

Fabrication of 5 nm linewidth and 14 nm pitch features by nanoimprint lithography

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We report advances in nanoimprint lithography, its application in nanogap metal contacts, and related fabrication yield. We have demonstrated 5 nm linewidth and 14 nm linepitch in resist using nanoimprint lithography at room temperature with a pressure less than 15 psi. We fabricated gold contacts (for the application of single macromolecule devices) with 5 nm separation by nanoimprint in resist and lift-off of metal. Finally, the uniformity and manufacturability of nanoimprint over a 4 in. wafer were demonstrated. © 2004 American Institute of Physics. [DOI: 10.1063/1.1766071]

The field of nanotechnology is advancing rapidly. Applications of nanotechnology include subwavelength optical elements, biochemical analysis devices, photonic crystals, high-density single-domain magnetic storage, and single-molecule devices, to name a few. Yet, key to the commercial success of these nanotechnology applications are low cost and high throughput manufacturing capabilities. State-of-the-art manufacturing photolithography patterning tools are both too expensive and incapable of producing the necessary pitch and feature sizes of these applications. Thus, presently, researchers have been largely constrained to using low-throughput lithography tools, such as electron-beam lithography (EBL), atomic force microscopy (AFM), and ion-beam lithography. For high-throughput and low-cost lithography, various “nanoprinting” technologies have been developed.^{1–3} Here, we report our investigation of the resolution limit of nanoimprint lithography, where we demonstrated a nanoimprint record of 5 nm linewidth features and 14 nm pitch over a large area, its applications in nanogap metal contacts, and a study of fabrication yields.

In photocurable nanoimprint lithography (P-NIL) (shown in Fig. 1), a mold is pressed into a low viscosity photocurable resist liquid to physically deform the resist shape such that it conforms to the topology of the mold. The resist is cured with exposure to UV light, crosslinking the various components in the resist liquid, producing a uniform, relatively rigid polymer network. The mold is then separated from the cured resist. Finally, an anisotropic reactive ion etch (RIE) removes the residual resist in the compressed area, exposing the substrate surface.

In order to explore the performance of P-NIL, a variety of molds were fabricated to test specific attributes, including minimum pitch (maximum density), minimum feature size, and large-area uniformity patterning. Previously, 10 nm dots and 40 nm pitch have been demonstrated by NIL¹ with the resolution limited by our ability to fabricate the mold, as proximity effects inherent with EBL make sub-35 nm pitch patterning very difficult. To produce a mold with a pitch resolution surpassing EBL capabilities, we fabricated a NIL mold by selectively wet etching $\text{Al}_{0.7}\text{Ga}_{0.3}\text{As}$ from a cleaved edge of a $\text{GaAs}/\text{Al}_{0.7}\text{Ga}_{0.3}\text{As}$ superlattice [grown by

molecular-beam epitaxy (MBE)] with a dilute solution of hydrofluoric acid (HF).^{4,5} This mold fabrication process offers many advantages, specifically very dense sub-50 nm pitch topologies can be manufactured over a large area with vertical and smooth sidewalls, low defect and linewidth variation, and the pitch and duty cycle are controllable to atomic precision. In addition, the GaAs mold has multiple MBE superlattice growths of varying pitch, thus allowing us to determine the minimum pitch resolution of P-NIL.

The GaAs mold was pressed into a P-NIL resist on a transparent quartz substrate, and the resist was exposed to UV light through the quartz, curing the resist, allowing the mold to be released, leaving the resist patterned on the substrate. After imprint, the cured polymer was sputter-coated with 4 nm of Ir to aid in scanning electron microscopy (SEM) imaging, however, thermal damage to the patterned structures by the SEM electron beam limited our ability to resolve the imprint patterns. Figure 2(a) shows a SEM image of the P-NIL polymer after imprint with 14 nm pitch and 7 nm linewidth pattern, the densest patterning we were capable of confirming with SEM analysis of the polymer, but

