

Titania Deposition on PMR-15

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Received November 22, 2004. Revised Manuscript Received March 19, 2005

The formation, degree of crystallinity, and adherence of dense titania (TiO₂) thin film coatings on a high-temperature polyimide resin (PMR-15) can be influenced by the chemical composition of the polymer surface. Furthermore, solution deposition conditions can be adjusted to provide additional control over the morphology and crystallinity of the titania films. Recipes for solution-based titania deposition that used a slowly hydrolyzing titanium fluoride salt in the presence of boric acid as a fluoride scavenger allowed growth of films up to 750 nm thick in 22 h. By adjusting solution pH and temperature, either amorphous titania or oriented crystalline anatase films could be formed. Surface sulfonate groups enhance the adhesion of solution-deposited oxide thin film coatings. While most sulfonation procedures severely damaged the PMR-15 surface, the use of chlorosulfonic acid followed by hydrolysis of the installed chlorosulfonyl groups provided effective surface sulfonation without significant surface damage. In some cases, the oxide deposition solution caused partial hydrolysis of the polymer surface, which itself was sufficient to allow adhesion of the titania film through chelation of titanium ions by exposed benzoic acid groups on the polymer surface.

Introduction

High-performance polymers and polymer–matrix composites (PMCs) are finding increasing use in demanding applications,¹ in part as metal replacements. Polyimide-based PMCs (typically with graphite fiber reinforcement) are thus far the most promising candidates. In general, the thermal-oxidative stability (TOS) of the resin limits the high-temperature performance of the PMC. Good polymers for high-temperature applications, combining TOS, processibility, and good mechanical properties, are PMR (polymerization of monomer reactant) polyimides.^{2–5} PMCs are attractive materials for various structural applications because of their high strength-to-weight ratio. Unfortunately, PMCs are limited to applications which avoid prolonged exposure to oxidizing atmospheres at temperatures > 300 °C because surface oxidation leads to weight loss and degradation of mechanical properties.

A promising approach to improve PMC performance is the use of inorganic barrier coatings which physically block the interaction of oxygen and oxy-radicals with the polymer surface. The effectiveness and life of the coatings depend on the inherent properties of the coating material (thermal stability, compactness, and uniformity) as well as the interaction between the coating and the PMC. Hard-coated PMCs can also show improved abrasion resistance.^{6,7}

Progress in the deposition of ceramic thin films has been made possible by advances in film deposition technology, involving chemical vapor deposition, sputtering, laser ablation, and evaporation.⁸ However, these techniques have significant shortcomings. Capital equipment cost can be prohibitively high, especially for large-area applications, and considerable art is associated with the design of the deposition systems and with controlling the operating parameters. The most common techniques still involve line-of-sight deposition, making them applicable only to simple surfaces and shapes. Most importantly, temperatures above 400 °C (i.e. where organic polymers will not survive) are usually required to convert the as-deposited material into well-ordered crystalline films. Sol–gel techniques, which have

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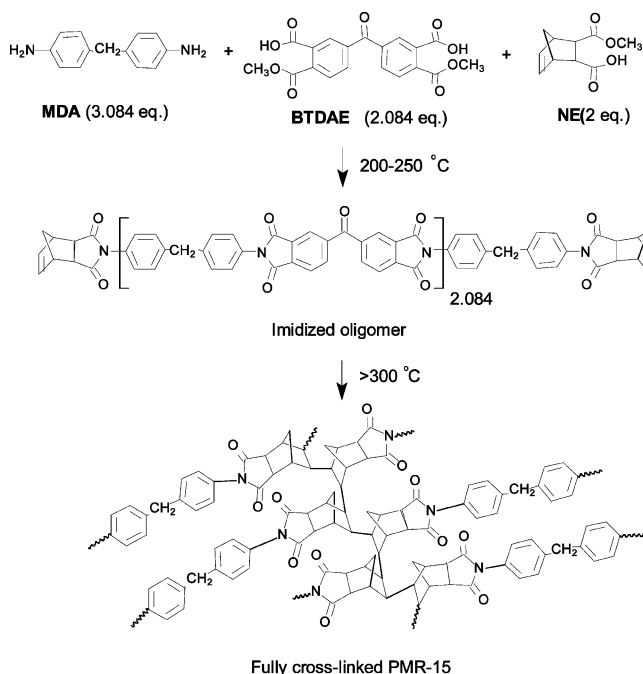
also undergone extensive development in the past 3 decades, are typically subject to similar high-temperature requirements. These significantly limit existing film-synthesis technologies for many metal and polymeric substrates.⁹

Liquid-phase deposition (LPD) is an aqueous technique for deposition of oxide films that has been widely used for silica¹⁰ but is being increasingly used to form films of other oxides such as titania.^{11–16} The distinguishing characteristic of LPD is the use of a solution of metal–fluoride complexes whose hydrolysis in water is modulated by adding boric acid (H₃BO₃) or aluminum metal. The fluoride ligand provides for a slower and more controllable hydrolysis, while the boric acid or the aluminum function as F[−] scavengers.¹⁷ Most of the LPD work has been done on silanol-bearing surfaces (silicon wafers and glass).

