In situ real time monitoring of nanosecond imprint process

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Using a real time imprint monitoring system (RIMS), the authors measured the process time for laser assisted nanoimprint lithography to be about 200 ns. They found that during this short period of time, the mold had been fully pressed into the resist, resulting in a full pattern transfer with high fidelity. Their results also demonstrated the capability of RIMS for monitoring an ultrafast imprint process. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2335952]

As a low-cost, high throughput patterning technique with sub-10-nm resolution, nanoimprint lithography[1–4] (NIL) is playing an important role for nanotechnology development. NIL has recently been added to the International Technology Roadmap for Semiconductors as one of the next generation lithography technologies.[5] In NIL, a mold (template) is used to physically deform a thin layer of deformable material (resist), creating a thickness contrast pattern in the resist.[1,2] The resist can be either thermoplastic or photocurable.[1,6] In either case, understanding the speed of polymer deformation is important to the optimization of the imprint process.

A recent development in NIL is the use of a laser pulse as the heating source in thermal NIL.[7] The laser irradiation with a suitable wavelength can melt a material's surface (e.g., Si) in less than 1 ns.[8] This approach has been used for direct imprint of hard solids, such as Si, SiC, SiGe, and metals,[9,10] and for imprint polymeric resists without direct heating of the underlying substrate,[7] thereby, reducing thermal expansion effects. The imprint time of ~250 ns or longer in these experiments was estimated from the total molten time of the imprinted material,[7,9] which might be inaccurate. Hence, a method for the direct measurement of the imprint time with nanosecond resolution is highly desirable.

The real time imprint monitoring system (RIMS) can monitor the flow of an imprinted material into a mold *in situ*. It has been proposed and demonstrated for flow characterization of both thermal and photocurable polymers or monomer mixtures in conventional NIL.[11,12] In RIMS, a surface relief diffraction grating is created on the imprint mold and the diffracted light intensity from the grating, which depends on resist filling of the grating trenches, is monitored continuously during the imprint process. Previous work has demonstrated that RIMS was capable of monitoring NIL processes which finished in less than 1 s.[12] In this letter, we report experimental study using RIMS to directly monitor an ultrafast NIL process. We demonstrate the capability of RIMS to characterize nanosecond imprint processes and find that the imprint time of laser assisted NIL in polymer materials is about 200 ns.

A schematic of the RIMS experimental setup is shown in Fig. 1. The substrate, resist, and mold in our experiments were prepared as follows. A clean silicon substrate with native oxide was spin coated with a 210 nm thick resist that was custom made by modifying the commercially available Nanonex resist NXR-1023 with an UV light absorber. The spun resist was then baked at 70 °C for 30 min to drive out the residual solvent. The mold was an optical grade fused silica (0.5 mm thick, UV transparent, and refractive index of 1.46) having parallel 300 nm wide grating lines of 950 nm pitch and 150 nm depth over the entire mold area (1.2×1.2 mm^2). The mold was fabricated by NIL using a master grating mold and reactive ion etching to transfer the pattern from an imprinted resist into the silica. The finished mold was coated with an antisticking monolayer for easy mold release after imprint.

During the imprint, the mold was placed on top of the resist and was pressed into the resist by two parallel plates. There was a hole in the center of top plate and it was large enough for the laser beams to pass through. An excimer laser pulse (308 nm wavelength, 20 ns pulse width, and 2.5×2.5 mm^2 spot size) was used to melt the resist. A HeNe laser (632.8 nm wavelength, continuous wave, and beam diameter 0.5 mm) was used to monitor resist imprint by RIMS process. The incident angle of the HeNe laser beam was 60° relative to the surface of the silica mold. The angle between the incident plane and the grating lines was 45°. This arrangement ensured that the diffracted beam was directed to a different path from the reflected beam. The negative first order diffraction signal was collected by a high-speed Si *p-i-n* detector (Newport, 818-BB-21A, rise time <500 ps and fall time <500 ps) with a bandpass filter (Andover Corp, 633FS02-25, center wavelength of 632.8 nm and bandwidth

