Viscosity Measurement of Spin-coated UV Nanoimprint Resin

Hiroshi Hiroshima\textsuperscript{a,b} and Hidemasa Atobe\textsuperscript{a,b,c}

\textsuperscript{a}National Institute of Advanced Industrial Science and Technology
1-2-1 Namiki, Tsukuba, Ibaraki 305-8564, Japan
\textsuperscript{b}Japan Science and Technology Agency, CREST
5 Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan
\textsuperscript{c}Tokyo University of Science
2641 Yamazaki, Noda, Chiba 278-8510, Japan
hiroshim@ni.aist.go.jp

Despite of the importance for understanding or predicting resin filling in UV nanoimprint, viscosities of UV curable resins used in UV nanoimprint were not well known and considered as same as those of UV curable resins in the bulk state. In UV nanoimprint, UV curable resin is commonly spin-coated on a wafer and a thin UV curable resin film is created. The ratio of surface to volume of a spin-coated film is extremely large in comparison to that in the bulk status. Therefore, it is possible that the viscosity of the spin-coated UV curable resin is changed by evaporation of some volatile components, for example. We constructed viscosity measurement apparatus for a thin liquid film, simply based on laminar shear of fluid between two plates. By using the viscosity measurement apparatus, it was found that the viscosity of UV curable resin supplied on a wafer by a droplet or by spin-coating with thickness larger than 2.3 \textmu m showed almost the same viscosity as that in the bulk state, however, when a thin film was created by spin-coating with a thickness smaller than that, the viscosity clearly increased. It was also found that viscosity of spin-coated UV curable resin increases with time or by heating and becomes 6 times of that in the bulk state for PAK-01. We succeeded in viscosity measurement of PAK-01 with a thickness of 0.58 \textmu m prepared from diluted PAK-01 (PAK-01-1000) and found that the UV curable resin was exactly Newtonian fluid in these thickness ranges.

\textbf{Keyword: viscosity, thin film, UV-curable resin, PAK-01, spin-coat, pentafluoropropane}

1. Introduction

UV nanoimprint lithography \cite{1-3} is a promising candidate of the next generation lithography due to high resolution at a low cost. UV nanoimprint lithography has potentially high throughput, however, the throughput is still not high enough to introduce UV nanoimprint into LSI production. We proposed high throughput UV nanoimprint using pentafluoropropane (PFP) enabling the use of spin-coated UV curable resins \cite{4}. In the PFP system, UV curable resin quickly fills mold recesses without accompanying rise in pressure of the trapped PFP due to condensation phenomenon. In the analysis of the filling process, we would like to use a viscosity of spin-coated UV curable resin (ToyoGosei PAK-01) but had to use a value of the viscosity of PAK-01 in the bulk state. In the case of UV

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nanoimprint, a unique and precise alignment called “in-liquid alignment” can be available, where the in-plane position of a mold is adjusted after making contact of the mold and UV curable resin on a wafer. A calculation tells that the viscous force generated in the in-liquid alignment is negligible small when the length for adjustment of a mold position is in the μm range. The calculation also tells that the force can be large enough to be detected if the velocity of in-plane motion of a mold is enough high. To move a mold initially at rest and finally at a high speed, the traveling length of the mold must be in the mm range and the travelling area of the wafer and the surface of the mold should be flat. We use molds with a flatness error of less than λ/20 and Si wafers of which flatness is not known but may be good for viscosity measurement. These conditions let us to measure the viscosity of thin liquid film on a wafer.

2. Viscosity measurement system [5]

2.1 Principle

A viscosity \( \mu \) of fluid between two plates and under laminar shear is determined from the following equation:

\[
\mu = \frac{Fh}{US}
\]  

(1)

where \( S \) is plate area, \( h \) is distance of plates, \( U \) is relative velocity of plates, and \( F \) is viscous force. From the relation between force and velocity, we can determine whether the fluid is Newtonian or not. For Newtonian fluid, a linear relation is obtained and a viscosity \( \mu \) is determined independent from velocity.

