Fabrication of Polymer-Derived Ceramic Nanostructures by Imprint Lithography

B. Duong[*], P. Gangopadhyay[**], J. Brent[**], S. Seraphin[**], R. O. Loutfy[***] and J. Thomas[*]

[*]University of Central Florida, Orlando, FL, USA, binh.duong@ucf.edu, jayan.thomas@ucf.edu
[**]University of Arizona, Tucson, AZ, USA, palash@optics.arizona.edu, jbrent42@email.arizona.edu, seraphin@email.arizona.edu
[***]Materials and Electrochemical Research Corporation, Tucson, AZ, USA, rloutfy@mercorp.com

ABSTRACT

The conventional technique used for manufacturing miniaturized ceramic components is the powder route which typically does not allow the fabrication of feature sizes smaller than 0.1mm. With the availability of pre-ceramic polymers, processed by various lithographic methods, it is possible to realize feature sizes below 1μm in size on polymer derived ceramics (PDC). Recently, sub-500nm structures have been fabricated by soft lithography which uses a sacrificial mold. This method is not commercially viable for the production of sub-100nm feature devices in large numbers due to the tedious pre- and post processing steps involved. Currently, no studies are present in the direction of simply printing the nanostructures below 100nm on Si_3N_4/SiO_2 to the best of our knowledge. Here, we present an easy method of fabricating sub-100nm photonic devices in polysilazane which is a precursor for preparing Si_3N_4 and SiC.

Keywords: polymer-derived ceramics, imprint lithography, sub-100nm features, photonic structures.

1 INTRODUCTION

Advanced ceramics are very attractive for a variety of applications because they can be used in high pressure[1], high frequency[2], high temperature[3] and in harsh environments[4], which are not possible with other materials. The ability to fabricate these multifunctional materials into nanoscale structures has become indispensable to the development of various fields, including energy[5], biomedical components[6], and micro-nano-electro-mechanical systems (MEMS/NEMS)[7]. However, the smallest feature produced by conventional techniques using powder routes is 0.1mm[8], which significantly contrains technical applications. This disadvantage has been overcome after the invention of polymer-derived ceramics (PDCs) [9]. The liquid ceramic-precursors are not only suitable to pattern complex features but also offer high tailorability of chemical composition on molecular level. For instance, polysilazane can be converted to silicon nitride (Si_3N_4) or silicon carbide (SiC) by changing from argon (Ar) to ammonia and nitrogen heating environment, respectively.

The two main approaches to fabricate ceramic structures from polymer precursors are (i) photolithographic techniques and (ii) non-photolithographic techniques such as micromolding in capillaries (MIMIC)[10], micro transfer molding (μTM)[11] and nanoimprint lithography (NIL)[12]. Conventional lithography typically utilizes different kinds of radiation including visible to extremely UV light, electron beam or ion beam, to generate a pattern on a precursor thin film. Although defect-free ceramic features with diameter smaller than 50μm and thickness of 20μm were obtained after pyrolysis using UV- and deep X-ray lithography [13], it is not a feasible approach in commercial process due to technical challenges, high capital and operating costs.

Non-photolithographic methods have gained significant attention in recent years. For instance, the smallest PDC patterns below 1μm have been achieved by MIMIC[10]. NIL is another technique that has proved to be a powerfull tool with a potential of fabricating devices at sub-10nm scale[12]. Despite the fact that liquid ceramic precursors are well suited for NIL, the technique has not received much attention in the field due to several critical challenges. For instance, typical NIL was found to be impossible to produce pre-ceramic polymer structures because they are thermosetting materials[14].

In this work, we present an easy technique to print PDC nanostructures which are an order of magnitude smaller than that reported previously.

