

Inorganic polymer photoresist for direct ceramic patterning by photolithography†

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A novel negative, inorganic polymer photoresist was demonstrated to be suitable for simple and direct fabrication of tribological SiCN-based ceramic microstructures *via* UV photolithography and subsequent pyrolysis at 800 °C.

Photolithography has become the mainstay for small feature patterning, in which the chemical structure of a thin photoresist is modified by radiation. Following the incredible advances in photolithography, various organic photoresists are being used in a wide range of applications such as semiconductor processing, optical circuits, microfluidic devices, and microelectromechanical systems (MEMS).^{1–6}

Despite the widespread use of organic photoresists, demand is increasing for the simple fabrication of robust, inorganic micro- to nano-structures because the material properties of organic polymers are inadequate, in many cases, for devices in a harsh environment due to their weakened resistance to high temperature, corrosion, and friction. There is, therefore, great benefit to be gained in the development of an inorganic photoresist that is able to support robust ceramic structures on a micro- to nano-scale. Currently, sophisticated fabrication techniques, including surface, bulk, laser and electro discharge micromachining, have been demonstrated for the direct patterning of metal, glass, and Si without the use of photolithography. However, these techniques are slow, complicated and difficult to apply for the patterning of non-oxide ceramics with high corrosive resistance and mechanical strength. Relevant to this obstacle are the reports on the preparation of tribological ceramics from various preceramic polymers as processible ceramic precursors and subsequent pyrolysis for structural applications such as fibers and composites.^{7,8} Recently, our group reported for the first time the fabrication of three-dimensional, SiCN ceramic objects of 5–9 micrometer size *via* two-photon absorption photo-crosslinking, *i.e.*, stereolithography, using a newly developed inorganic polymer photoresist with low viscosity and high optical transparency, and subsequent pyrolysis at 600 °C.⁹ This fabrication technique has shown promise for diverse applications of ceramic micro-devices. However, the low viscosity of the developed photoresist was inappropriate for a typical ultraviolet (UV) photolithography

process due to a stiction problem of the mask in the proximity of the photoresist. In this paper, therefore, we report a novel development of a solid, solvent-soluble, highly photosensitive polymer *via* the synthesis of high molecular weight, methacrylated polyvinylsilazane (HM-PVS) as a precursor for SiCN ceramic. The negative version of the solid inorganic photoresist is demonstrated to be a suitable candidate for simple and direct microstructuring of tribological SiCN ceramic features *via* UV photolithography and subsequent pyrolysis at 800 °C. In particular, closed contact with no air gap between the photomask and the photoresist on the substrate overcomes the limited resolution caused during the photoimaging step of the liquid-based photoresist.

A high molecular weight, photosensitive polyvinylsilazane was synthesized by modification of a solid polyvinylsilazane (KiON Ceraset Ultra, KiON Corp.) *via* linkage or insertion reaction routes through the addition of 2-isocyanatoethyl methacrylate (Hestia Laboratories Inc.) at a content of 20 wt%, as in our own report of the synthesis of low molecular weight methacrylated polyvinylsilazane (LM-PVS, $M_n = 551$).⁹ The obtained product is a solid-soluble polymer which can be diluted in various common organic solvents such as tetrahydrofuran, toluene, and acetone. As determined by GPC measurements, the molecular weight of the initial polymer ($M_n = 8940$) slightly increased ($M_n = 10366$) due to the addition of the methacrylate groups.