LPD from aqueous solution, under mild conditions of temperature (≤55 °C) and pH (2.88–3.88), can produce thin (0.1–1.0 μm), adherent, titania films. We have studied LPD titania films deposited on silicon wafers and on variously sulfonated surfaces.¹⁸ The growth rate and crystallinity of these films could be controlled by careful manipulation of solution parameters and surface functionality of the substrate. For example, room-temperature deposition¹⁹ from 0.3 M H₃BO₃ and 0.1 M (NH₄)₂TiF₆ with an initial pH of 3.88 (method 1) gave amorphous films that adhered well to silicon wafers but not to sulfonated surfaces. Alternatively, deposition¹⁴ at 50 °C from a solution of 0.15 M H₃BO₃ and 0.05 M (NH₄)₂TiF₆, at an initial pH of 2.88 (method 2) produced oriented anatase films at a faster growth rate but with poor adherence to silicon substrates and excellent adherence to sulfonated surfaces.

Applying LPD to polymer substrates, Dutschke et al.^{20,21} deposited titania via LPD (method 2) on variously treated polystyrene (PS). Continuous, adherent anatase films form on PS either after hydroxylation in aqueous sodium peroxodisulfate or after surface grafting with 2-(acrylamido)-2-methylpropane-1-sulfonic acid (AMPS). Nonadherent but continuous films deposit on untreated PS under identical conditions. Continuous films are not observed on polystyrene etched by sulfuric acid or SO₃ gas. On polyamide microcapsules, LPD (method 2) yielded continuous anatase coat-

Scheme 1. Preparation and Structure of PMR-15 Polyimide Resin



ings which after heat treatment at 600 °C were 200 nm thick.²²

Herein we further explore the influence of polymer surface chemistry on LPD film deposition. Polymer substrates provide an organic matrix, and our surface chemistry will attach directly to the polymer backbone. The polymer substrate chosen for this work is PMR-15, a cross-linked polyimide based on the condensation of three monomer reactants: 2-carbomethoxy-3-carboxy-5-norbornene (the monomethyl ester of nadic diacid, NE, nadic-end-capped), 4,4'-methylenedianiline (MDA), and the diacid diester of benzophenone-3,4,3',4'-tetracarboxylic 3,4:3'4'-dianhydride (BTDA). These components and an idealized picture of their oligomer formation (other dimeric and oligomeric structures likely exist as well) are shown in Scheme 1.²³

PMR-15 surfaces were initially treated using various sulfonation procedures, after which titania films were deposited using the two LPD recipes described above. For combinations that led to adherent films, the thickness, morphology, and crystallinity of the films were characterized. The interplay of the surface chemistry of the polymer and the deposition solution conditions are a focus of this work. This study opens new possibilities for the application of such ceramic layers to polymer substrates as thermooxidative and/or abrasion barriers.

Experimental Procedure

A. Chemicals. Fuming sulfuric acid (65%) (oleum) was obtained from Merck. Other chemicals were obtained from Aldrich.

B. Equipment. Solution pH was measured using a Metrohm model 691 pH meter. X-ray photoelectron spectroscopy (XPS)

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Table 1. Film Thickness Obtained by LPD Method 2 (0.15 M Boric Acid, 0.05 M (NH₄)₂TiF₆, pH Adjusted to 2.88, 50 °C) on Various Treated PMR-15 Substrates, As Determined Using RBS Calibrated against Cross-Sectional TEM^a

surface type	4 h deposition		22 h deposition	
	thickness ± roughness (nm)	composition	thickness ± roughness (nm)	composition
untreated PMR-15	230 ± 300	Ti, O (2.0), F (0.4)	520 ± 200	Ti, O (2.5)
untreated PMR-15 (duplicate run)			630 ± 300	Ti, O (3.0)
chlorosulfonic acid treated	230 ± 400	Ti, O (2.0), F (0.4)	660 ± 300	Ti, O (2.9)
chlorosulfonic acid treated (duplicate run)			690 ± 300	Ti, O (3.0)

^a Values for “thickness ± roughness” of, e.g., 230 ± 300 nm indicates a film that was at least 230 nm thick but whose point-to-point thickness variation can be 300 nm large.

analyses were done on a Kratos AXIS-HX spectrometer with a monochromatic Al X-ray source, at 75 W. Due to the nonconducting nature of the samples, an electron flood gun was used for charge neutralization. All spectra were calibrated versus C 1s = 286.6 eV (for the main peak). Energy-dispersive X-ray analyses (EDAX) were recorded on a JEOL JSM-B40 microscope. EDAX data acquisition and analysis were performed using Link ISIS (Oxford) software. Grazing incidence X-ray diffraction (XRD) analysis at 0.5 and 1° incidence was done on a SCINTAG XI advanced diffraction system composed of a 40 kV ultrastable generator, a 1.8 kW X-ray tube (Cu target), and a θ - θ wide angle goniometer. The system is also equipped with a thin-film grazing-angle collimation attachment. A Bruker D8 ADVANCE X-ray diffractometer in grazing-angle mode equipped with a GÖBEL mirror was also used. A Philips CM-20 analytical transmission electron microscope (TEM) equipped with a high-purity intrinsic Ge Noran EDAX detector and a JEOL 4000-EX high-resolution electron microscope operating at 400 keV were used for TEM analysis. Cross-sectional thin foils for TEM analysis were made by cutting the polyimide substrates bearing the titania films in half and gluing the titania-coated faces together using epoxy resin. The thickness of the specimens was reduced to less than 25 μ m by hand-polishing. The samples were then mounted on a 3 mm copper grid and further thinned via conventional ion-thinning using a Gatan PIPS ion thinner. Tape tests for film adhesion were performed using carbon tape, which was analyzed by EDAX before and after the test.

