FABRICATION OF SILICON CARBIDE NANOROD ARRAYS USING NANOPOROUS ALUMINA FILMS[1]

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Abstract

This study investigates the application of nanoporous alumina to fabricate nanorod arrays by using pre-ceramic polymers. Anodized thin films of aluminum supported on silicon could have several applications that involve integrating the nanoporous structures into chemical and biological sensors and as templates for creating hierarchically complex nanostructures that are integrated with microelectronic circuits. A new fabrication method for making nanorod arrays was introduced. In this method, nanoporous alumina was used as a casting mold for being filled by a preceramic polymer. To understand the changes in the chemical structure during the different steps of curing process of these pre-ceramic polymers and also to find a better process for fabrication of nanorod arrays, the effect of curing conditions on these preceramic polymers were investigated.

Key words: Nanoporous; Alumina; Silicon carbide; Nanorod arrays; Pre-ceramic polymer; Curing.

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1 INTRODUCTION

There are several applications for nanoporous structures synthesized during the anodization of alumina. Nanoporous structures obtained from anodized alumina have been used in tissue engineering as substrates for cell cultivation, to immobilize drugs in pores in drug delivery systems, in biosensors and as templates to fabricate nanowires or nanotubes[1-4]. The use of nanoporous alumina membranes for the fabrication of silicon nanorod arrays was investigated in the present paper.

Anodized alumina membranes provide advantageous characteristics such as uniformity, high pore density, controllable pore dimensions, highly ordered structure and simple synthesis procedures [1, 5-8]. One of the fascinating aspects of anodized alumina nanoporous structures is its tunability in pore size, pore density, inter-pore distance and pore depth by simply changing the anodizing parameters, such as current, voltage, time, electrolyte chemistry, electrolyte concentration and temperature [1,9,10]. Pore sizes of the anodized aluminum can vary in a wide range of 5 to 500 nm [1,9,10]. In anodized alumina, the pore aspect ratio (pore diameter vs. pore depth) can reach values more than 1:1000 and these pores could have a narrow size distribution[1]. Controlling the anodizing of aluminum in turn could permit the fabrication of nanorods with different geometrical attributes and film densities. A new fabrication method for making nanorod arrays was introduced. In this method, nanoporous alumina was used as a casting mold for being filled by a preceramic polymer.

Preceramic polymers can be converted into ceramics in system of Si-C-N-O materials[11]. These preceramic polymers have many advantages such as simplicity, cost efficiency, lower input energy and flexibility for complex shapes in comparison to traditional methods of making SiC [12]. Since the last 2 decades, organometallic compounds or simply pre-ceramic precursors are highly focused due to their promising potentiality in forming high purity non-oxide Si based ceramics and surface coatings [13]. Preceramic polymers can be processed at low temperatures, using polymer processing techniques. These polymers can be cross-linked and then pyrolyzed into amorphous covalently bound ceramics at the temperature range of 800-1,000°C generally under inert atmosphere. A recent study used micromolds to fabricate SiCN ceramic MEMS [14].

In this study, a polyureasilazane (PUSZ) was used as the pre-ceramic polymer for nanorod fabrication. It is a clear liquid with low viscosity. Figure 1 shows the chemical structure of PUSZ. The effects of process conditions on the chemistry and morphology of the nanorod structures were investigated in the present study using scanning electron microscopy, thermogravimetric analysis and infrared spectroscopy.
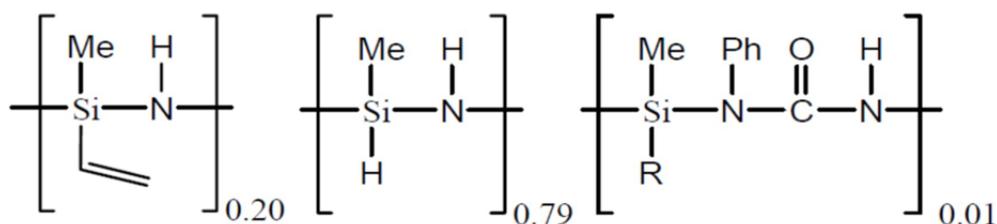
Figure 1. Chemical structure of PUSZ.

