Nickel Electroplating for Nanostructure Mold Fabrication *

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Abstract. We demonstrated a practical process of fabricating nickel molds for nanoimprinting. Dual-side polished glass is chosen as the substrate on which nickel nanostructures are successfully electroplated. Photonic crystal structures with 242nm diameters and other nanoscale pillars down to 90nm diameters are achieved over a large area. The electroplating parameters are investigated and optimized. This process extends the feasibility of electroplating process to nanoscale and shows great potential in nanoimprint mold fabrication with its low cost, straightforward process and controllable pattern structures.

Key Words. nickel electroplating, electron beam lithography, nanostructure

1. Introduction

The fabrication of nanostructures has been a challenge over past decades. Although electron beam lithography (EBL) has always been a possible solution, every EBL run is time consuming and cost intensive. Thus, many organizations do not have the luxury of using EBL and it is also not suitable from the mass production point of view. Therefore, nano imprint lithography (NIL) has drawn much attention recently. A successfully fabricated mold can be used to replicate many devices thus reduces the cost of per unit noticeably. Actually, this low-cost and high-throughput technique has been successfully applied to make sub-10nm scale features for compact disks[1]. Photonic crystal structure has also been reported by Belotti et al. to be successfully nanoimprinted via etched glass/silicon mold with 10nm minimum feature sizes[2]. In the light emitting diode (LED) industry, nanoimprint technology is also booming[3, 4]. When performing NIL process using ultraviolet, two commonly fabricated molds are rigid quartz stamps[5] and flexible stamps[6]. Rigid stamps are suitable for small scales down to 20nm or 10nm while flexible stamps (normally PDMS based) are suitable for a large area with lower resolutions.

Electroplating, a low cost metal deposition method, is widely used in molding parts scaled from microns to meters. In micro machining, electroplating is a key step in LIGA and pseudo LIGA processes (German acronym for Lithographie/Lithography, Galvanoformung/Electroplating, Abformung/Molding) to replicate the master photo resist mold with high aspect ratio structures[7]. LIGA process is used to create high-aspect-ratio microstructures. A typical LIGA process is composed of pattern exposure, development, electroforming, resist stripping and replication steps with the purpose of fabricating various structure in micron scale[8-11]. Sub-micron and nanoscale electroplating has been demonstrated in fabricating molds for NIL use. Actually some groups have performed related experiments to fabricate nanoimprint mold by electroplating. Kuczko used template-based method to electroforming nanowires[12]. Kouba et al. from Germany demonstrated a nanoimprint stamp for photonic crystal [13]. In their research, features were patterned in silicon stamps and were followed by nickel seed layer deposition. On top of the seed layer, nickel mold was electroplated and formed its own back support. Another group, Chen et al. presented their method of electroplating using a seed layer pre-buried in the substrate. After patterning, the electroplated metal grew only in zones where the seed layer was exposed. The final imprinting mold was also fabricated by over-electroplating[14]. Burek et al. [15] reported recently using electroplating and electron beam lithography to fabricated gold and copper nanoscale specimens for mechanical testing purpose.

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Compared to other works, our inspiration stemmed from bringing the LIGA process to nanoscale. We also use pre-buried seed layer to electroplate Ni on areas confined by electron beam resist directly. This method can be use to fabricate many nanoscale structures including photonic crystal structures, gratings. In our work, by controlling the electroplating condition precisely, we have successfully achieved nickel mold with nanoscale pillars down to 90nm in diameter and a photonic crystal structure mold with input/output waveguides as well as the line defect. This method, featured by its straightforward process, shows great potential in fabricating nanoimprint molds that make low cost device manufacturing possible.

2. Experimental

Figure 1 sketches the entire idea and process of device fabrication using the nanoimprint method, starting from the mold fabrication. After the mold fabrication, it can be used in an imprinting machine to define patterns on other polymers or resist layers that served as etch mask, followed by etching step to get functional devices. The details are discussed below.

Square, dual-side polished 1” × 1” glass slices were used as the nanostructure mold substrate. They are carefully cleaned with acetone and IPA then transferred to piranha solution (H_2O_2:H_2SO_4=1:2 by volume) for 20min to remove organic matter. Electron-beam evaporation was used to coat a uniform 50nm nickel film on the glass surface which serves as the pre-buried seed layer for electroplating. The diagonal resistance is around 14 ohms.

