

Two-dimensional Photonic Crystals Fabricated by Nanoimprint Lithography

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Abstract — We report on the process parameters of nanoimprint lithography (NIL) for the fabrication of two-dimensional (2-D) photonic crystals. The nickel mould with 2-D photonic crystal patterns covering the area up to 20mm² is produced by electron-beam lithography and electroplating. Periodic pillars as high as 200nm to 250nm are produced on the mould with the diameters ranging from 180nm to 400nm. The mould is employed for nanoimprinting on the poly-methyl-methacrylate (PMMA) layer spin-coated on the silicon substrate. Periodic air holes are formed in PMMA above its glass-transition temperature and the patterns on the mould are well transferred. This nanometer-size structure provided by NIL is subjective to further pattern transfer.

I. INTRODUCTION

A photonic crystal^[1] is a periodically repeating structure made of two materials of different dielectric constants. Such index modulated structures can provide so-called photonic band gap, and photons with frequencies within the gap are not allowed to propagate. In recent years two-dimensional (2-D) photonic crystal slab structures attract a lot of interest and a variety of applications have been demonstrated such as 2-D photonic crystal defect lasers, 2-D photonic crystal band edge lasers, 2-D photonic crystal waveguides and 2-D photonic crystal light-emitting diodes^[2-10].

Despite novel high-performance optical devices achieved by the employment of 2-D photonic crystals, the commonly used fabrication method of electron-beam lithography (EBL) refrain them from real commercial applications. Therefore, alternative nanometer-size patterning techniques are under research, among which nanoimprint lithography (NIL) is promising in terms of its low-cost and high-throughput. Basically NIL involves a physical deformation of a thin layer of polymer deposited on a substrate by using a rigid mould, followed by a pattern

transfer and the complete removal of the residual polymer in the recessed areas of the pattern^[11].

Passive photonic devices especially polymer photonic crystals has been successfully fabricated by NIL^[12-14].

In this paper, the fabrication of 2-D photonic crystals using NIL is illustrated. The nickel (Ni) mould used for nanoimprinting is produced by EBL and electroplating. 2-D photonic crystal patterns designed for light-emitting diodes are defined as air holes on poly-methyl-methacrylate (PMMA), which is spin-coated on the silicon substrate with metal seeding layers. Electroplating is then performed on top of the patterned PMMA, and Ni pillars form through the air holes. As the electroplating goes on, the whole PMMA region is covered by Ni, and the mould with designed fine pillar structures is obtained after releasing from the substrate. The mould can be used for nanoimprinting after being cut to desired shapes, deburring, backside polishing and cleaning. The polymer used for nanoimprinting is also PMMA, which is able to flow above its glass-transition temperature and can readily be deformed by the pillars on the mould. 2-D photonic crystals are thus formed as periodic air holes in PMMA by nanoimprinting, which serves as a good fabrication technique for nanometer-size patterning.

The experimental details and results are discussed in the next two sections. The optimization of the process parameters are described in details and several problems involved in the process are also illustrated. Some conclusions are reached and suggestions for improvement are provided in the last section.

II. EXPERIMENTAL DETAILS

The fabrication of 2-D photonic crystal slab structures is composed of mould fabrication and nanoimprinting. The rigid Ni moulds used for nanoimprinting are produced by EBL and electroplating processes, which are advantageous in terms of high strength and good reliability, but more subjective to residual stress compared with silicon (Si) moulds. Nanoimprinting is carried out on the PMMA layer

spin-coated on the semiconductor substrate, with the polymer deformed by external force applied above glass-transition temperature. The structure patterned by nanoimprinting is subjective to Inductively Coupled Plasma (ICP) etching and other processes to further transfer the patterns down to the semiconductor layers.

A. Ni mould fabrication

Ni moulds for nanoimprinting can be fabricated by EBL and electroplating, as is schematically shown in Fig. 1.

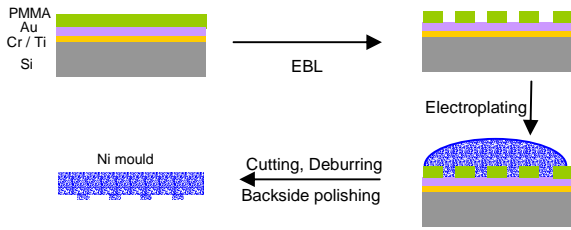


Fig. 1. Process flow chart for Ni mould fabrication

First, Au/Cr or Au/Ti double layers with the thickness of 30nm and 10nm respectively are deposited on the Si substrate by sputter deposition or e-beam evaporation. The Au layer will act as the electroplating seed and the Cr layer can enhance the adhesion to the Si substrate by forming silicide.