2 MATERIALS AND METHODOLOGY

The process sequence to fabricate SiC nanorod arrays is shown in Figure 2. To prepare nanorod arrays, commercial membrane (Whattman, AnodiscTM 47, 60μm thickness, 200nm pore diameter) was used as a mold and filled with PUSZ. Vacuum was typically applied for 5 minutes. The filled membrane was exposed to 2.5 mW/cm^2 UV light for 9 hours to cross-link and solidify the ceramic precursor polymer. The alumina membrane was removed by etching in aqueous H3PO4 (6 wt%) and H2CrO4 (1.8 wt%) mixture at 50°C for 4-5 minutes. The fabricated nanorod arrays pre-ceramic polymers were pyrolyzed in argon atmosphere at 1,000^{o}C for 2 hours at a heating rate of 1.2^{o}C/min.

For evaluating the nanoscale structure of nanorod arrays and investigating the effect of different parameters on these structures, scanning electron microscopy (SEM) was used. SEM characterization of the nanorod arrays was performed using a Hitachi S-4700 Cold Cathode Field Emission Scanning Electron Microscope. The SEM was conducted using a 5 kV accelerating voltage and 10-11 mm working distance. Various sections of the membrane were scanned at different magnifications in each case. To look at the cross-section of the samples a dual beam FIB microscope (Hitachi S-4700 Cold Cathode Field Emission SEM) was used.

In order to study film properties during cross-linking, PUSZ was polymerized byUV exposure followed by heating. For curing under UV radiation, 5 wt% Irgacure-651 (2,2-dimethoxy-2-phenylacetophenone) was added as a photoinitiator. The films were exposed to 2.5 mW/cm^2 UV light for one hour, 5 hour and 9 hours. After polymerization under UV radiation or heat, cross-linking was completed by heating the samples under argon atmosphere to 200, 400 and 600°C for 0.5, 2 and 4 hours at a heating rate of 1.2^{o}C/min. To convert this polymer to SiC, cross-linked polymers required to be pyrolyzed at 1000°C in an argon atmosphere. After each step, all samples were analyzed by energy dispersive X-ray (EDAX), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). For EDAX analysis, a Hitachi S-4700 cold cathode field emission scanning electron microscope was used. FTIR analysis was performed using a Nexus 470 FTIR spectrometer (Thermo Nicolet, Madison, WI) and for TGA analysis a TA Instruments 2950 TGA was used.
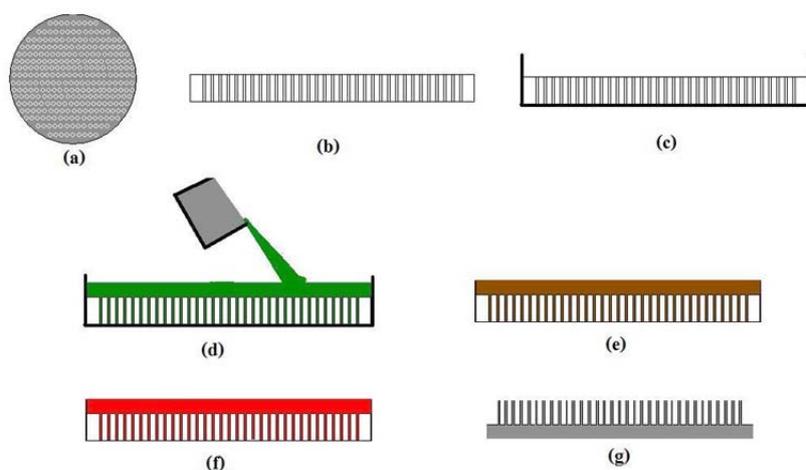
Figure 2. Schematic process of fabrication of nanorod arrays using alumina membranes as a mold: (a) Top view and (b) side view of nanoporous alumina membrane whichwas used as the mold, (c) alumina membrane inside a petridish as a holder, (d) pouring the polysilazaneinto the mold, (e) curing the polysilazane, (f) pyrolysis and (g) the resulting nanorod arrays following etching of the membrane.

3 RESULTS AND DISCUSSION

Figure 3 shows the surface and cross-section of the alumina membrane used as mold for the fabrication of nanorod arrays. For this purpose, the pores were filled with PUSZ.

