Laser-assisted Fabrication of 3-D Structures on Polymer Film

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3-D photonic bandgap (PBG) crystals were fabricated by laser assisted imprinting of self-assembled silica particles on polymer film. Pulses (pulse duration 23 ns) of a KrF excimer laser instantaneously heated the silicon substrate under polymer film, which transferred the heat to the polymer film and melted it. With the force applied on the quartz, the melted polymer infiltrated and solidified over the assembled silica particles. By removing silica particles embedded in the silicon using hydrofluoric acid, inverse-opal photonic crystal was produced. This technique enables us to fabricate micrometer-order deep structures and 3-D hemispherical cavities structures.

Keywords: photonics bandgap, nano-structure, polymer, self-assembly, laser-assisted imprinting
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1. Introduction

Photonic bandgap (PBG)[1-2] crystal is a promising topic which attracts the interests of many researchers due to its applications in a variety of fields like optoelectronics, photonic materials, sensors, photo catalysts and energy harvesting coatings [3]. Many fabrication methods have been investigated and developed on various materials. Polymer material is one of the popular substrate materials. In this paper, we present a new approach to fabricate 3D PBG structures on the polymer of organic composite IC28T3 [(Benzene dimethyl (1330-20-7) cyclized polyisopropene (68441-13-4) benzene ethyl (100-41-4)), Arch Chemicals, Inc.]

Conventional techniques used for building 3-D PBG structures on polymer include focused-ion beam etching [4], soft lithography [5], photolithography [6] and laser ablation techniques [7]. Although these techniques provide structures with high resolution [4] and have high through-put [2], they have some limitations. They require costly equipment, such as masks [2], which make the whole process very expensive. Also, these processes are very slow. 3D structures need to be fabricated layer-by-layer in some conventional methods. And the depth of etching was also a major obstacle [6]. But there is another attractive area in which extensive research is being carried out, the use of colloidal microspheres to make inverse opal structures [8-15].

Monodispersed colloidal suspensions of silica can be self-assembled into close-packed structures at optical wavelength scales, with excellent long range periodicity [10]. Recently, it has been reported that inverse opals stacked in f.c.c. structures are good candidates for complete inhibition of transmission in the near-infrared and visible frequency range [14]. Several methods have been proposed to construct these inverse opals based on infiltration of foreign materials and calcination techniques [10-11, 16]. Although they are able to achieve inverse opal structures, they suffer from one common limitation, i.e., they are all slow processes. Some may even take two to three days [11-12, 14]. The infiltration of another foreign material into colloidal crystals is also a very difficult task as the infiltration rate has to be kept around 20~30% which is very difficult to control [11-12, 16, 20].

Laser-assisted nanoimprinting is an efficient way to fabricate ordered array of hemispherical cavities on silicon using the colloidal microspheres [16, 20]. This led us to explore the possibility of fabricating three dimensional photonic band gap structures on polymer. Compared to its counterpart techniques, this method is faster, cheaper and simpler. We have fabricated inverse-opal structures made of silica microspheres with diameters of 0.97 and 0.81 μm using laser-assisted nanoimprinting. It has been proposed that the photonic crystals with operating frequencies commonly used in optical communications can be readily fabricated [15].

2. Characteristics of polymer IC28T3

IC28T3 is an organic composite which has being used in semiconductor industry for several years as negative photoresist. Its wide spread use can be attributed to some of the advantages it has over its counterparts. These advantages include low cost, excellent adhesion, high photo-speed and outstanding resistance to etchants like buffered hydrofluoric (HF) acid. Some of the important physical properties of IC28T3 [17] are listed in Tab. 1. Its absorption characteristics can be seen in Fig. 1. The absorption range is located between 300 to 400 nm wavelength. IC28T3 does not absorb the photon energy of 248 nm which has been used for imprinting process. This means that the chemical and physical properties will not be changed during laser-assisted imprinting.

