

Large area direct nanoimprinting of SiO₂-TiO₂ gel gratings for optical applications

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We demonstrated an economical way of fabricating gel-film-based devices by combining nanoimprint lithography (NIL) and a sol-gel technique. A novel imprinting procedure, new mold surface passivation, and an effective surfactant added to sol were developed. Gratings with 300 nm pitch and 80 nm linewidth and waveguide gratings with varying periods were imprinted in a single step and with excellent uniformity into the gel films coated on a quarter of 4 in. wafers, respectively. Surface roughness measurements of waveguide gratings by atomic force microscope showed smooth profiles with root mean square roughness less than 6 nm. NIL is an excellent patterning technology for gel-film-based optical devices. © 2003 American Vacuum Society.
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I. INTRODUCTION

Sol-gel techniques have been known as an economical and quick way to obtain artificial ceramics with engineered properties. Their low-temperature characteristics and good film quality have attracted much interest. Silica films, prepared by sol-gel technique, possess low optical loss,^{1,2} and adjustable refractive index. Sol-gel derived silica films functioned as antireflective coatings,³ waveguides,^{1,4-10} power splitters,^{10,11} optical filters,¹² distributed Bragg reflector,² resonator,¹³ diffraction gratings,^{14,15} and fiber-optic gas sensors.¹⁶ Also reported were a dye-doped sol-gel silica laser^{4,17-20} and erbium-doped sol-gel planar waveguide²¹ for optical amplifiers. Gel-film-based devices are, therefore, very promising for all-optical telecommunications.

Patterning gel-film-based optical devices usually requires at least one lithographic step and one etching step. As a comparison, direct patterning of gel films shows great advantages for cost-effective mass productions. Many research efforts²²⁻²⁶ have been directed toward this direction. However, direct patterning of gel films over a large area and the surface smoothness of patterned waveguide devices have not been investigated yet, although they are significant for sub-wavelength optical elements and performance of optical devices. In this article, we report direct nanoimprinting²⁷ of SiO₂-TiO₂ gratings with 300 nm pitch and 80 nm linewidth and SiO₂-TiO₂ waveguide gratings with varying periods. Excellent uniformity and smooth pattern profiles were obtained over a quarter of 4 in. wafers.

II. FABRICATION DETAILS

A. Mold fabrication

The two molds used in our experiments are both a quarter of a 4 in. wafer in size. Gratings with 300 nm pitch were

patterned on the first mold by interference lithography,^{28,29} and waveguide gratings with varying periods (4 μm, 6 μm, and 10 μm) were patterned on the second mold by contact optical lithography. After exposure, development, electron-beam evaporation of chromium (Cr), and lift off in warm acetone, resist gratings on both molds were transferred to chromium. With chromium serving as an etch mask, metal gratings were transferred to the underlying oxide by reactive ion etching with CHF₃/O₂ gas chemistry. The chromium was then stripped off in chromium etchant (CR-7), and both molds were passivated by 4 nm thick fluoroalkylsilane. The protrusions on the molds are 210 nm high.

B. Preparation of solution

First, tetraethoxysilane (TEOS) was mixed with 2-propanol to a molar ratio of 1:3 and stirred at 60 °C for 15 min. Then, a catalyst, 0.15 M hydrochloric acid, was added to the mixture to make TEOS:H₂O with molar ratio 1:2. Second, a mixture of titanium tetrabutoxide and 2,4-pentanedione in a molar ratio of 1:2 was stirred at room temperature for 20 min. The titanium tetrabutoxide solution was then mixed with the TEOS solution. By varying the molar ratio of TEOS and titanium tetrabutoxide, the refractive index of the derived film varies between 1.46 (pure silica) and 2.20 (pure titanium oxide). The solution (sol) contains 0.1 mol TEOS and 0.15 mol titanium tetrabutoxide. The sol was left to react for four days, and then diluted in 2-propanol to a volume ratio of 1:1. For successful direct imprinting over a large area, we found it essential to modify the sol²⁵ by adding a small amount of perfluoroalkyl surfactant.

