶ With this technique, we compared the fluidity of the resins with different kinds of fluorine-containing monomers through the comparison of the viscous parameters (damping parameters) of the resins. There are some reports on the resin with fluorine-containing materials for the UV-NIL. Bongiovanni et al. reported that the fluorine-containing materials were segregated at the resin-mold interface due to the surface energy difference between the resin and the fluorine-containing materials.^{7,8} Furthermore, Bender et al. showed that because the segregated layer has low surface energy and small interaction with the mold, multiple imprints

Received: April 15, 2013

Accepted: August 9, 2013

Published: August 9, 2013

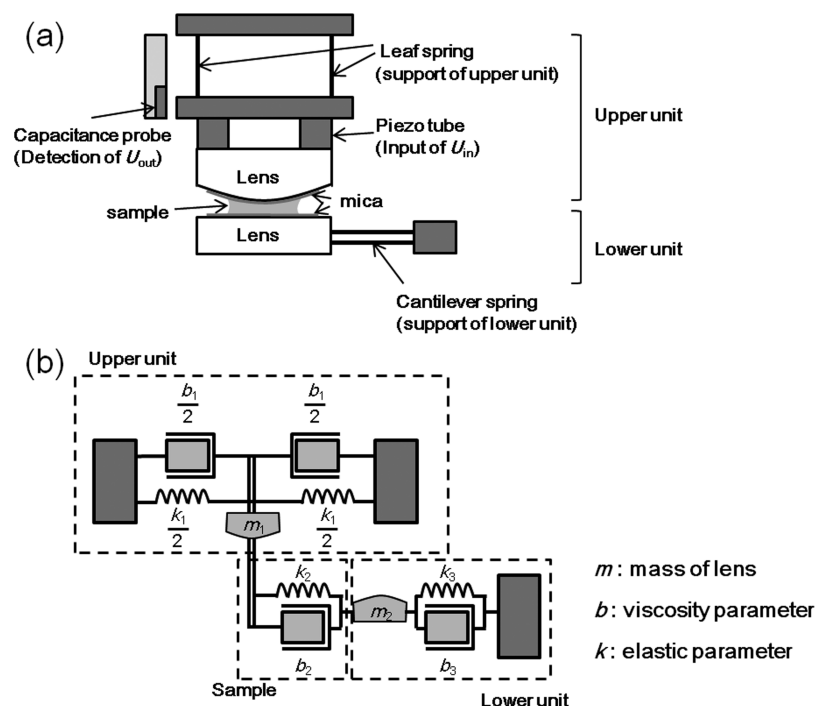


Figure 1. (a) Setup for the shear resonance measurement and (b) schematic illustration of physical model.

up to 50 times could be achieved onto the resin with the fluorine-containing material without mold cleaning.⁹ Given that the formation of the segregated layer would be also effective for the reduction of the interaction that retards the resin flow, the fluidity enhancement of the resin would be possible by the addition of the fluorine-containing materials. The fluidity enhancement of the resin would be beneficial for the reduction of the thickness of the residual layers that leads to the successful preparation of the fine patterns in the device.

EXPERIMENTAL SECTION

Figure 1a shows the setup of the shear resonance measurement. We used the system which was commercially available (RSM-1, ULVAC Inc.). Detailed explanation of this measurement can be found elsewhere.¹⁰ In brief, the sample was sandwiched between the cleaved mica surfaces on the round glass lenses. In this study, we used mica surfaces as a substrate due to the technical reasons such as the requirement of the molecularly smooth surface for this measurement. The upper lens was equipped with a piezo-electric tube that could generate a horizontal input vibration on the sample. The distance between the mica surfaces was adjusted through the observation of the fringes of equal chromic order (FECO). The intensity of the output vibration from the system was monitored by the capacitance probe located on the side of the upper lens. The ratio of the output voltage to the input voltage (U_{out}/U_{in}) was measured as the frequency of the input vibration, ω , was varied. The U_{out}/U_{in} value is expressed as eq 1¹¹

$$\frac{U_{OUT}}{U_{IN}} = \frac{C}{\alpha} \frac{((K_2 - m_2\omega^2)^2 + \omega^2 B_2^2)}{([(K_1 - m_1\omega^2)K_2 - \omega^2 B_1 B_2 - k_2^2 + b_2^2 \omega^2]^2 + \omega^2 [(K_1 - m_1\omega^2)B_2 + (K_2 - m_2\omega^2)B_1 - 2k_2 b_2]^2)^{1/2}} \quad (1)$$

where the parameters are based on the analytical model shown in Figure 1b and $B_1 = b_1 + b_2$, $B_2 = b_2 + b_3$, $K_1 = k_1 + k_2$, and $K_2 = k_2 + k_3$. The values of the parameters were evaluated by the

least-squares fit of the data, and the fluidity of the sample was evaluated from the viscous parameter of the resin, b_2 , which becomes larger with the decrease in resin fluidity. The values of the elastic parameter of the sample, k_2 , was not discussed in this paper because the values of k_1 and k_3 , the spring constants of the upper and lower systems, respectively, were much larger than k_2 and the system did not have a sensitivity to discuss the dependence of k_2 on the experimental parameters.¹² The parameters associated with the system, k_1 , k_3 , b_1 , and b_3 , were measured in a separate experiment where no resin sample was placed between the upper and lower lenses.