The chemical change of the solid HM-PVS was investigated by Fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR) studies. The conversion of isocyanate to urea in the product was monitored by the new IR absorption peaks as assigned to the urea group (CO–NH) at 1690 cm^{-1} (overlapped with C=O peak), 1543 cm^{-1} (N–H) and 1440 cm^{-1} (C–N); and the nearly disappeared peaks of the isocyanate group (–NCO) at 2272 and 1363 cm^{-1} . Further, the introduced methacrylate contents appeared at 1714 cm^{-1} (C=O) and 1639 cm^{-1} (C=C). In the product's NMR spectra,¹⁰ both new peaks at 5.4 ppm of the ¹H-NMR spectrum, and at 155–159 ppm of the ¹³C-NMR spectrum could be assigned to the urea group.⁹

The final product of the reaction process can be demonstrated by a 2D ¹H–¹H-NMR (COSY) spectroscopy experiment which confirmed that the linkage reaction of the isocyanate group at the amine site was the major reaction route due to the presence of three peaks at 5.3, 4.2 and 3.5 ppm. Otherwise, the peaks at 4.3 and 3.9 ppm correspond to the insertion reaction of the isocyanate group into the Si–N bond of cyclic silazane.^{9,10} In addition, the relative peak intensity in the ¹H-NMR spectrum showed that the linkage reaction was the dominant route for the introduction of methacrylate groups, with a yield of 81.2% at a reaction temperature of 50 °C. The mechanism of the proposed reaction

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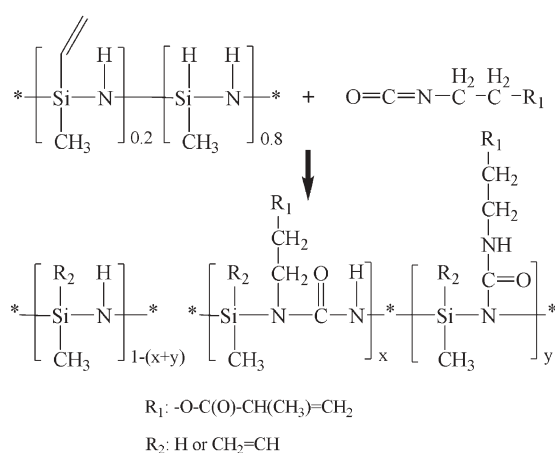
† Electronic supplementary information (ESI) available: Characterization of HM-PVS: NMR, TGA, nano-indentation test, experimental details. See DOI: 10.1039/b708480c

routes is presented in Scheme 1, which is similar to the chemistry of our previous work.⁹

We propose that the as-synthesized HM-PVS polymer possesses dual functions as both an intrinsic, preceramic polymer and a novel, photoresist resin with enhanced photosensitivity. The photosensitivity of the HM-PVS was comparatively evaluated by measuring the UV-absorbance spectrum (UV spectrometer, SINCO) and photo-DSC thermogram (DSC2910). Fig. 1a shows the UV-absorption spectrum of the HM-PVS, with a much stronger absorption peak clearly evident in the wavelength region of 205–240 nm, in comparison with that of the initial solid PVS. Furthermore, in the photo-DSC measurement at a wavelength of 250 nm, the initial solid PVS showed negligible photosensitivity with no exothermic peak. However, the HM-PVS resin exhibited a dramatically greater photosensitivity with a large exothermic peak (Fig. 1b), indicating enhanced photopolymerization kinetics.^{11,12} The synthesized polymer clearly displayed the typical behavior of a negative photoresist resin in the presence of both vinyl groups and additional methacrylate groups.

However, the HM-PVS resin exhibited only a two-fold smaller exotherm than that obtained for the liquid type of low molecular weight methacrylated polyvinylsilazane, LM-PVS resin ($M_n = 551$). To evaluate the effect of molecular weight on the photopolymerization reactivity, the two photosensitive polymers cured under identical UV exposure conditions (wavelength 365 nm, intensity 20 mW cm^{-2}) underwent $^1\text{H-NMR}$ measurement to determine the conversion yield of C=C bonds in the polymer samples, with an internal reference peak of non-reacted Si-CH₃. Fig. 2 shows that the conversion yields of C=C bonds in the HM-PVS resin were consistently lower than those in LM-PVS at every illumination time. This can be interpreted as indicating that the limited translation movement of the extended polymer chains caused higher steric hindrance, and thereby a lower degree of crosslinking. However, we consider that the high molecular weight resin readily formed an insoluble phase even with a low degree of crosslinking reaction, while the liquid resin type of negative photoresist needs a higher photosensitivity to form an insoluble crosslinked phase.

