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Fabrication of Sub-50 nm Au Nanowires using Thermally Curing Nanoimprint Lithography

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As narrow as 50 nm metal nanowire array patterns were successfully fabricated by nanoimprint lithography (NIL) using thermally curable monomer based resin. Compared to conventional hot embossing lithography, which has used thermoplastic polymers such as PMMA as an imprint resin and thus process temperature and pressure are over 180°C and 50 bar, respectively, thermally curable monomer based resin enabled imprint process at relatively lower temperature (120°C) and pressure (20 bar). Due to the highly fluidic nature of monomer based liquid phase resin, residual layer was not observed after imprinting. Imprinted resist pattern was then treated with oxygen plasma for 5 seconds and 5 nm of Ti layer and 15 nm of Au layer was deposited by e-beam evaporation. The imprinted resist pattern was lifted-off by dipping into an organic solvent, such as acetone. As the result, as narrow as 50 nm Au nanowire array pattern with area of 30 mm×40 mm was fabricated on a Si substrate. 30 mm × 40 mm of nanowire pattern area was not limited by nanoimprint process, but the laser interference lithography process, which was used to fabricated the master template for imprinting.

Keywords: nanoimprint lithography, hot embossing lithography, zero-residual imprint, thermally curable liquid phase resin, Au nanowire array, lift-off process

1. INTRODUCTION

Integrated nano-scale patterns are essential elements for the fabrication of semiconductor devices, optical components such as wire grid polarizer and nano-bio devices. In order to fabricate nano-scale patterns, various techniques, including e-beam lithography,[1] extreme UV lithography[2] and laser interference lithography (LIL)[3] have been applied. However, those nano-patterning techniques were not successfully adopted for mass production of nano scale patterns, due to high process cost and insufficient throughput.

Nanoimprint lithography (NIL) can fabricate nano-sized patterns at lower cost and higher throughput.[4-6] Wafer to wafer scale transfer of nanometer sized patterns can be done by NIL process[7] and the same sized metal patterns can be formed using NIL and lift-off process.[8] Thus, NIL is considered to be a next generation nano-scale patterning technique. Fabrication of as small as 10nm patterns on Si substrate using NIL has been demonstrated.[9]

NIL can be categorized into two groups, hot embossing lithography and UV nanoimprint lithography. Conventional hot embossing lithography uses solid phase thermoplastic polymers, such as polymethylmethacrylate (PMMA) as an imprint resin, due to its ability to form high-resolution patterns. However, PMMA resin requires high imprint temperature (>170°C) and an imprint pressure also needs to be as high as 50 bar, in order to transfer nano-scale patterns to the PMMA layer. Although, imprinting was conducted at high temperature and high pressure, a few tens of nanometer thick residual layer is inevitably remained after imprinting, due to limited fluidity of PMMA resin. Such residual layer can easily be removed by oxygen plasma treatment, however, lateral dimension and profile of imprinted resin can be degraded during this step. UV nanoimprint lithography uses UV curable liquid phase imprint resin. Since liquid phase imprint resin can be solidified by UV exposure, imprinting can be done at room temperature and imprint pressure can be lowered drastically. Since UV light is used to polymerize the resin, either substrate or imprint template must be transparent to UV light.

In this work, highly fluidic, thermally curable, liquid phase monomer-based resin was formulated and used, in order to lower the imprint temperature to 120°C and imprint pressure to 20 bar. With this imprint resin, near-zero residual imprint-

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ing can be achieved and metal nanowire array can be made by combining nanoimprint lithography and lit-off process.

2. EXPERIMENTAL PROCEDURE

The overall process flow to fabricate metal nanowire array pattern is summarized in Fig. 1. Single droplet of thermally curable liquid resin (0.5 ul) was dispensed between the substrate and imprint template by micropipette and 20 bar of isotropic pressure was applied for 10 min in order to fill the nano-sized cavities of the template uniformly and to squeeze off the excess imprint resin. During this stage, fluidic imprint resin fills the nanometer sized cavities of imprint stamp without forming the residual layer by applying pressure and the excessive resin was moved to outside of the stamp. The temperature was then increased to 120℃ to initiate the polymerization reaction by activating the thermal radical generator. Finally, the imprint template was released from the cured polymer patterns. Imprinted resist pattern was then treated with oxygen plasma for 5 seconds and 5 nm of Ti layer and 15 nm of Au layer was deposited consecutively. Au nanowire array pattern can be formed by lifting off the resist using organic solvent, such as acetone.