The chemical compositions and thicknesses of the films were measured using Rutherford backscattering spectroscopy (RBS) with 2 MeV α particles from an NEC 5SDH ion beam accelerator. The backscattered α particle spectra were detected with a silicon surface barrier detector and analyzed with RUMP software. Thickness values obtained from RBS analysis were calibrated as follows. For one specimen, thickness was measured using cross-sectional TEM. (See Results.) This value of thickness was used as input in the RBS analysis of that specimen to obtain values for atomic density of Ti and O. These values were then used as input in RBS analysis of all other specimens to obtain values of film thickness. Film roughness was estimated from the RBS data as described previously.¹⁸ The results are presented (Table 1) as [thickness] ± [roughness] in nanometers. In the cases where titania films were deposited on surface-modified silicon wafers, oxide thickness was measured by ellipsometry as previously described.¹⁸

C. Substrate Preparation. Silicon wafer substrates with sulfonic and benzoic acid self-assembled monolayers (SAMs) on silicon wafers were used as models for the work on polyimides. The sulfonic acid SAMs were prepared and characterized as previously described.²⁴ Details on the preparation and characterization of the benzoic acid SAM are reported elsewhere.^{25,26} They involve

preparing Cl₃Si-(CH₂)₁₁-O-Ph-COOCH₃ and depositing it on clean silicon wafers. In-situ conversion of the methyl ester to the free acid used AlI₃.^{25,27} The free benzoic acid monolayer data are as follows: contact angles, 56° advancing and 43° receding; IR data (ATR) CH₂antisym = 2923 cm⁻¹, CH₂sym = 2852 cm⁻¹, C=O = 1686 cm⁻¹ (protonated), C=O = 1536 cm⁻¹ (nonprotonated).

PMR-15 resin coupons were prepared by published procedures.²⁸ They were cut to the desired size and polished using 0.05 μ m aluminum oxide powder (BDH). They were then washed and sonicated twice in water, rinsed with ethanol, and dried under a filtered nitrogen flow. PMR-15 samples for XPS were gently abraded with the edge of a glass microscope slide to remove the upper layers.

D. Surface Activation of the PMR-15. (D.1) *Sulfonation by Oleum.* PMR-15 coupons were dipped into oleum solution (fuming sulfuric acid) for times up to 30 min. The samples were then rinsed with water until the wash water was neutral. Samples were stored under distilled water until use.

(D.2) *Sulfonation by SO₃ Gas.* PMR-15 coupons were held (using Teflon tweezers) for 45–120 s over an open bottle of oleum into which there was a slow bleed of dry nitrogen to increase the outflow of SO₃ gas. The sample was then washed and stored as above.

(D.3) *Sulfonation by Chlorosulfonic Acid.*²⁹ PMR-15 coupons were immersed for 30–60 s into a freshly prepared solution of 30% chlorosulfonic acid in concentrated sulfuric acid. They were rinsed with water and then soaked in water for 48 h to ensure full hydrolysis of the sulfonyl chloride to sulfonic acid. The sample was then washed and stored as above. Note: All three of the above sulfonation methods gave PMR coupons that were completely wetted by water, though water uptake into the polymer was not quantified. EDAX measurements were used to determine the level of incorporated sulfur.

E. Titania Deposition Procedures. (E.1) *LPD Using TiF₄ (Method 1).*¹¹ The procedure involves immersing a sample (vertically) into 0.3 M H₃BO₃ and 0.1 M (NH₄)₂TiF₆ solution kept at room temperature. Substrates were left in the solution for 4–48 h, after which they were washed with water and blown dry with filtered nitrogen.

(E.2) *LPD Using TiF₄ with Added HCl*¹⁴ (Method 2). The procedure involves immersing (vertically) a sample (either a silicon wafer or PMR-15 resin) into a 0.15 M H₃BO₃ and 0.05 M (NH₄)₂TiF₆ solution. HCl was added to adjust the pH to 2.88, and the solution was kept at 50 °C. Substrates were left in the solution for 4–22 h, after which they were washed with water and blown dry with filtered nitrogen.

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Results

A. Surface Activation of the PMR-15. Previous work using SAM templates^{18,30–32} suggested that sulfonate groups can be effective in initiating and sustaining the growth of an oxide thin film. Working on a polymeric substrate, we wanted to use sulfonation chemistry that would work directly on the surface of the polymer. We surmised that since the aromatic rings of MDA (Scheme 1) and the imides it produces are activated toward electrophilic aromatic substitution, we could use them to attach sulfonate groups directly onto the surface.