Table 1 Physical properties of IC28T3

Physical Property	Value
Midpoint viscosity	28 centipoise
Refractive Index (solution)	1.5035
Refractive Index (dry film)	1.5465
Soft bake conditions	85 ^{o}C for 10-20 minutes
Hard bake conditions	135 ^{o}C for 15-30 minutes

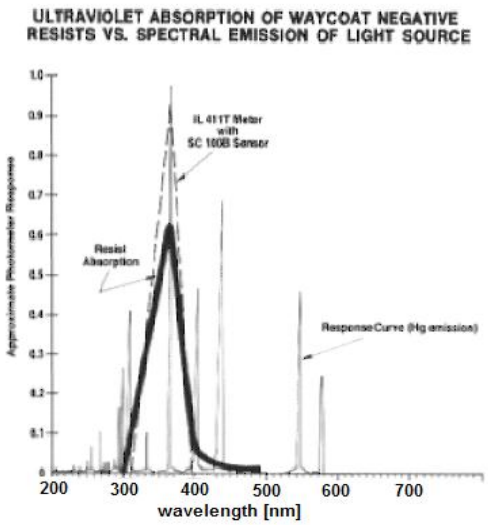


Fig. 1 UV absorption spectrum of IC type III resists [18].

The coating properties of polymer materials are determined by their viscosity. Since IC28T3 has the same viscosity as HR 200 resist [17], the curve which demonstrated the relation of spin speed and film thickness of HR 200 was referred.

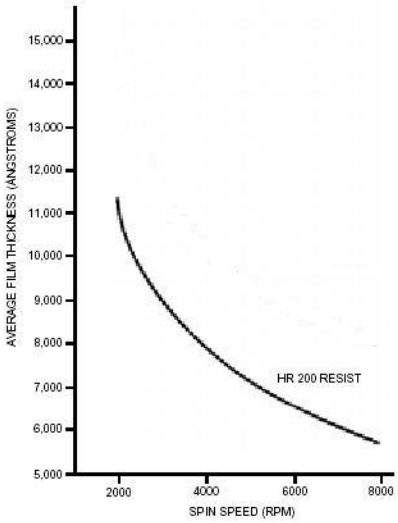


Fig. 2 Spin speed vs. pre-baked film thickness of negative HR resist [18]

3. Experimental details

We have used silicon substrates to hold the polymer film (IC28T3). The silicon substrates were thoroughly cleaned by ultrasonic agitation in methanol, acetone and deionized water sequentially for five minutes each. Then the substrates were treated with HF acid for a few minutes. A spin coater (Headway Research), which can spin up to a speed of 10,000 rpm, was used for coating the polymer on Si substrates. After the polymer was dried, the substrates were used for the self assembly of silica particles. A mixture of triton X and water in a ratio of 1:400 was used to wet the polymer surface, which made the surface more suitable for self assembly of particles. The substrate was later air dried.

The prepared substrates were placed in a tilted position making an angle (40^o~ 60^o) with the base. The schematic of the setup is shown in Fig. 3. After the surfactant is air dried, a drop of monodisperse suspensions (10% solution of silica microspheres, Bangs Laboratories, Inc.) containing silica (SiO_2) microspheres with a diameter of 0.97 or 0.81 μm was dropped on the tilted samples to obtain a hexagonally close-packed assembly over an area around several hundred square microns. When the samples were dried they were again wetted by the surfactant and the silica microspheres were dropped to form a second layer. The schematic drawings of the top view and the side view of the silicon substrate with an assembly of two layers of silica particles are shown in Fig. 4.

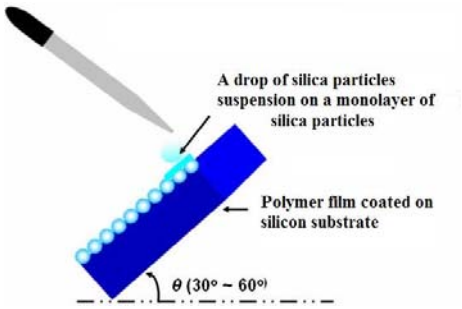
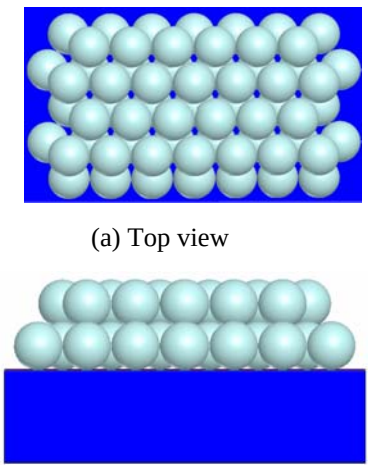


Fig. 3 Schematic of the set up for self-assembly of two layers of silica microspheres.



(a) Top view

(b) Side view

Fig. 4 Schematic of top view and side view of two layers assembled on silicon substrate.

