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**NEGATIVE THERMAL EXPANSION IN ULTRATHIN
PLASMA POLYMERIZED FILMS (PREPRINT)**

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14. ABSTRACT Owing to 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. In a recent study the glass transition of a free standing and supported PS film was found to vary significantly with thickness. Other studies have unveiled several interesting phenomena such as the depth dependent glass transition temperature and thickness dependent thermal expansion. It has been reported that substrate interactions alter the thermal properties of ultrathin poly-(2)-vinylpyridine films. A non monotonic thermal behavior was observed in ultrathin polycarbonate films with a negative and positive thermal expansion below and above glass transition temperature, respectively.					
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Negative Thermal Expansion in Ultrathin Plasma Polymerized Films

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Owing to 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.^{1,2,3,4,5,6,7,8} 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.^{11,12,13,14,15,16} 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 glass transition temperature respectively.¹⁸

Properties of ultrathin polymer films strongly depend upon the fabrication routines. Plasma Enhanced Chemical Vapor Deposition (PECVD) is one of the popular fabrication techniques which is a solvent less (dry) process that results in organic films with high solvent, scratch, and corrosion resistance, and excellent thermal and chemical stability.¹⁹ Plasma polymerization allows the deposition of ultra thin polymers films compatible with lithographic fabrication methods, finding applications in sensing devices, MEMS, and

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optical devices,^{20,21,22,23} 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. Due to the fragmentation of the chains and irregular crosslinking, plasma polymers could display very intriguing 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 which 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 thermally induced stress release of grainy microstructure. We compare this behavior of conventional spin-cast films as well as to 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 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 Supporting Information for technical details).^{22,30,31,32,33} (Table 1). All the PECVD polymer films were deposited on freshly cleaned (100) silicon wafers within argon (99.999%) atmosphere. FTIR was used to confirm the chemical composition of the polymer films and their crosslinked 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 Fig 2 (see additional data in SI). The plasma polymerized films exhibited a well-developed grainy surface morphology with

grain sized below 100 nm as compared to the smooth surfaces of spin-cast films with no specific features (SI). 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). 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 which 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 hours) in Fig 3(a). In all the experiments the first heating and cooling cycle 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 $1.6 \times 10^{-4} \text{ K}^{-1}$ which is slightly higher but close to that for the bulk film (Figure 3c, Table 1).

However, all the plasma polymerized polymers exhibited a significantly non-linear variation of thickness with temperature while cooled (Figure 3b,d,e). The final thickness was 0.3-0.5 nm higher than the initial immediately after cooling (for the sake of clarity cycle 3 was normalized to the same elevated temperature thickness in Figure 3b,d,e). However, the film restored to original thickness after long relaxation time (~ 8 hours). This behavior was observed for all the plasma polymerized films while the spin-cast films exhibited no such hysteresis. We suggest that the observed hysteresis followed by relaxation might be due to the stresses 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 accounted to different rates of relaxation.^{35,36,37}

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 vertical direction during heating (Figures 3d, e). Furthermore, this negative thermal expansion was found to be reversible with some hysteresis followed by relaxation as discussed above for ppPS. The thermal expansion coefficient calculated from 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 high residual stress in the polymer film common for plasma polymerized materials combined with developed grainy surface morphology as depicted in Figure 3f. The high in-plane compressive strength common for plasma polymerized polymers might originate from specific, wedge-type of their growth.^{38,39} The residual stresses arise due to 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/exceeds yield strength of polymeric materials.²⁰ Figure 2(f) shows a schematic representation of the plasma polymer films with wedge-shaped individual grains in highly compressive state. Increase in the temperature causes these polymer grains to expand laterally with a simultaneous vertical contraction of the entire film. It is worth to note 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 C \equiv N group which should lead to a higher degree of crosslinking and different topology in comparison with ppPS.

In fact, NTE has been previously observed in some special cases. E.g., NTE was reported 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 non-equilibrium state will be a key issue. By designing composite materials comprising of elements with negative thermal expansions, effective temperature variations in the nanocomposite materials could be eliminated. These materials can find interesting applications in microelectronic and optical devices as means to control and compensate the conventional materials thermal expansion.

