

Negative Thermal Expansion in Ultrathin Plasma Polymerized Films

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Because of the increasing applications of polymer films with nanoscale thickness, it is imperative to fully characterize the physical properties in these films, which could be significantly different from the bulk properties due to the surface and interfacial effects. Interactions with the substrate and high specific surface area (film/air and film/substrate) can cause peculiar properties of the ultrathin polymer films.^{1–8} In a recent study, the glass transition of a free-standing and supported PS film was found to vary significantly with thickness.^{9,10} Other studies have unveiled several interesting phenomena such as the depth-dependent glass-transition temperature and thickness-dependent thermal expansion.^{11–16} It has been reported that substrate interactions alter the thermal properties of ultrathin poly-(2)-vinylpyridine films.¹⁷ A non-monotonic thermal behavior was observed in ultrathin polycarbonate films with a negative and positive thermal expansion below and above the glass-transition temperature respectively.¹⁸

Properties of ultrathin polymer films strongly depend on the fabrication routines. Plasma-enhanced chemical vapor deposition (PECVD) is one of the popular fabrication techniques that is a solventless (dry) process, resulting in organic films with high solvent, scratch, and corrosion resistance and excellent thermal and chemical stability.¹⁹ Plasma polymerization allows the deposition of ultrathin polymer films compatible with lithographic fabrication methods, finding applications in sensing devices, MEMS, optical devices,^{20–23} and nanoscale photonics,^{22,24} or as biocompatible interfaces.²⁵ The chemical reactions during the plasma polymerization are significantly different from those observed in conventional polymerizations.^{19,26} Excited organic species, free radicals, and ions react with each other to produce high-molecular-weight and highly crosslinked chains. The technique offers a unique advantage of the ability to polymerize almost any organic molecule, some of which are impossible otherwise. Because of the fragmentation of the chains and irregular crosslinking, plasma polymers could display very intriguing and novel physical properties.²⁷ An additional aspect of plasma polymers is that when deposited as thin films, they inevitably possess residual stresses due to their growth mechanisms that can significantly alter their physical behavior.^{28,29}

In this communication, we report on the unusual thermal behavior of ultrathin plasma-polymerized polymer films on silicon wafers. Remarkably, a large, reversible negative thermal expansion of plasma polymerized polyacrylonitrile (ppPAN) and polytrimethyl silyl acetonitrile (ppPTSA) in the normal direction was observed and related to the thermally induced stress release of a grainy microstructure. We compare this to the behavior of conventional spin-cast films as well as that of polystyrene (PS) spin-cast and plasma films.

The chemical structures of the monomers used as precursors for the plasma polymerization are shown in Table 1. The polymer films were deposited by the PECVD technique in a custom built PECVD reactor and thoroughly characterized with FTIR, AFM, and XPS according to the procedures described in detail elsewhere (see the Supporting Information

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

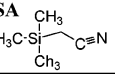
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Table 1. Thermal Characteristics of Nanoscale Polymer Films^a

Polymer	Ultrathin films from present study							Bulk films (obtained from literature)
	Plasma polymerized				Spin-cast			
	α (K^{-1}) 10^{-4}	t (nm)	R (nm)	C (deg)	α (K^{-1}) 10^{-4}	t (nm)	R (nm)	α (K^{-1}) 10^{-4}
PS 	1.9	148	1.5	69	1.7	169	0.25	0.8–2.8 ^b [Ref. 11,43]
PAN 	-3.1	95	1.7	55	1.6	20	0.20	1.0 [Ref. 44]
PTSA 	-2.5	97	0.5	75	NA ^c	-	-	-

^a α , Linear thermal expansion coefficient below T_g ; t , thickness; R , rms roughness over $1 \times 1 \mu\text{m}^2$ area; C , contact angle. ^b Thickness dependent. ^c Cannot be polymerized by conventional techniques.