The Si substrates with a polymer coating and a two-layer of self-assembled silica particles were then used for laser-assisted imprinting. A KrF excimer laser (Lambda Physik

Compex 205, wavelength = 248 nm, pulse duration = 23 ns) was used for imprinting, with a fluence of 480 mJ/cm^2, 3 pulses. The experiment setup is shown in Fig.5.

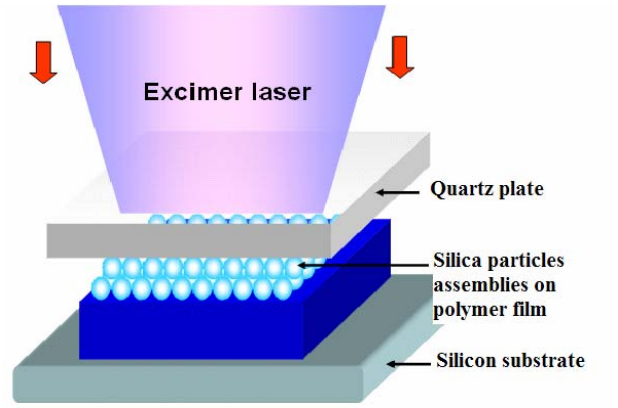


Fig. 5 Schematic of the set up for laser assisted nano-imprinting.

The quartz plate is transparent to excimer laser. The silica particles were imprinted into the polymer film as the molten polymer rose through the gaps between the silica particles. This is shown in Fig. 6. Ultrasonic cleaning was used to remove the silica particles and hydrofluoric-acid (HF) solution was then used to remove the remaining silica particles to get clear structures. Three dimensional hemispherical cavities were thus formed on the polymer film. The schematic drawings of the top view of thus formed structures looks similar as Fig. 7.

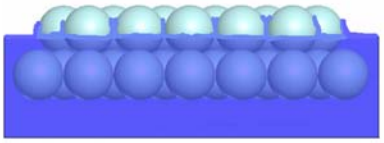


Fig. 6 Side view of 3D structures fabricated on polymer film with self assembly and laser assisted imprinting.

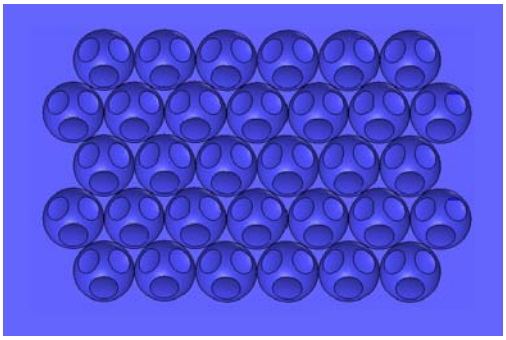


Fig. 7 Schematic of the top view of the 3-D hemispherical cavities formed in the polymer substrate after removing the imprinted silica microspheres.

4. Results and Discussions

AMBIOS Tech XP2 Profilometer was used to characterize the thin polymer coating on Si substrates. For self-assemblies of particle and the imprinted PBG structures with Philips XL30 ESEM and Hitachi S-4700 field emission scanning electron microscope were used.

4.1 Polymer film.

Profile graph generated during the measurement of the thickness of an unbaked polymer film is shown in Fig. 8. The spin speed for this sample was 2000 rpm and the coating time was 60 sec. We have used same parameters for spin coating all the samples, which we have used in this study. The average thickness of the films for different samples was found to be around in the range 1300 to 1500 nm. These results agree with the curve of Fig. 2.

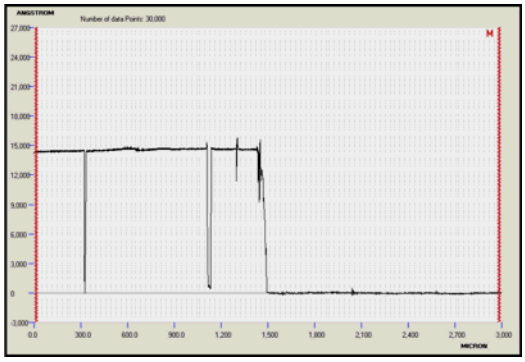


Fig. 8 Profile graph generated during the measurement of the thickness of an unbaked polymer film

4.2 Self assembly of silica particles on polymer surface

Figures 9(a) - (d) show the top view of the monolayer and double-layer assemblies of silica particles under different magnifications. Although the SEM micrographs shown in Figures 9(c)-(d) have some defects, they clearly show that the two-layer assemblies were formed. Note that in Fig. 9(d), the lower layer was formed with line defects, which were also found in upper layer. For this tilt self assembly method, the upper layer inherits defects form lower layer. Wide and uniform area assemblies can be easily achieved by the self assembly technique discussed earlier in the experimental procedure.

