

Supporting Information

Negative Thermal Expansion in Ultrathin Plasma Polymer Films

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The polymer films were deposited in custom built PECVD reactor described in detail elsewhere.¹ All the PECVD polymer films were deposited on freshly cleaned (100) silicon wafers. Argon (50-200 cm³/min, 99.999%), used as the noble gas for generating a plasma, flows into a 10-cm diameter reactor at 0.02-0.5 Torr vacuum through a capacitively coupled radio frequency (RF, 13.56 MHz) discharge of 45 W power. The plasma density is controlled to approximately 10⁸ cm⁻³ in the afterglow region. The precursor gas/vapor is added 10 cm downstream from the plasma generation zone. The substrate is located about 2 cm further downstream from the precursor inlet. The precursor flow rate of 1.125 cm³/min was employed during all the depositions.

Wet deposited ultrathin films of PS ($M_w = 250,000$ g/mol) were spin coated (3000 rpm) on a silicon substrate from 3% solution in toluene while PAN films ($M_w = 3,500$ g/mol) were spin coated from 2% solution in DMF. The spin-casting was carried out in class 100 clean room condition and the substrates were priority treated in piranha solution and rinsed thoroughly with nanopure water as typically employed in our lab.²

Chemical compositions of the plasma-polymerized films were identified through Fourier transform infrared (FTIR) analysis. FTIR was performed on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer in the transmission mode. A range of 400 to 4000 cm⁻¹ was scanned 128 times with 1 cm⁻¹ resolution and averaged.

The chemical structures of the monomers used as precursors for the plasma polymerization are shown Figure 1(a). FTIR analysis was used to identify the chemical composition of the polymer films under investigation. The FTIR spectra of the plasma polymer films of PAN, PTSA and PS are shown in Fig. 1. The FTIR of the PS (Fig. 1(b))

was characterized with aromatic ring stretching mode (1600 cm^{-1} and 1450 cm^{-1}), aliphatic C-H stretch mode (2930 cm^{-1}), C-H out of plane vibration (760 cm^{-1}) and ring out-of-plane deformation (690 cm^{-1}).³ However, it is interesting to note the absence of =C-H aromatic ring vibrations between $3000\text{--}3100\text{ cm}^{-1}$ which indicates that the double bonds of the phenyl ring underwent dissociation leading to a high cross-linking in the polymer. The PAN spectrum (Fig 1(c)) shows the characteristic $\text{C}\equiv\text{N}$ stretch at 2240 cm^{-1} corresponding to the cyano group. The spectrum also displays a strong C=N stretching mode at 1650 cm^{-1} and N-H stretching at 3300 cm^{-1} suggesting a high degree of cross linking in the polymer film. The spectrum displays other characteristic bands such as $\text{-CH}_2\text{-}$ stretch (2920 cm^{-1}), C-C stretch and C-H bending (1450 cm^{-1}). The FTIR spectrum obtained from PTSA (Fig 2(d)) shows the representative $\text{-Si-(CH}_3)_3\text{-}$ band ($770\text{--}860\text{ cm}^{-1}$), $\text{-Si-CH}_2\text{R-}$ group (1250 cm^{-1}), cyano group (2220 cm^{-1}) and CH_3 stretch (2960 cm^{-1}). The interesting aspect is the presence of a strong band at 1050 cm^{-1} which corresponds to C-N indicating the cyano group dissociation causing a highly crosslinked network. A relatively weak band corresponding to C=N stretch (1650 cm^{-1}) also indicates cross linking of the polymer. Several other weak bands correspond to the small amount of oxygen impurity, the presence of which is confirmed with XPS (not shown here).

