Resolution Enhancement in Nanoimprinting by Surface Energy Engineering

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ABSTRACT

Nanoimprinting lithography was initiated as an alternative way to achieve nanoscale structures with high throughput and low cost. We have developed a UV-nanoimprint process to fabricate 34×34 crossbar circuits with a half-pitch of 50 nm (equivalent to a bit density of 10 Gbit/cm^2). Our resist was of a single layer, which required fewer processing steps than any bi-layer process, but yielded high quality results.

We devised a technique that exploits the opposite free energies of the mold and substrate surfaces to produce a very uniform resist film without any trap air. Sixty-six by sixty-six crossbar structures with a half-pitch of 30 nm were produced recently by improving the resist adhesion to the substrate with a surface linker.

Keywords: nanoimprint, lithography, drop method, surface linker, UV process

1 INTRODUCTION

Optical lithography has been used to pattern semiconductor circuits for over 3 decades. However, as the feature sizes shrink to a small fraction of the wavelength of the light used, new challenges are emerging to drive the cost up dramatically. Hot embossing and its descendant nanoimprint have shown promise as new disruptive technologies to displace photolithography in patterning electronic circuits.[1,2] These methods are attractive because of their potential for high throughput with easy operation at a low cost. It has now been incorporated into the 2003 version of the International Technology Roadmap for Semiconductors (http://public.itrs.net/) for post 45 nm half-pitch manufacturing (sometime after 2010). However, because of its direct contact printing process, resist thickness non-uniformity and resist adhesion to the stamp remain as some of the challenges to overcome before the nanoimprint technique can become volume lithography tool.

To achieve high yield, a very uniform resist film after imprinting is important, especially to make devices by a subsequent lift-off process. As the feature-size decreases, the imprinted resist is likely to adhere to the gap on the mold features after mold-substrate separation. This paper focuses on how to overcome these challenges in the nanoimprint process by exploiting the opposite free energies of the mold and substrate surfaces.

2 NANOIMPRINT LITHOGRAPHY

Figure 1 shows the procedure to make electrodes by imprint lithography and subsequent lift-off.

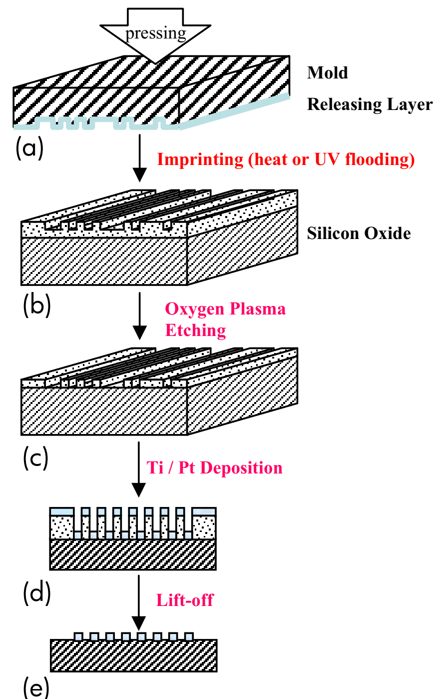

Figure 1. Process flow for fabricating bottom electrodes by nanoimprint lithography: (a) the mold coated with a releasing layer; (b) imprint lithography on the polymer film; (c) oxygen plasma etch to remove the residual polymer layer at the bottom of imprinted trenches; (d) Ti (4nm) / Pt (6 nm) metal evaporation; (e) lift-off process to define the bottom electrodes.

The features on the mold which consisted of raised mesas of nanowires was patterned on a silicon or silicon oxide substrate by e-beam lithography with a bi-layer resist and reactive ion etching.[3] The mold surface was treated with a releasing agent, which prevented the resist polymer from adhering to the gaps between the mold features after mold detachment from the substrate.[4] The mold is pressed onto a resist-coated substrate, and then the resist is cured by UV irradiation or elevated temperatures to produce a

replica of the mold on the polymer layer. The residual resist layer under the trenches is removed by an oxygen plasma treatment to expose the substrate in the patterned area before metal evaporation. The metal deposited on the resist is lifted off with a suitable solvent in an ultra-sonic bath while the metal deposited in the trenches remains and becomes the electrodes.

