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# RIMS (real-time imprint monitoring by scattering of light) study of pressure, temperature and resist effects on nanoimprint lithography

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**Abstract**
To optimize nanoimprint lithography (NIL), it is essential to be able to characterize and control the NIL process *in situ* and in real time. Recently we have developed a real-time imprint monitoring by the scattering-of-light (RIMS) approach, which allows us to detect the degree of resist deformation and the duration of resist penetration by a mould during the imprint process in real time. In this paper we report the performances of RIMS under a broad range of working conditions. RIMS data shows that the resist penetration is facilitated by increasing processing temperature, pressure and the resist film thickness; a prolonged pre-NIL resist baking step, on the other hand, has the effect of slowing it down. Our results provide further demonstration of the effectiveness of this method under different working conditions. RIMS measurements show not only how long an imprint takes to complete, but also how an imprint progresses with time and how it is affected by differences in processing parameters. These measurements provide information crucial for a better understanding and process optimization in NIL.

(Some figures in this article are in colour only in the electronic version)

Nanoimprint lithography (NIL) is a high throughput, low-cost lithography tool with the potential to become a mass manufacturing process for nanoscale devices and systems [1]. It has been investigated vigorously and has recently demonstrated a 5 nm linewidth resolution at 7 nm half-pitch [1–4]. Unlike other conventional lithographies, polymer deformation plays a critical role in nanoimprint lithography. Instead of using radiation, NIL patterns by physically deforming a resist thin film using a mould with three-dimensional topography to form a negative replica, which can be done either by embossing a thermoplastic polymer at an elevated temperature (thermal-NIL) or by pressing a low-viscosity photocurable resist at room temperature and curing it with UV exposure (UV-NIL) [4, 5].

Clearly, a good understanding of the polymer flow during NIL is essential for the rational design of NIL tools and the optimization of NIL processes. Specifically, questions such as how is the speed of resist penetration affected by differences in processing parameters (temperature, pressure, type and thickness of the resist, pre-NIL baking conditions, etc) need to be answered. Previously, effects of resist thickness, resist viscosity and mould geometry have been studied by simulations or indirect measurements. The usefulness of this kind of investigation is limited because it does not provide the crucial time-dependent information on the transient state in the NIL process [6, 7]. Without an effective means for *in situ* NIL process detection, to ensure a complete deformation of the resist, it was a common practice to hold the mould and resist at a high processing temperature (in some cases ∼100 °C above $T_g$) under a high pressure for a long duration of time. Obviously, these processing parameters should be optimized: on the one hand, high temperature and pressure may not be

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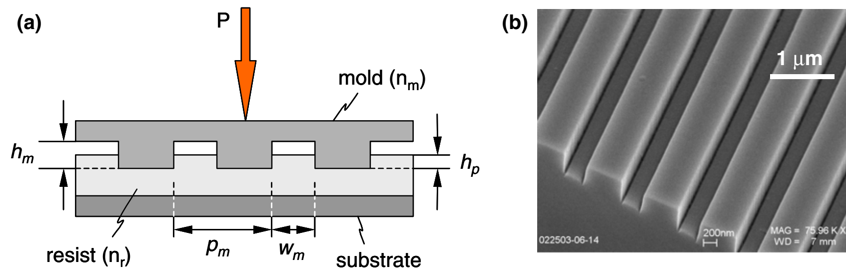


**Figure 1.** (a) Schematic of the NIL system to be studied by RIMS and (b) a scanning electron micrograph showing a cross-sectional view of the 1.0 $\mu$m period fused silica grating mould used in the experiment.

compatible with some processes and applications (molecular electronic devices, organic light-emitting diodes, etc); on the other hand, shorter processing time is always desirable in a manufacturing environment or even in a research lab because it means higher throughput.

In our recent publications, we have demonstrated a real-time imprint monitoring by a scattering-of-light (RIMS) approach where a surface relief diffraction grating is fabricated on a transparent mould, and the intensity of light diffracted from the grating is monitored continuously during the imprint process. These measurements provide valuable information not only on how long an imprint takes to complete, but also on how an imprint progresses with time [8]. However, there is still a great need to know how this new method performs under different processing conditions. In this paper we report, for the first time, real-time measurements of imprinting processes under different working conditions (pressure, $T_g$, imprint temperatures, materials, etc). We present a further study of RIMS in characterizing both UV- and thermal-NIL processes. New data on the effects of various processing conditions on the duration of resist penetration, an understanding of which is critical for the optimization of NIL processing parameters, will be analysed and studied.