C. Imprint wet gel film

Prior to spin coating of the sol, (100) silicon substrates were soaked in trichloroethylene for 5 min, rinsed by acetone, methanol, 2-propanol, and blown to dry by nitrogen. The silicon substrates were then baked at 200 °C on a hot-

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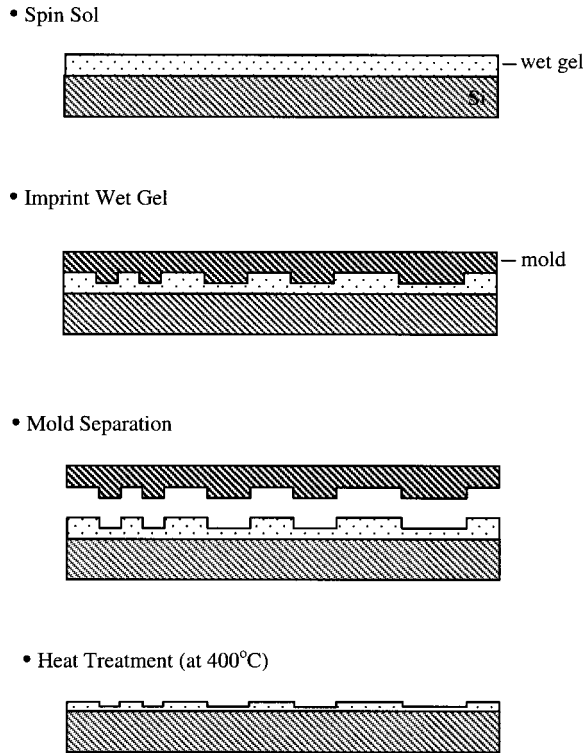


FIG. 1. Schematic of patterning of $\text{SiO}_2\text{-TiO}_2$ gel film using nanoimprint lithography: (1) Spin sol onto a silicon wafer; (2) ramp up temperature after gel film is patterned by a mold; (3) separate the mold from the patterned gel film; and (4) transform the patterned gel to ceramic by heat treatment.

plate in atmosphere for 10 min to make their surfaces hydrophilic. Sol was spun at 3000 rpm for 30 s, and about 635 nm thick wet gel film was left on silicon wafers due to solvent evaporation during spinning. Imprints were immediately carried out, using the two grating molds, respectively. The process of patterning $\text{SiO}_2\text{-TiO}_2$ gel by nanoimprint lithography (NIL) is schematically depicted in Fig. 1. With an applied pressure of 645 psi, the mold and patterned wet gel were heated up from 17 °C (room temperature) to 200 °C at 9 °C per minute. During the ramp-up procedure, the temperature was kept at 100 °C, 150 °C, and 200 °C for 7 min, respectively. Pressure was then released, and the mold was separated from the imprinted wafers. The patterned gel was further heat treated on a hotplate at 400 °C in atmosphere for 15 min, reaching the end point of the quick-shrinkage phase.⁷

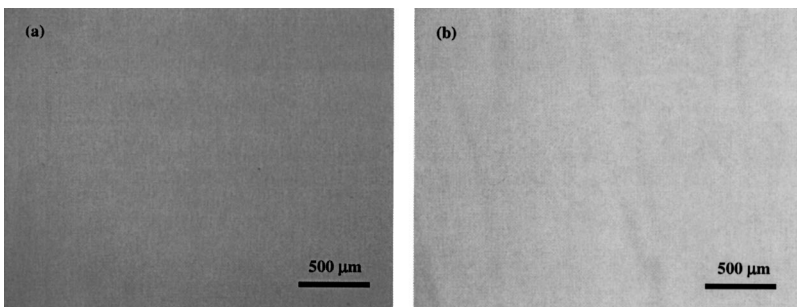
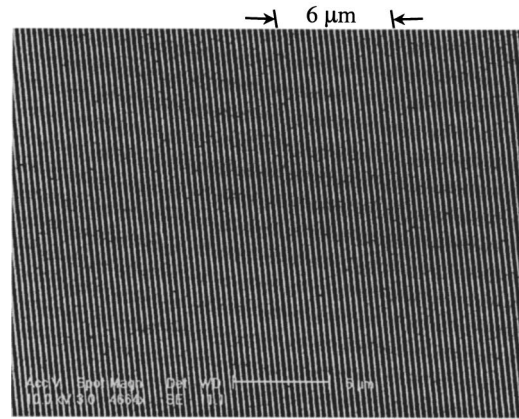
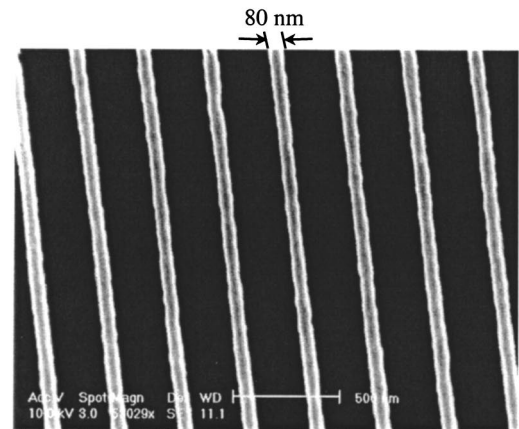


