Large area direct nanoimprinting of SiO$_2$–TiO$_2$ 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, and adjustable refractive index. Sol–gel derived silica films functioned as antireflective coatings, waveguides, power splitters, optical filters, distributed Bragg reflector, resonator, diffraction gratings, and fiber-optic gas sensors. Also reported were a dye-doped sol–gel silica laser and erbium-doped sol–gel planar waveguide 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 efforts 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 nanoimprinting of SiO$_2$–TiO$_2$ gratings with 300 nm pitch and 80 nm linewidth and SiO$_2$–TiO$_2$ 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, 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 CHF$_3$/O$_2$ gas chemistry. The chromium was then stripped off in chromium etchant (CR-7), and both molds were passivated by 4 nm thick fluoroalkysilane. 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:H$_2$O 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 sol 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-
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 SiO\(_2\)–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.\(^7\)

### 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

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**Fig. 1.** Schematic of patterning of SiO\(_2\)–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.

**Fig. 2.** Optical pictures of the planar SiO\(_2\)–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.

**Fig. 3.** (a) Directly imprinted 300 nm pitch and 70 nm deep SiO\(_2\)–TiO\(_2\) gratings (after heat treatment). (b) A detailed view of (a) under high magnification. The average linewidth is 80 nm.
quarter of 4 in. wafers. Figure 3 shows scanning electron micrographs of SiO$_2$–TiO$_2$ 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 from the imprinted wafers. Third, heat-accelerated gelation during imprint keeps distorted gel films, and simultaneously delays aging of the wet gel. First, our mold turns gel into a single-step duplications of micro- and nanostructures in wet gel. Under our imprint conditions 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.

IV. CONCLUSION

We directly imprinted gratings with 300 nm pitch and 80 nm linewidth and waveguide gratings with varying periods in SiO$_2$–TiO$_2$ 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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