2 EXPERIMENTAL PROCEDURE

Steps involved in the precursor printing are illustrated in Figure 1. To demonstrate the capability of our technique, polysilazane was used as the ceramic precursor. The master mold was first wet with a commercial anti-adhesive agent. Then, the pre-ceramic polymer film was cast onto a pre-heated Si master mold by spin coating or drop casting. A substrate coated with the precursor was placed on top of the mold before curing the precursor completely. The compact assembly was cooled down to room temperature followed by mold removal. These pre-ceramic polymer nanostructures were converted to ceramics by heating in the presence of Ar at 1100°C. We have successfully transferred the defect-free pre-ceramic films onto four different substrates: glass, silicon, tungsten foil, and carbon cloth. The conversion of pre-ceramic polymers to amorphous SiC_xN_y was confirmed by X-ray diffraction

(XRD), Fourier transform infrared spectroscopy (FTIR), and X-Ray photospectroscopy (XPS).

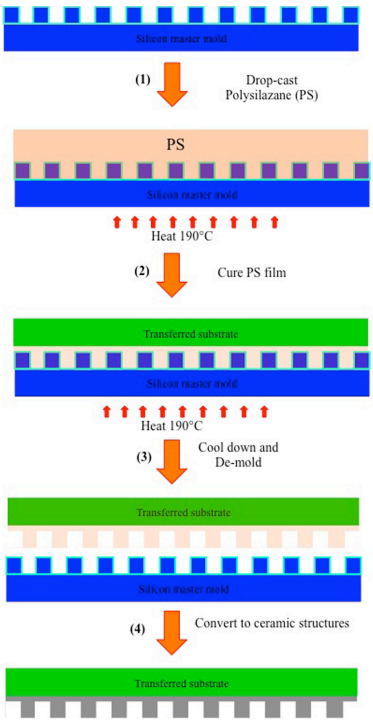

Figure 1: Schematic illustrates steps involved in the PDC printing process.

3 RESULTS AND DISCUSSION

The key advantage of using a ceramic precursor as printing medium is that low viscosity (0.05-0.2Pa.S) polysilazane enables efficient low pressure filling over a broad range of nanodimentions with relatively high aspect ratio. We have successfully printed pre-ceramic pillars with diameters as small as 80nm (Figure 2). We have transferred the defect-free pre-ceramic polymer films onto glass, silicon, tungsten foil and carbon cloth. It is worth pointing out that the master mold was not damaged even after repetitive (more than 30) printing. Furthermore, the ability to imprint nanostructures near and on top microstructures without any defect is a major improvement over the existing NIL techniques (Figure 2c and d)[15]. The feasibility of printing versatile nanodevices is demonstrated by fabricating a photonic crystal-like structure (Fig. 2e, f). This structure has been converted into ceramics.

The conversion of pre-ceramic polymers to amorphous SiCN nanostructures was confirmed by different analytical techniques as shown in Figure 3. Chemical changes during pyrolysis were revealed by FTIR analysis. Significant reduction in intensities of all peaks were observed after polysilazane was cross-linked at 190°C (Figure 3a). Moreover, the disappearance of –C-H absorption peaks of vinyl group at 3048cm^{-1} and CH=CH$_2$ group at 1592cm^{-1} indicates that complete cross-linking took place after curing