FIG. 2. Optical pictures of the planar $\text{SiO}_2\text{-TiO}_2$ gel film on a silicon substrate (a) before and (b) after heat treatment. The film thickness shrank from 635 to 247 nm. No cracking was observed over a quarter of a 4 in. wafer.



(a)



(b)

FIG. 3. (a) Directly imprinted 300 nm pitch and 70 nm deep $\text{SiO}_2\text{-TiO}_2$ gratings (after heat treatment). (b) A detailed view of (a) under high magnification. The average linewidth is 80 nm.

III. RESULTS AND DISCUSSION

For a planar gel film, the refractive index (at 633.2 nm wavelength) increased from 1.50 to 1.71 after heat treatments, and the thickness decreased from 635 to 247 nm, resulting in a 61% shrinkage in the film thickness. Figure 2 shows optical pictures of the planar gel film spin coated on (100) silicon wafer [Fig. 2(a)] before and [Fig. 2(b)] after heat treatments, respectively. No cracking of the film was observed over a quarter of a 4 in. wafer.

Excellent uniformity was obtained in gel patterning over a

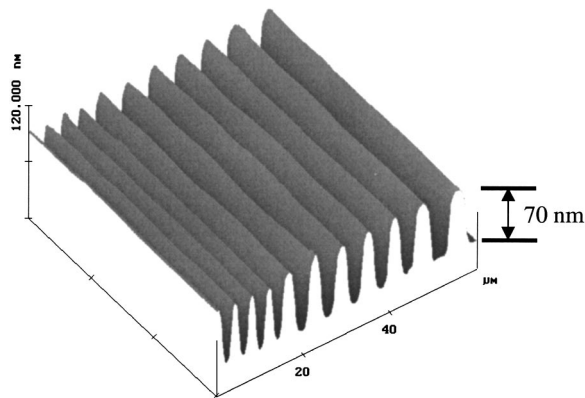


FIG. 4. Directly imprinted 70 nm deep SiO₂-TiO₂ waveguide gratings (after heat treatment) were inspected by AFM. Root mean square of less than 6 nm was obtained in roughness measurements. From the left- to right-hand side, the grating period varies from 4 to 10 μm .

quarter of 4 in. wafers. Figure 3 shows scanning electron micrographs of SiO₂-TiO₂ gratings with 300 nm pitch and 80 nm linewidth. The depth of the trenches is about 70 nm. The minor variations in linewidth come from the mold made by interference lithography. It is the size of the mold that limits the patterning area, and we do not see any difficulty in scaling up the patterning of gel film to 4 in. wafer level.

Directly imprinted SiO₂-TiO₂ patterns also have smooth profiles. Contact mode atomic force microscope (AFM) was used to inspect 70 nm deep SiO₂-TiO₂ waveguide gratings, as shown in Fig. 4. A root mean square (rms) of less than 6 nm was obtained in the roughness measurements around grating peak areas. The obtained smoothness will not cause unacceptable scattering losses in gel-film-based waveguide devices. The smoothness and hydrophilic surface property of the patterned silica film make it potentially useful for providing spatial confinement for micro- and nanofluidic^{30,31} applications.

