Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Fabrication of Three-Dimensional SiC Ceramic Microstructures with Near-Zero Shrinkage via Dual Crosslinking Induced Stereolithography

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1. Inorganic Polymer as a SiC Precursor

Allylhydridopolycarbosilane (AHPCS, SMP-10®, Starfire system, USA) and organometallic ((η^5-cyclopentadienyl-methyl)-trimethylplatinum ($CpPtMe_3$), Strem chemicals, USA) were used to prepare an inorganic polymer photoresist. AHPCS was mixed with 1 wt% of $CpPtMe_3$ and stirred for 15 min. AHPCS has no absorption at 780 nm, which is the center wavelength of the femtoseconds laser. This makes it possible to focus the laser beam into the resin without causing a curing reaction. All reactions were carried out in a nitrogen atmosphere.

2. Fabrication of Three-Dimensional SiC Ceramic Microstructures

A drop of the inorganic polymer photoresist resin was placed between two cover glasses with a 100 μm thick polymer (Kapton) film as a spacer. The 2D patterns and each layer of the horizontally-sliced 3D data were fabricated by the accumulation of 2D patterns. The dose for the photocuring reaction at each unit volume pixel (voxel) was controlled by changing the laser power and exposure time (150 mw and 1 ms in this work). After the stereolithography process, the photocured features on the plate were developed using a normal hexane solvent, which dissolved and removed the uncured polymer resin. The

developed solid polymer samples were annealed in a tube furnace at 600 ℃ for 2 hr in a nitrogen atmosphere at a heating rate 2 ℃/min to produce the ceramic phase. The use of a cover glass plate limited the highest pyrolysis temperature to 600 ºC.

3. Preparation of Thin Film for Conversion Chemistry

The effect of $CpPtMe_3$ on the curing and pyrolytic conversion chemistry was examined by preparing two types of thin film samples on a Si wafer using spin-coating process at 3000 rpm for 30 sec. One (designated the AHPCS-Pt film) was a AHPCS mixture with 1 wt% $CpPtMe_3$, and the other (AHPCS film) was AHPCS only. Both polymer films were cured by 365 nm UV exposure for 1 hr with no heating effect and then cured thermally at 160 ℃ for 12 hr. Subsequently, the samples were pyrolysed at 600 ℃ under the above mentioned conditions.

4. Characterization

The three-dimensional microstructures were examined using field emission scanning electron microscopy (FE-SEM, FEI co., Netherlands). To prevent charging, the samples were coated with a 10 nm platinum layer prior to analysis. The hardness and Young's modulus of the pyrolysed film samples were measured at room temperature using a nanoindentation system (Nanoindenter XP, MTS Nano instruments, USA). The ceramic yield was determined by TGA (TGA 2050, TA instruments, Austrailia) up to 1000℃ at a heating rate of 2 ℃/min in a nitrogen atmosphere. The conversion chemistry was examined by preparing a mixture using 15 wt% of the two types of polymer, AHPCS with 1wt% of $CpPtMe_3$ and no polymer in $CDCl_3$ solvent. Solid samples were prepared by scratching a polymer thin film on a Si wafer. The samples were then placed into a nuclear magnetic resonance (NMR) spectrometer (Solid state NMR Spectrometer-200MHz, Varian) tube. The progress of polymerization by UV exposure was monitored after exposing the samples to UV radiation for 0, 5, 10, 20, 40, 60, 90 min.