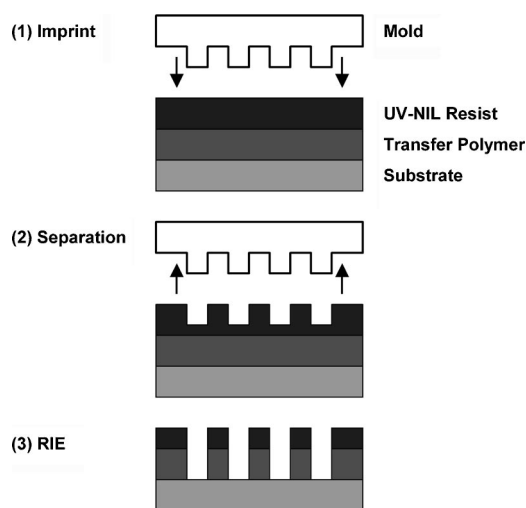


FIG. 1. Schematic of the nanoimprint lithography process: (a) A low viscosity resist film is pressed with a mold to create a thickness contrast in the resist. The resist is then exposed to UV light, curing it to produce a rigid and durable tightly bonded polymer network that conforms the mold features. (b) The mold is separated from the polymer film. (c) Pattern transfer using anisotropic etching to remove residue resist in the compressed troughs.

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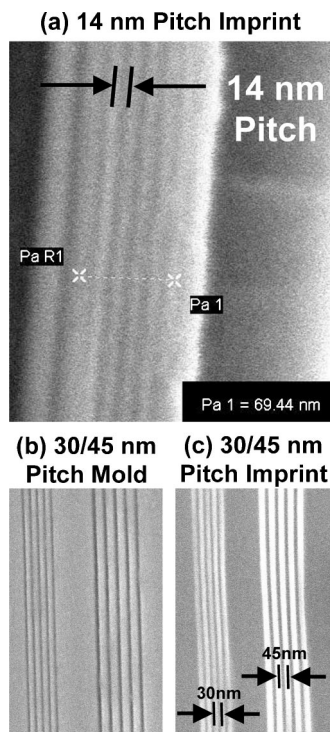


FIG. 2. (a) Demonstration of ultrahigh density photocurable nanoimprint lithography with a SEM image of cured P-NIL polymer patterned by a mold with a 14 nm pitch grating with 7 nm linewidth. (b) SEM of a P-NIL mold showing 30 and 45 nm pitch troughs. (c) SEM of cured P-NIL polymer with protruding 30 and 45 nm pitch lines continuous over several hundred microns in length. These lines were fabricated from the mold shown in (b), clearly showing that no residue polymer remains in the mold after separation, and the pattern transfer fidelity is high.

which may not represent the ultimate resolution limit of P-NIL.

Figure 2(b) shows the troughs of 30 and 45 nm pitch GaAs molds after imprint, and Fig. 2(c) the cured imprinted P-NIL polymer with the reproduced 30 and 45 nm pitch lines. The fidelity of the pattern transfer is excellent as the lines extend for several hundreds of microns without defects or variation in width, mirroring the troughs of the GaAs mold. P-NIL resist adhesion to the GaAs mold after separation was reduced by treating the mold with an alkanethiol self-assembled monolayer (SAM) to reduce its surface energy.^{6,7} As Fig. 2(b) shows, the mold troughs are clear of polymer residue after imprint.

Further investigation of the minimum size capability of P-NIL was performed with a silicon wafer mold fabricated using EBL patterning. Here, EBL is advantageous as sparse small features can be reliably patterned on a silicon substrate. These patterns are then transferred into the silicon substrate, as described in Ref. 1 with a dry RIE etch producing a mold.

The silicon mold consists of nanogap contacts for potential use as traps for single-molecule self-assembly, as shown in Fig. 3(a). Figure 3(b) shows an SEM image of the imprinted and cured P-NIL resist. The smallest feature size on the mold of 5 nm was reproduced in the resist without tearing the polymer between the contacts. As this was the smallest feature size on the mold obtainable by EBL patterning, the ultimate resolution of P-NIL is still unknown.