The sinusoidal profile of waveguide gratings, as seen in Fig. 4, indicates that wet gel does not flow as well as thermoplastics [such as poly(methylmethacrylate)] used in conventional nanoimprint lithography. Under our imprint conditions, however, the gel was able to flow to such an extent that gratings with varying pattern densities can be successfully imprinted simultaneously.

The planar or patterned gel film did not crack during heat treatment, although ripples were visible only within a long range. When the strain energy release rate of the sol-gel film reaches its critical value,^{32,33} film cracking occurs. Although the critical thickness of gel film depends on its processing and composition, a reasonable order of magnitude estimate of the critical thickness is 1.0 μm ,^{34,35} which is much thicker than the films prepared in our experiment.

We found a 61% shrinkage in the direction perpendicular to wafer surface. There was no obvious shrinkage observed in the direction parallel to the wafer surface. Heat treatment resulted in the complete evaporation of solvents, and hence collapses of the cross-linked polymer network. Increasing the feature height on the molds can compensate for the

shrinkage of gel films in the vertical direction. Meanwhile, the addition of organics into an inorganic matrix^{36,37} reduces shrinkage and increases its cracking resistance.

Three factors are crucial to large area single-step duplications of micro- and nanostructures in wet gel. First, our mold surfaces were uniformly passivated with nanometers thick surfactant, which greatly reduces their surface energy, and thus preventing monomers (such as TEOS) in the gel from bonding to the mold surfaces. Second, the surfactant added to the sol further helps to release our molds from the patterned gel films, and simultaneously delays aging of the wet gel. Third, heat-accelerated gelation during imprint keeps duplicated structures from being distorted when we separated the molds from the imprinted wafers.

IV. CONCLUSION

We directly imprinted gratings with 300 nm pitch and 80 nm linewidth and waveguide gratings with varying periods in SiO₂-TiO₂ gel films with excellent uniformity and smoothness over a quarter of 4 in. wafers. A new patterning procedure along with good mold surface passivation and the surfactant added to sol was developed. NIL is an excellent patterning technology for gel-film-based optical devices.

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- ¹P. Coudray, J. Chisham, A. Malek-Tabrizi, C. -Y. Li, M. Andrews, N. Peyghambarian, and S. Najafi, *Opt. Commun.* **128**, 19 (1996).
- ²M. A. Fardad and M. Fallahi, *Opt. Commun.* **163**, 33 (1999).
- ³C. J. Brinker and M. Harrington, *Sol. Energy Mater.* **5**, 159 (1981).
- ⁴P. Yang, G. Wirsberger, H. C. Huang, S. R. Cordero, M. D. McGehee, B. Scott, T. Deng, G. M. Whitesides, B. F. Chmelka, S. K. Buratto, and G. D. Stucky, *Science* **287**, 465 (2000).
- ⁵E. A. Mendoza, D. J. Ferrell, S. J. Syracuse, A. N. Khalil, and R. A. Lieberman, *Proc. SPIE* **2288**, 580 (1994).
- ⁶L. Weisenbach, T. Davis, B. Zelinski, R. Roncone, and L. Weller-Brophy, *Mater. Res. Soc. Symp. Proc.* **180**, 377 (1990).
- ⁷P. Coudray, J. Chisham, M. Andrews, and S. Najafi, *Opt. Eng.* **36**, 1234 (1997).
- ⁸S. Toyoda, N. Ooba, M. Hikita, T. Kurihara, and S. Imamura, *Thin Solid Films* **270**, 311 (2000).
- ⁹P. Innocenzi, A. Martucci, M. Guglielmi, L. Armelao, S. Pelli, G. C. Righini, and G. C. Battaglin, *J. Non-Cryst. Solids* **259**, 182 (1999).
- ¹⁰A. Fardad, M. Andrews, G. Milova, A. Malek-Tabrizi, and I. Najafi, *Appl. Opt.* **37**, 2429 (1998).
- ¹¹M. Fardad and M. Fallahi, *IEEE Photonics Technol. Lett.* **11**, 697 (1999).
- ¹²J. Keddlle and E. Giannelis, *Mater. Res. Soc. Symp. Proc.* **180**, 383 (1990).
- ¹³K. M. Chen, A. W. Sparks, H. Luan, D. R. Lim, K. Wada, and L. C. Kimerling, *Appl. Phys. Lett.* **75**, 3805 (1999).
- ¹⁴D. Blanc and S. Pelissier, *Thin Solid Films* **384**, 251 (2001).
- ¹⁵E. A. Mendoza, D. J. Ferrell, and R. A. Lieberman, *Proc. SPIE* **2288**, 621 (1994).
- ¹⁶J. T. Remillard, J. R. Jones, B. D. Poindexter, C. K. Narula, and W. H. Weber, *Appl. Opt.* **38**, 5306 (1999).
- ¹⁷A. Arena, S. Patane, G. Saitta, G. Rizzo, S. Galvagno, and G. Neri, *J. Mater. Res.* **17**, 2095 (2002).
- ¹⁸S. K. Lam, D. Lo, and K. Wong, *Appl. Opt.* **34**, 3380 (1995).
- ¹⁹D. Lo, S. K. Lam, C. Ye, and K. S. Lam, *Opt. Commun.* **156**, 316 (1998).