2-D photonic crystal patterns are designed for the enhancement of light extraction in light-emitting diodes. The basic idea is to put the photonic crystals around the electrode, which can Bragg-scatter the photons traveling sideways so that more light can be directed upwards and thereby get extracted. The design for a single device is illustrated in Fig. 2a with the photonic crystal region plotted in red. Alignment marks are employed in correspondence with those on the electrode masks, as is shown in Fig. 2b and 2c. Eight sets of photonic crystal patterns with square and hexagonal lattices and a variety of lattice constants are incorporated on one piece of mould, with each set including nice devices for characterization purposes.

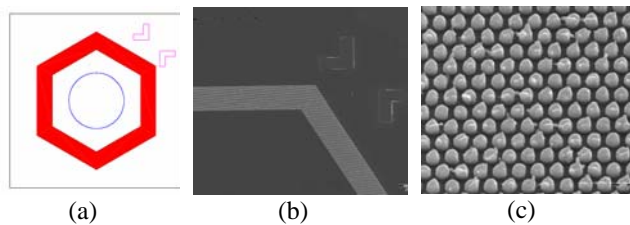


Fig. 2. Designed and real 2-D photonic crystal structures for light-emitting diodes; (a) Schematic design for a single device; (b), (c) SEM picture for patterns on the mould

The nanometer-size patterns are defined in PMMA by EBL. PMMA 950K A5 (molecular weight of 950kg/mol, 5% dissolved in anisole) is used as the resist for EBL. The PMMA solution is spin-coated on the substrate with a velocity of 2000rpm for 45 seconds, followed by prebaking for two hours. The target resist thickness is around 300~350nm. The nanometer patterns are written by JC Nability Nanometer Pattern Generation System (NPGS) v9.0 at 30keV energy on the PMMA layer. The development is carried out in a 1:3 solution of MIBK: IPA, IPA and DI water for 70s, 20s and 20s respectively. Oxygen plasma is then used to remove the resist residue. Normally the resist thickness is around 250~300nm at 20sccm O₂ flow rate, 25W power and 1min plasma time.

The Ni electroplating is then performed in the M-O-T μ Galv system. The samples are fixed to a four-inch Ni plate with electroplating tapes and soaked in the Ni electrolyte with PH=3.7 and T=50°C. The fine structures are first electroplated from the Au layer through the holes in the PMMA, followed by overplating across the whole sample since the electroplating process is isotropic.

The Ni mould will release from the seed layers and substrate after being cut to a rectangle shape with 10~15mm along each side, with the pattern area of roughly 6mm \times 4mm. The deburring and backside polishing is then performed and the mould is soaked in acetone to remove the PMMA residue before use.

B. Nanoimprinting

The nanoimprinting process is carried out in Jenoptik Mikrotechnik HEX 01 system. The same type of polymer as EBL, PMMA 950k is used for nanoimprinting. The PMMA solution is spin-coated with a speed as high as 2500rpm to achieve the resist thickness of about 250nm, which is slightly bigger than the pillar height on the mould. The residue PMMA layer is required to protect the mould from touching the substrate, but the layer thickness should be kept small enough for the benefit of further pattern transfer via dry etching.

Since the glass transition temperature for PMMA is around 110~120°C, the nanoimprinting is performed at the temperature from 120°C to 180 °C and the mechanical force applied ranges from 500N to as high as 3000N for a square-shape mould with 10~15mm along each side.

Normally there will be some PMMA sticking to the mould after a few runs, and the mould will then be cleaned by O₂ plasma, washed by chloroform and rinsed by acetone, IPA and DI water. Surface treatment will be applied if necessary.

III. RESULTS AND DISCUSSION

The fine structures and curvature of the Ni mould fabricated were characterized and it is found that the quality

of the fine structures are influenced by the controlling parameters of EBL and electroplating recipe, while the curvature of the mould are mainly determined by the current density of electroplating.

A. Ni mould fabrication

1) Electron-beam lithography

The controlling parameters for e-beam writing include beam current, line spacing, resist thickness and dose. Although higher beam current leads to shorter writing time in favor of patterning of bigger areas, the shape of designed patterns will somehow be distorted when the beam current goes too high and a trade-off is thus required. The results of e-beam writing under different current were investigated and some were shown in Fig. 3. It can be seen that the circular shape was distorted at a beam current as high as 600pA either under circular (Fig. 3a) or line-by-line writing mode (Fig. 3b), whereas both writing modes generated good circular shape at a beam current as low as 38.5pA as shown in Fig. 3c and 3d. Finally the beam current of about 100pA is employed for the good quality of the fine structures as well as acceptable writing time. The corresponding line spacing is optimized as 20~30nm.