On the other hand, a nano-indentation test showed that only UV cured HM-PVS film had a Young's modulus of 4 GPa,¹⁰ which is four times stronger than the UV cured LM-PVS in identical conditions.⁹ It is noteworthy that the increased strength



Scheme 1 A schematic mechanism of linkage and insertion reaction routes for solid photoresist HM-PVS with high molecular weight.

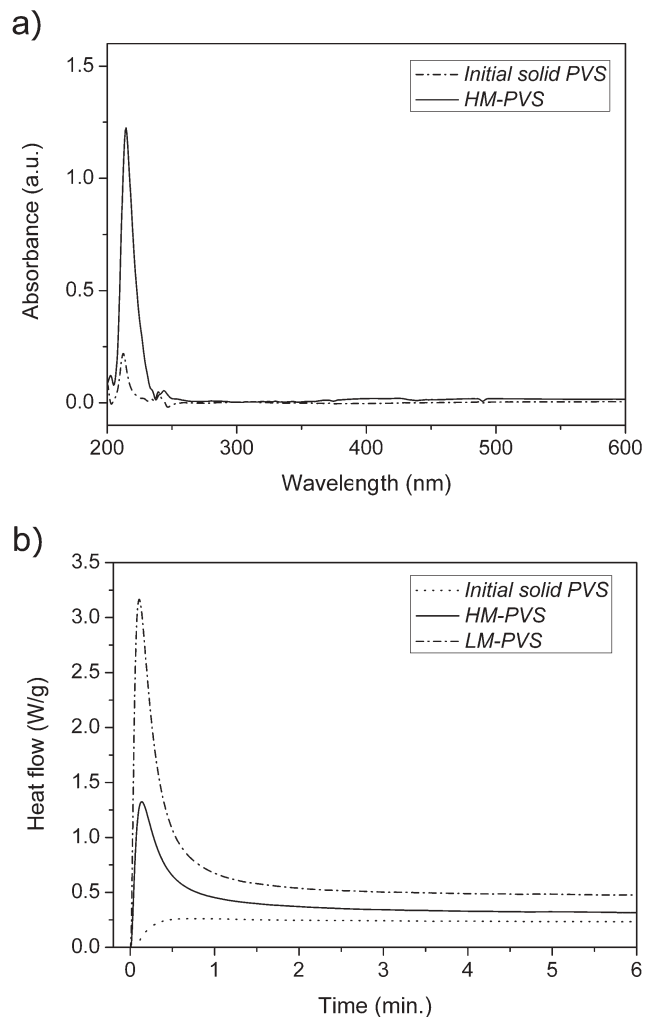


Fig. 1 (a) UV-absorbance spectra and (b) photo-DSC thermogram comparing the initial solid PVS and the photosensitive HM-PVS resin in THF ($10^{-3} \text{ g ml}^{-1}$), and the samples with 2 wt% Irgacure 369 were placed in an uncovered aluminium pan, respectively.

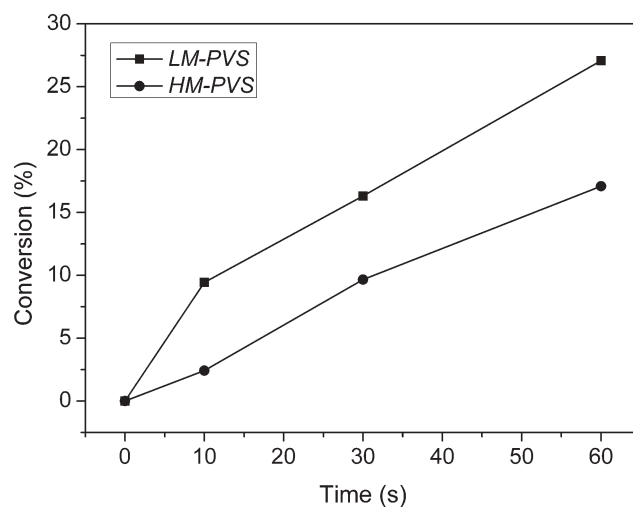


Fig. 2 Comparative curing chemistry of two photoresist resins, LM-PVS and HM-PVS, as a function of UV exposure time.