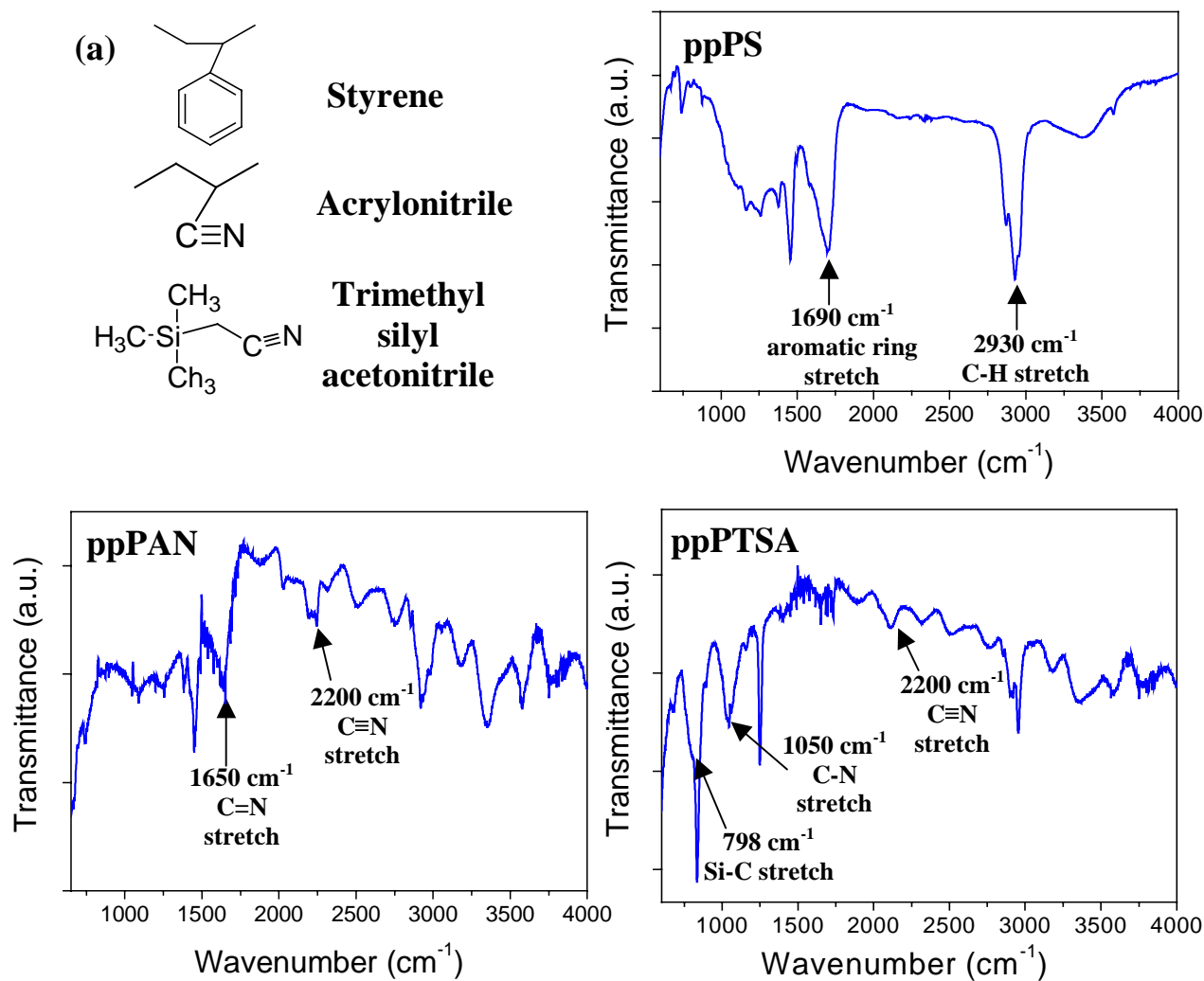
The surface morphology of polymer films was studied in the light tapping mode in the range of magnifications (from 1×1 to $30\times 30\text{ }\mu\text{m}$) with a Dimension 3000 Atomic Force Microscope (AFM) according to the procedure adapted in our lab.⁴ AFM scratch test was used as an independent technique to confirm the thickness of the polymer films obtained from the ellipsometry with the refractive indices from independent measurements.⁵ The thickness of the polymers films at various temperatures was measured using COMPEL automatic ellipsometer (InOmTech, Inc.) equipped with a He-Ne laser with collimated beam of 1 mm diameter. The thickness at different temperatures was computed using a two layer model (polymer film on 1.4 nm SiO_2 layer). The refractive indices of the polymer films used for computing thickness were obtained using Woollam variable-angle spectroscopic ellipsometer system including a VB-200 ellipsometer control module and a CVI Instruments DigiKrom 242 monochromator with a 75-W xenon light source. The reflected polarization states were acquired over the

range of 300-900 nm at 1-nm intervals and at angles of incidence equal to 53°, 55°, and 57°.

Selected AFM images of the polymer films obtained under different conditions are shown in Fig 2. The plasma polymerized (ppX) polymer films exhibited a well-developed grainy surface morphology compared to the much smoother spin deposited counterparts.