The dose plays an important role in determining the dimension of the holes. Considering that the dimensions may change during the processes followed such as electroplating, nanoimprinting and ICP etching, a variety of dose from $120\mu\text{C}/\text{cm}^2$ to $200\mu\text{C}/\text{cm}^2$ was originally chosen and the desired dose can be obtained by measuring the final dimensions of the holes after the whole process.

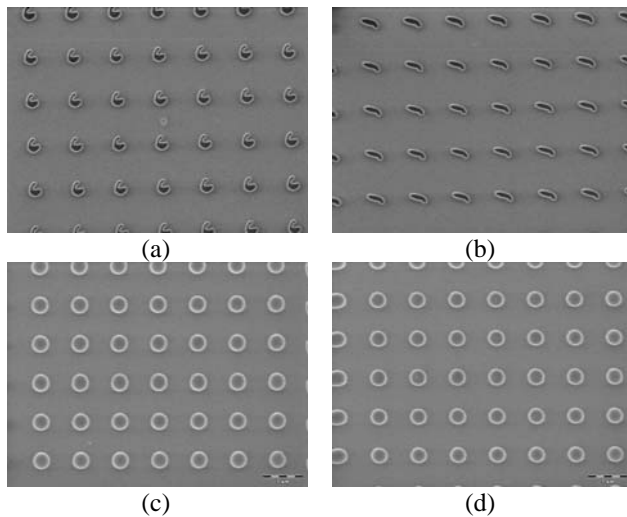


Fig. 3. SEM pictures of square arrayed holes in PMMA after EBL, dose = $240\mu\text{C}/\text{cm}^2$, line spacing = 22nm; beam current=600pA for (a) and (b), and 38.5pA for (c) and (d); (a), (c) written in a circular way while (b), (d) written line-by-line

2) Electroplating

Another key process for Ni mould fabrication is electroplating. The electroplating recipe, i.e. the current versus time curve, has to be carefully selected.

The flatness of the Ni mould is highly desired for nanoimprinting, as will be further explained in the next part. Any stress developed during electroplating will cause bending of the mould, thus degrading the results of nanoimprinting. The stress-free current density in our system proves to be $0.4\text{mA}/\text{mm}^2$, below which tensile stress is developed while above which compressive stress is developed. Fig. 4 shows the surface profiles of the patterns on the Ni mould electroplated at different current density measured by WYKO-NT 1100 optical profiler. It is evident that much better surface flatness was achieved at the current density of $0.4\text{mA}/\text{mm}^2$. However, slight curvature was still observed across the whole pattern region of more than 20mm^2 .

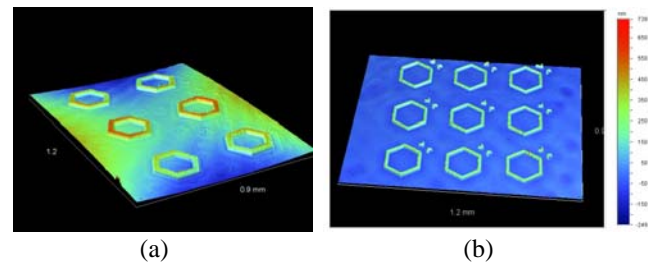


Fig. 4. Surface profiles of Ni moulds electroplated current density $\sim 0.45\text{mA}/\text{mm}^2$ and not well controlled for (a), while kept at $0.4\text{mA}/\text{mm}^2$ for (b)

Fig. 5 shows the SEM pictures of the Ni mould electroplated at $0.4\text{mA}/\text{mm}^2$ for 15 hours. The total thickness after electroplating was estimated to be $720\mu\text{m}$ and the mould more than $500\mu\text{m}$ thick was obtained after polishing, which turned out to be enough for the handling of nanoimprinting. The height of the mould is around $200\sim 250\text{nm}$, which is slightly smaller than the resist thickness after EBL and plasma cleaning.

