A Dynamic System to evaluate the UV Shrinkage Characteristics of UV Photopolymers used for Nanoimprint

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Knowledge of shrinkage is important for fabricating a successful replication with high resolution and optimizing the conditions of a UV nanoimprint process. A dynamic system to evaluate the UV shrinkage characteristics of photo-curable resin is proposed to study the shrinkage of the UV photo-curable resin with UV exposure time. This system provides a way to evaluate not only the saturation resin shrinkage induced by UV exposure, but also in-situ dynamic shrinkage with a time resolution of 100µs. It is found that the shrinkage-induced displacement of thin film resin by UV exposure has a linear relation with the thickness of the thin film resin. The shrinkage of PAK-01 resin at 250ml/cm² is approximately 8.4% by fitting the displacement data using a linear model. The dynamic shrinkage analysis reveals that the stronger UV intensity gives a lower conversion rate at the same exposure dose.

Keyword: photoresist, shrinkage, nanoimprint, thin film, UV-curable resin

1. Introduction

UV nanoimprint lithography using UV photo-curable resin gives a low-cost process for fabricating sub-100nm patterns with high resolution and has been becoming an alternative to traditional photolithography [1]. Nanostructures in a quartz mold are transferred to silicon wafers following a photo-polymerization of UV photo-curable resin with a low viscosity upon a short time UV exposure. The advantage of UV photo-polymerization is that cross-linking reaction is fast, and more importantly the reaction can be carried out at room temperature. This enables UV nanoimprint lithography to be a high-throughput process for fabricating nanostructures. However, shrinkage is inevitable accompanying the photo-polymerization, as a result of chemical bond formation from monomer to polymer of the curing resin [2]. The polymerization-induced shrinkage brings about some practical problems in applying nanoimprint lithography with high accuracy. Shrinkage induced stress may peel out the polymerized resin from some certain transfer substrates, especially metals and plastics [2, 3]. The size and shape of replicated features are affected by the shrinkage. Colburn [4] reported a high shrinkage in the direction normal to the substrate surface. A defect of scooped features was found due to the shrinkage after demolding [5]. The defects in size and shape may become worse in fabrication of hybrid patterns of nano- and micro-meter scale [6], because the shrinkage around the large-scale (hundreds of microns and larger) patterns may distort the nanoscale patterns. The shrinkage of feature size is dependent on the size and shape of the pattern and the property of UV

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curable resin and this relation becomes more complicated in a two-step replication process and makes the two-step nanoimprint process difficult to control [7]. These studies reveal that knowledge of the shrinkage is critical to obtain a successful replication using a nanoimprint process with high resolution.

A variety of methods have been developed to measure the shrinkage of resin polymerization. Density determination by pycnometry is often used to measure the shrinkage of resin polymerization by comparing the change of resin densities before and after polymerization[8,9]. Dilatometry is another widely used method to measure directly the volume change during polymerization[10-12]. The measured resin is surrounded during the polymerization period with a non-reacting liquid, generally mercury in a capillary vessel[13,14]. The volume change is determined from the shift of the liquid meniscus level in the capillary vessel. Recently a video imaging system is developed to determine the volume change from the imaging of resin in polymerization [15]. Different from the aforementioned two methods measuring a volume shrinkage of resin during polymerization, bonded disk method [16,17] and linometer [18,19] are used to measure a one-dimension linear shrinkage by monitoring the displacement of the bonded disk induced by the volume change during polymerization. Haider et al. [20] proposed a combined rheology and shrinkage measurement system in which the shrinkage is determined from the normal force control of a rheometer.

Comparison studies on these measurement methods found that measured shrinkage values were highly dependent on the measurement methods [21]. So it is difficult to compare the shrinkage values in the literatures using different methods. One of the reasons for this can be related to different physical basis for the measurement methods. Another important reason is the geometry difference of the measured samples [16]. This should be especially emphasized when measuring the shrinkage of the photo-curable resin used in nanoimprint process, because the resin is used as a very thin film pressed between a quartz mold and a silicon substrate wafer. Therefore, to measure accurately the shrinkage of the photo-curable resin used in a nanoimprint process, the samples should be prepared and held in the same conditions as used in the nanoimprint process. Otherwise, we cannot obtain a correct shrinkage result from measurements.

For a thin resin film used for nanoimprint, an ellipsometer is used to measure the shrinkage by comparing the thicknesses before and after UV exposure [6,7,22]. However, using an ellipsometer can only give us a final shrinkage value. To understand thoroughly the characteristics of resin shrinkage, a dynamic analysis of shrinkage with the exposure time during polymerization is necessary and important when optimizing the UV nanoimprint process. Some researchers have reported dynamic methods to measure the shrinkage. For example, de Gee[23] described a modified dilatometer allowing the dynamic measurement of volumetric shrinkage. This measurement was then improved by using video-imaging system to measure the volumetric shrinkage [24]. But no report has been presented about a dynamic shrinkage studied using the samples of thin film liquid photo-curable resin in the same way.