Figure 1(a) shows a schematic of the NIL system to be analysed in this study. The grating has a period of $p_m$, a trench width of $w_m$ and a trench depth of $h_m$. The initial resist thickness is $h_r$ (which is determined by ellipsometry in our experiment prior to NIL). During NIL, the mould is pressed into the polymer under an applied pressure $P$ and the penetration depth $h_p$ is defined as the height of the resist protruding into the mould cavities. In our experiment, the mould body is made of a 0.5 mm thick fused silica substrate and is square-shaped with a size of 1.5 cm $\times$ 1.5 cm. It is patterned with a surface relief grating using a process we have previously reported [9]. Cross-sectional SEM of the grating (figure 1(b)) is used to determine the mould parameters: grating period $p_m$ = 1.0 $\mu$m, trench width $w_m$ = 350 nm and trench depth $h_m$ = 400 nm. During experiments, the mould is first placed on top of a resist thin film spin-coated on a silicon substrate, a He–Ne laser beam with a wavelength of 632.8 nm is incident upon the grating at a 30° angle of incidence (the plane of incidence is parallel to the grating lines) and the intensity of the first diffraction order is monitored continuously during the NIL process [8]. The imprint is performed using a modified NX-2000 imprint system (Nanonex Corp., Monmouth Junction, NJ), which provides control of the processing pressure and temperature.

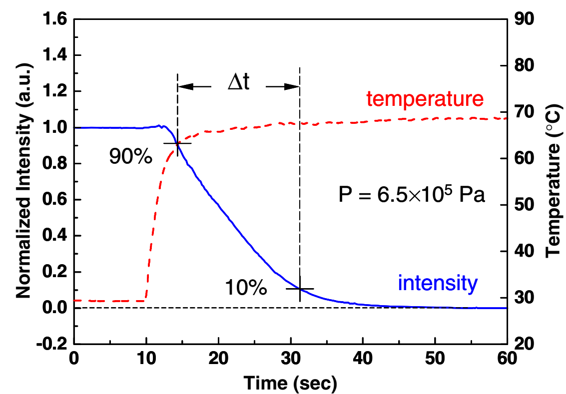


**Figure 2.** Measured first diffraction order intensity and substrate temperature as functions of time in a typical thermal-NIL process cycle. The diffraction intensity decreases as the mould is being pressed into the resist. The NIL transit time $\Delta t$ is defined as the time it takes for the intensity signal to go from 90% to 10% of the total transition.

Measured first diffraction order intensity and substrate temperature as functions of time in a typical thermal-NIL process cycle are shown in figure 2. First, the mould and the substrate are brought into contact at room temperature by an external pressure. In our experiment, the applied pressure increases from 0 Pa to its preset value (which is $6.5 \times 10^5$ Pa in the case shown in figure 2) and then it remains constant throughout the NIL process. Before heating starts, the polymer is rigid and the pressure alone cannot deform the resist, hence, the measured diffraction intensity stabilizes at an initial value. Next, the resist and the mould are heated (the NXR-2000 system has a heating element which brings the substrate temperature to a set value within a few seconds), the polymer softens, the mould is pressed into the resist under the applied pressure and the diffraction intensity decreases. Upon completion, the grating grooves are completely filled by the polymer and the diffraction intensity reaches its near-zero minimum because of the close match between the refractive indices of the polymer ($n_r$ = 1.46) and the fused silica mould ($n_m$ = 1.46) [8].

To simplify our discussion, here we also define the NIL 'transit time' $\Delta t$ as the time it takes for the intensity signal to go from 90% to 10% of the total transition (figure 2). Clearly, $\Delta t$ is of the same order as the mould cavity fill time [7]. Currently our system has a data acquisition rate of $\sim$5 Hz and can easily detect a $<$1% change in diffraction intensity

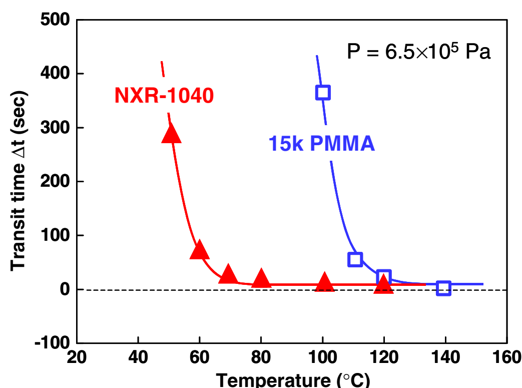


**Figure 3.** Measured $\Delta t$ as a function of imprinting temperature for two different thermal NIL resists (NXR-1040 and 15k molecular weight PMMA). RIMS data shows that the speed of resist penetration is highly sensitive to processing temperature. It is very difficult to deform the resist by pressure alone when the processing temperature is lower than the glass transition temperature $T_g$ of the resist.