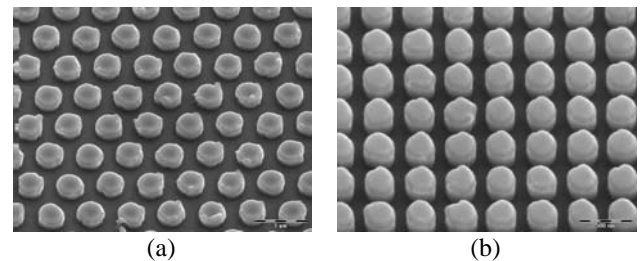


Fig. 5. SEM pictures of photonic crystal patterns with different lattice constants from the same Ni mould; current density for electroplating is $0.4\text{mA}/\text{mm}^2$

The fine pillar structures in Fig. 5 seemed not well controlled probably due to the electroplating current as high as 0.4 mA/mm^2 . Hence new recipes were devised and smaller current was employed throughout the electroplating of the fine structures, while higher current was used for overplating. Fig. 6 shows a typical current-time curve during the electroplating using this method.

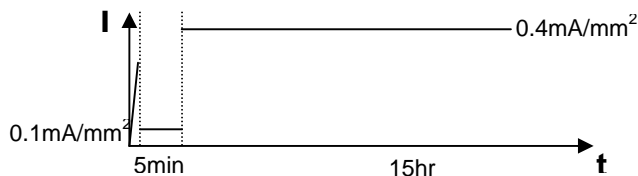


Fig. 6. Current density Vs time curve for Ni electroplating

The result of surface flatness is acceptable as shown in Fig. 7a. And some improvement was also obtained for the fine pillar structures, as is shown in Fig. 7b. Nevertheless, there is still room for improvement by further fine-tuning the recipe.

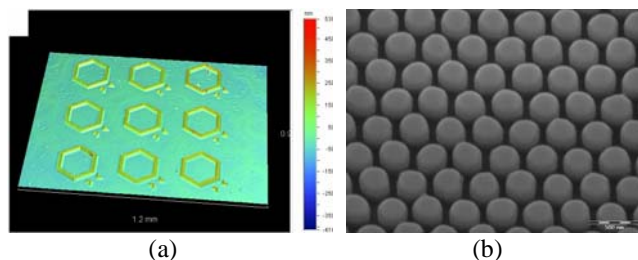


Fig. 7. Pictures of Ni mould electroplated under the condition shown in Fig. 6

(a) surface profile; (b) SEM of photonic crystal patterns

B. Nanoimprinting

The main parameters for nanoimprinting include the imprinting temperature, pressure and time. And the separation temperature also plays a role. A lot of experiments under different conditions were dedicated to the nanoimprinting on the PMMA/Si samples using the Ni moulds we fabricated. The PMMA thickness was kept around 250nm, which is slightly bigger than the pattern height on the mould. Such small pattern height as 200~250nm on the mould makes the nanoimprinting process very sensitive to the flatness of the mould as well as the substrate. Big particles on the substrate or prominent curvature of the mould would prevent the patterns being imprinted on the thin PMMA layer. The baking time and temperature of PMMA was varied but no distinguished difference was observed.

It was found that PMMA tended to peel off from the substrate and stick to the pattern region on the Ni mould

during imprinting and only some parts of the patterns were transferred to the substrate, as is shown in the OM pictures of Fig. 8a. This sticking issue may be probably caused by the defects on the mould surface which increase the surface energy. Surface treatment using silane was therefore tried out for the Ni moulds to reduce the surface energy: the moulds are soaked in the solution made by 0.3g silane and 50mL heptane for 10min and rinsed by heptane and acetone. The sticking problem was alleviated as is shown in Fig. 8b. More improvement is expected if the defects on the mould surface are reduced.

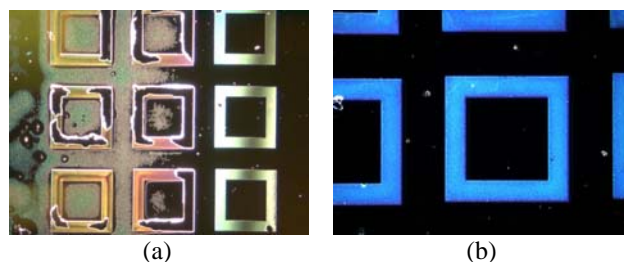


Fig. 8. OM pictures of PMMA/Si nanoimprinted by Ni mould; the mould used for (b) is surface treated by silane, while no surface treatment is applied for the mould in (a)

When inspected by SEM, the fine structures of nanometer-size holes in PMMA after nanoimprinting seemed to be slanted, as is shown in Fig. 9. This is probably owing to the curvature across the whole mould. The pillars on the mould were not vertical to the substrate surface when touching and pressing the substrate, so there would be shear stress involved during the imprinting process and tilted holes would be formed. The problem could be solved either by reducing the curvature of the mould or by applying the force more uniformly.