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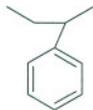
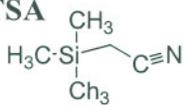
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Figure captions

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

Figure 2: Film thickness vs temperature for plasma polymerized and spin coated polymer films for 2nd and 3rd heating and cooling cycles (a-e) and schematics of the plasma polymer film with the wedge-shaped morphology undergoing a stress release with heating which causes lateral expansion and normal contraction of the wedges. (f).

Table1. Thermal characteristics of nanoscale polymer films

Polymer	Ultrathin films from present study							Bulk films (obtained from literature)
	Plasma polymerized				Spin-cast			
	α (K ⁻¹) 10 ⁻⁴	<i>t</i> (nm)	<i>R</i> (nm)	<i>C</i> (deg)	α (K ⁻¹) 10 ⁻⁴	<i>t</i> (nm)	<i>R</i> (nm)	
PS 	1.9	148	1.5	69	1.7	169	0.25	0.8-2.8 * [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 **	-	-	-

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; * Thickness dependent

** Cannot be polymerized by conventional techniques

Figure 1

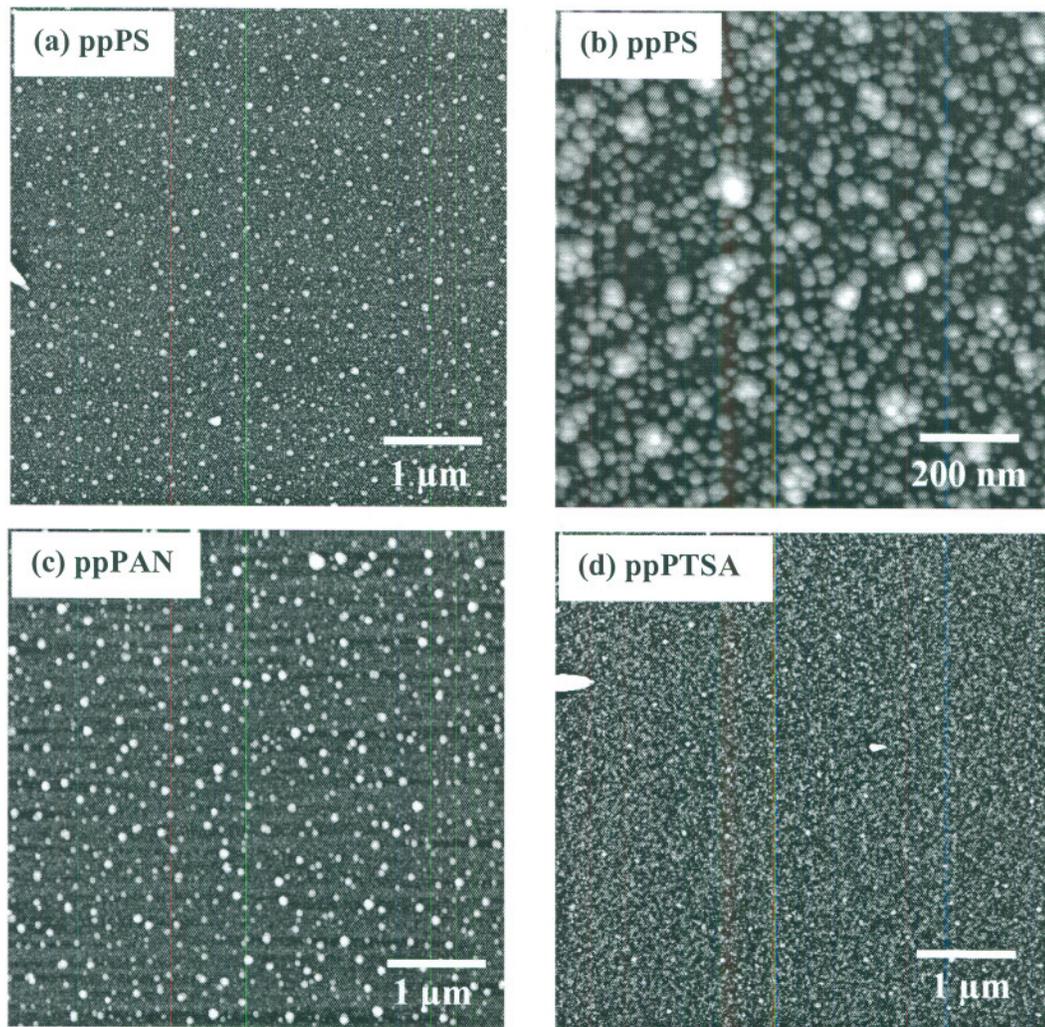
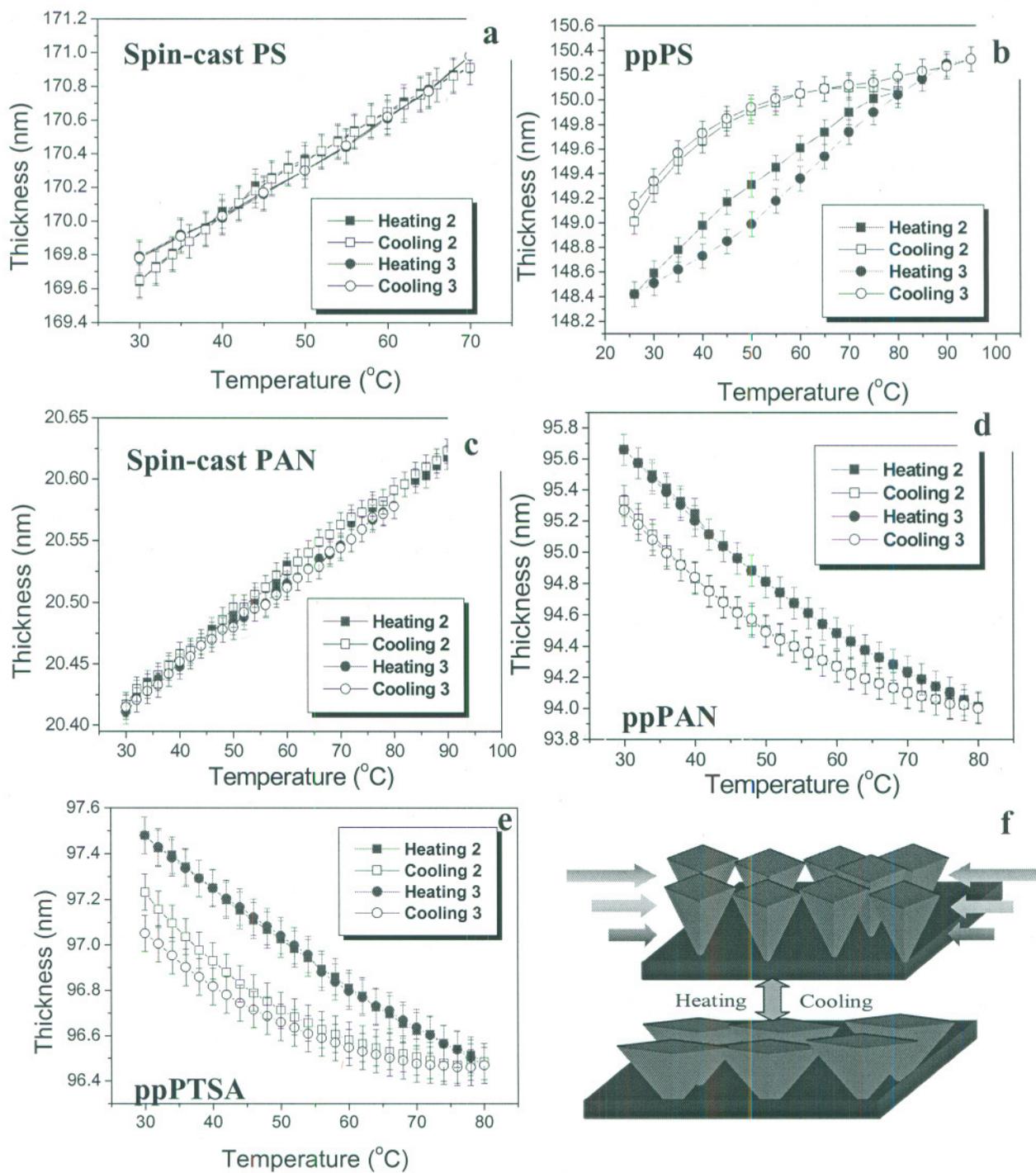


Figure 2



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TOC:

An intriguing large negative thermal expansion behavior was observed in ultrathin plasma polymer films. The thermal expansion of plasma polymerized films exhibited a profound hysteresis between the heating and cooling cycles. The surprising thermal behavior was explained as a consequence of high residual stresses caused by the “wedging” phenomenon.