![Fig. 1. Schematic of shrinkage measurement system using a laser displacement sensor.](image1)

![Fig. 2. Picture of shrinkage measurement system using a laser displacement sensor.](image2)
conditions as used in the nanoimprint process.

In this paper, a system to analyze the dynamic shrinkage with the UV exposure time is proposed. The shrinkage variation with the UV exposure time in a very short time after the exposure is studied. The necessary exposure dose at different UV strengths for a successful nanoimprint is discussed.

2. Experimental Details

Double-side mirror-polished silicon wafers were cut into 20mm x 20mm squares as measurement substrates. These substrates were sonicated in acetone for 30 min and rinsed carefully in deionized water for 15 min to remove cutting particles. A commercial UV curable resin (Toyogosei PAK-01) was used to study its UV-induced shrinkage. The PAK-01 resin was spin-coated on silicon substrates with different resin film thicknesses. Then the spin-coated resin on the silicon substrate was conformably contacted with a quartz mold treated with a silane-coupling agent (Gelest Aquaphobe CF). Prior to the contact, the surface of the quartz mold was self-cleaned using the photo-curable resin, PAK-01. The PAK-01 resin was sandwiched between the quartz mold and a clean glass slide and cured with UV exposure. The glass slide and solidified photo-curable resin were detached from the quartz mold to clean dusts from the quartz surface. Repeating this self-cleaning process several times gives us a clean mold surface free from particle contamination, and this ensures a precise measurement of resin shrinkage.

Figure 1 schematically depicts the measurement system of UV curable resin shrinkage using laser displacement sensor (Keyence LK-G08). The as-prepared UV photo resin samples on silicon small substrates are exposed to UV light from bottom through the quartz mold. Displacement of silicon wafer induced by resin UV shrinkage is recorded every 100 us. To suppress noise during measurement, the sample stand with a glass window and the laser displacement sensor are fixed on a stable upright pillar, as shown in Fig. 2. An example of the displacement recorded during UV exposure in 5 second is shown in Fig. 3. The top graph in Fig. 3 shows the UV exposure period and the lower graph shows its corresponding displacement induced by UV shrinkage of the photo-curable resin. The displacement before UV exposure is enlarged and shows that the background noise of displacement is around plus minus 10 nanometers. This makes the system possible to measure shrinkage of a thin resin film at several micrometers and to catch the dynamic shrinkage variation in a very short time during UV exposure.

3. Results and Discussion

Shrinkage of thin film resin is evaluated
induced by UV exposure and the thickness of resin layer on silicon substrate after the exposure. The thickness of the residual layer is measured with a film thickness measurement system based on spectrophotometry (Otsuka Electronics FE-3000). The UV-induced shrinkage rate of thin film resin is calculated with the following formulation,

$$\frac{k}{h + d} = \frac{d}{h + d}, \quad (1)$$

where \( k \), \( d \) and \( h \) are the evaluated shrinkage, total displacement induced by UV exposure, and the thickness of film resin after UV exposure, respectively.

Relation of shrinkage-induced displacement and shrinkage rate with the thickness of UV-curable film resist is shown in Fig. 4. We can find that the shrinkage rate calculated from Equation (1) is independent on the initial thickness of the photo-curable film resin. To reduce measurement error, the shrinkage characteristic of the thin film resin is also deduced from resin films of different thicknesses. It may be seen that the total displacement induced by UV exposure has a linear relationship with the thickness of thin film resin, as shown in Fig. 4. Fitting the displacement data using linear model, we find that the shrinkage fitting result is in agreement with the shrinkage evaluated directly using displacement induced by UV exposure and the thickness of film resin after UV exposure at different film thicknesses. For the UV curable resin (Toyogosei PAK-01), the shrinkage is approximately 8.4% at UV exposure dose of 250mJ/cm² and UV exposure intensity of 50mW/cm². This agrees with the results measured using ellipsometer where the shrinkage of PAK-01 resin was reported to be around 6-8% [25]. Their results were calculated from the initial thickness of resin before mold contacting and post UV exposure using an unpatterned mold. So only a final shrinkage value can be obtained using their measurement method.