The glass substrate coated with Ni film was then spin coated with adhesion promoter hexamethyldisilazane (HMDS) and high resolution positive electron beam resist ZEP520A. The spin speed and time were carefully controlled so that a resist thickness of 400nm is maintained. JEOL 6000 E-Beam system was employed to expose the resist. After e-beam writing, the sample was developed and then followed by isopropanol alcohol rinse.

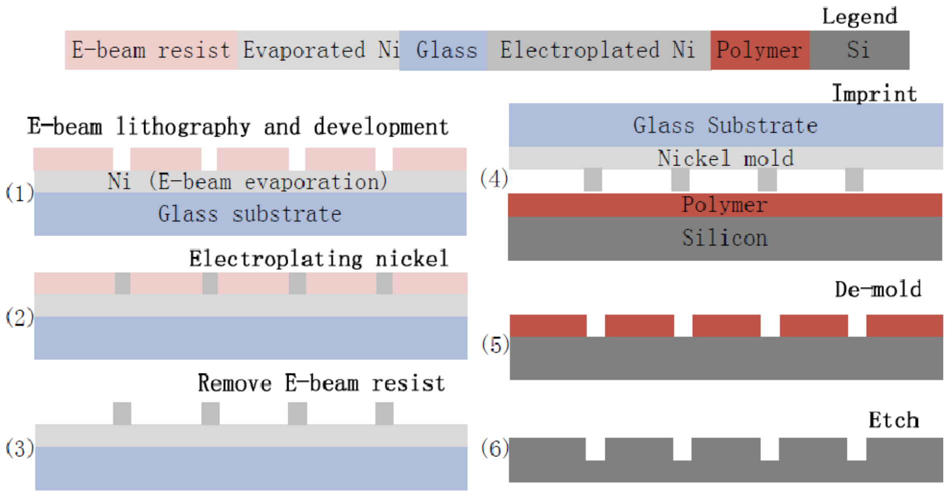

Figure 1 Fabrication process. Step (1) ~ (3) shows the mold fabrication process using nanoscale electroplating. Step (4) ~ (6) shows applying the mold in a nanoimprint process.

In order to make a contact for the electroplating process, we used Oxford Reactive-Ion-Etching to open a contact area of 330mm^2. The area containing nanoscale features was protected from to ion beam exposure during the etching process. The ZEP520A resist served as the confinement. The electroplating environment is critical for nanoscale features to be grown. In our experiment, we maintained the bath temperature at 45^{o}C and pH value at 4. The current density was set to 0.1mA/mm^2. Electroplating time varied from 3 to 60 minutes.

The ZEP520A resist was then removed by a solvent stripper called NANO^{TM} REMOVER PG after electroplating to expose the nanostructure. To finalize the mold for imprinting process, dicing saw was employed to cut out a square area of around 8mm×8mm in order to remove the edge defect during fabrication. After dicing, the sample can be used as a nanoimprinting mold.

The main advantage of using a pre-buried seed layer before patterning features is that the electroplated nickel will only grow on areas where the seed layer is exposed. Chen's et al. [14] stated that a seed layer will also help reduce voids formed during the electroplating process, compared post-patterning seed layer sputtering. In the process outlined above, a pre-buried layer is necessary as the entire surface is not over-electroplated for back support. Instead, the back support of the presented nickel mold is the dual-side polished glass substrate. Furthermore, no extra step is necessary to polish the back support of the mold for handling purpose after dissolving the resist.

3. Results

We started from fabricating pillar array to test the feasibility of electroplating nickel in sub-micron and nanometer scale. With optimized nickel parameters, electroplating were executed on holes arrays with 500nm diameter (1000nm period). Figure 2(a) shows the results of electroplating with current density of 0.1mA/mm2 for 60min. As shown in the picture, a uniform nickel cylinder array was successfully fabricated across the entire electroplated area. The inset picture in Figure 2(a) shows the detailed zoomed in view of a single pillar. The top surface is relatively rougher than the substrate due to immature electroplating termination control. However, from the device point of view, this roughness is acceptable during the imprinting process.

The cross-section image of the 500nm pillar array is shown in Figure 2(b), demonstrating the height of electroplated nickel to be 400nm, which is identical to the thickness of the spin coated e-beam resist. Electroplating conditions shall be carefully controlled to prevent the nickel over-electroplating. Otherwise all the pillars will start to have mushroom like shape and finally connect to each other and cover all the zones. The cross section picture also reveals the pre-buried Ni seed layer underneath the structure which is measured to be 48nm thick. Employing nickel as seed layer can help eliminate the internal stress that may weaken the adhesion strength if two different materials are used. We noticed that in the nickel mold, the measured diameters of those pillars are around 600nm, which are larger than designed. This is due to the electron scattering effect in the electron beam writing system causing larger areas to be exposed to electrons. Thus, ZEP520A electron beam writing and development yielded a larger size of holes that were later filled by electroplated nickel. This difference can be eliminated by offset the design dimension and optimize the EBL parameters (i.e. dosage, current and expose time) to account for electron scattering effects.

