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Fabrication of Refractive Index Tunable Polydimethylsiloxane Photonic Crystal for Biosensor Application

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Abstract

Photonic crystal based nanostructures are expected to play a significant role in next generation nanophotonic devices. Recent developments in two-dimensional (2D) photonic crystal based devices have created widespread interest as such planar photonic structures are compatible with conventional microelectronic and photonic devices. Various optical components such as waveguides, resonators, modulators and demultiplexers have been designed and fabricated based on 2D photonic crystal geometry. This paper presents the fabrication of refractive index tunable Polydimethylsiloxane (PDMS) polymer based photonic crystals. The advantages of using PDMS are mainly its chemical stability, bio-compatibility and the stack reduces sidewall roughness scattering. The PDMS structure with square lattice was fabricated by using silicon substrate patterned with SU8-2002 resist. The 600nm period grating of PDMS is then fabricated using Nano-imprinting. In addition, the refractive index of PDMS is modified using certain additive materials. The resulting photonic crystals are suitable for application in photonic integrated circuits and biological applications such as filters, cavities or microlaser waveguides.

Keywords: Photonic crystals; Nanoimprint lithography; PDMS; SU8 template; Variable Refractive Index; TiO2 Nanoparticles; PDMS dilution

1. Introduction

Recent and significant developments in the area of photonic crystals (PCs) have demonstrated the ability of these devices to be able to manipulate and process light in compact integratable devices. PCs have a regular array of perturbations which provides them the ability to control the propagation of light through it efficiently. This ability to control the propagation of light with particular wavelength is referred to as photonic bandgaps (PBGs) and they find their applications in wideband filters and waveguides [1-3]. Defects can be incorporated in the periodicity to achieve wave guiding properties in photonic crystals. By eliminating a row or column of holes or pillars along a particular symmetric direction we can obtain a W1 defect waveguide. There can be other various techniques applied to enhance the wave guiding properties by application of principles of total internal reflection by varying the dielectric properties of the material [3].

Periodic structures can be made by stacking micro machined semiconductor wafers or self-assembly of polymers in two-dimensions (2D) and three-dimensions (3D). Recently a branch of holographic lithographic
methods has been under review [7]. Planar waveguides or PC slabs are emerging as some of the most suitable candidates for controlling light propagation in 3D [4-6]. In this paper we report a process methodology to create submicron patterns on PDMS while addressing various issues related to its processing.

2. Materials and Methods

Primarily four issues related to PDMS polymer PC fabrication and processing is addressed in this paper. The first is the fact that fabrication of nanoscale dimension optical materials such as arrayed PCs requires a highly precise and reproducible nanolithographic technique with early turn-around times. To achieve precision in the structures and to reduce scattering losses mostly the use of electron beam lithography (EBL) has been resorted to. Though EBL provides the unique advantage of exquisite precision in nanoscale dimensions it is time-consuming direct-writing technique which is unsuitable for mass fabrications. In this paper we report the use of a direct writing method using Microtech LW 405 Laser Writer (Fig. 3) to create a master which can be used for creating subsequent diffractions which reduces process times significantly.

The second is the usability of the hugely popular polymer composite PDMS (Sylgard 184, Dow Corning Corp., Midland, MI) in the fabrication of sub-micron features [8-10]. The fundamental phenomenon is based on the principle of diffraction. The periodicity of the photonic crystal has to be congruous with the length-scale of half the wavelength of the light or electromagnetic waves. For example, for a PC filter for blue light has to have a grating in the range of 350 nm approximately and likewise for red it has to be 700 nm to target the visible spectrum. To achieve these gratings is difficult and cumbersome. PDMS is a viscoelastic fluid, meaning that at long flow times it acts like a viscous liquid and at short flow times it acts like an elastic solid. This material property is highly beneficial for many MEMS applications and also due to the inherent advantage it has of being highly chemically stable and bio-compatible, which makes is more than ideal for lab-on-chip and biomedical applications.

In the instances of using PDMS for patterning sub-micron features, it is almost incapable in conforming to the patterns created on the template. The patterns suffer from low aspect ratio and deformation as was seen in our initial experiments. In such instances, it is necessitated to dilute the PDMS to lower its viscosity and allow it to flow and conform to the template provided. Most organic solvents will diffuse into the polymer and cause it to swell to varying degrees. The swelling ratio is inversely proportional to the parameter of solubility of the solvent. It has been found that solvents such as chloroform and ether swell the material to a large extent and are thus best avoided while solvents such as acetone, 1-propanol, methanol and glycerol and water do not swell the polymer appreciably. Solvents also cause the bubbling and expansion of the polymer upon the application of heat. Commonly hexane is used a solvent and dilutant for PDMS for thin-film deposition, but the use of hexane causes swelling in the cured substrate. In this report we confirm the effective usage of a typical industrial solvent tert-butyl alcohol (TBA) as a dilutant for PDMS. We show that sub-micron features can be achieved using TBA.

Diluting PDMS is an effective strategy to get the polymer to conform to the template but this reduces the rigidity of the polymer. A flexible polymer affords the advantage of nano-patterns being bendable during peel-off without the use of non-adhesive layers like DC-20 which prevents breakage as can be seen from Fig. 4 below. At the same time, a flexible substrate might not be ideal for many applications where rigidity is required. The other purpose of this report is to highlight the use of a dual-tone PDMS process. The first layer, which conforms to the patterns, is the diluted polymer with lower viscosity. Upon development, a second layer of thick polymer is applied on top and allowed to cure effectively acting as a single thick polymer layer.