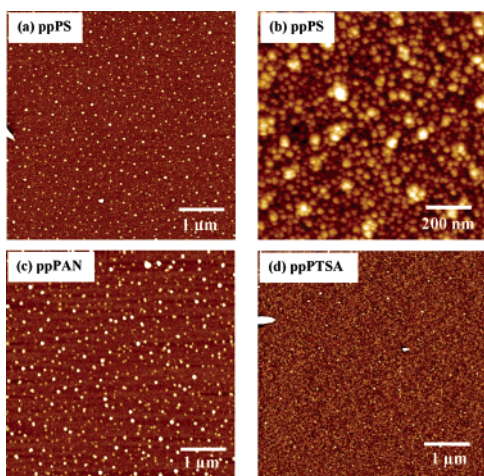


Figure 1. AFM images showing the surface morphology of (a,b) pp PS, (c) pp PAN, and (d) pp PTSA. The z range is 20 nm for all images.

for technical details).^{22,30–33} (Table 1). All the PECVD polymer films were deposited on freshly cleaned (100) silicon wafers within an argon (99.999%) atmosphere. FTIR was used to confirm the chemical composition of the polymer films and their cross-linked structure.³⁴ Thermal expansion of the polymer films was studied by measuring the thickness of the films in the course of heating and cooling using ellipsometry, and the thickness value was independently confirmed by AFM.

AFM images of the polymer films are shown in Figure 1 (see additional data in the Supporting Information). The plasma-polymerized films exhibited a well-developed grainy surface morphology with grain sizes below 100 nm as compared to the smooth surfaces of spin-cast films with no specific features (see the Supporting Information). The rms surface microroughness was found to be 1.5 and 1.7 nm for pp PS and ppPAN, respectively, with ppPTSA displaying the lower microroughness at 0.5 nm. In all cases, the microroughness of plasma-polymerized films is much higher than that observed for spin-cast films (around 0.2 nm; Table

1). A contact angle within 55–75° corresponds to modestly hydrophilic surfaces, which is well below that expected for bulk polymers (e.g., 90° for PS) and indicated the presence of polar groups at the surface that could be generated by post-plasma reaction with ambient.

Thermal expansion of spin-cast PS films is plotted for second and third thermal cycles (each cycle was acquired within 6–8 h) in Figure 2a. In all the experiments, the first heating and cooling cycles were disregarded to eliminate preparation pre-history. The thermal expansion coefficient was found to be $(1.7 \pm 0.3) \times 10^{-4} \text{ K}^{-1}$ for spin-cast PS film and $(1.9 \pm 0.3) \times 10^{-4} \text{ K}^{-1}$ for ppPS, which is within a conventional range of values (Table 1). Thermal expansion of the spin-cast PAN with a thickness of 20.5 nm is also linear with a thermal expansion coefficient of $1.6 \times 10^{-4} \text{ K}^{-1}$, which is slightly higher than but close to that for the bulk film (Figure 2c, Table 1).

However, the plasma-polymerized polymers exhibited a significantly nonlinear variation of thickness with temperature when cooled (Figure 2b,d,e). The final thickness was 0.3–0.5 nm higher than the initial thickness immediately after cooling (for the sake of clarity, cycle 3 was normalized to the same elevated temperature thickness as that in Figure 2b,d,e). However, the film restored to original thickness after a long relaxation time (~ 8 h). This behavior was observed for all the plasma-polymerized films, whereas the spin-cast films exhibited no such hysteresis. We suggest that the observed hysteresis followed by relaxation might be due to the stresses that developed in the polymer during the deposition process. In fact, a hysteresis behavior of residual stresses in plasma-deposited thin films during thermal cycling was previously reported and attributed to different rates of relaxation.^{35–37}

Moreover, the thermal behavior of two plasma-polymerized films was absolutely uncharacteristic for conventional polymers. In both cases, we have observed thermal contraction of the film in the vertical direction during heating (Figure 2d, e). Furthermore, this negative thermal expansion was found to be reversible, with some hysteresis followed by