4.3 Laser-assisted nano imprinting

Mendu *et.al* [20] has shown that 1,500mJ/cm^2 was sufficient for efficient laser-assisted nanoimprinting of a doublelayer of silica particles into the silicon substrate. Given the thermal sensitivity of polymer materials, we have arrived at an optimum value of laser fluence, around 500 mJ/ cm^2, 3 pulses, for the laser-assisted nanoimprinting of two layers of silica particles. When the laser is shined the quartz being transparent to excimer laser allows the laser to be incident on the assembly of silica particles. Each silica

particle acts as a converging lens and enhances the optical intensity at the point of contact. The polymer film dose not

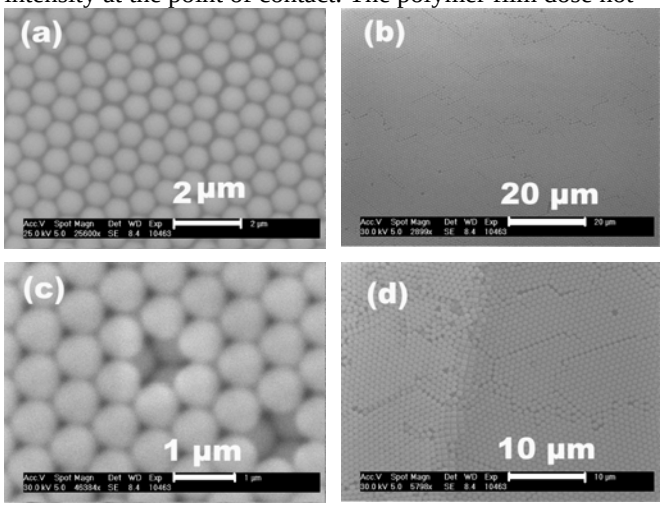


Fig. 9 SEM micrographs of the one and two layer assemblies of 0.97 µm silica particles on polymer substrate under different magnifications.

absorb laser energy as stated in the previous section. The light intensity enhancement excited by the silica particles contributes to the rapid heating of silicon substrate. The silicon substrate transfers the heat back to the polymer film and melts it. The SEM micrographs of the imprinted 0.81 µm silica particles are shown in Fig. 9(a) and 9(b). The ultra thin molten polymer covering the 0.81 µm silica microspheres can be observed in figure 9(b). The structure wall is about 50~100 nm. The two-layer nano structures imprinted on polymer film are shown in Fig 10(a) and (b). In Figures 11(a) - (b) the silica particles were aligned in [111] orientation which is very common.

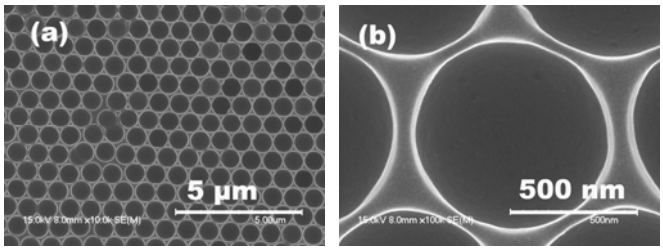


Fig. 10 The SEM images of monolayer semi-spherical cavities under different magnifications.

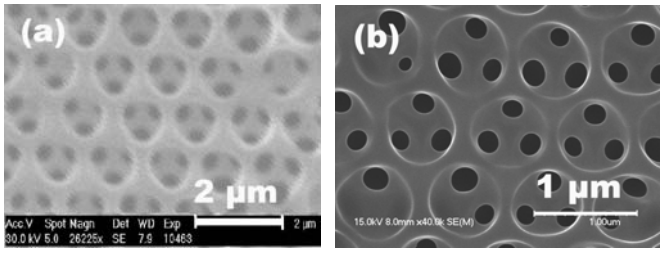


Fig. 11 The SEM images of 3D semi-spherical cavities under different magnifications.

5. Conclusions

We have demonstrated an alternative method for fabricating three dimensional PBG structures using colloidal suspensions on polymer film. Laser-assisted nanoimprinting is fast, simple and cost efficient. Our structures are highly porous and possess of three dimensionality compared to its expensive counterparts. These structures provide an inexpensive optical integrated circuit technique. Further work is being done to develop such structures in various sizes and polymer materials for further applications.

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