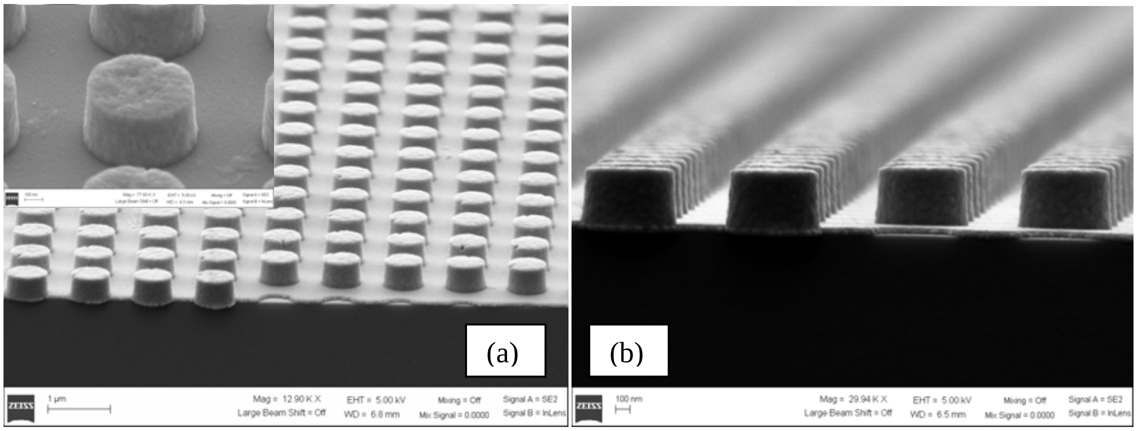

Figure 2 (a) Nanoscale pillar array with 500nm in diameter, with a pillar zoomed in. (b) Cross section view of electroplated Ni pillar array

Electroplating speed varies according to different environmental settings. In the present work, the relation between electroplating thickness and time was investigated. Table 5 contains data indicating the nickel thickness deposited versus time under fixed electroplating conditions by setting the electroplating bath temperature to 45°C, the pH value to 4 and the current density to 0.1mA/mm^2 after stabilizing the current source. The relation is very close to linear and the speed is roughly estimated to be 6-8nm/min. Because of the nanoscopic thicknesses involved in the investigation, care must be taken in extrapolating to microscale thicknesses, as this linear may not hold.

Table 1 Thickness of electroplated Ni inside nanoscale holes versus time

Electroplating Time (minute)	5	15	30	45	60
Electroplated Nickel Thickness(nm)	45	113	254	362	400

With the success in the 500nm diameter pillar, we continued to try smaller sizes integrated with practical photonic crystal design. Figure 3 shows a mold for hexagonal array of photonic crystal structures with a line defect, electroplated on a Ni coated glass substrate. The sub-picture (a) shows the overview of the entire photonic crystal Ni template area under scanning electron microscope (SEM) after developing and removal of the e-beam resist. The length of the photonic crystal area is 58.03µm. The sub-picture (b) shows the topography of the area where light is coupled in/out the photonic crystal area. The sub-picture (c) shows the 90^{o} rotated view of hexagonal array of the nickel pillars inside the photonic crystal area. The device design includes two straight waveguide areas with a photonic crystal area in- between. As can be seen clearly from above pictures, the lithography patterns were successfully transferred into a nickel mold with remarkable uniformity. The electroplating condition is optimized to 0.07mA/mm^2 at 45^{o}C accordingly. The air holes have been designed to have diameters of 212nm and period of 465nm to let through light ranged from 1515nm to 1565nm wavelength.