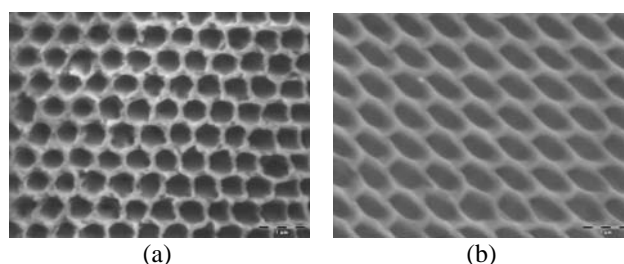


Fig. 9. SEM pictures of PMMA/Si nanoimprinted by Ni mould at 160°C , $F=1000\text{N}$ for 5min, separated at 70°C

IV. CONCLUSION

In summary, Ni moulds with the designed photonic crystal patterns covering the area of $6\text{mm} \times 4\text{mm}$ were fabricated by EBL and electroplating. Little residue stress and small curvature was achieved by controlling the electroplating recipe. 200~250nm high pillars were produced with the diameters ranging from 180nm to 400nm. Pulse

electroplating is under development and moulds with improved quality are expected under alternative currents. Annealing of the mould to reduce the residue stress is also under consideration.

NIL was realized for PMMA/Si samples using the Ni moulds we fabricated. Although some parts of the imprinted patterns got transferred, the problem of PMMA sticking to the mould during nanoimprinting process was not well controlled so far. Silane surface treatment has showed some effects, and more experiments will also be carried out using other nanoimprinting systems utilizing high-pressure gas to apply the force more uniformly.

The fabrication of Si moulds is also under progress, for which standard surface treatment recipes are well developed and many applications for NIL have been demonstrated. Lift-off process has proved successful and the Reactive Ion Etching (RIE) of Si with chromium (Cr) mask is being performed.

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REFERENCES

- [1] E. Yoblonovitch, *Phys. Rev. Lett.* 58, 2059 (1987).
- [2] H. Y. Ryu, J. K. Hwang, D. S. Song, I. Y. Han, Y. H. Lee, and D. H. Jang, *Appl. Phys. Lett.* 78, 1174 (2001).
- [3] H. Y. Ryu, Y. H. Lee, R. L. Sellin and D. Bimberg, *Appl. Phys. Lett.* 79, 3573 (2001).
- [4] A. Erchak, D. J. Ripin, S. H. Fan, P. Rakich, J. D. Joannopoulos, E. P. Ippen, G. S. Petrich, and L. A. Kolodziejski, *Appl. Phys. Lett.* 78, 563 (2001).
- [5] Han-Youl Ryu, Jeong-Ki Hwang, Yong-Jae Lee, and Yong-Hee Lee, *IEEE J. Sel. Top. Quantum Electron.* 8, 238 (2002).
- [6] H. Ichikawa and T. Baba, *Appl. Phys. Lett.* 84, 457 (2004).
- [7] T. N. Oder, J. Shakya, J. Y. Lin, and H. X. Jiang, *Appl. Phys. Lett.* 83, 1231 (2003).
- [8] T. N. Oder, K. H. Kim, J. Y. Lin, and H. X. Jiang, *Appl. Phys. Lett.* 84, 466 (2004).
- [9] J. Shakya, K. H. Kim, J. Y. Lin, and H. X. Jiang, *Appl. Phys. Lett.* 85, 142 (2004).
- [10] J. J. Wierer, M. R. Krames, J. E. Epler, N. F. Gardner, M. G. Craford, J. R. Wendt, J. A. Simmons and M. M. Sigalas, *Appl. Phys. Lett.* 84, 3885 (2004).
- [11] S. Y. Chou, P. R. Krauss, W. zang, L. J. Guo and L. Zhang, *J. Vac. Sci. Technol. B* 15, 2879 (1997).
- [12] J. Seekamp, S. Zankovych, A.H. Helfer, P. Maury, C. M. Sotomayor Torres, G. bottger, C. Liguda, M. Eich, B. Heidari, L. Montelius and J. Ahopelto, *Nanotechnology* 13, 581 (2002).
- [13] D. Pisignano, L. Persano, G. Gigli, P. Visconti, T. Stomeo, M. De Vittorio, G. Barbarella, L. Favaretto and R. Cingolani, *Nanotechnology* 15, 766 (2004).
- [14] M. Belotti, M. Galli, D. Bajoni, L.C. Andreani, G. Guizzetti, D. Decanini and Y. Chen, *Microelectron. Eng.* 73, 405 (2004).