3. RESULTS AND DISCUSSION

A master imprint template, used in this study, was made of a 100-mm diameter silicon wafer. Prior to patterning, the cleaned silicon wafer was oxidized with steam in order to grow a 250 nm thick oxide layer. Then, Shipley SPR-508A resist was spin-coated. 200 nm pitch line and space type photo-resist pattern was formed by Laser interference lithography. He-Cd laser with 325 nm of wavelength was used as the light source. The pattern area was limited to 30 mm × 40 mm. After LIL process, the underlying oxide was then selectively removed by reactive ion etching using fluorocarbon (CF3-CF2-CHF3) plasma. [10] The remaining photo-resist was then cleaned off.

Top view and cross-sectional view scanning electron microscopy (SEM) images of the 50 nm features on the master template is shown in Fig. 2. The feature consists of 50nm narrow line with 150 nm narrow spacing. The pattern was made of SiO_2 and its height was about 250 nm. Prior to imprinting, a monolayer of (hepta-decafluoro-1,1,2,2-tetrahydrodecyl) trichlorosilane molecules was formed on the surface of the imprint template by conventional liquid-based, self-assembled monolayer (SAM) coating.[11,12] According to lateral force AFM, less frictional force is measured on SAM coated Si surface, compared to bare Si surface.[13] In Fig. 3(a), (b), and (c), the contact angle of deionized water and imprint resin on the SAM coated Si surface and imprint resin on non SAM coated Si surface are shown, respectively, in order to evaluate the hydrophobicity and non-stick property of SAM coated Si master template. A contact angle of deionized water on the SAM coated Si wafer was as high as 140° and this implies that SAM coated Si master template is fairly hydrophobic. According to Fig. 3(b) and (c), (a) contact angle of thermally curable liquid phase imprint resin, used in this study was about 5° on Si wafer, non-coated with SAM antistiction layer and about was increased to 88° on the SAM coated Si surface, which means imprint resin has the strong tendency not to wet on SAM coated master template and this

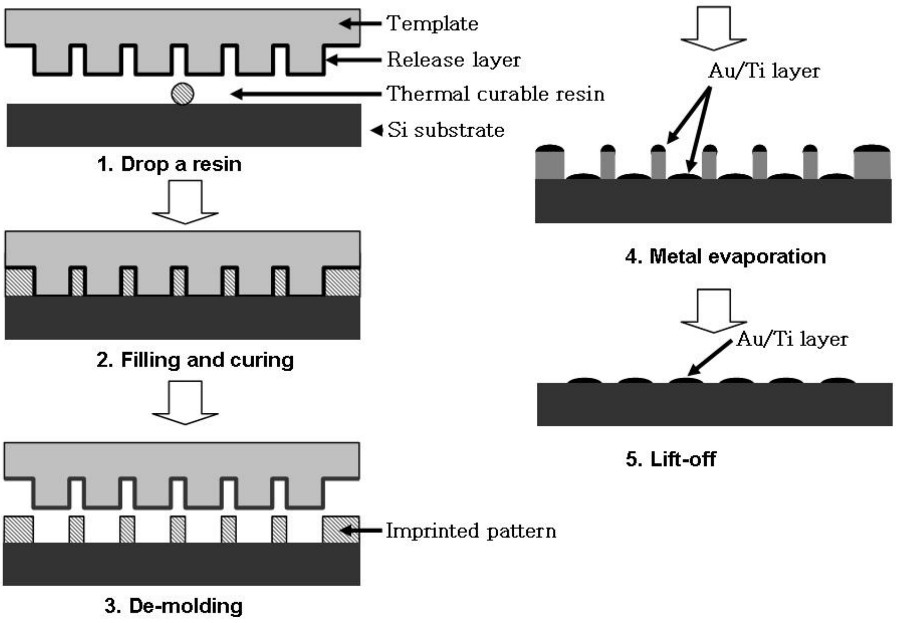

Fig. 1. The schematic diagram of thermal curing nanoimprint lithography and lift-off process.