After filling the pores, the membranes were exposed to UV light in order to solidify the PUSZ by cross-linking. Further heating helped to increase the cross-linking, accompanied by increased shrinkage of the formed nanorods. Cross-linking changed the chemical structure as well as physical properties such as color, transparency and the thermal stability of the PSZ/PUSZ. Shrinkage provided accessibility to the membrane walls. At this stage, the alumina membrane was etched to expose the nanorod array. These nanorods were further pyrolyzed to form a material that was primarily SiC.

(a)   (b)
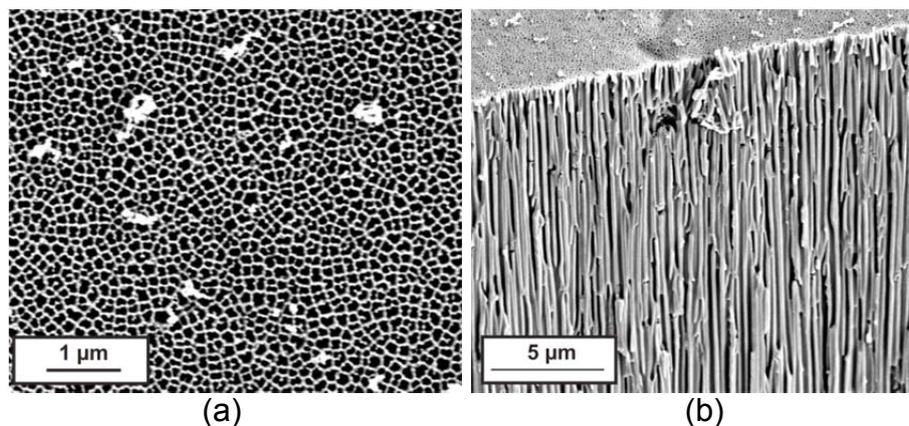
Figure 3. SEM image of (a) surface and (b) cross-section of alumina membrane (200 nm pore size).

The effect of vacuum on pore-filling behavior was investigated for PUSZ. Although PUSZ only appeared to partially fill the pores in the absence of vacuum (Figure 4a), applying vacuum for 3 minutes facilitated a more uniform filling of the pores (Figure 4b). It is possible that the pressure gradient under vacuum could result in a shear force to the liquid pre-polymer. Since polymers display non-Newtonian flow behavior, applying shear force could further decrease their viscosity and increase the polymers flow into the pores. Further studies on the rheological behavior of the pre-polymers may help understand the differences in their pore-filling behavior.

(a)   (b)
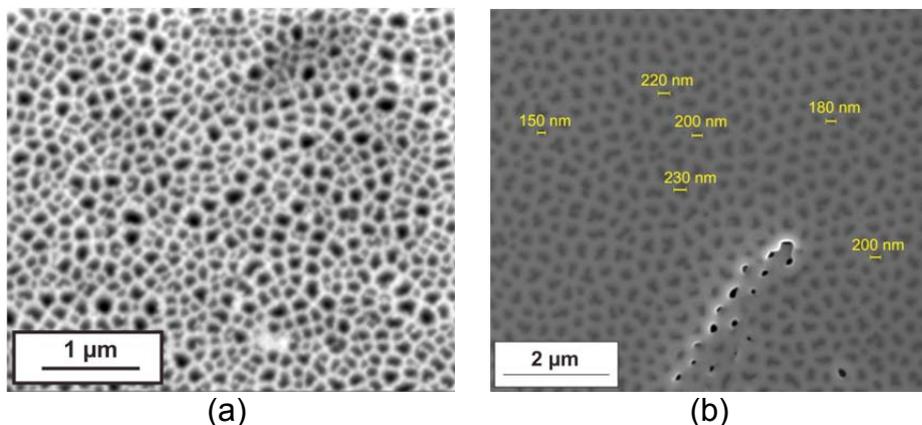
Figure 4. SEM image of alumina membrane filled with PUSZ followed by 9 hr UV curing (a) no vacuum (b) 3 minutes vacuum

The PUSZ-filled alumina membranes were cured by exposure to UV for 9 hours. Figure 4 show that this solidification was not accompanied by shrinkage after UV curing. After solidification of PUSZ inside the pores, the next step for fabrication of nanorod arrays was to dissolve the membrane in an appropriate etchant in order to expose the nanorod array. The etching conditions used for the dissolution of the alumina membrane involved soaking the sample in an aqueous mixture of H_3PO_4 (6 wt%) and H_2CrO_4 (1.8 wt%) mixture in 50^oC for 4-5 minutes. Figure 5a shows the SEM of a PUSZ-filled membrane (UV cured for 9 hours) that was heated to 200^oC at a heating rate of 1.2^oC/minute and held for 2 hours. When shrinkage of the polymer was low as in Figure 5a, the dissolution of membrane only occurred near the surface of the membrane. Presumably, the membrane walls could not be removed completely due to lack of accessibility of the etchant to the membrane pore walls.