- ²⁰S. K. Lam, X. L. Zhu, and D. Lo, *Appl. Phys. B: Lasers Opt.* **68**, 1151 (1999).
- ²¹X. Orignac, D. Barbier, X. Du, and R. Almeida, *Appl. Phys. Lett.* **69**, 895 (1996).
- ²²W. Lukosz and K. Tiefenthaler, *Opt. Lett.* **8**, 537 (1983).
- ²³K. Heuberger and W. Luosz, *Appl. Opt.* **25**, 1499 (1986).
- ²⁴N. Tohge, A. Matsuda, T. Minami, Y. Matsuno, S. Katayama, and Y. Ikeda, *J. Non-Cryst. Solids* **100**, 501 (1988).
- ²⁵R. Roncone, L. Weller-Brophy, L. Weisenbach, and B. Zelinski, *J. Non-Cryst. Solids* **128**, 111 (1991).
- ²⁶H. Krug, N. Merl, and H. Schmidt, *J. Non-Cryst. Solids* **147**, 447 (1992).
- ²⁷S. Y. Chou, P. R. Krauss, and P. J. Renstrom, *Appl. Phys. Lett.* **67**, 3114 (1995); *Science* **272**, 85 (1996).
- ²⁸E. H. Anderson, C. M. Horwitz, and H. I. Smith, *Appl. Phys. Lett.* **43**, 874 (1983).
- ²⁹W. Wu, B. Cui, X. Sun, W. Zhang, L. Zhuang, L. Kong, and S. Y. Chou, *J. Vac. Sci. Technol. B* **16**, 3825 (1998).
- ³⁰J. Han and H. G. Craighead, *J. Vac. Sci. Technol. B* **17**, 2142 (1999).
- ³¹H. Cao, Z. Yu, J. Wang, J. O. Tegenfeldt, R. H. Austin, E. Chen, W. Wu, and S. Y. Chou, *Appl. Phys. Lett.* **81**, 174 (2002).
- ³²A. Atkinson and R. M. Guppy, *J. Mater. Sci.* **26**, 3869 (1991).
- ³³L. A. Chow, Y. H. Xu, B. Dunn, K. N. Tu, and C. Chiang, *Appl. Phys. Lett.* **73**, 2944 (1998).
- ³⁴C. J. Brinker and G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing* (Harcourt, Brace, and Jovanovich, Boston, 1990), p. 507.
- ³⁵R. K. Roeder and E. B. Slamovich, *J. Mater. Res.* **14**, 2364 (1999).
- ³⁶Y. Wei, D. L. Jin, C. C. Yang, and C. Wei, *J. Sol-Gel Sci. Technol.* **7**, 191 (1996).
- ³⁷K. A. Vorotilov, V. A. Vasiljev, M. V. Sobolevsky, and N. I. Afanasyeva, *Thin Solid Films* **288**, 57 (1996).