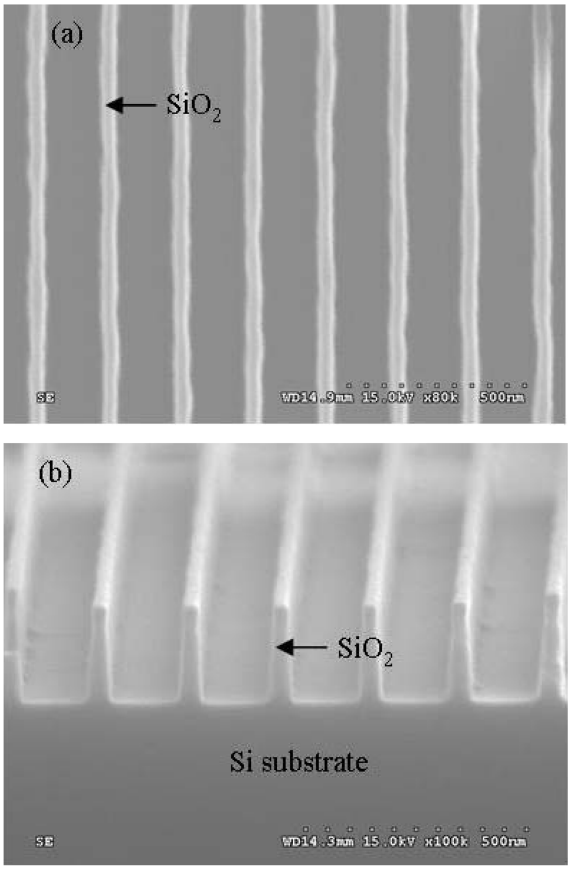

Fig. 2. SEM micrograph of Si template with 50 nm features (a) top-view (b) cross-sectional view.

results in repeatable imprinting process without detachment problem of master template.

A thermal curable, liquid phase monomer-based imprint resin, used in this study contains base monomer (benzyl-methacrylate, $C_{11}H_{12}O_2$), 7% of its polymer, poly benzyl-methacrylate and 3% of thermal radical generator (tert-butyl peroxy-2- ethylhexanoate, commercial product name: trigonox™ 21).[14] No solvent was added to minimize the out-gassing. Since base monomer is very volatile, polymer form of base monomer (poly benzyl-methacrylate) is added to prevent vaporization during process and to adjust viscosity. Trigonox™ 21LS, used as a thermal radical generator, can initiate the polymerization reaction of base monomer at 80 °C, which is lower than glass temperature of commonly used thermoplastic polymers. By using thermally curable liquid phase resin, imprinting can be done at much lower temperature without noticeable residual layer.

During imprinting process, a holding period was necessary to fill the cavities of the template and to remove the excess resin, both of which are very essential for obtaining zero residual imprinting. Just for pattern transfer, holding time and pressure can be as low as 1 min and 2 bar, respectively. A holding time of 10 min at 20 bar pressure was set for a high fidelity pattern transfer without any noticeable residual layer. Figure 4 presents top view and cross-sectional view SEM micrographs of the imprinted resist pattern. Although single droplet of liquid resin was applied, high fidelity pattern transferring was obtained over 30 mm × 40 mm area. Compared to the SEM micrographs of the imprint template shown in Fig. 2, a reversed image pattern of master template was formed. A 50 nm narrow lines of template become 50 nm narrow trenches. According to cross-sectional SEM micrograph of the imprinted resist pattern, residual layer was not observed. This implies that residual layer is too thin to be observed by SEM. This is also confirmed by that lifted-off metal nanowire pattern can be obtained by depositing the metal layer on the imprinted resist pattern, after 5 seconds of oxygen plasma treatment. A PlasmaTherm™ 790 series reactive ion etching system was used for oxygen plasma treatment. 100 watt of plasma power and 40mT of pressure was maintained with 40 sccm of oxygen flow. Under this oxygen plasma condition, the etch rate of cured imprint resin was about 270 nm/min. Cross-sectional SEM micrograph of imprinted resist pattern also confirms nearly vertical sidewall profile, which enables successful fabrication of metal nanowire array pattern using lift-off process. Figure 5 shows SEM micrograph and an atomic force microscopy (AFM) image of Au nanowire array pattern, fabricated by the nanoimprint and lift-off processes. 50 nm narrow metal nanowires with 150 nm spacing, which was identical to original master template pattern, was formed on Si substrate.

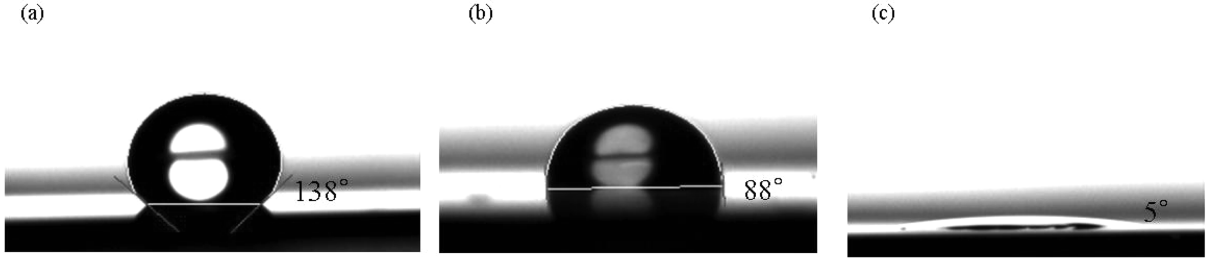

Fig. 3. Contact angle of (a) de-ionized water on SAM coated Si wafer, (b) thermally curable resin on SAM coated Si wafer and (c) thermally curable resin on Si wafer without SAM coating.