(a)   (b)
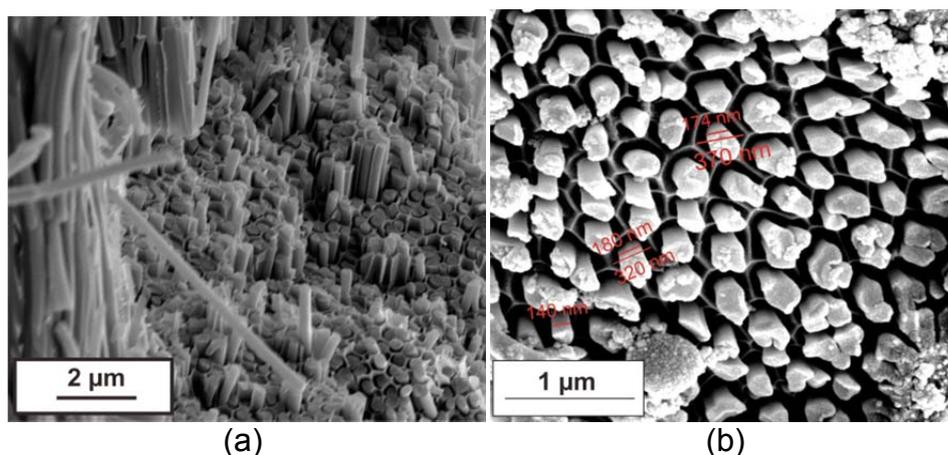
Figure 5. Alumina membrane filled with PUSZ after 9 hr UV curing followed by heat treatment at (a) 200^oC and (b) 600^oC (heating rate of 1.2^oC/min) for 2 hours under argon.

Figure 5b shows that heat treatment of the PUSZ-filled membrane at 600^oC for 2 hours under argon resulted in a diametrical shrinkage of over 50% by comparing the pore diameter with the nanorod diameter. Figure 6 shows a nanorod array formed by using PUSZ in the above manner, after it was further pyrolyzed at $1,100^oC$ for 2 hours under argon and etched to remove the alumina membrane. Fully formed nanorod arrays could be observed. EDAX characterization confirmed the presence of SiC.
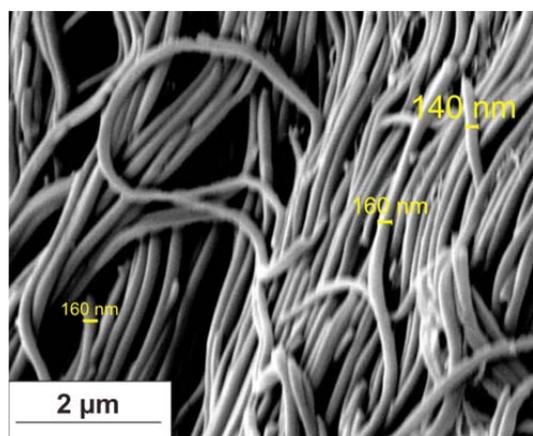
Figure 6. Alumina membrane filled with PUSZ after 9 hr UV curing followed by heat treatment at 600^oC (heating rate of 1.2^oC/min) for 2 hours under argon. A further pyrolysis to $1,100^oC$ (heating rate of 1.2^oC/min) for 2 hours under argon.