2.2 Apparatus

Figures 1(a) and 1(b) are a front view and a side view of the developed viscosity measurement apparatus, respectively. The upper unit holds a 10×10 mm\(^2\) quartz mold on a window of a mold holder via a rotatable joint. The upper unit has a gas inlet for efficient supply of gas (i.e. PFP) around the mold for simulation of actual UV nanoimprint. A Si wafer is held with the lower unit mount on a base unit by viscous coupling. A parallel contact between the mold and the wafer can be realized by the rotatable upper unit and the movable lower unit. Once a contact is created, the contact is maintained by the wettability of UV curable resin between the mold and the wafer.

2.3 Viscous force measurement

The upper unit is connected to a fatigue testing machine (Shimadzu MMT-101NB-10) via a load cell. The testing machine can move the actuator position according to a selected wave form (i.e. sine wave, triangle wave, block wave, and so on). We chose sine wave because of differentiability of position and variability of speed. Ten cycles of sine wave with amplitude of 0.5 – 2.0 mm and frequency of 2 Hz were applied and the position and force data were recorded at intervals of 10 ms. After the viscosity measurement, thickness distribution of the UV curable resin was frozen by UV light through the mold for thickness measurement.

2.4 Assessment of apparatus performance

The analysis of viscosity characteristics is described here taking polydimethylsiloxane with
a viscosity of 100 mPa·s as an example. As polydimethylsiloxane is not UV curable, we cannot freeze the thickness distribution in the viscosity measurement by UV exposure. Therefore, in this case, the thickness of polydimethylsiloxane contained between the mold and the wafer was estimated from the dispensed volume divided by the area of the mold.

Figure 2 shows time evolution curves of force and position for polydimethylsiloxane with a thickness of 1 μm. The position curve was clear sine wave and the force was nearly cosine wave. Figure 3 shows a Lissajous trajectory of the force and position where the inner 8 of 10 oscillation cycles in Fig. 2 are plotted so that transient data are excluded. The form of a slightly oblique ellipse means the main component of the force is originated in viscosity and force other than that is included a little. From Fourier analysis, the other component was found to be inertia force produced by the motion of the upper unit.

Since the position curve shown in Fig. 2 is virtually sine wave, velocities and accelerations at given times can be accurately determined. The inertia forces included in the obtained forces are subtracted by calculations and the relation between viscous force and velocity shown in Fig. 4 is derived. It is found that the polydimethylsiloxane with a thickness of 1 μm is Newtonian fluid since the viscous force is proportional to the velocity. The viscosity obtained from the slope of the regression line of the data was 90 mPa·s. Namely, the 1 μm thick polydimethylsiloxane film maintains the original viscous characteristics in the bulk state. From the above discussions, we also found that the viscosity measurement apparatus works well.

3. Viscosity of UV curable resin [5, 6]

3.1 UV curable resin dispensed as a droplet

Figure 5 shows time evolution curves of force and position obtained by viscosity measurement apparatus in the case that 0.1 μL of UV curable resin PAK-01 was supplied as a droplet. Similar sine waves as those of polydimethylsiloxane were obtained. By the same data processing described above, we can know the viscosity characteristics of a thin film of PAK-01 supplied as a droplet as shown in Fig. 6. It is found that the 1 μm thick PAK-01 film is Newtonian fluid.
The determined viscosity was 48 mPa·s and it is smaller by 30% than the viscosity of 71 mPa·s in the bulk state measured using a rheometer (CBC VM-10A-L). We cannot distinguish whether this discrepancy is really happened or not. However, we can conclude that the PAK-01 keeps Newtonian fluid characteristics with a viscosity not much different from the bulk value when UV curable resin PAK-01 is supplied as a droplet and the thickness of PAK-01 film is about 1 μm.

3.2 UV curable resin supplied by spin-coating

In UV nanoimprint, UV curable resin is commonly spin coated on a wafer and a thin UV curable resin film is created. The ratio of surface to volume of a spin-coated film is extremely large in comparison to that in the bulk state. Therefore, it is possible that the viscosity of the spin-coated UV curable resin is changed by evaporation of some volatile components and so on.