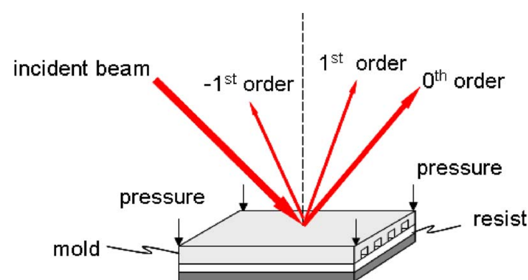

FIG. 1. (Color online) Schematic illustration of the experimental setup (after Ref. 11). An UV laser spot (λ=308 nm) covers the mold/resist/substrate sandwich, which was pressed by two parallel metal plates (not shown here). A HeNe laser beam (λ=632.8 nm) is incident on the mold at an angle of 60° to the mold surface. The angle between the HeNe laser beam incident plane and the grating lines was 45°. The diffracted signal (negative first order) passes through a red filter and is collected by an ultrafast photodetector. The captured signal is analyzed by an oscilloscope.

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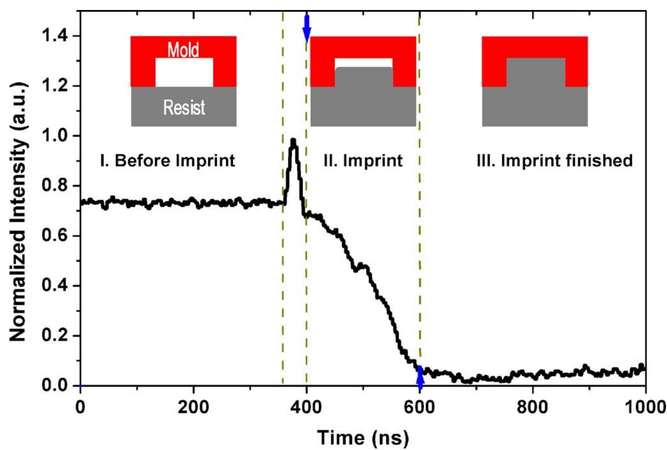

FIG. 2. (Color online) Typical curve of normalized diffraction intensity vs time during RIMS. This curve was obtained when imprinting a 210 nm thick NXR 1023 thin film on Si substrate at a laser fluence of 380 mJ/cm^2. Three zones are defined on the curve, which represent the stages before, during, and after imprinting. The schematics of polymer filling into the grating trenches in each of the three stages are drawn as insets. Blue arrows indicate the start and end points of imprint. The whole imprint process takes about 200 ns.

of 1.0 ± 0.2 nm) mounted in front of the detector. The signal was sent to an oscilloscope (Tektronix, TDS 220, bandwidth of 100 MHz and sample rate of 1 Gsample/s) for analysis. The detector and oscilloscope together have a time resolution better than 10 ns.

In RIMS, the intensity of diffracted light depends on the filling ratio of the polymeric resist to the mold trench. As the resist flows into the mold trenches, the diffracted signal decays monotonically because the imprint resist has an index almost the same as that of the mold (1.46 at 632.8 nm in our experiments). The diffraction will disappear when the resist fills the mold grating trenches completely. By calibrating the measured diffraction on a known grating with simulation software such as G-SOLVER, one can accurately measure *in situ* the average filling of a resist into a grating trench.

Figure 2 is a typical curve of the diffracted light intensity as a function of time obtained during the real time monitoring of the ultrafast imprint process. Before imprint, the grating mold and resist were in contact at room temperature and the resist was rigid with almost no deformation. No polymer filled into the trenches at this stage and the diffraction intensity stayed constant (Fig. 2, zone I). As the resist was heated by an excimer laser pulse, it became soft and started to flow into the grating trenches under the external pressure, causing