Figure 7 shows that the PUSZ nanorods were transformed to spheres when directly heating polymer-filled membranes that were UV cured only for 5 hours and heated directly to 1,100°C at 5°C/min without an intermediate thermal curing stage. This result implies that an intermediate thermal cross-linking step is necessary in without a heat treatment stage as discussed in the previous paragraphs. Based on the FTIR and TGA results discussed below, it is likely that cross-linking had not progressed sufficiently causing the semi-liquid polymer to convert to spherical shapes to minimize its surface tension prior to pyrolysis at higher temperatures.
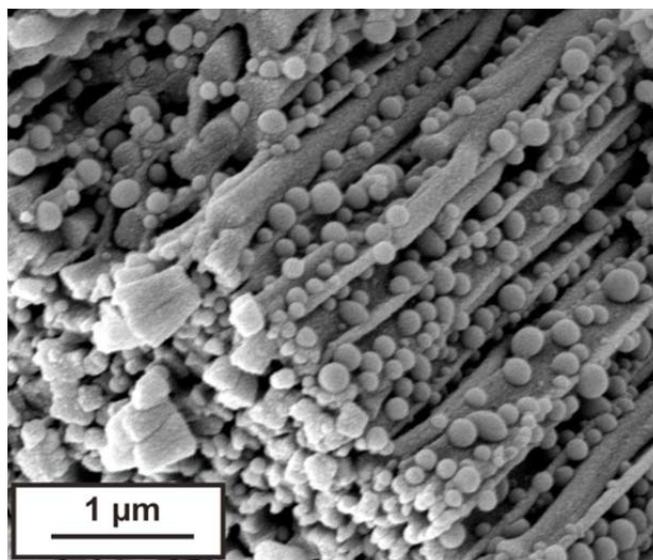
Figure 7. Alumina membrane filled with PUSZ after 5 hr UV curing followed by pyrolysis at 1100°C for 2 hours in argon. Eliminating an intermediate thermal curing step resulted in the formation of spheres.

Figure 8 shows the FTIR results for PUSZ cured by UV exposure for different times. The peak at 787 cm^{-1} assigned to Si-C is distinguishable in PUSZ after 1 and 5 hours UV curing. The peak at 1,596 cm^{-1} assigned to the vinyl group had a relatively lower intensity in PUSZ, suggesting that the vinyl group may have undergone cross-linking in PUSZ. Increase of UV exposure duration of PUSZ to 5 and then 9 hours slightly increased the intensity of the peaks at 752 and 871 (associated with C-H deformation) as well as at 897 cm^{-1} (assigned with -Si-N-Si- group). In addition, the intensity of the peak at 1,018 cm^{-1} assigned to C-H wagging in -Si-CH$_2$-Si- increased with increase of UV exposure time and it shifts to smaller wavenumbers. Increase of UV exposure time slightly increased the intensity of the peak related to Si − C in Si − CH3 at 1,259 cm^{-1}. Further slight shifts in the silyl peak at 2,150 cm^{-1} were observed. In addition, strong bands associated with C-H stretching could be observed for all samples in the 2,950-3,050 cm^{-1} region[15].
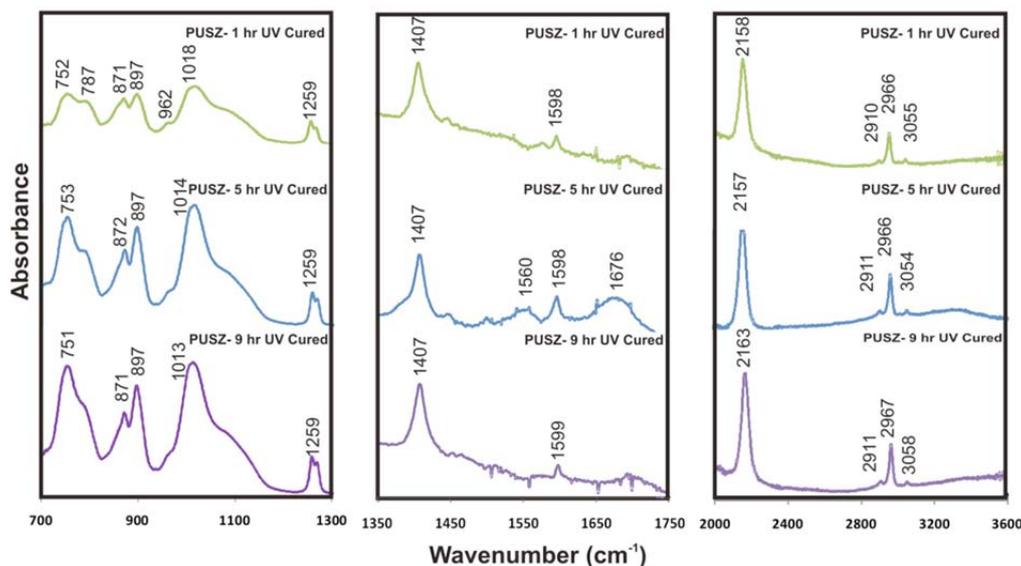
Figure 8: FTIR spectra for PUSZ UV cured for different times (1, 5 and 9 hours).