3 UNIFORM RESIST SPREADING BY CAPILLARY ACTION

Resist formulation is one of key issues in nanoimprint lithography. It should have a low viscosity to facilitate spreading under a low imprinting pressure and a strong adhesion to the substrate for clean mold detachment. When a mold is in contact with a substrate on which the UV-curable monomer is spin-coated, air bubbles are likely to be trapped between them as shown in figure 2, because the mold and substrate are not perfectly conformal. These air bubbles were detrimental to the fidelity, and caused non-uniform resist film thickness after imprinting.

Figure 2. Trapped air in imprinted resist which was spin-coated on the substrate. The mold was a piece of plane quartz through which UV was flooding to polymerize the monomer film.

A very uniform resist without any trapped air is desired before imprinting for the high device yield. For this purpose, we devised a new method in which we engineered surface energies of the mold and the substrates to be opposite of each other, and applied the resist in a way that exploit one surface's ability to localize it and the other's to spread it.[5] The resist was first dropped onto the mold surface which had been made very hydrophobic with a monolayer releasing material. The resist stayed as a small bead due to high surface tension. To spread the resist, we made the glass substrate surface very hydrophilic with water vapor plasma treatment, then placed it on the mold. The hydrophilic surface spread the resist uniformly and systematically through the nanoscale channels by capillary action (figure 3(a)). Initially, there were interference fringes caused by non-uniform resist thickness and air trapped near the edge of the contact, but they disappeared with time (figure 3(c)), which illustrated the flow of the resist solution from the overloaded to the empty areas. Our method resulted in a uniform film across the whole active area.

Figure 3. Still photos show resist spreading with time. Interference fringes spread out and disappear with time after contact between the mold and substrate: (a) 2 min; (b) 5 min; (c) 30 min.

After the spreading was complete, the mold and substrate were adhered together so well that they could not be moved even with a strong lateral force. The sample was then loaded into imprint machine and pressed for 10 minutes with a pressure of 20 psi to displace any residual resist layer beneath the mold features. The sample was irradiated with UV light for 15 minutes while the pressure was maintained. The bottom electrodes were metalized by evaporating Ti (4nm) / Pt (6nm), followed by a lift-off process. Then the active memory layer was deposited on them by the Langmuir-Blodgett technique.[3] The top electrodes were patterned on top of the molecular layer, with the mold rotated 90° relative to the bottom electrodes. Figure 4 shows a 34 by 34 crossbar array at 50 nm half-pitch fabricated with the method above.

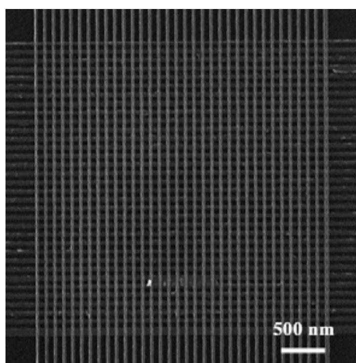

Figure 4. Thirty-four by thirty-four crossed nanowires fabricated by UV nanoimprint lithography. The half-pitch of the nanowires is 50 nm. The cell density is 10 Gbit/cm^2.

4 SURFACE LINKER TO ENHANCE RESIST ADHESION TO SUBSTRATE

We have successfully imprinted patterns down to 50 nm half-pitch. However, as the feature size was further reduced, another new challenge appeared: the resist was prone to detach from the substrate surface and adhere to the mold during mold separation. Figure 5b, which is a SEM image of the resist after mold detachment, shows that at 30 nm half-pitch region the hydrophobic treatment on the mold surface was no longer sufficient. Only the patterns of the sparser 60 nm half-pitch fan-out wires remained on the substrate, whereas the denser patterns at 30 nm half-pitch had completely detached from the substrate and adhered to the mold.

A new strategy was applied to the substrate to improve the resist adhesion to the substrate. We applied a monolayer of “surface linker” to the substrate surface, which not only served to decrease the free energy of the resist-substrate interface to help the resist spread, but more importantly, it also formed a chemical bond between the resist and the substrate, thus greatly improving resist adhesion.

The surface linker molecule we chose has a silane group on one end and methacrylate group on the other end, as shown in figure 6. The former forms a chemical bond with the hydroxyl group on the substrate surface by self-assembly and the latter co-polymerizes with the resist during UV exposure, thus forming a link by chemical bonding between the substrate and the imprinted resist.