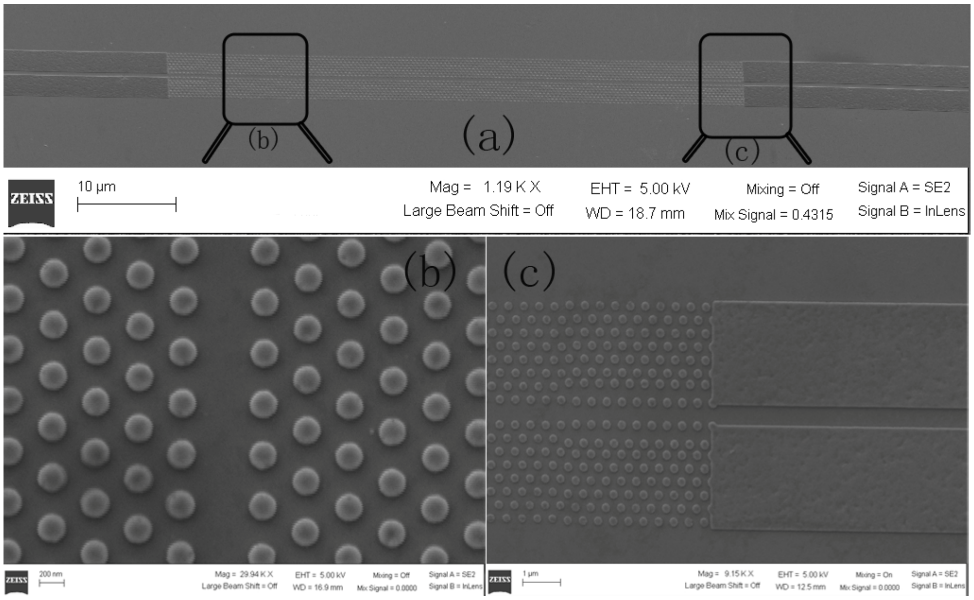

Figure 3 Photonic crystal pattern and electroplated Ni mold. (a) Overview of the device template; (b) zoomed in hexagonal array of photonic crystal structure template (rotate by 90^{o}), scale bar: 200nm; (c) light input/output coupling area, scale bar: 1µm

The fabricated mold is featured with both good bulk mechanic properties and surface chemical properties. The glass substrate is pretty solid while not as brittle as silicon substrate. High Young’s module of pure nickel using LIGA process has been tested and reported to be over 1000GPa[16] which is also our estimation that needs to be confirmed in our future work. Besides, the adhesion force between glass and nickel is high enough to sustain the temperature up to 200^{o}C. As an imprinting mold, the surface needs to be hydrophobic where the presented sample is well featured with a hydrophobic surface that renders easy de-molding process when imprinting.

In fact, electroplating as a low-cost fabrication technique is able to deposit metal into even smaller structures. Figure 4 shows the nanoscale features with 90nm diameters that are successfully electroplated in glass substrate with nickel coating.

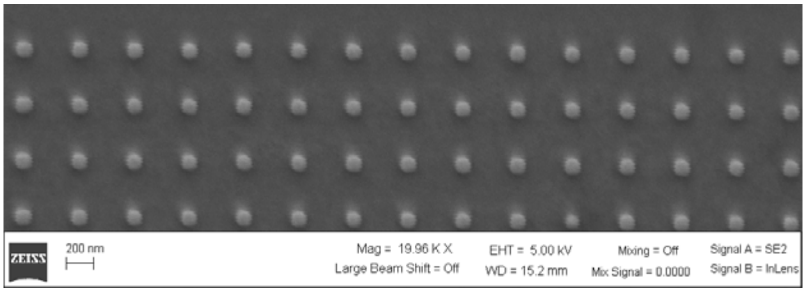

Figure 4 electroplated Ni pillars with 90nm pillars, scale bar: 200nm

4. Conclusion

We have demonstrated the process of fabricating Ni mold for the purpose of nanoimprinting. Arrays of nanoscale Ni pillars in photonic crystal patterns were successfully achieved with remarkable uniformity. Smaller mold feature dimensions of 90nm were demonstrated and the smallest size we can achieve now were mainly limited by the electron-beam lithography process, but subsequent designs can be tailored to achieve intended dimensions. Mold thickness was accurately characterized over a wide range of nanoscopic thicknesses, ongoing work on electroplating termination shall decrease roughness in future molds.

The main advantage of this process includes: (1) It is a simple fabrication process. (2) Compared with other methods, the supporting substrate is not formed by electroplating, thus no post-polish step is necessary. (3) After electroplating, REMOVER PG is used to dissolve the e-beam resist, and no further mold release step is necessary. (4) The Ni seed layer is pre-buried in the substrate, enabling tighter control of features. Electroplating Ni on Ni also minimizes the internal stress that would be induced if using two different materials.

Future work shall include but not limited to the improvement of the adhesion strength between different layers, more precise thickness control over the entire mold, better controlled electroplating termination for improved surface roughness, and more investigation into the imprinting process such as surface energy reduction, mold protection, etc.

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