We sought a sulfonation method that would be convenient and provide maximum surface sulfonation with minimum surface damage. We investigated three approaches: (1) dipping the polymer into oleum for times up to 30 min; (2) exposing the polymer to the SO₃ gas evolved from oleum for times up to 2 min; and (3) dipping the polymer into a mixture of sulfuric and chlorosulfonic acid for times up to 1 min to obtain sulfonyl chloride groups which are then hydrolyzed in water. A combination of scanning electron microscopy (SEM; Figure 1) and EDAX analysis allowed us to assess sulfur incorporation and surface damage. The relative amounts of sulfonation in these three methods were determined by EDAX to be approximately 600:3:1, respectively.

These results showed that while immersion in liquid oleum provided the most extensive sulfonation, it is also the most destructive method (Figure 1a). Varying the exposure time and sulfuric acid concentration showed the expected variation in degree of sulfonation. The rate of sulfonation seemed to vary with the degree of water absorbed into/onto the PMR-15 sample. Samples that had been predipped in water were much more extensively sulfonated, with correspondingly increased damage to the surface. This is likely due to acid-catalyzed hydrolysis of the imide bonds in the polymer when the moist samples were exposed to sulfonation conditions. In summary, we could not identify conditions that used oleum and that yielded substantial sulfur incorporation without a great deal of surface damage, as was reported for polystyrene.²¹

A slightly milder approach used a 2-min exposure of the PMR-15 to SO₃ vapors coming out of liquid oleum. This gave effective sulfonation but was also accompanied by substantial surface degradation (Figure 1b), again, as with polystyrene.²¹ The most successful sulfonation result was obtained by dipping the PMR-15 into a mixture of chlorosulfonic acid and sulfuric acid (30:70) for 0.5 min and then soaking the sample in water for 48 h to fully hydrolyze the surface sulfonyl chloride groups. This approach gave substantial sulfonation without significant surface damage (Figure 1c).

It is likely that the PMR-15 absorbs significant amounts of water during both the sulfonation procedures and the

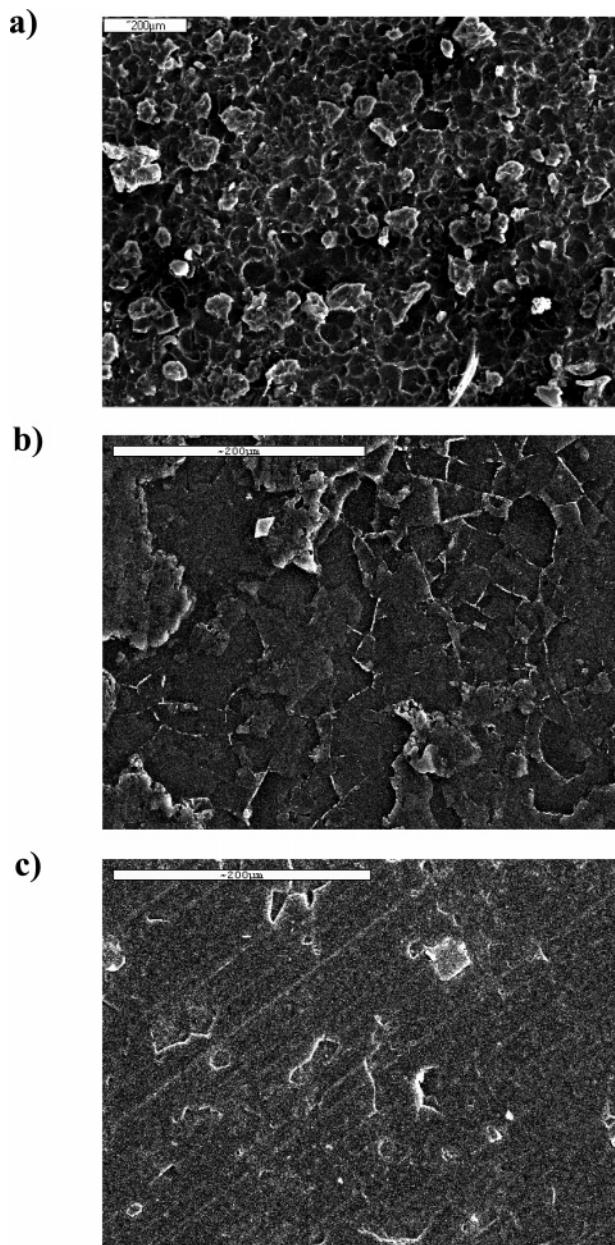


Figure 1. SEM micrographs of variously sulfonated PMR-15: (a) PMR-15 treated with oleum; (b) PMR-15 treated with SO₃ vapors; (c) PMR-15 treated with ClSO₃H/H₂SO₄.

subsequent TiO₂ deposition. While future work on the robustness and thermal cycling of the coated PMR-15 will have to address this question, the present study focused on understanding the surface chemistry and the TiO₂ deposition and did not explore the extent or consequences of water absorption.