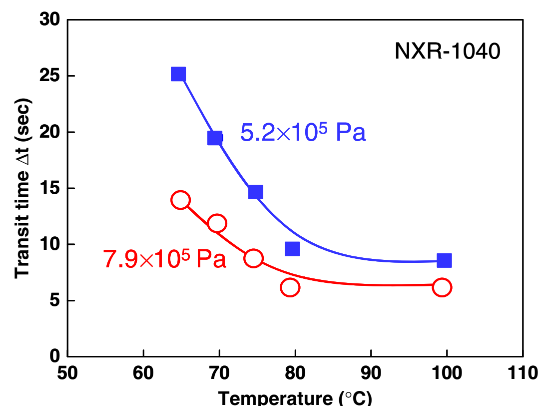


**Figure 4.** RIMS data showing the effects of NIL pressure on the speed of resist penetration. The samples are imprinted under a pressure of either $5.2 \times 10^5$ or $7.9 \times 10^5$ Pa. RIMS measurement shows that the speed of resist penetration is increased by applying a higher pressure.

in real time (both the speed and sensitivity of our system can be further improved). Information on the mould penetration depth can be extracted in real time with ~5 nm sensitivity and the transient state in NIL can be detected with ~0.2 s time resolution [8].

In our study, both types of NIL processes (UV- and thermal-NIL) have been analysed and characterized. In UV-NIL, the resist has a very low $T_g$ and is in a liquid state when pressed by a mould at room temperature. We have found that the resist penetration in UV-NIL is usually very fast (with $\Delta t < 1$ s in our set-up) and its speed is not sensitive to variations in pressure or temperature. However, in the case of thermal-NIL, the resist is in a solid state at room temperature and can be deformed only at elevated temperatures close to or above its $T_g$. As a result, the duration of resist penetration in thermal-NIL is much longer (from a few seconds to a few minutes) and is very sensitive to changes in processing temperature or pressure. For this reason, we will focus our discussion on thermal-NIL.

Central questions to answer here are how much time it takes for the mould features to completely deform the resist and how the deformation process is affected by the difference in processing conditions (temperature, pressure, resist, etc). To start with, we have first studied the effects of temperature on the speed of resist penetration. In this experiment, two resists are tested: a commercially available thermal-NIL resist NXR-1040 from Nanonex with a nominal flow temperature of 60 °C and 15k molecular weight polymethylmethacrylate (PMMA) with a glass transition temperature $T_g$ of 105 °C. These resists are chosen because they have refractive indices close to the quartz mould, which simplifies analysis of the measurement data [8]. The resist thin films are baked at 90 °C for 60 min after spin-coating, and have the same film thickness of 210 nm after baking. The imprints are done under the same processing pressure of $6.5 \times 10^5$ Pa. The measured transit time $\Delta t$ as a function of imprinting temperature for these resists is shown in figure 3. The RIMS data clearly shows that, for a thermoplastic resist, the speed of resist penetration is highly sensitive to the processing temperature: it is very difficult to deform the resist by pressure alone when the processing temperature is lower than the glass transition temperature of the resist; the speed of resist penetration increases dramatically when the temperature is increased close to the $T_g$ of the resist. Different resists show a similar transit time–temperature dependence, although for a high $T_g$ resist, the required processing temperature increases correspondingly. For that reason most of our experiments discussed in this paper are conducted using the low $T_g$ NXR-1040 resist instead of PMMA.

Second, the effects of pressure on the speed of resist penetration are studied by comparing $\Delta t$ for imprints done under different processing pressures. The results are shown in figure 4. NXR-1040 resist is used in this experiment and all the samples are baked at 90 °C for 60 min after spin-coating and the resist film thickness is 210 nm (after baking). The samples are imprinted under a pressure of either $5.2 \times 10^5$ or $7.9 \times 10^5$ Pa at different processing temperatures. The data shows that the speed of resist penetration increases with increasing imprinting pressure. This effect is more pronounced especially when the processing temperature is low.

In our study, we have also found that the RIMS measurement is very sensitive in detecting small changes in $\Delta t$ caused either by differences in pre-NIL baking conditions or variations in resist properties. For example, figure 5 shows the NIL transit time $\Delta t$ as a function of pre-NIL resist baking time in one of our experiments. The NXR-1040 resist films are spun under the same conditions with the same initial thickness of 220 nm (before baking). Before imprinting, these samples are baked at the same temperature of 90 °C, but for different durations of time. The difference between these resist films in NIL is easily detected by performing a RIMS measurement. The data shows that it takes longer to deform a hard-baked film under the same imprinting conditions because, as the baking step drives out the remaining solvent in the film, it effectively increases the $T_g$ of the polymer, making the resist more rigid.