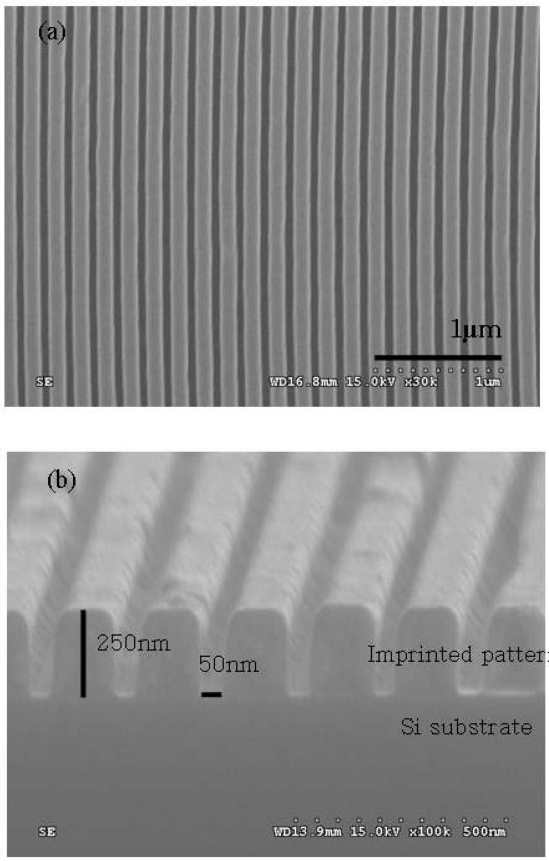

Fig. 4. SEM micrographs of imprinted pattern (a) top-view (b) cross-sectional view.

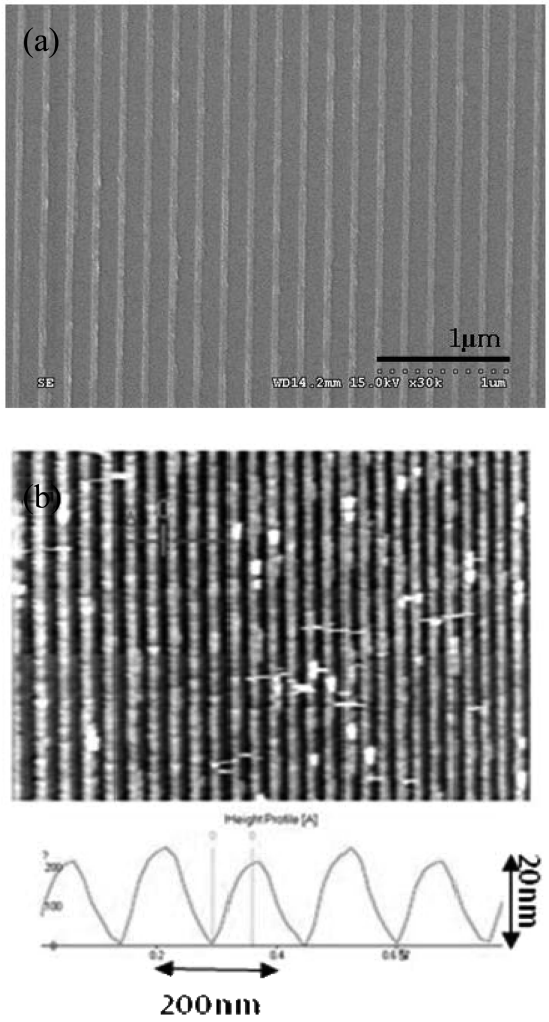

Fig. 5. SEM micrograph and AFM image of 50nm Au nano-wires fabricated on Si substrate.

4. CONCLUSION

A thermally curable liquid phase monomer resin was formulated for thermally curable imprint lithography, in order to lower imprinting temperature and pressure and to ensure near zero residual imprinting. In this work, 50 nm narrow metal nanowire array was fabricated by using thermally curable imprint lithography and lift-off process. Due to the nature of lift-off process without double layer, lifted off metal nanowire patterns were slightly wavy.

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