Figure 9 shows the TGA results for PUSZ, following UV exposure for different times. The results indicate that the samples exposed to UV for shorter times show higher weight loss presumably due to lower cross-linking reaction and accompanying gas evolution. This provided an explanation of different nanorod structural stability following further heat treatment. The release of H_2, NH_3, CH_4 and other hydrocarbons have been reported to caused a shrinkage of about 30-60% in converting the PUSZ and PSZ to a ceramic. If the heating rate is high or for insufficient times, then gas formation is not expected to be complete. This phenomenon has also been reported to cause defects in the pyrolyzed sample and affect its mechanical properties negatively.
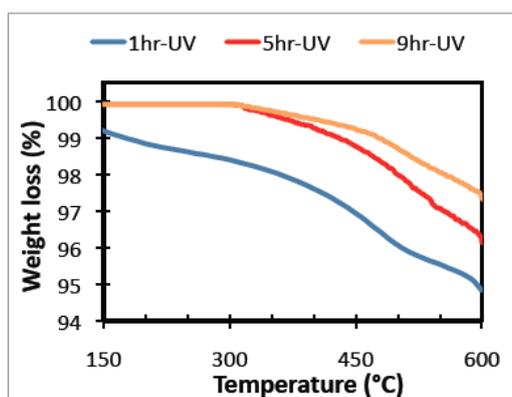
Figure 9. TGA curves for PUSZ UV cured for different times (1, 5 and 9 hours).

PUSZ cured at 200ºC changed from transparent/white (depending on UV exposure time) to a bright yellow color. Following heating to 400ºC, the color changed to a darker yellow with a more glassy appearance compared to a flexible film before thermally activated curing. After heating at 600ºC, the color changed to brown and it was completely glassy. Figure 10 shows FTIR results for PUSZ exposed to UV for one hour and heated for 4 hours at different temperatures. The principal observation is the virtual elimination of hydrocarbon peaks at 1,400, 2,900, and 2,960 cm^{-1} and retention of S—C and Si-N peaks after heating at 600ºC[15].
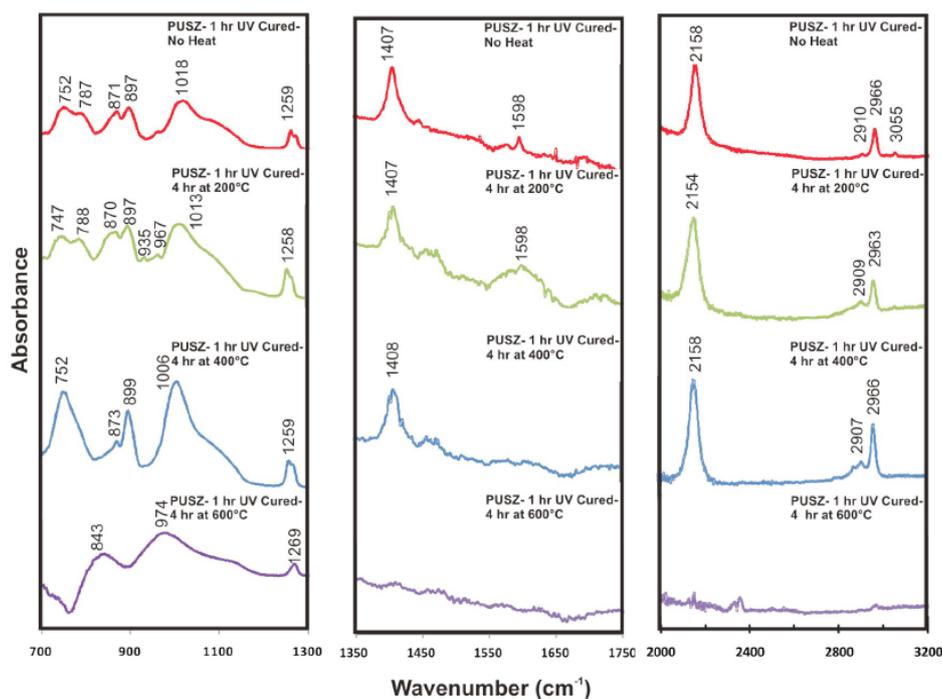
Figure 10. FTIR spectra for PUSZ thermally cured for 4 hours at various temperatures.
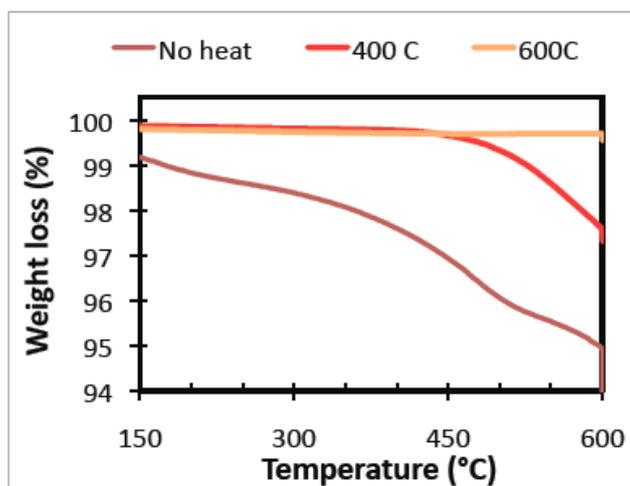
Figure 11. TGA curves for PUSZ thermally cured for 4 hours at various temperatures.