The third is flexibility in using polymerized composites such as PDMS in the fabrication of arrayed pillars. The use of PDMS affords significant flexibility and greater turnaround times in the process but it suffers from low dielectric constant. Since essentially, photonic crystals contain regularly repeating regions of high and low dielectric constant, a high dielectric differential is necessitated. The ability to control the photonic band structure and consequently their optical properties is crucial to fully exploit the optical properties of PCs. In this paper we show the ability to modulate the dielectric variation of PDMS using TiO2 nanoparticles dispersed in a butyl alcohol base. The base provides for dilution of PDMS for patterning small structures.
3. Fabrication

3.1. Fabrication of silicon template

A polished silicon sample was first piranha cleaned for 10 minutes followed by a dehydration bake at 200 deg C for 20 minutes. The substrate was spin-coated with SU8 2002 at 9000 rpm for 50 seconds to achieve a thickness of about 1.5 um. This was followed by soft exposure bake at 65 deg C for 1 minute and 95 deg C for 1 minute. The pattern was directly written on the sample by ‘Microtech LW 405 Laser Writer’. As this Laser writer operates at 405nm where sensitivity of SU-8 is low, 9 times writing of the pattern at an optimized setting of the Laser writer parameters was carried out to ensure proper cross-linking. The sample was post exposure baked at 65 deg C for 1 minute and 95 deg C for two minutes. The SU8 was finally hard baked for 20 minutes at 300 deg C.

![Image of SU8 template with a square array of holes and a period of 1 um. The die is 5mm*5mm](image)

3.2. TiO2 nanoparticle

TiO2 nanoparticles were made by dissolving titanium isopropoxide in water and stirred and kept for sometime till the solution turned yellow. This process was repeated with regular dilution of 2-methoxyethanol and finally it was let to dry for 2 hours at 300 degrees C. Using this process it was possible for us to achieve nano-particles in the dimensions of 30-70 nm.

3.3. Polymer processing

A dilute PDMS mold is made by mixing the respective components of PDMS, TBA and curing agent in the proportion of 10:10:1. 10mg of TiO2 nanoparticles, which is used to increase the refractive index is dispersed in a diluant of 5gms of TBA and agitated for in an ultrasonic for a couple of seconds. After this, the TBA is mixed with 5gms of PDMS and stirred in a clean petri-dish using a spatula for about 12mins. Now 0.5gms of curing agent is mixed with original polymer for another couple of minutes. The polymer mixes well without any observable bubbles. Now this mixture is poured over the patterned silicon kept in a petri-dish and allowed to cure for a day. We did not apply heat to the substrate since we had earlier noticed significant swelling of the polymer on the application of heat. The coefficient of expansion of the TBA mixed polymer after cooling is 1.05. The process can be optimized to reduce the curing time by the application of heat which we plan to consider later.

After curing, another layer of PDMS was poured on the original to achieve a thick layer of PDMS mold. The second layer was made without dilution, with just PDMS and curing agent in the ratio of 10:1 respectively. The new layer adheres to the original layer to form homogenous interface and can thus be peeled off easily. The substrate was then checked for patterns.
4. Results and Discussion

4.1. Optical characterization

To measure the dielectric property of the PDMS by ellipsometry, the thickness of the polymer was measured accurately by means of an optical profilometer. The ellipsometry measurement was done to get a good fit and the refractive index ‘n’ was determined to be 1.51. The refractive index of pure PDMS is 1.43. Thus we were able to effectively increase the refractive index of the polymer.

4.2. Silicon template patterning with SU8

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4.3. Nano-imprint using the SU8 template

Using the silicon template patterned with SU8 photoresist we were able to achieve 600 nm wide pillars on PDMS and height of 1.5 um. The structures showed very low side-wall roughness as expected and exhibited consistency in the arrays without breakage. The main reason that could be attributed to the success in achieving low pillar breakage even while peeling without using a non-adhesive compound such as DC-20 maybe attributed to the lowered rigidity of the diluted PDMS compound. While enhancing the optical characteristics by additive nanoparticles of TiO2 certainly improves its applicability in PC devices and micro lenses. As can be seen it was possible to achieve 600 nm features.

4.4. Refractive index measurements

| TiO2 (mg) | Refractive Index measurements |
|-----------|------------------------------|
| 5         | 1.46                         |
| 10        | 1.51                         |
| 15        | 1.57                         |
| 20        | 1.63                         |

Fig. 4. Microscope images of PDMS nanopillars using a template of a variety of patterns done on SU8.

Fig. 5. Plot showing refractive index measurements versus milligrams of titanium oxide mixed.
5. Conclusion

We have fabricated sub-micron PDMS photonic crystals for biosensor applications and further we used dual-tone methodology to fabricate a two layer PDMS with different viscosities. The structures showed very low side-wall roughness as expected and consistency in the arrays without breakage. We have also investigated the refractive index variation using TiO2 nanoparticle additives. The PDMS is suspected to exhibit a contraction of the patterns and further investigation on this is in progress.

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