Key to this lithography technology is the photocurable NIL resist and its associated processing. Unlike Ref. 3, our resist was spin-coated, thus ensuring a uniform thickness

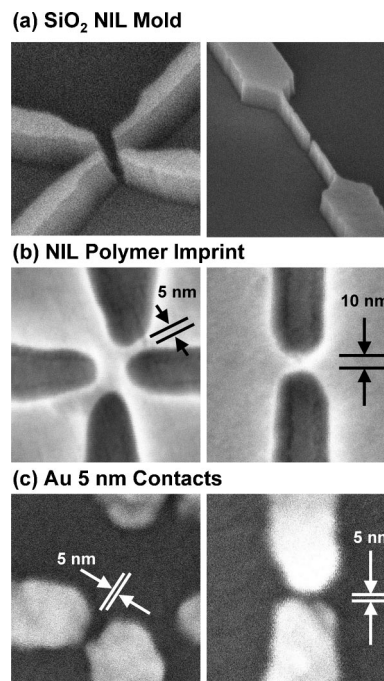


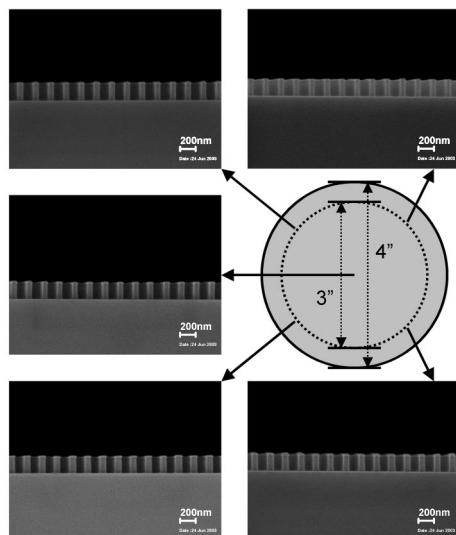
FIG. 3. Demonstration of 5 nm resolution photocurable nanoimprint lithography with application for single-molecule contacts. (a) SEM images of a silicon oxide mold. (b) SEM images of the imprinted P-NIL resist after UV curing and mold separation. Mold features as small as 5 nm were reliably reproduced in the resist. (c) SEM images of Au contacts after evaporation of metal and lift-off of the resist. Contact gaps as narrow as 5 nm can be fabricated.

over the entire surface of the substrate. Tight control over the resist thickness is vital to maintaining control over patterned critical dimensions. The thickness of the film depends on the mold depth, but is typically 100 nm. The resist consists of multiple components whose exact composition is proprietary and can be purchased from Nanonex Inc. The primary component is a reactive silicon containing oligomer whose function is to provide high etch resistivity to an oxygen plasma RIE etch, and reduce surface energy to aid in mold separation. A photoinitiator component initiates polymerization upon exposure to UV by allowing a crosslinking agent to form bonds with neighboring reactive oligomers, thus producing a tightly bonded polymer network. An acrylate monomer provides high solubility for the various components, a low viscosity of approximately 100 cp before curing, and prevents shrinkage during curing.

The P-NIL resist solution is spin-coated over a transfer layer polymer film of poly(methylmethacrylate) (PMMA) on a silicon substrate. The transfer layer material can be varied to suit the specific application required. Here, PMMA was chosen for its high solubility in acetone for a lift-off process. The NIL mold is then pressed into the low viscosity P-NIL resist at room pressure (15 psi) allowing the solution to conform to the patterns of the mold. Polymerization of the P-NIL resist is then performed by exposing the film to a broad band xenon UV lamp source, ensuring a dose of greater than 40 mJ/cm². After exposure, the mold is released, leaving the P-NIL polymer patterned. Polymer adhesion to the silicon mold is prevented by reducing surface energy with a fluoroalkyltrichlorosilane SAM.