B. Titania Deposition. (B.1) *Method 1.* Given their relatively low acidity and low temperature, LPD methods are ideally suited to polymer substrates. We applied method 1 (pH = 3.88; room temperature) to unactivated PMR-15. RBS analysis showed that the deposited titania was 90 nm thick after 24 h and a 450 nm film was deposited in 48 h. Variability in the onset time for film formation may account for the seemingly slower initial growth. We note that titania growth by this method on clean silicon wafers, for approximately these same time intervals, gave 250 and 450 nm, respectively. All samples were amorphous, as had

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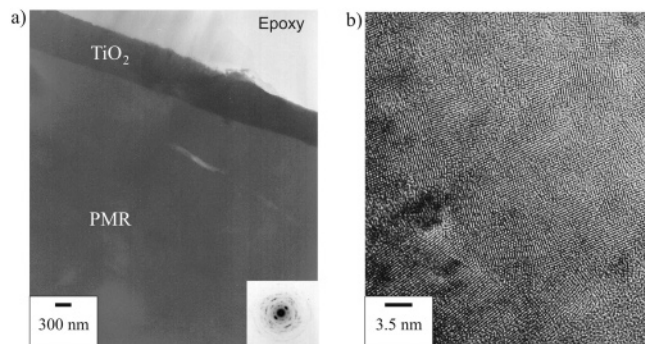


Figure 2. TEM of method 2 LPD TiO₂ on chlorosulfonic acid-treated PMR-15: (a) cross-sectional view of the substrate and the titania layer; (b) HRTEM of the titania shown in a.

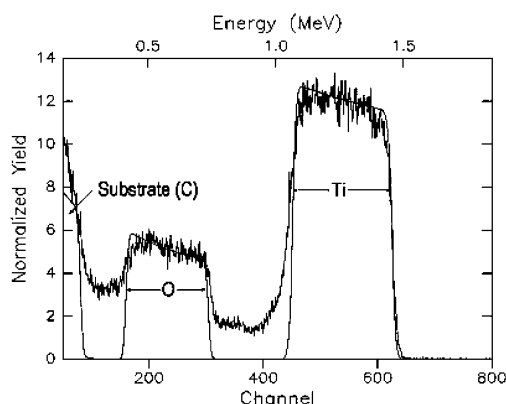


Figure 3. RBS analysis of the TiO₂-coated PMR-15 specimen shown in Figure 2. The film is measured to be 750 nm thick, with an O/Ti ratio of 3.6:1 and a film density of 0.6 E23 atoms/cm³.

been previously reported for this method on variously treated silicon wafers.¹⁸ An adherent, amorphous, titania film (420 nm thick in 48 h) also formed on a PMR-15 surface that had been sulfonated by exposure to SO₃ gas. Formation of such a film at a sulfonated surface is in contrast to our previous work, where method 1 did not form a stable titania film on sulfonated silicon wafers. A possible explanation for this contrast will be considered in the discussion section below.

(B.2) *Method 2.* Method 2 (pH 2.8; 50 °C) was used to deposit (22 h) TiO₂ on chlorosulfonic acid-activated PMR-15. It yielded a film that was 750 nm thick in TEM (Figure 2). The rings in the electron diffraction pattern (inset with Figure 2a) confirmed that the film was polycrystalline anatase with some degree of texture, consistent with XRD. The high-resolution image (Figure 2b) indicates that typical crystals in this region of the film were generally smaller than 10 nm in diameter (consistent with other studies using method 2^{21,33}), but some larger crystals are visible.

The sample of Figure 2 also was used to calibrate the use of RBS to evaluate film thickness. Using the thickness of 750 nm obtained from TEM, RBS analysis (Figure 3) for the same film yielded values for the atomic density of 1.3×10^{22} Ti atoms/cm³ and 4.7×10^{22} O atoms/cm³, compared to 2.89×10^{22} Ti atoms/cm³ and 5.79×10^{22} O atoms/cm³ for fully dense anatase. (The oxygen in excess

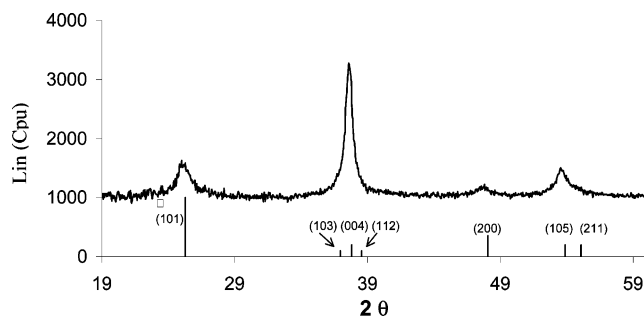


Figure 4. XRD analysis of the specimen of TiO₂-coated PMR-15 shown in Figure 2. The reference spectrum for anatase (JCPDS 84-1286) is indicated at the bottom of the figure.

of a Ti/O ratio of 1/2 is assumed to be associated with water in the film.) These values of atomic density were then used in the RBS thickness calculations, giving calibrated thickness values for all films reported herein. Using the RUMP software alone to estimate the thickness of the 750 nm film from its chemical composition yielded an uncalibrated thickness value of 950 nm. This magnitude of discrepancy between the TEM and an uncalibrated RBS thickness determination is consistent with comparable observations in SnO₂ films, which yielded TEM thickness values that were 55–75% of those from uncalibrated RBS measurements.³⁴