Another example is the effect of film thickness on $\Delta t$. The data is shown in figure 6. In this experiment, NXR-1040 films with different thicknesses are imprinted at 70 °C under the same pressure of $6.5 \times 10^5$ Pa. These films are baked at 90 °C for 30 h before imprinting to ensure they are similar in solvent concentrations (the film thickness shown in figure 6

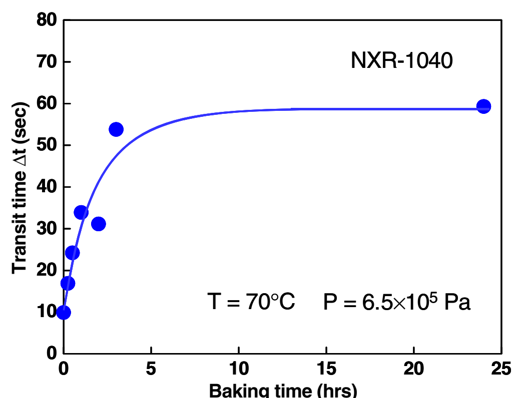


**Figure 5.** RIMS data showing the effects of pre-NIL baking time on $\Delta t$. The data shows that it takes longer to print a hard-baked film under the same imprinting conditions, because driving out residual solvent in the resist makes it more rigid.

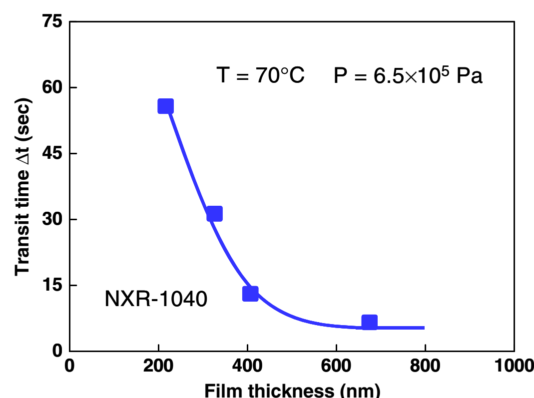


**Figure 6.** RIMS data showing the effects of resist film thickness on NIL. NXR-1040 films with different thicknesses are imprinted at 70 °C under the same pressure of $6.5 \times 10^5$ Pa. The data shows that increasing film thickness significantly speeds up resist penetration.

is the 'final' thickness after baking). RIMS measurement shows that, when other conditions are the same, increasing film thickness significantly speeds up resist penetration. This effect can be explained by the observation that, in NIL, the pattern is formed not only by compressing the resist under the protruding mould features but also by squeezing resist into the cavities in the mould. Thicker film means more abundant resist supply to fill the cavities, it also means a wider opening between the mould features and the substrate through which the resist can flow. Both of these factors should facilitate that process. This effect has previously been predicted by other theoretical studies [6, 7]. Our RIMS study provides a direct experimental observation of this effect for the first time.

It is worth mentioning here that, for the data shown in figure 5, as the solvent is being driven out, the baked films are also slightly thinner (2–5%, depending on baking conditions) than the unbaked film. The decrease in film thickness may also contribute to the observed increase in $\Delta t$. However, as our data in figure 6 indicates, a 2–5% difference in film thickness is too small to be considered as a significant factor in that experiment.

Finally, it should be pointed out that, although the data presented in this paper is based on results obtained with a 1.0 $\mu$m period grating and a light source with a wavelength of 632.8 nm, other grating periods and two-dimensional mould patterns can also be used in RIMS. For example, by using a He–Ne laser with a wavelength of 543.5 nm, we have successfully applied the same principle to a 300 nm period grating mould. RIMS study of gratings with different periods and linewidths could provide useful information on the effects of mould geometry and pattern density on the speed of NIL. These results will be presented in our future publications.

In summary, we have presented a new RIMS approach to *in situ* NIL process characterization. A surface relief diffraction grating is used as the imprint mould, and the diffracted light intensity is monitored continuously during the imprint process. Performances of the RIMS method under a broad range of working conditions (pressure, $T_g$, imprint temperatures, materials, etc) have been investigated. RIMS data shows that the resist penetration in thermal-NIL is facilitated by increasing the processing temperature, pressure and the resist film thickness; a prolonged pre-NIL resist baking step, on the other hand, has the effect of slowing it down. Our results provide further demonstration of the effectiveness of the RIMS method, which can be used to provide information crucial for a better understanding and process optimization in NIL.

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