Figure 2 shows the chemical structures of the fluorine-containing monomers. In this study, fluorine-containing acrylic

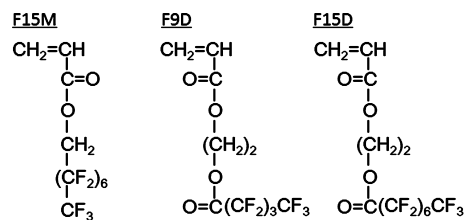


Figure 2. Chemical structure of the fluorine-containing monomers used in this study.

monomers with the different number of carbons in the perfluoroalkyl chains were used to investigate the dependence of the chain length of the additive on the resin fluidity in the quasi-2D space. F15M was purchased from Aldrich. F9D and F15D were synthesized by the esterification reactions of 2-hydroxyethyl acrylate with perfluorobutanoyl chloride and perfluoroheptanoyl chloride, respectively. These monomers were purified by the column chromatography, and the formation was verified by ¹H NMR and ¹⁹F NMR. The mixture of polyurethane with acrylic groups (EB8405, $M_w = 3 \times 10^3$, DAICEL-CYTEC Co. Ltd.) and neopentyl glycol diacrylate (A-NPG, Shin-Nakamura Chemical) was used as a base resin. The

combination of a functionalized urethane resin with a cross-linker such as A-NPG is often used as a standard component of the resist resin, which is the reason why we chose this combination as a base resin. For the composition of the samples, the concentration of EB8405 in A-NPG was 33 wt %, and the concentration of the fluorine-containing monomers was 3 wt % against the base resin. We confirmed that all the fluorine-containing monomers used in this study were soluble in the base resin.

RESULTS AND DISCUSSION

Figure 3 shows the measured data and the fitting curves for the samples with F15M. In Figure 3, the data were fitted well with

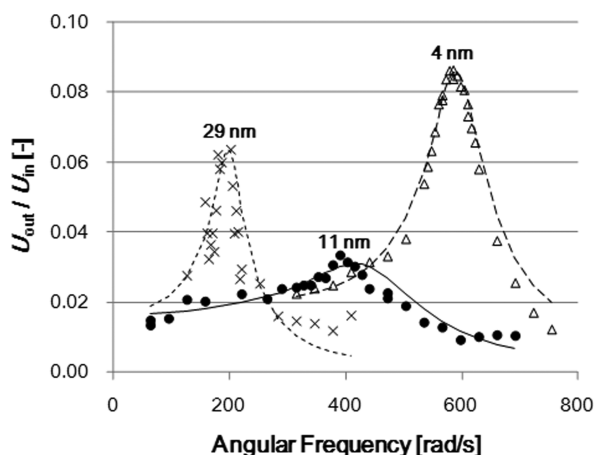


Figure 3. Resonance curves of the shear resonance measurement for the resin with F15M. The distances between mica surfaces are denoted in the figure.

the equation. Furthermore, the resonance peak shifted toward higher frequency when the distance between mica surfaces became smaller. The shift of the resonance frequency indicates the stronger viscoelastic coupling between mica surfaces and suggests the decrease in the fluidity of the resin between these surfaces. The peak intensities for 29 and 4 nm were stronger than that for 11 nm, because the strong resonances took place at these frequencies; the resonances of the upper system (29 nm) and the system where the upper and lower mica surfaces interact strongly (4 nm).

Figure 4 shows the viscous parameters of the resins with and without F15M as a function of the distance between mica

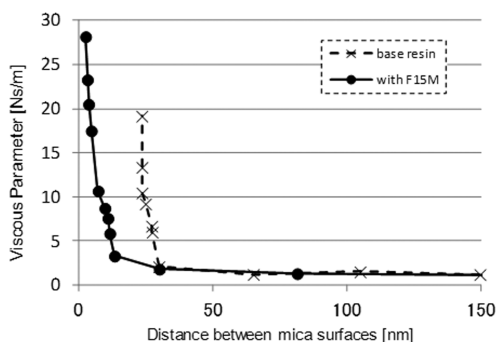


Figure 4. Dependence of viscous parameter on the distance between mica surfaces for the base resin (cross symbol) and the resins with F15M (filled circle).