XRD analysis (Figure 4) of the sample from Figure 2 showed enhanced intensity of the (004) peak (which normally has a relative intensity of 20) compared to the (101) and (200) peaks (the strongest peaks in a random powder pattern, with relative intensities of 100 and 35, respectively). This indicated significant *c*-axis texturing perpendicular to the substrate. Using the same deposition route, a similar degree of texturing has been observed in films on variously treated substrates.^{18,21,33} The full widths at half-maximum (fwhm) of the XRD peaks were used to estimate crystal size *t* from the Scherrer formula:³⁵

$$t = 0.9\lambda / (b \cos \theta)$$

where λ is the X-ray wavelength (Cu K α , 0.154 nm), *b* is fwhm (in radians of 2θ), and θ is the diffraction angle. The (101), (004), (200), (105), and (213) peaks yielded values of the crystal size of 6.7, 10, 12, 11, and 10 nm, respectively. These data suggest that the crystals with their *c*-axis aligned normal to the substrate were not appreciably larger than the unaligned crystallites; i.e., there was no tendency for columnar growth of these crystals, consistent with the TEM images (Figure 2). Similar calculations on comparable films from deposition times of 4–22 h (below) yielded grain sizes of 10–14 nm; i.e., there was little dependence of crystal size on growth time.

Though method 2 had been reported by us¹⁸ to give adherent titania films only on sulfonated surfaces, we compared chlorosulfonic acid-activated PMR-15 to untreated PMR, side-by-side, in a 22 h deposition. Adherent anatase

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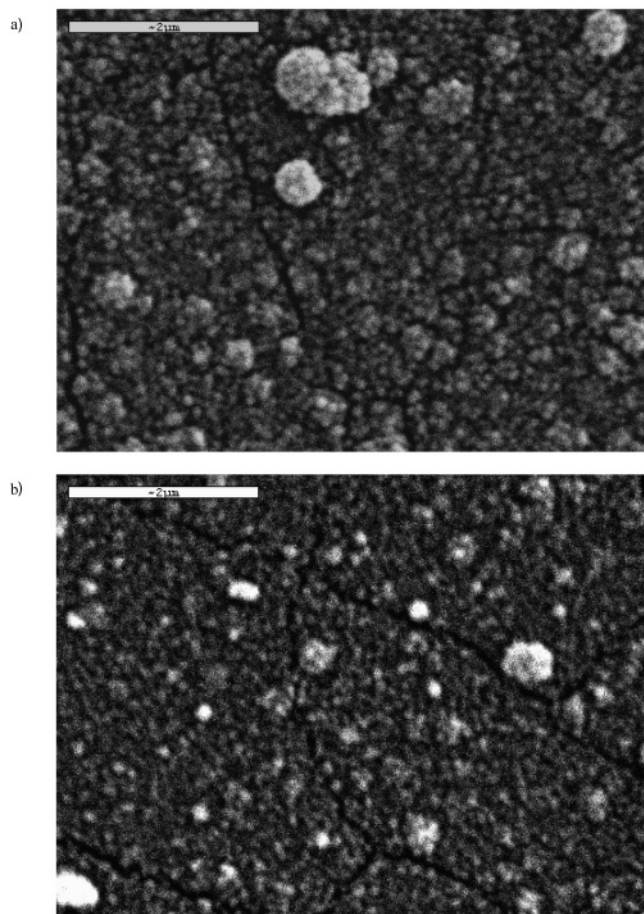


Figure 5. SEM micrographs of method 2 films deposited in 4 h on (a) PMR-15 treated with $\text{ClSO}_3\text{H}/\text{H}_2\text{SO}_4$ and (b) untreated PMR-15. The white bar is 2 μm long in each image.

films with significant (004) orientation formed on both coupons, 660–690 nm thick on the sulfonated surface and 520–630 nm thick on the untreated substrate (Table 1). In a similar study using PS substrates,²⁰ films did deposit on the polymer with or without grafted sulfonic acid groups on the surface, but adherence was adequate only on the treated surface. The issue of method 2 providing an adherent film on a nonsulfonated surface is addressed below.

SEM images of the surface of films deposited on chlorosulfonic acid-activated PMR-15 (Figure 5a) and on an untreated substrate (Figure 5b) showed virtually identical features. The films (both 230 nm thick, Table 1) consisted of densely packed particles (~50–100 nm in diameter). The XRD data indicating crystal sizes on the order of 10 nm suggest that the particles seen in Figure 5 are probably agglomerates of the 10 nm crystals. In addition, a few larger surface agglomerates up to ~500 nm can be seen. A few cracks ~50 nm wide are evident in both films. On silicon substrates, method 2 films 270 nm thick exhibited only closed cracks.¹⁸

C. TiO_2 on Benzoic/Sulfonic Acid Surfaces. The observation that TiO_2 could deposit at pH 2.88, 50 °C (method 2) directly onto untreated PMR-15 is in contrast to our earlier demonstrations that this method is best suited for sulfonated surfaces. One possibility is that functional groups other than sulfonic acids could promote the growth of oriented anatase.