Using our system the shrinkage variation against exposure time can be investigated. To understand the effects of UV intensity on the resin shrinkage, we carried out the measurements at different UV intensities. The shrinkage variation against the UV exposure time at different UV intensities is shown in Fig. 5. It can be found that the UV intensity has no strong effects on shrinkage after 0.8s. However, the shrinkage just after UV exposure start is strongly affected by the UV exposure intensity. The shrinkage increases greatly from starting UV exposure for higher exposure intensity. This means that high UV exposure intensity results in a fast crosslinking of photo curable monomer resin. The shrinkage of UV-curable resin is a result of photopolymerization reaction process in which monomer of the UV-curable resin is changed to polymer with absorbing UV lights. Assuming that the photopolymerization reaction kinetics may be expressed in the context of the first-order reaction kinetics, the rate of monomer conversion to polymer during the
photopolymerization is described as [26]

\[ p(t) = 1 - \exp(-kt). \]  

(2)

Here \( t \) is the time of UV exposure. \( k \) is the overall reaction rate constant related to UV intensity and the reaction rate constants of propagation and termination. Fitting the shrinkage variation with UV exposure time in Fig. 5, we can find that the shrinkage can be fitted with the first-order reaction kinetics given by Equation (2). The shrinkage at lower UV intensities is fitted very well, whereas shrinkage at higher UV intensities is fitted well only in a short period just after UV exposure. The overall reaction rate constant in Equation (2) represents the reaction rate at the beginning of photopolymerization reaction. The dependency of reaction rate on the UV intensity can be obtained from the reaction rate constants obtained at different UV intensities shown in Fig. 6 where the log type axes are used. The results show that there is a linear relation between the log of the reaction rates and the log of UV intensities. The slope of the linear fitting line in Fig. 6 is approximately 0.4. This means that the photopolymerization of UV-curable film resin is a classic radical polymerization in which the overall reaction rate has an exponential relation to the UV intensity expressed as [27]

\[ k = \lambda I^{1/2}, \]  

(3)

\[ \lambda = k_p \left( \frac{k_p \varepsilon}{k_t} \right)^{1/2}. \]  

(4)

Here \( k_p \) and \( k_t \) are the reaction rate constants of propagation and termination, respectively. \( \varepsilon \) represents the quantum absorbing efficiency, \( k_e \) the coefficient of radical reaction, and \( I \) the intensity of UV light. From the relation of reaction rate constant of polymerization with UV intensity in Fig. 6, the reaction rate constant increases with the increase of UV intensity. This is in agreement with the formulation in Equation (3).

Using the dynamic system to evaluate the UV shrinkage proposed in our paper, we can easily obtain dynamic shrinkage characteristics for different UV exposure doses comparing the traditional method by carrying out several experiments of varying the exposure time [25]. To obtain the necessary UV exposure dose during nanoimprint process, the effects of the exposure dose on the shrinkage of thin film resin by the UV exposure is investigated. The shrinkage variation with the UV exposure dose is shown in Fig. 7. This shrinkage variation during the UV exposure is corresponding to the rate of monomer conversion to polymer during the photopolymerization. From Equations (2) and (3), the rate of monomer conversion to polymer with the relation to the UV exposure dose can be expressed as

\[ p(t) = 1 - \exp\left( -\frac{\lambda}{I^{1/2} d} \right), \]  

(5)

where \( d \) represents the dose of UV exposure. From the Equation (4), parameter \( \lambda \) is only related to the reaction rate constants of propagation and termination, the quantum absorbing efficiency, and the coefficient of
radical reaction and is independent to the UV intensity. So Equation (5) means that the stronger UV intensity gives a lower conversion rate at the same exposure dose. The same phenomenon is successfully depicted in the shrinkage variation to UV intensity shown in Fig. 7.

For higher UV exposure intensity, the shrinkage increases gradually comparing with that at lower UV exposure intensity, as shown in Fig. 7. The UV exposure triggers the crosslinking of photo monomer resin. But the higher UV exposure intensity has no definite contribution in shortening the crosslinking completing time. We find that the shrinkage has no more increase after 100mJ/cm² for PAK-01 resin. This gives us the appropriate UV exposure dose during the nanoimprint process using PAK-01 resin.

4. Conclusion
A dynamic system to evaluate UV curable resin shrinkage is proposed to study the shrinkage characteristic of thin film resin in the similar condition as used in nanoimprint process. This system provides a way to evaluate not only the saturation resin shrinkage induced by UV exposure, but also in-situ dynamic shrinkage with a time resolution of 100us. The displacement of thin film resin by UV exposure has a linear relation with the thickness of thin film resin. The shrinkage of PAK-01 resin at 250mJ/cm² is approximately 8.4% by fitting the displacement data using a linear model. The dynamic shrinkage analysis reveals that the stronger UV intensity gives a lower conversion rate at the same exposure dose.

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