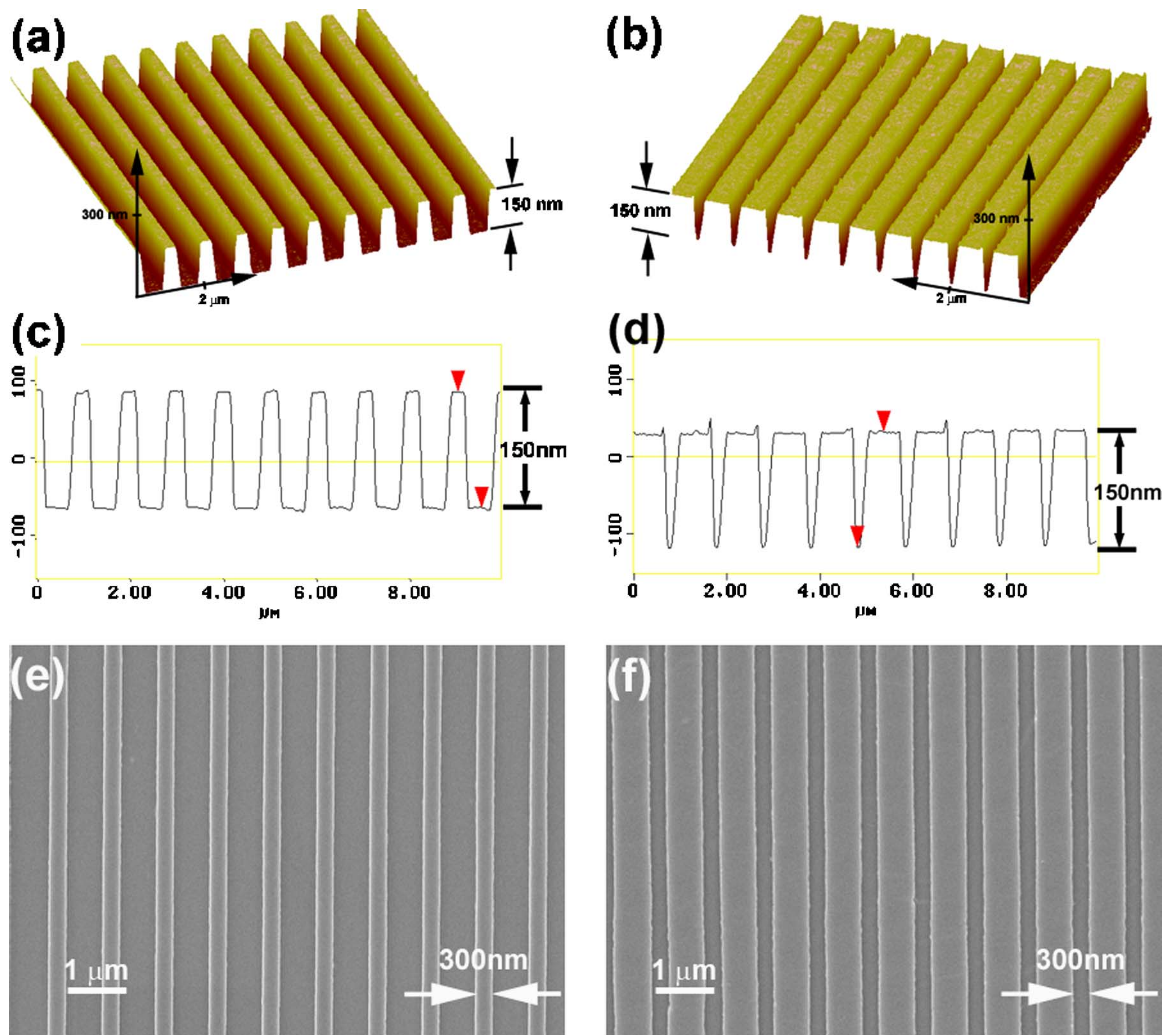

FIG. 3. (Color online) AFM and SEM images of the mold used [(a), (c), and (e)] and the imprinted resist [(b), (d), and (f)]. The flat tops and bottoms and vertical sidewalls in the mold were fully transferred to the resist during imprint. Cross-sectional analyses of the mold (c) and the imprinted resist (d) showed that mold grating height was the same as resist trench depth (both at 150 nm), indicating a full pattern transfer. Linewidth of the raised area in the mold (e) was also the same as the resist trench width (f) (300 nm), suggesting high process fidelity.