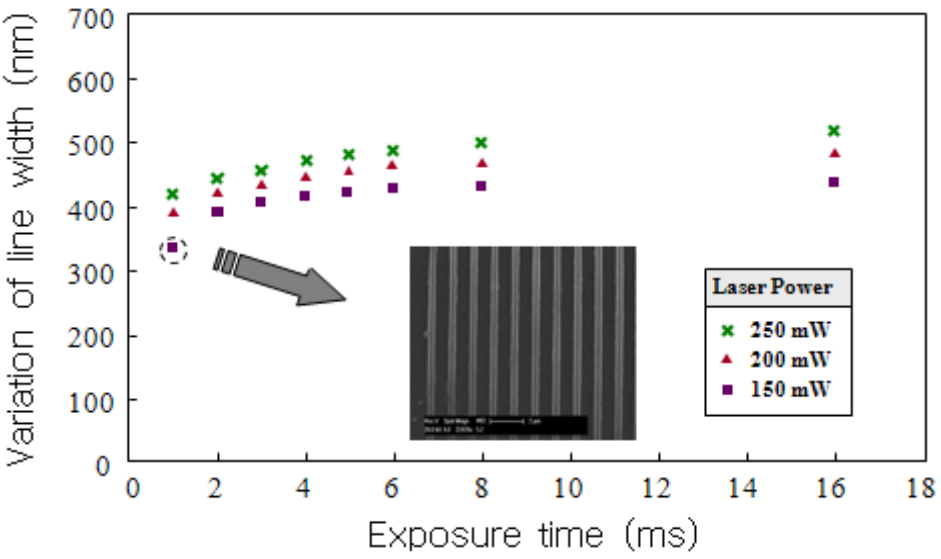

Figure 1s Polymer line width as a function of the laser power and exposure time

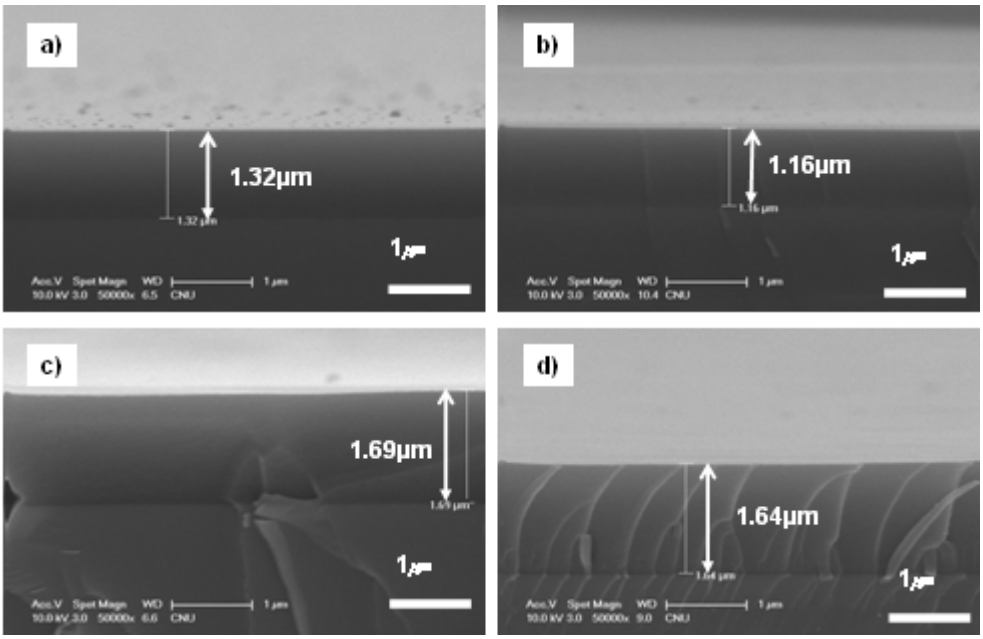

Figure 2s SEM images of the spin coated and pyrolysed film at 600 ℃ after UV curing at 365 nm and thermal curing at 160 °C for 12 hr: AHPCS derived film (a) only after UV and thermal curing, (b) after pyrolysis; AHPCS-Pt film (c) after UV and thermal curing, and (d) after pyrolysis

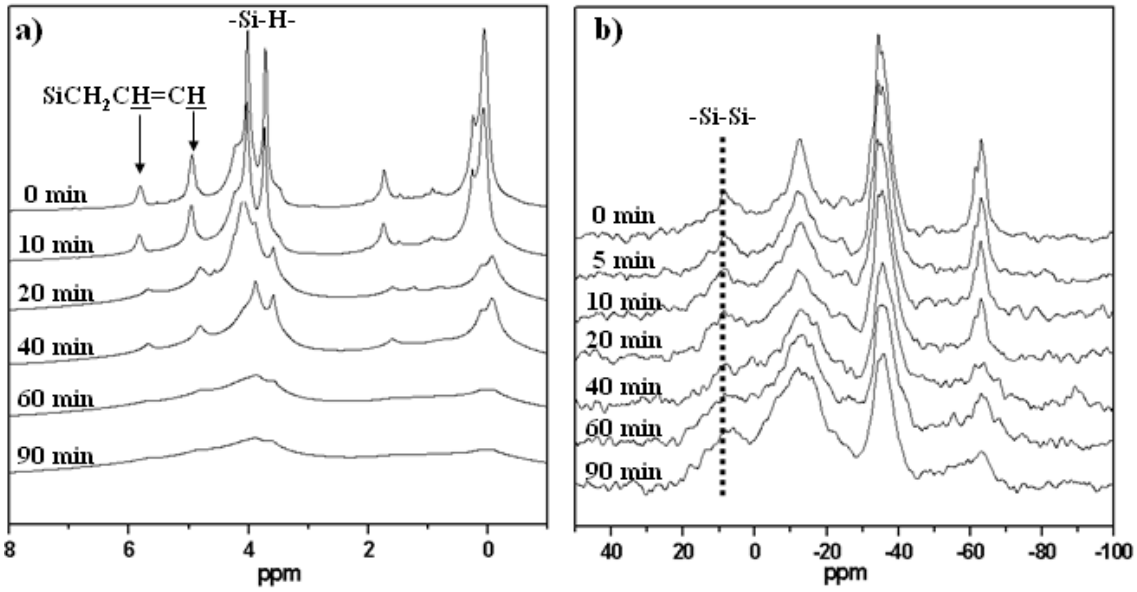

Figure 3s NMR spectra of the UV cured AHPCS-Pt samples at different exposure times: (a) ^{1}H-NMR; (b) ^{29}Si-NMR