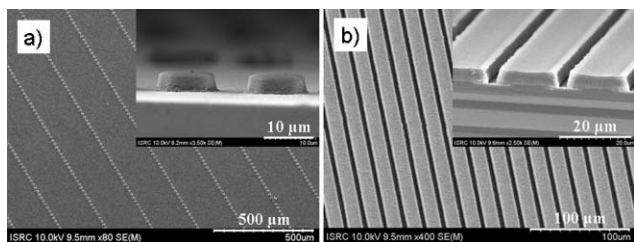


Fig. 3 Inorganic polymeric microstructures fabricated by photolithography: a) 10 μm dots (spacing \sim 10 μm) and b) 15 μm lines (spacing \sim 5 μm). Inset images show a cross-sectional view at a higher magnification.

of the cured HM-PVS can promote the stability of patterned structures towards the mechanical deformation caused by the surface tension of liquid developers. In addition, when the spin-coated HM-PVS films were annealed at 600 and 800 $^{\circ}\text{C}$, the modulus steeply increased to *ca.* 15 GPa and 45 GPa, respectively, due to conversion of the polymer to the ceramic phase. This increment supports the application of the films in microdevices operated under harsh conditions. During the thermal conversion to the ceramic phase, the HM-PVS resin showed a ceramic yield of 75.5 wt% at 1000 $^{\circ}\text{C}$, which was slightly lower than the 80.4 wt% of the starting solid PVS due to the additional presence of the organic methacrylate. Nevertheless, the synthesized polymers still showed a relatively high ceramic yield, which is advantageous for obtaining a dense ceramic product with less shrinkage.

In order to examine the potential applications for the patterning of ceramic features, the HM-PVS resin with high ceramic yield was used to fabricate the SiCN ceramic patterns by photolithography. Fig. 3 shows the 10 μm dots and 15 μm line patterns that were formed uniformly on a large area ($5 \times 5 \text{ cm}^2$). As can be seen, the microstructures were neatly fabricated with excellent pattern fidelity and without any residual layer, as judged by the sharp interface between the resist and the substrate. These results demonstrate that the inorganic precursor could be equally applied to photolithography without any required modification of the protocol. In contrast, the photolithography with liquid resin LM-PVS was mostly troublesome due to stiction between the mask and the resin.

To evaluate the shrinkage upon pyrolysis, the formed patterns were compared before and after pyrolysis at 800 $^{\circ}\text{C}$ (Fig. 4). The width and height of the ceramic dot patterns after pyrolysis were 8.4 μm and 2.3 μm , which were smaller than the values for the cured dot patterns of 10.4 μm and 3.4 μm , respectively. This result is readily explained by the volume shrinkage that is undergone by the ceramic structures during pyrolysis due to the thermal conversion from a low-density polymer to a high-density ceramic phase. The findings of 19% and 32% shrinkage in width and height, respectively, after pyrolysis are comparable with the data reported in the literature.^{13,14} However, these shrinkage rates were much lower than the 41% of the low molecular weight resin LM-PVS.⁹ The elemental composition of the SiCN ceramic (atomic %) analysed by SEM/EDS was 34.1% Si, 26.7% C, 27.1% N and 12.1% O at 800 $^{\circ}\text{C}$, corresponding to $\text{SiC}_{0.78}\text{N}_{0.80}\text{O}_{0.35}$. It is nearly consistent with ceramic phase $\text{SiC}_{0.61}\text{N}_{0.55}\text{O}_{0.11}$ obtained from initial solid PVS under the same conditions, but the higher oxygen content is presumably correlated