surfaces. The viscous parameter of the sample without F15M increased rapidly as the distance was reduced down to 30 nm, and the distance could not be reduced below 20 nm due to the low fluidity of the resin. The increase in the viscous parameter can be explained as follows. As the distance between mica surfaces decreased, the ratio of polyurethane molecules near the mica surfaces increased. Therefore, the contribution of the polar–polar interaction between urethane group and mica surfaces¹³ was not negligible. This resulted in the increase in the degree of confinement of the EB8405 chains at the resin–mica interface, leading to the increase in energy required for the resin to flow and, thus, the viscous parameter. However, the viscous parameter for the resin with F15M did not increase until the distance between mica surfaces became 15 nm, and the distance could be reduced down to 4 nm. One of the possible reasons is that the interaction between the resin and the mica surface was reduced by the existence of the fluorine-containing segregated layer at the interface, and the energy required for the resin to flow was not influenced much by the interaction until the distance between the mica surfaces became 15 nm. Also, the reduction of the bulk viscosity would have to be taken into account to explain the fluidity enhancement because the bulk viscosity of the resin with F15M (1.1×10^2 mPa s) was somewhat smaller than that without F15M (1.3×10^2 mPa s).

We also investigated the dependence of F15M concentration on the viscous parameter, and found that the reduction in the viscous parameter took place when the concentration of F15M was more than 0.3 wt % against the base resin. Assuming that all the F15M molecules are segregated near the hypothetical surface layer whose thickness is 1.3 nm (full-stretched length of the F15M molecule), the concentration of F15M in the hypothetical surface layer is calculated to be 1.7 wt % when the mica–mica distance is 15 nm. This calculation suggests that the reduction in the interaction between the resin and the mica surface take place at a rather small concentration of F15M where the F15M molecules would not form packing structure.

Next, the viscous parameters for the resins with F9D and F15D were measured to investigate the dependence of the resin fluidity on the length of the perfluoroalkyl chain in the fluorine-containing monomers. Figure 5 shows the viscous parameters (on the logarithmic scale) for the resins with F9D and F15D as a function of the distance between mica surfaces. Because the bulk viscosities of the resin with F9D was the same as that with F15D (1.0×10^2 mPa s), the effect of the bulk resin viscosity

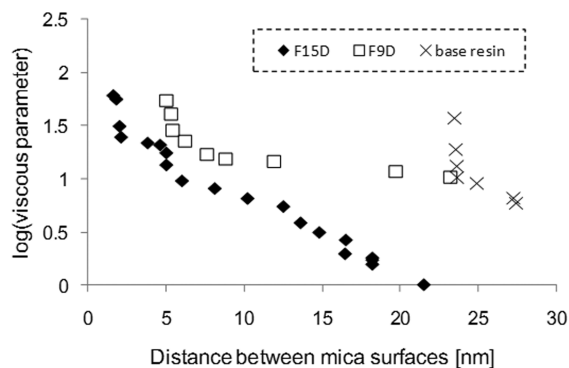


Figure 5. Dependence of viscous parameter on the distance between mica surfaces for the base resin (cross symbol) and the resins with F9D (unfilled square) and F15D (filled diamond).

on the discussion was minimized. In Figure 5, the viscous parameters of the resin with F9D had an increasing trend which was almost on the same line as that of the base resin, but the smallest distance between mica surfaces was as small as 5 nm, whereas the distance was 23 nm in the case of the resin without the fluorine-containing monomer. However, for the case with F15D, the viscous parameters as well as the smallest distance between mica surfaces became smaller than those of the base resin. This trend was also observed for the resin with F15M. These results suggest that the local viscosity of the resin is reduced when the fluorine-containing monomer with the longer perfluoroalkyl chain, which is soluble in the base resin, is applied to the resin. One of the possible explanations is that the perfluoroheptyl chain of F15D and F15M, which is concentrated at the interface because of the segregation, reduces the entanglement of the polyurethane molecules (EB8405) at the interface, resulting in the reduction in the viscosity of the resin in the small gap.

CONCLUSION

In conclusion, the fluidity of the resin for the nanoimprint lithography was investigated in a quasi-2D space by the shear resonance measurement. With this technique, we could observe that the addition of the fluorine-containing monomer enhanced the fluidity of the resin in the gap between mica surfaces. Two reasons possibly explain the result: (i) the interaction between the resin and mica was reduced by the existence of the fluorine-containing segregated layer at the interface, and (ii) the reduction in viscosity took place by the addition of the fluorine-containing monomer that reduced the degree of chain entanglement in the resin because of its small intermolecular interaction force. The monomer with the longer perfluoroheptyl chain (F15D and F15M) reduced both the viscous parameters and the smallest distance between mica surfaces, while the monomer with the shorter perfluorobutyl chain (F9D) reduced the smallest distance between mica surfaces only. The investigation is ongoing to clarify the reason of smaller viscous parameters of the resin with fluorine-containing monomers with the longer perfluoroalkyl chain.

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Notes

The authors declare no competing financial interest.

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