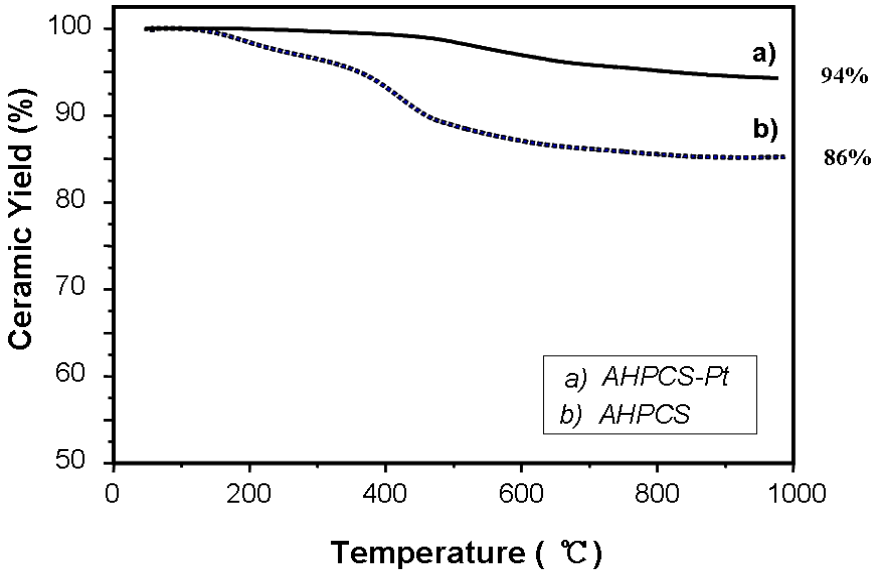

Figure 4s TGA analysis results showing the ceramic yield of (a) AHPCS-Pt and (b) AHPCS after UV curing 1 hr and thermal curing at 160 ºC for 12 hr in N_2

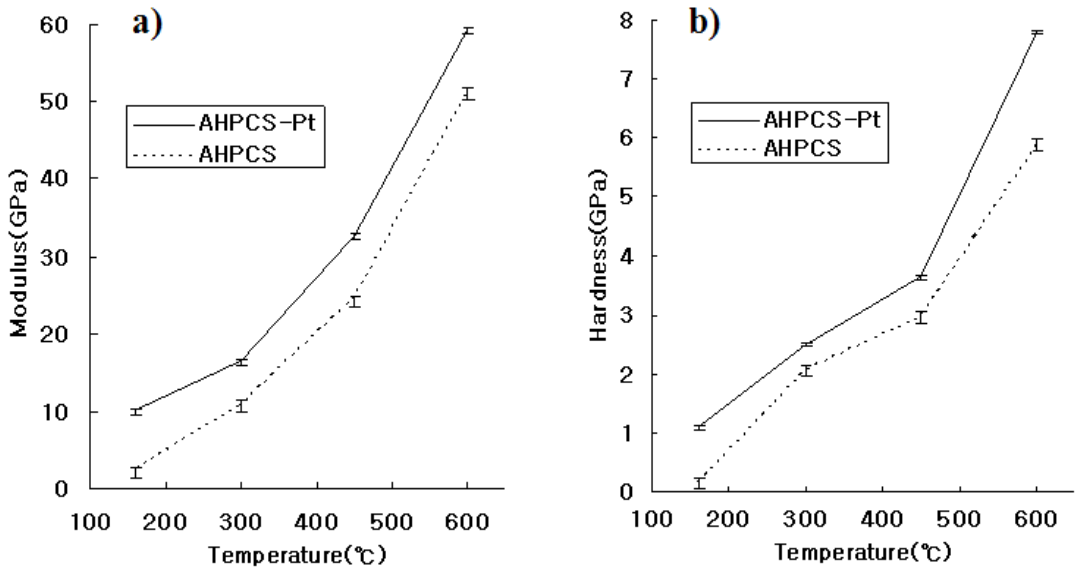

Figure 5s Mechanical strength of the spin-coated AHPCS-Pt and AHPCS films pyrolysed at different temperatures: (a) modulus; (b) hardness