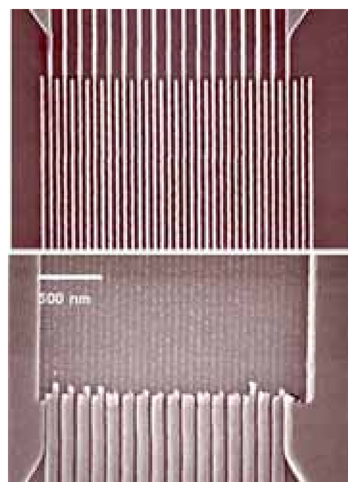

Figure 5. a) SEM image of the mold in a region in which wires of two different pitches exist. The feature sizes are 60 nm half-pitch in the fan-out region and 30 nm half-pitch in the nanowire region. b) SEM image of the imprinted nanowire pattern in the resist, showing the nanowire patterns with larger pitch remained but those with smaller pitch have completely detached.

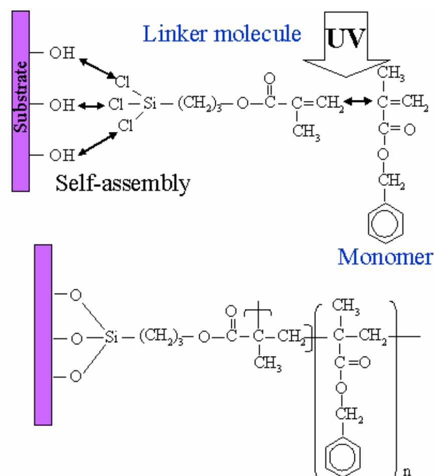

Figure 6. Schematic diagram illustrating the mechanism of the silanation reaction of the linker with hydroxyl groups on the glass during initial SAM formation and of the co-polymerization between the methacrylate groups in the linker and in the resist during UV irradiation.

The linker monolayer on the substrate was produced by first treating the substrate with piranha solution to produce hydroxyl termination and then dipping it into a toluene solution that contained 0.2 wt % methacryloxy propyl-trichlorosilane for one hour. The presence of the linker monolayer was confirmed by FTIR spectroscopy, and the

thickness of monolayer was measured to be 1.2 nm by ellipsometry.[6]

With the modified substrate surface, nanoimprint lithography was performed with the resist utilizing the drop method. Every process parameter was same as the previous experiment, which gave a poor resist adhesion to the substrate at 30 nm half-pitch, to compare the effect of the monolayer of surface linker on the substrate surface. Figure 7 is the SEM image of a imprinted resist on the functionalized substrate with thirty-seven distinct nanowire impressions at 30 nm half-pitch and the transition to the fan out region. When compared to the results in figure 5b, it shows the use of a surface linker has dramatically improved resist adhesion to the substrate surface.

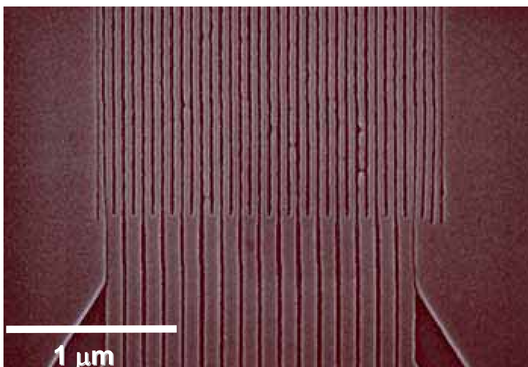

Figure 7. SEM image of imprinted resist on the surface treated with the linker molecule, demonstrating the good resist adhesion to the substrate and detachment from the mold in both dense and sparse regions.

5 SUMMARY

We devised a technique that exploits the opposite free energies of the mold and substrate surfaces to produce a very uniform resist film without any trapped air. We applied the resist onto the mold surface to take advantage of its ability to localize the resist and then use the substrate surface to spread it. Further, we functionalized the substrate with a linker molecule that chemically bonds the resist to the substrate after UV exposure. The linker monolayer enabled the successful imprinting of 30 nm half-pitch nanowire patterns on the polymer resist layer.

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