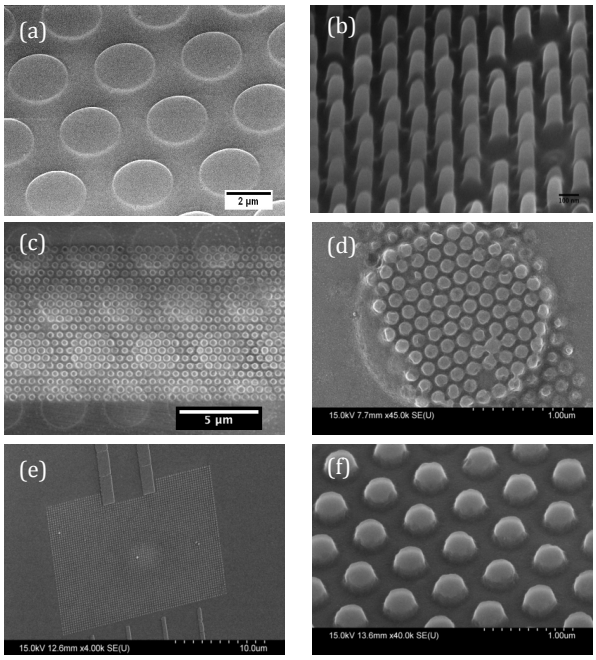

Figure 2: SEM micrographs show printed pillars with diameter of about (a) 3µm and (b) 80nm. Nanopillars printed on and near micropillars are shown in (c) and (d), respectively. A ceramic photonic structure after pyrolysis is shown in (e) with a close-up view in (f).

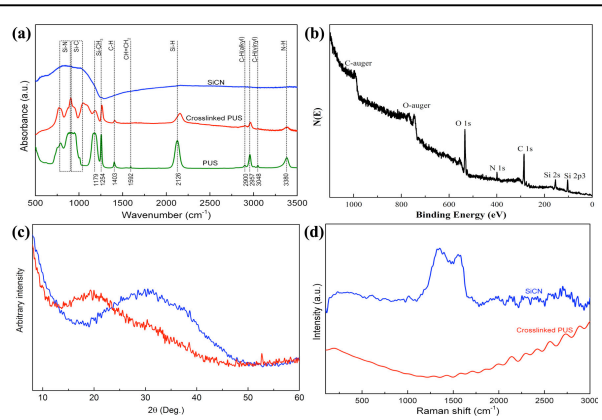

Figure 3: (a) FTIR, (b) XPS, (c) XRD and (d) Raman results of the samples before and after pyrolysis.

the sample at 190°C. After pyrolysis, there is only one broad band between 600 and 1200 cm^{-1} which attributes to the Si-C, Si-N networks. XPS spectrum shows the presence of Si, C, N and O in both before and after pyrolyzed samples (Figure 3b). The binding energies of all elements were found to be about 0.6eV lower than those of the ones before pyrolysis. Results collected from four different samples suggest the existence of Si-C, Si-N and Si-O networks. The atomic concentration collected from these

samples (after pyrolysis) also show consistent compositions of about 13% Si, 55.2% C, 5.2% N and 26.6% O. X-Ray diffraction patterns shown in Figure 3c indicates structural changes from the cross-linked polymers to amorphous ceramics due to the shifting of the broad peak at ~20° to 30°. Raman spectrum shown in Figure 3d confirms that the existence of carbon network in the pyrolized sample due to the visibility of the characteristic D-band and G-band at around 1400 cm^{-1} and 1600 cm^{-1}, respectively.

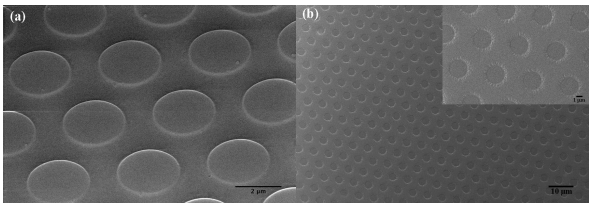

Figure 4: SEM images show (a) polysilazane micro-structures and (b) a second generation microhole array printed on a PMMA film.

The benefit of making PDC structures by this approach is that it can also serve as a very reliable replica of the silicon mold for NIL and other lithographic techniques. Figure 4a shows the 30-degree angle view of the polysilazane printed micro-pillars. This replica served as a mold to print the pattern on PMMA film as shown in Figure 4b.

4 CONCLUSIONS

We have demonstrated for the first time that patterning of thermosetting ceramic liquid precursor is possible. Easy and simple steps involved in our printing technique enable the fabrication of large area PDC nanostructures. Moreover, this technique can be a viable alternative to the expensive photolithographic technique for the fabrication of semiconductor device platforms and photonic devices.

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