

Nanopatterning of silica sol-gel thin films by soft thermal nanoimprint lithography

C. Peroz^{a,*}, C. Heitz^a, V. Goletto^b, M. Foresti^a, L. Billot^c, E. Barthel^a, E. Sondergard^a

^aLaboratoire mixte CNRS / Saint-Gobain, BP 135, 93303 Aubervilliers France

*christophe.peroz@saint-gobain.com

^bSaint-Gobain Recherche, BP 135, 93303 Aubervilliers France

^cLaboratoire de Photonique et de Nanostructures, CNRS 91460 Marcoussis, France

ABSTRACT

We report on results on a simple and direct route to nanopattern inorganic-organic sol gel films by soft thermal nanoimprint over large areas. Silica nanostructures are obtained with a good conservation of initial features and sizes down to 150nm.

Keywords: nanoimprint, glass, sol-gel

1 INTRODUCTION

Structuration of surfaces at the sub-micrometer scale over large areas is a challenge for the emergence of a wide variety of applications from physics to biology. The next generations of glass or polymer substrates will integrate nanopatterns such as photonics structures for future displays or windows. Conventional methods developed by semiconductor industry such as UV extreme lithography or electron/ion beam lithography are time consuming and will be not suitable for mass production over large areas. Unconventionnal nanofabrication methods are required to develop manufacturing processes at low cost and high throughput. One of the most attractive alternatives is the thermal nanoimprint lithography [1] (NIL) to replicate nanostructures into various kinds of materials (thermoplastics or UV reticulated films) at potential low cost and over large area. Standard thermal NIL technology is based on the deformation of a thermoplastic materials (resist) in contact with a rigid stamp (silicon or nickel) containing nanostructures. Patterning resolution by thermal NIL has been demonstrated so far as 5 nm into polymer resist [2]. Whereas molding of polymer materials is largely studied and spreads up in academic and industrial laboratories, few works are reported on imprinting of sol-gel films.

The sol-gel chemistry is very versatile and structuring sol-gel materials will allow a fine tuning of chemistry, electromagnetic, optical and mechanical properties. Direct

nanoimprinting of silica sol-gel films involving only inorganic reaction (no-hybrimers) is a convenient method but actual works require complex (high pressures and temperatures, plasma treatment) and/or long time procedures [3-7]. In this paper, we demonstrate a simple route to fabricate inorganic-organic silica nanopatterns by soft thermal nanoimprint over large areas.

2 EXPERIMENTAL DETAILS

Our process consists in replicating nanopatterns from a flexible PDMS (Poly-dimethylsiloxane) stamp into a liquid sol-gel resist. The principle of the soft thermal nanoimprint is schematically shown in Figure 1.

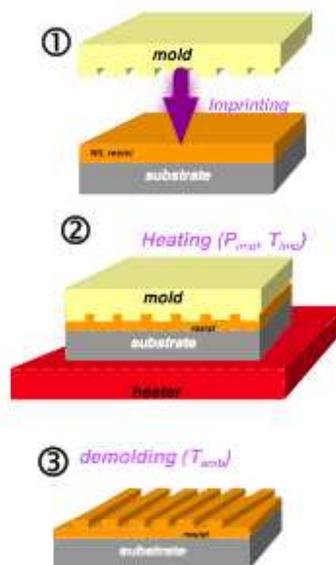


Figure 1: Schematic representation of the soft thermal NIL process

The soft PDMS stamps[8] are simply replicated by casting of liquid PDMS (Poly-dimethylsiloxane) on nanostructured nickel or silicon of several cm^2 area. The silicon master molds in substrates are defined in a resist layer by electron beam lithography and transferred into substrate by reactive ion etching. Nickel shims are purchased from 3DAG[9] company and are replicated by nickel electroless plating from photoresist patterns. The silicon surface of the master molds is then treated with trimethylchlorosilane (TMCS) by vapour deposition which forms a self-assembling monolayer for as release agent. Whereas nickel molds are treated with Zonyl FSP (Du Pont de Nemours) solution for anti-adhesion. The soft PDMS stamps have the advantage of being compliant with surface which minimizes the pressure needed to obtain contact with the substrate. The hybrid silica thin films are obtained from a MTEOS (Methyltriethoxysilane) sol prepared in acidic conditions and mixed during several hours. MTEOS resist is first deposited by spin-coating on glass or silicon substrates. Thicknesses of MTEOS films are included between 400 and 800nm. The imprinting step is then performed at low pressures and temperature is increased up to a stable imprint temperature. This stage temperature is kept of few minutes. After a cooling ramp-down to ambient temperature, the stamp and substrate are separated. No clean room access and photolithographic facilities are required for NIL technology.

3 RESULTS AND DISCUSSION

Different nanopattern sizes and geometry have been successfully replicated in MTEOS thin films over large area. As example, Figures 2 displays Scanning Electron Microscope (SEM) images of imprinted gratings with 340 nm and 150nm linewidth for pitch of 1 μm (Figure 2a) and 600 nm (Figure 2b), respectively. Actual resolution is limited by PDMS resolution and has to be improved in using adequate hard PDMS. The features are imprinted with a good homogeneity over several square centimeters and are in good accordance with initial sizes from stamps. Figure 3 shows diffracted light from imprinted gratings on glass substrate. The actual patterning area limitation is fixed at several cm^2 due to our imprinting facility. Important parameter for NIL technology is conformity between initial and imprinted features. Atomic Force Microscopy (AFM) is used to compare patterns sizes. Example of AFM profiles for imprinted nanostructures are reported in Figure 4. The depth of imprinted trenches is found to be about 150nm which is close to initial pattern depth for master molds (about 160nm). We remark also that nanostructures are crack-free and their refractive index is close to glass value.