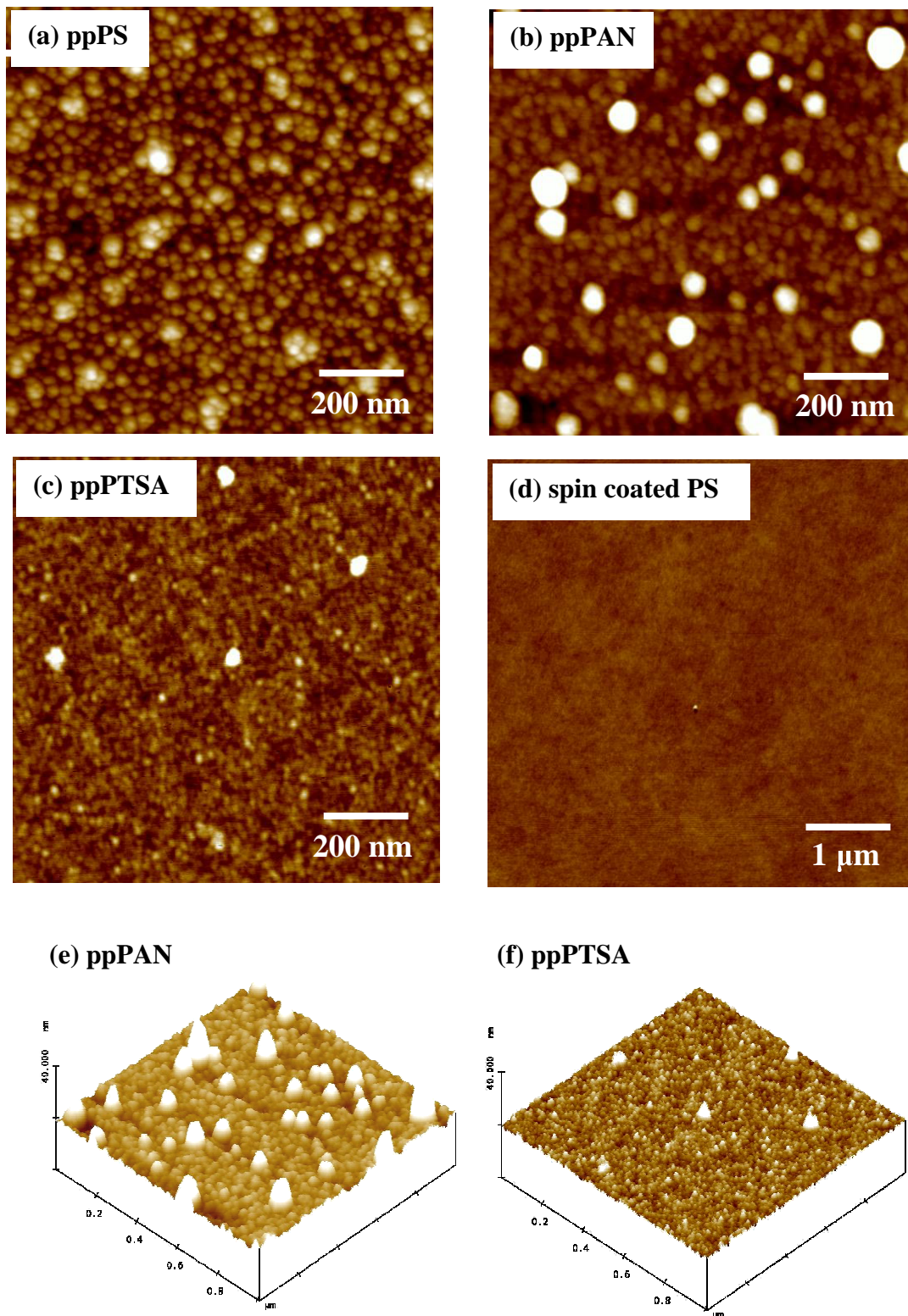
To study thermal expansion the samples were heated using a Nanoscope heater (DI) and the sample temperature was controlled with a precision of ± 0.1 K. The sample located directly on the ellipsometry stage was held for 10 min at each temperature and the thickness recorded. The heating-cooling cycles (each about 6 hrs long) were repeated 3-4 times. Prior to the thermal expansion measurements the polymer films were annealed at 50° C under vacuum for 15 hours to remove a residual solvent and allow stress relaxation.

Figure 1: (a) Chemical structures of various monomers under study. FTIR spectra of pp



PAN, pp PS and pp PTSA showing the characteristic bands.

Figure 2: AFM images showing the surface morphology of pp PS (a), pp PAN (b), pp PTSA (c), spin coated PS (d), 3-D ppPAN (e), and ppPTSA (f) The z range is 10nm for image (a) and (d), and 5 nm for images (b) and (c).



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