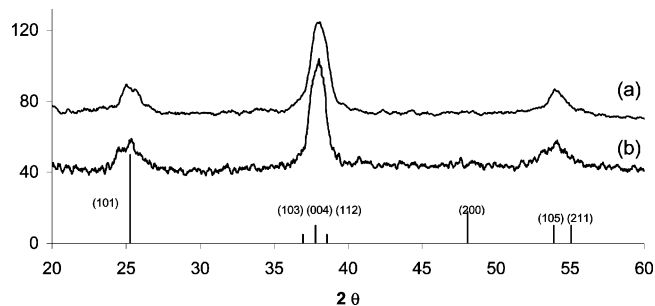


Figure 6. XRD analysis of titania deposited on silicon wafers coated with different monolayer-forming silanes: (a) $\text{SiCl}_3(\text{CH}_2)_{16}\text{SO}_3^-$ and (b) $\text{SiCl}_3(\text{CH}_2)_{11}\text{O}(\text{p})$ -benzoic acid. The reference spectrum for anatase (JCPDS 84-1286) is indicated at the bottom of the figure.

Specifically, imide hydrolysis on the PMR-15 surface can provide new surface functionality in the form of amides and carboxylic acids (amic acid).

Since in situ hydrolysis of the PMR-15 imides would lead to the formation of benzoic acid derivatives, we examined a model benzoic acid surface—i.e., a siloxane-anchored SAM on silicon wafers with benzoic acid groups on the exposed surface. These samples were immersed for 19 h, alongside a sulfonic acid SAM on silicon, in method 2 solution. Both surfaces gave adherent titania films that were stable to sonication for 20 min. XRD showed that both samples consisted of oriented anatase (Figure 6). Ellipsometry showed that the titania deposited on the sulfonate SAM was somewhat thicker than that on the benzoic acid SAM (630 nm vs 537 nm). This is consistent with the difference reported above between sulfonated and nonsulfonated PMR-15.

D. XPS Analysis of the PMR-15 Surface. Polyimides are known to be sensitive to alkaline hydrolysis, leading to erosion of the polymer matrix at a rate of 16 nm h^{-1} in 0.25 M NaOH solution.³⁶ There are comparable data on the sensitivity of polyimides to acid conditions.³⁷ Although we find no independent tests of PMR-15 degradation in acid solution, acid hydrolysis of such imides is reasonable and the conditions of our titania deposition might effect partial hydrolysis of the PMR-15 surface. The alkaline hydrolysis of a number of polyimides has been systematically studied.^{38,39} Plechty and Thomas⁴⁰ used XPS to monitor polyimide hydrolysis. Other groups subjected polymers such as pyromellitic dianhydride oxydianiline (PMDA-ODA)⁴¹ and Upilex S^{42,43} to alkaline hydrolysis (0.25 M NaOH, 2–5 h) followed by neutralization with acetic acid (0.1 M for 2–5 h) and monitored changes in the C, O, and N XPS spectra. These data provide useful models for the behavior of PMR-

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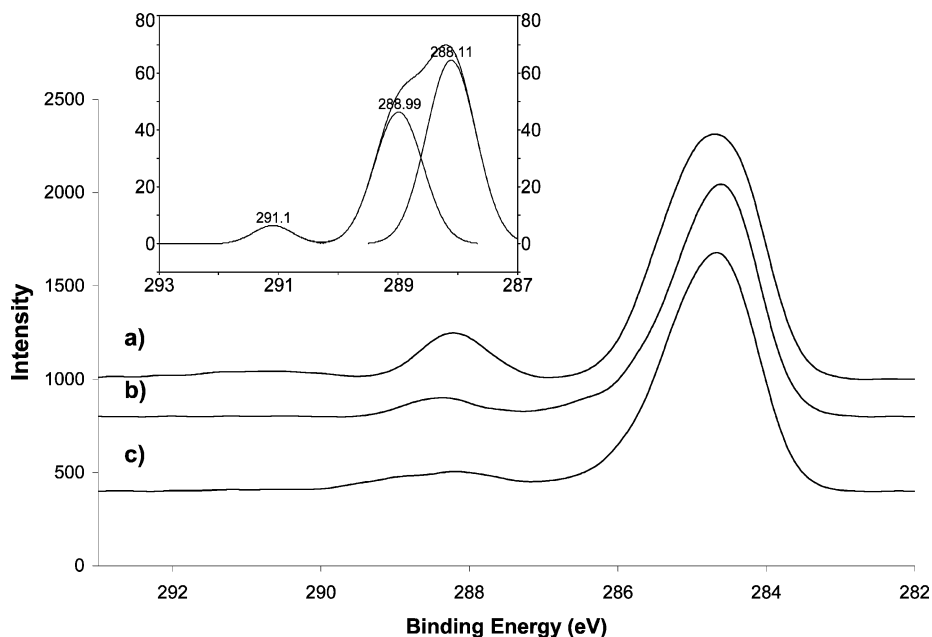


Figure 7. Carbon 1s XPS spectra of variously treated samples of PMR-15: (a) untreated PMR-15; (b) PMR-15 after soaking for 50 min in pH 2.88/50 °C LPD solution; (c) PMR-15 after soaking for 50 min in 0.5 M NaOH solution and then 10 min in 0.5 M acetic acid. The insert is a magnification and curve resolution of the 287–293 eV region of trace c.