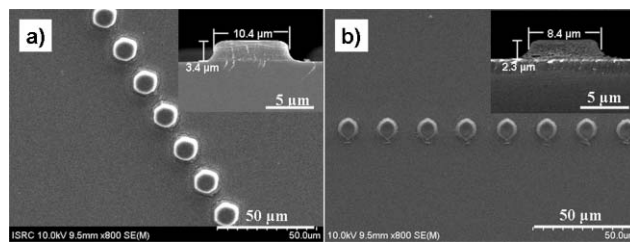


Fig. 4 (a) 10 μm polymeric dot patterns before pyrolysis and (b) the corresponding ceramic patterns after pyrolysis at 800 $^{\circ}\text{C}$ in nitrogen atmosphere. Inset images show a cross-sectional view of the samples at a higher magnification.

with the addition of methacrylate groups and also possible moisture contamination during the photolithography step. Finally, further investigation will focus on improving the dimensional stability by controlling the formulation of the synthesized resin as well as addition of nanoparticles as fillers. This proposed microfabrication process is expected to enable the preparation of a variety of microstructures without the need for high resolution imaging material.

In summary, a solid inorganic polymer photoresist resin was simply synthesized *via* one step of linkage and/or insertion reaction routes. The ceramic microstructure was readily fabricated without any residual layer *via* direct UV photolithography and subsequent pyrolysis at 800 $^{\circ}\text{C}$. The synthesized inorganic polymer photoresist is a suitable candidate for the fabrication of tribological SiCN ceramic microstructures with high modulus, which have great promise for high temperature SiCN MEMS devices applications.

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Notes and references

- H. Ma, A. K. Y. Jen and L. R. Dalton, *Adv. Mater.*, 2002, **14**, 1339.
- R. Yang, W. Wang and S. A. Soper, *Appl. Phys. Lett.*, 2005, **86**, 161110.
- M. Agirregabiria, F. J. Blanco, J. Berganzo, M. T. Arroyo, A. Fullaondo, K. Mayora and J. M. Ruano-López, *Lab Chip*, 2005, **5**, 545.
- S. W. Jeon, J. U. Park, R. Cirelli, S. Yang, C. E. Heitzman, P. V. Braun, P. J. A. Kenis and J. A. Rogers, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 12428.
- J. H. Daniel, B. Krusor, R. B. Apte, M. Mulato, K. Van Schuylenbergh, R. Lau, T. Do, R. A. Street, A. Goredema, D. C. Boils-Boissier and P. M. Kazmaier, *J. Vac. Sci. Technol., A*, 2001, **19**, 1219.
- M. C. Gather, A. Kohnen, A. Falcou, H. Becker and K. Meerholz, *Adv. Funct. Mater.*, 2007, **17**, 191.
- M. Horz, A. Zern, F. Berger, J. Haug, K. Mueller, F. Aldinger and M. Weinmann, *J. Eur. Ceram. Soc.*, 2005, **25**, 99.
- M. Zemanova, E. Lecomte, P. Sajgalik and R. Riedel, *J. Eur. Ceram. Soc.*, 2002, **22**, 2963.
- T. A. Pham, D. P. Kim, T. W. Lim, S. H. Park, D. Y. Yang and K. S. Lee, *Adv. Funct. Mater.*, 2006, **16**, 1235.
- Supporting information.
- J. W. Stansbury and S. H. Dickens, *Polymer*, 2001, **42**, 6363.
- E. W. Nelson, J. L. Jacobs, A. B. Scranton, K. S. Anseth and C. N. Bowman, *Polymer*, 1995, **36**, 4651.
- L. A. Liew, Y. Liu, R. Luo, T. Cross, L. An, V. M. Bright, M. L. Dunn, J. W. Daily and R. Raj, *Sens. Actuators, A*, 2002, **95**, 120.
- Y. Liu, L. A. Liew, Y. Liu, R. Luo, L. An, M. L. Dunn, V. M. Bright, J. W. Daily and R. Raj, *Sens. Actuators, A*, 2002, **95**, 143.