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a monotonic reduction of the effective trench depth and hence a reduced diffraction intensity (Fig. 2, zone II). After completion of the imprint process, the trenches were completely filled with resist and the diffraction intensity remained constant near zero, due to the refractive index match between the mold and resist (Fig. 2, zone III). From the measurement, the entire imprint process was completed in about 200 ns.

Furthermore, a spike was observed in the diffracted light curve (between zone I and zone II in Fig. 2). The spike came from the scattering of the excimer laser pulse, since we found that the spike had a pulse width almost the same as the excimer laser (20 ns) and the spike height could be reduced greatly by improving the UV filtering. The spike, which marks the time of the excimer laser beam, is very useful to establish the time relationship of laser melting and the imprint. Since the diffracted light intensity drops immediately after the spike, it reconfirms our previous observation that a resist melts in less than 20 ns after the excimer laser pulse, which was obtained by time resolved reflectivity measurement using the same photodetector and oscilloscope as in this study.[13]

Based on the measured imprint time, the average speed of the imprint is estimated to be 0.5 m/s. The imprint speed is related to several factors such as viscosity and surface tension of the polymer melt, imprint pressure, and mold geometry. Faster imprint speeds can be achieved by using polymers that intrinsically have low viscosity. Higher laser fluence can be used to raise the imprint temperature and lower the viscosity of the polymer melt.[14] Raising the imprint temperature also decreases the surface tension of the polymer melt,[14] resulting in increased imprint speeds. Improving the mold geometry and using thicker polymer film may also be helpful for polymer flow in NIL according to recent experimental and numerical simulation results.[15,16]

Compared with conventional NIL, laser-assisted NIL has a processing time several orders of magnitude shorter and has the direct heating primarily to the resist, but not the substrate nor the mold. Hence, during laser assisted NIL, only the surfaces of the substrate and mold are heated, while their bulks remain at room temperature. As a result, laser assisted NIL has much less thermal expansion mismatch between the mold and substrate, leading to better alignment accuracy, which is necessary for multilevel electronic device fabrication. Because little heat is transferred to the mold and substrate, higher resist temperature can be used and it is not a problem for thermal expansion. This will result in lower viscosity, better filling of polymer melt into the mold, and hence better imprint quality in laser assisted NIL.

The imprint quality and fidelity of ultrafast NIL remain excellent, as in traditional NIL. We examined both the mold and imprinted resist using a scanning electron microscopy (SEM) and an atomic force microscope (AFM). Geometrical features such as flat tops and vertical sidewalls were fully transferred from the mold into the resist [Figs. 3(a) and 3(b)]. More importantly, the height of resist lines was the same as the trench depth in the mold [Figs. 3(c) and 3(d)], which suggests that the mold has been completely pressed into the resist within 200 ns. Further SEM characterization [Figs. 3(e) and 3(f)] showed that the linewidth of the protruding part in the mold was the same as the trench width in the resist (both are 300 nm). This demonstrates the high fidelity of the ultrafast imprint process.

RIMS can be extended to other imprint materials which have refractive indices different from that of the mold.[11] Smaller pitched grating for RIMS can be used as long as shorter wavelength monitor laser is used.

Our experiments here demonstrated the capability of RIMS for monitoring nanosecond imprint process. However, the ultimate time resolution of RIMS could be even higher. This can be achieved using an ultrafast photodetector together with an ultrafast oscilloscope. For example, commercially available high-speed photodetector can offer as high as 60 GHz bandwidth (PX-D7, Newport Corp., impulse response of 7 ps and wavelength range of 400–900 nm).[17] And digital storage oscilloscope with bandwidth up to 15 GHz (TDS6154C, Tektronix Inc., 28 ps rise time and 40 Gsample/s sample rate) is also on market.[18] Using the advanced equipment will extend the capacity of RIMS to monitor ultrafast process to tens of picoseconds.

In summary, using RIMS we directly measured the imprint time for laser assisted nanoimprint lithography, which is about 200 ns. During that short period of time, the mold was fully imprinted into the resist, resulting in high fidelity pattern transfer. Our results demonstrate that RIMS is capable of monitoring an ultrafast imprint process within nanoseconds and can be extended to picosecond processes with improvements to measurement equipment.

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