Figure 11 shows TGA results for the same films. A higher weight loss was observed for samples cured at lower temperatures while samples cured at 600ºC showed the least weight loss. The principal inference from these results is that curing for several hours at 600ºC produces a more thermally stable structure than those produced at lower temperatures and times. Accordingly, these results provide process design criteria for synthesizing nanorod arrays of the PUSZ.

4 CONCLUSIONS

A novel method to fabricate nanorod arrays of pre-ceramic polymers by using the nanopores as molds was introduced. For this purpose, polyureasilazane (PUSZ), was chosen. To have an understanding on the behavior of these polymers during the process and selecting appropriate processing conditions, the curing behavior of the

polymers under various combinations of UV, temperature and time combinations were studied.

It was observed that the selected UV curing condition (5wt% Irgacure 651 as a photo-initiator and 2.5 mW/cm^2 UV exposure) solidified PUSZ. An increase of UV exposure time reduced the flexibility of the polymer film and changed its color from transparent after one hour to white after five hours and yellow after nine hours. FTIR results did not show noticeable changes in chemical structure of these polymers by increasing the UV exposure time. TGA results showed that increase of time increased the thermal stability of the films, presumably due to cross-linking, but in qualitative agreement with the FTIR result, suggested that UV curing did not result in major reactions. In addition, SEM images after filling the pores of the membrane with PUSZ followed by UV curing alone did not show visible shrinkage, supports the idea of low levels of cross-linking by UV exposure alone.

Heating to 200ºC changed the color to bright yellow. FTIR results showed that heating the UV cured samples to 200ºC resulted in further cross-linking based on the reduction in intensity of the vinyl groups and formation of new peaks. Heating to 400ºC resulted in a dark yellow material with more glassy appearance. FTIR results for PUSZ heated at 400ºC, showed an intensity reduction in the peaks associated with the Si-H and Si-CH$_3$. Also, the Si-C and Si-N bands became broader. Heating tot 600ºC of PUSZ formed red glassy materials. Heating to this temperature completely removed Si-H and Si−CH3 related bands. After 600ºC, only Si-C and asymmetric Si-N bands are remained, suggesting in a residual material predominantly comprising of Si, N and C. These results qualitatively explained the differences in the ability to form nanorods following various UV-time-temperature combinations. Heating at a hold temperature of 600ºC was found to be effective in providing the necessary shrinkage to facilitate etchant penetration to remove the membrane. It was also observed that the viscosity of the liquid pre-ceramic polymer and the application of vacuum also played significant roles in uniformly filling the pores. Accordingly, PUSZ with less viscosity was able to fill the pores completely under the application of vacuum.

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