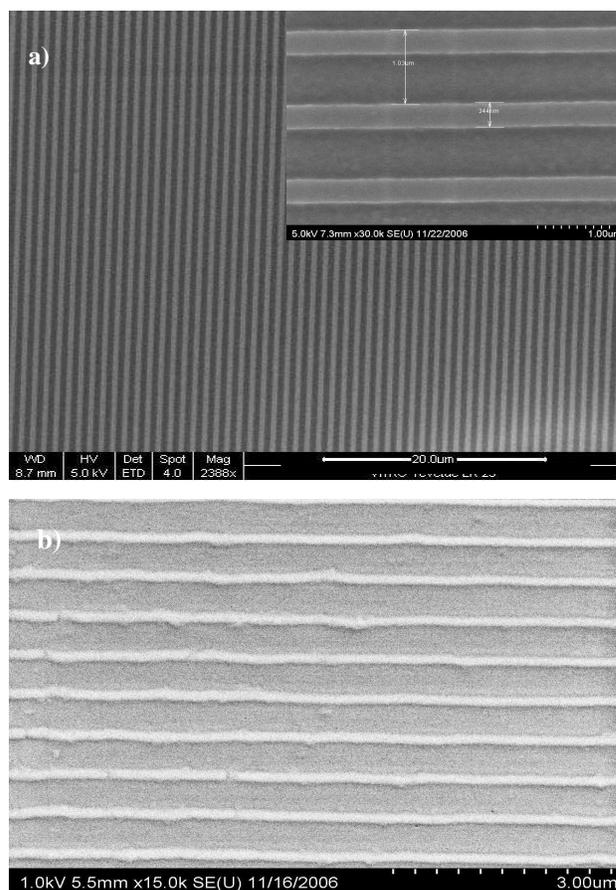


Figure 2: SEM pictures of lines arrays imprinted in MTEOS films with linewidth of 340nm (Figure a) and 150nm (Figure b) for pitch of 1 μm and 600nm

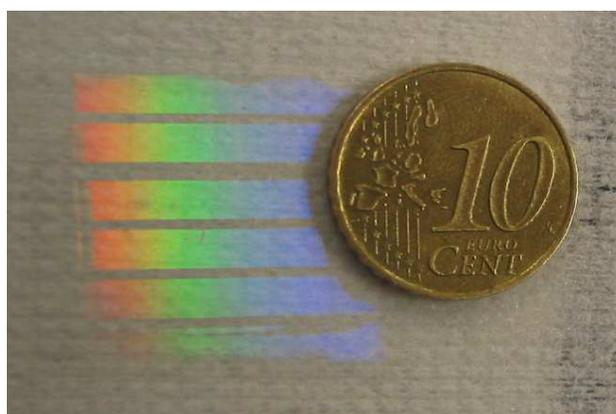


Figure 3: Optical picture of Bragg gratings ($w=340$ nm, $p = 1\mu\text{m}$) imprinted on glass substrate over large area.

4 CONCLUSION

We have reported on the fabrication of silica organic-inorganic nanostructures by a soft thermal nanoimprint. Patterning resolution of about 150 nm has been demonstrated. This potential cheap and high throughput route is very attractive for future optical applications on glass substrates. Future works will focus on high aspect ratio patterning and optical applications.

5 ACKNOWLEDGMENTS

We are grateful to S. Vassant for technical assistance.

REFERENCES

- [1] Chou, S.Y.; Krauss, P.R.; Renstrom, P.J. *Science* 272, 85, 1996
- [2] M.D. Austin, H. Ge, W. Wu, M. Li, Z. Yu, D.Wasserman, S.A. Lyon, S.Y. Chou, *Appl. Phys. Lett.* 84(26), 5299, 2004
- [3] R. Brendel, A. Gier, M. Menning, H. Schmidt, J.H. Werner, *Jnl. of Non-Crystal. Solids* 218, 391, 1997
- [4] C. Marzolin, S. P. Smith, M. Prentiss, G.M. Whitesides, *Adv. Mater.* 10(8), 571, 1998
- [5] M. Li, H. Tan, L. Chen, J. Wang, S.Y. Chou, *Jnl. Vac. Sci. Technol. B* 21(2), 660, 2003
- [6] C. Harnagea, M. Alexe, J. Schilling, J. Choi, R.B. Wehrspohn, D. Hesse, U. Gosele, *Appl. Phys. Lett.* 83(9), 1827, 2003
- [7] M. Okinaka, K. Tsukagoshi, Y. Aoyagi, *Jnl. Vac. Sci. Technol. B* 24(3), 1402, 2006
- [8] J. Shi, C. Peroz, D. Peyrade, J. Salari, M. Belotti, W.H. Huang, Y. Chen, *Micro. Elect. Eng.* 83, 1664, 2006
- [9] www.3dag.ch

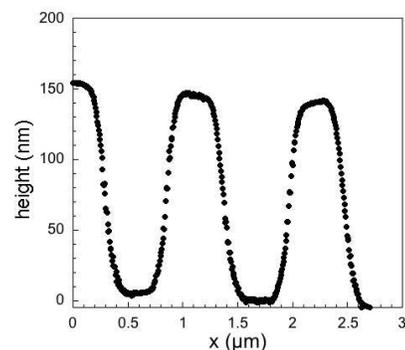
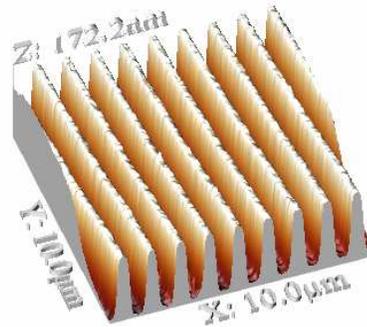


Figure 4: AFM image and profile of MTEOS nanostructures.