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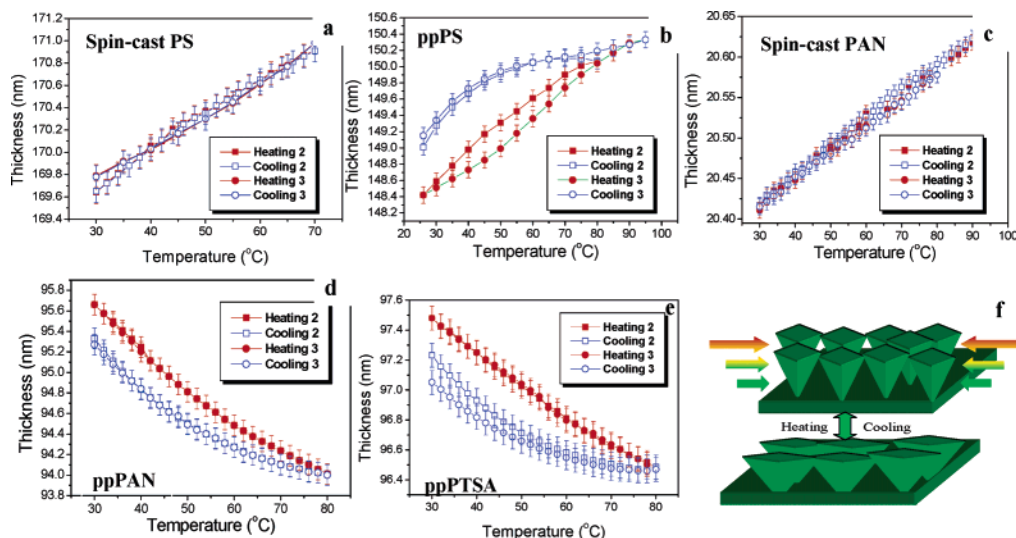


Figure 2. (a–e) Film thickness vs temperature for plasma-polymerized and spin-coated polymer films for second and third heating and cooling cycles and (f) schematics of the plasma polymer film with the wedge-shaped morphology undergoing a stress release with heating that causes lateral expansion and normal contraction of the wedges.

relaxation as discussed above for ppPS. The thermal expansion coefficient calculated from the linear portion below 50 °C was $(-3.1 \pm 0.2) \times 10^{-4} \text{ K}^{-1}$ for ppPAN and $(-2.5 \pm 0.2) \times 10^{-4} \text{ K}^{-1}$ for ppPTSA (Table 1).

This unusual negative thermal expansion (NTE) behavior is suggested to be caused by the presence of high residual stress in the polymer film, which is common for plasma-polymerized materials combined with developed grainy surface morphology as depicted in Figure 2f. The high in-plane compressive stress common for plasma-polymerized polymers might originate from their specific, wedge-type growth.^{38,39} The residual stresses arise because of the wedging effect during the deposition process, where the high-energy fragments wedge in the existing film. In fact, for some plasma-polymerized polymers, we estimated in-plane compressive stress to be as high as 50 MPa, which is close to/exceeds the yield strength of polymeric materials.²⁰ Figure 2f shows a schematic representation of the plasma polymer films with wedge-shaped individual grains in highly compressive state. An increase in the temperature causes these polymer grains to expand laterally with a simultaneous vertical contraction of the entire film. It is worth noting that although the residual stresses occur for all the plasma-polymerized polymers, the NTE phenomenon was only for ppPAN and ppPTSA. The actual cause for this remains uncovered, but we should note that both the NTE polymers possess a $\text{C}\equiv\text{N}$ group that should lead to a higher degree of cross-linking and different topology in comparison with ppPS.

In fact, NTE has been previously observed in some special cases, e.g., along the chain direction for fully aligned linear polyethylene chains.⁴⁰ A different effect exhibited by thermal stresses and elasticity in the negative axial thermal expansion of isotactic polypropylene has been discussed.⁴¹ Recently, it has been proposed that a decrease in the entropy associated

with expansion in some systems makes thermal contraction thermodynamically favorable.³⁵ However, the nature of NTE in amorphous polymer films studied here should be very different and similar to the case of high stresses comparable to the yield stress, which significantly alters the thermal expansion behavior of the polymer films.⁴²

The negative thermal expansion phenomenon in nanoscale polymer films may find applications in technologies requiring nanocoatings with zero thermal expansion. Harnessing these residual stresses either by refining the deposition procedures or by freezing in the nonequilibrium state will be a key issue. By designing composite materials comprising elements with negative thermal expansions, we could eliminate effective temperature variations in the nanocomposite materials. These materials can find interesting applications in microelectronic and optical devices as a means of controlling and compensating the conventional materials' thermal expansion.

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Supporting Information Available: Detailed experimental methods, FITR spectra of the polymers, additional AFM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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