After separation, the residual P-NIL polymer in the imprint trough is anisotropically etched with a RIE plasma of CHF₃ and O₂ until the PMMA is exposed. The PMMA is

(a) Uniform 200 nm pitch imprint over 4 inch wafer



(b) Cross section of 200 nm pitch imprint

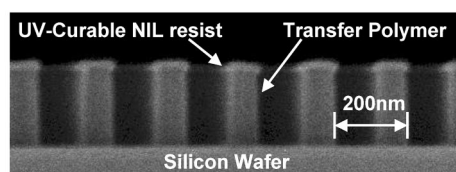


FIG. 4. Demonstration of large area and uniform imprint over a 4 in. silicon wafer: (a) After imprint of a 200 nm period grating, and anisotropic etching, sections of the 4 in. wafer were cleaved and examined under SEM. The patterned polymer bilayer shows no indication of variation in critical dimension control, thickness, sidewall roughness, or aspect ratio. (b) A high magnification SEM image of the polymer bilayer, showing the top P-NIL cured resist, and underneath, the transfer polymer layer.

then etched down to the substrate surface with an O_2 plasma using the P-NIL polymer as an etch mask. The etch selectivity of the O_2 plasma to the PMMA over the P-NIL polymer is greater than 10:1. The substrate is now patterned with a bilayer polymer film mirroring that of the mold. This patterned bilayer can be used for lift-off applications, or as an etch mask for the substrate itself. Because the polymer etching is a two-step process, the aspect ratio of the patterned polymer bilayer film can be greater than that of the original mold.

Next, pattern transfer was demonstrated with a lift-off process by evaporating 2 nm of Cr and 12 nm of Au directly on the sample, and then removing the bilayer film by dissolving the PMMA transfer layer in warm acetone. The quartz substrate was then patterned with gold contacts separated by as little as 5 nm, as shown in Fig. 3(c). The yields of the gold contacts exceeded 90% provided dust did not contaminate the process.

Fabrication of sub-10 nm contacts of sufficient resolution to trap complex macromolecules⁸ will substantially advance the emerging field of single-molecule devices by allowing the rapid production of multiple contacts in parallel. Typically, contacts are made one at a time with serial processing such as AFM probing,⁹ scanning tunneling microscope probing,¹⁰ electromigration,^{11,12} electrochemical growth,¹³ EBL,^{14,15} trapping colloidal gold particles with dielectric force,¹⁶ or shadow evaporating.¹⁷

Finally, we studied a large-area P-NIL imprint, and demonstrated excellent uniformity over a 4 in. silicon wafer. Figure 4(a) shows the P-NIL pattern transfer process over a 4 in. silicon wafer substrate after the two-step polymer RIE. Hence, the entire wafer was patterned with a 200 nm grating in a single step. SEM images at the center, and around the 3-in.-diameter circumference show patterned polymer uniformity can be obtained over the entire wafer with no noticeable variation in critical dimension, thickness, sidewall roughness, or aspect ratio. Figure 4(b) shows a higher resolution image of the polymer bilayers with the cured P-NIL resist on top, and transfer layer underneath. The sidewalls are almost perfectly straight due to the high resistivity of the P-NIL resist to the anisotropic oxygen plasma etch.

In summary, we have demonstrated that P-NIL is capable of 14 nm pitch lines, 5 nm critical dimension features, and can uniformly pattern an entire 4 in. wafer in a single step. The nanoimprint process is performed at room temperature and requires less than 15 psi pressure, thus allowing for a wide range of temperature- and pressure-sensitive applications. The bilayer polymer film, with the unique spin-coated application of the P-NIL resist, ensures tight process control over the entire substrate, aspect-ratio enhancement, no “tear-off,” and precise pattern transfer of metal with lift-off. Future work will involve further development of the P-NIL polymer, deep sub-micron alignment for multilayer NIL, and greater automation of the imprint process.

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