Figure 7 shows time evolution curves of force and position obtained by viscosity measurement apparatus in the case of UV curable resin PAK-01 was spin-coated with a thickness of 0.88 μm. In the measurement, we could reduce the noise level by selecting the optimal input range of the testing apparatus and thus results in
reduction of the amplitude of sine wave down to 0.5 mm. As the amplitude is rather smaller than the mold size, we expected to measure viscosities more accurately. Figure 8 shows the relation between viscous force and velocity of the spin-coated PAK-01. It showed Newtonian characteristics but showed viscosity of 250 mPas. The measurement reveals that the viscosity of spin-coated UV curable resin can become higher than that in the bulk state. In this case, the viscosity is 3.5 times larger than the bulk value.

3.3 Thickness dependence
Similar viscosity measurements were carried out for spin-coated PAK-01 films with larger thicknesses. The measurements were carried out as soon as spin-coated. Figure 9 shows the viscosity as a function of PAK-01 thickness. It was found that when PAK-01 thickness increases, the viscosity of the PAK-01 decreases down to 83 mPas at thickness of 2.3 μm and became constant at thickness larger than that. The viscosities of PAK-01 films with thicknesses larger than 2.3 μm are almost same as the viscosity of PAK-01 in the bulk state.

3.4 Stability of viscosity
Figure 10 shows the viscosity as a function of time after spin-coating where spin-coated PAK-01 films were measured after programmed times from spin-coating. The viscosity of 250 mPas just after spin-coating was 370 mPas in 10 min and became 450 mPas in 30 min. We think that some volatile components of PAK-01 are lost by evaporation and a change in composition of PAK-01 results in viscosity increase. The star indicated at a waiting time of 2 min in Fig. 10 is the result in the case of heating at 80°C for 2 min on hot plate. This result supports our speculation since the viscosity for heating is as same as that for keeping a sample in 30 min.

3.5 Measurement of thin resin film
As the original purpose of this study is to obtain viscous characteristics of thin films under UV nanoimprint conditions, it would be very attractive to measure UV curable resin films with a thickness far below 1 μm. Since the viscous force is inversely proportional to the thickness of fluid as indicated in equation (1), it becomes easier to detect the viscous force for the thinner UV curable resin. In contrast, it becomes more difficult to make a contact a thin UV curable resin film with a mold. We could make good contact for such thin UV curable resin films using a UV nanoimprint stepper [7] equipped

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![Graph](image1.png)

Fig. 9. Viscosity as a function of thickness just after spin-coating for PAK-01 and PAK-01-1000 (shown as a star).

![Graph](image2.png)

Fig. 10. Viscosity as a function of time after spin-coating. The result for heating at 80°C on hot plate is shown as a star.
with a special contact mechanism. However, it is difficult to realize such a contact in the viscosity measurement apparatus which has no such a sophisticated contact mechanism. The following are the results for the thinnest UV curable resin we could measure to date. Figure 11 shows time evolution curves of force and position obtained for PAK-01 with a thickness of 0.58 μm where the film was made from diluted PAK-01 (PAK-01-1000). As expected, larger forces are detected. Figure 12 shows viscous force as a function of velocity. The viscosity of this film was 330 mPa·s and it followed the viscosity trend as shown in Fig. 9. We found that UV curable resin PAK-01 was exactly Newtonian fluid in these thickness ranges.

3. Conclusion

We constructed viscosity measurement apparatus, which was simply based on laminar shear of fluid between two plates, for thin UV curable resin films and proved the performance through a measurement of polydimethylsiloxane as standard viscous fluid. By the viscosity measurement apparatus, it was found that the viscosity of UV curable resin PAK-01 supplied on a wafer by a droplet or by spin-coating with a thickness larger than 2.3 μm showed almost the same viscosity as that in the bulk state, while a thin film with a thickness smaller than that showed viscosity increase with decreasing the UV curable resin thickness. The viscosity of spin-coated UV curable resin showed increase with time or by heating and becomes 6 times of that in the bulk state for PAK-01. We succeeded in viscosity measurement of PAK-01 with a thickness of 0.58 μm prepared using diluted PAK-01 (PAK-01-1000) and found that the UV curable resin was exactly Newtonian fluid in these thickness ranges.

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