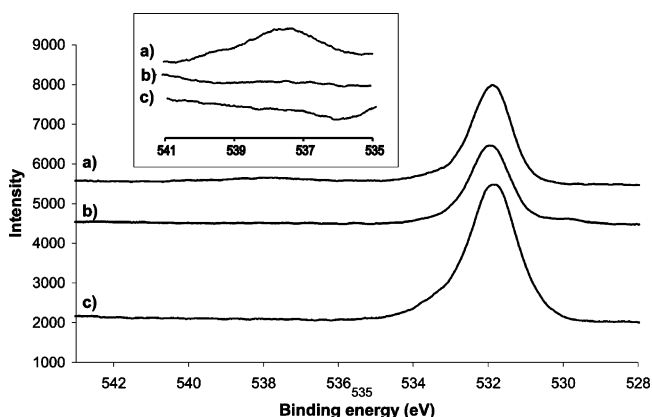


Figure 8. Oxygen 1s XPS spectra of variously treated PMR-15: (a) untreated PMR-15; (b) PMR-15 after soaking for 50 min in pH 2.88/50 °C LPD solution; (c) PMR-15 after soaking for 50 min in 0.5 M NaOH solution and then 10 min in 0.5 M acetic acid. The insert shows the range from 535 to 541 nm on an expanded vertical axis.

15 and supplement the studies of the PMR-15 hydrolysis and its effect on composite properties.^{2–5,44}

We subjected clean samples of PMR-15 to 0.5 M aqueous NaOH for 50 min at room temperature, followed by 0.5 M acetic acid for 50 min. We also put PMR-15 coupons into a freshly prepared titania deposition solution (method 2) for 50 min. Under these conditions, titania precipitation and/or surface film growth had not yet begun. Figures 6–8 and Table 2 summarize the XPS analyses of these experiments.

In the carbon 1s XPS spectrum, the main peak is at 284.6 eV. In untreated PMR-15 (Figure 7, trace a) the imide carbonyl appeared at 288.2 eV. After alkaline hydrolysis (Figure 7, trace c) the carbonyl carbon peak can be in terms

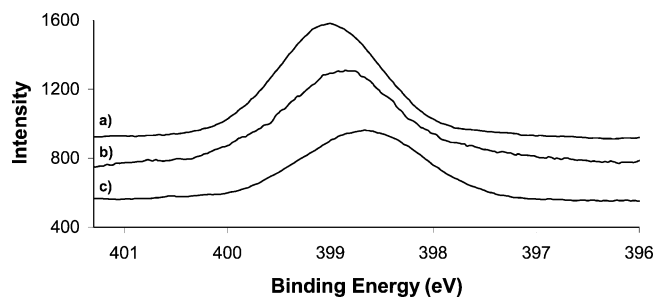


Figure 9. Nitrogen 1s XPS spectra of variously treated PMR-15: (a) untreated PMR-15; (b) PMR-15 after soaking for 50 min in pH 2.88/50 °C LPD solution; (c) PMR-15 after soaking for 50 min in 0.5 M NaOH solution and then 10 min in 0.5 M acetic acid.

of two peaks (Figure 7 insert): 288.1 eV (imide carbonyl) and 289.0 eV (carboxylic acid carbonyl). After exposure to the titania deposition solution (Figure 7, trace b), the carbonyl peak broadened. There are at least three contributing species: amide at 287.8 eV,⁴⁵ imide at 288.2 eV,⁴⁵ and acid at 289 eV.⁴⁵ The shake-up peak at 291 eV decreased noticeably after hydrolysis by either condition (Figure 7, traces b and c; Table 2).

In the oxygen 1s spectra (Figure 8 and Table 2), the biggest difference between untreated PMR-15 and the treated samples was the diminution of the shake-up peak (537.5 eV) relative to the main peak (531.9 eV). These effects on the carbon and oxygen spectra were also observed in the hydrolysis of PMDA-ODA⁴⁰ and are likely attributable to disruption of the conjugated C–N backbone.

In the nitrogen 1s spectrum, there was a single peak at 399.0 eV for untreated PMR-15. Upon alkaline hydrolysis or immersion in the titania LPD solution, this peak broadened and shifted to lower binding energy (Figure 9). This is consistent with imide cleavage to amide.

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Table 2. XPS Analysis of Imide Stability for Variously Treated PMR-15 Coupons

	carbon 1s			oxygen 1s	
	C–Y (Y = H, C, N) (%) (284.6 eV)	X–C=O (X = N, C, O) (%) (~288.2–289.0 eV)	shake up (%) (291.0 eV)	total C–O bonds (531.6 eV)	shake up (%) (537.7 eV)
bare PMR-15	85.8	10.2	4.0	92.2	7.8
alkaline hydrolysis (50 min in 0.5 M NaOH solution and then 10 min in 0.5 M acetic acid)	93.4	6.1	0.5	99.9	0.1
0.3 M boric acid (pH = 4.65)	89.9	8.8	1.3	98.3	1.7
water at pH 2.8, 50 °C	86.9	11.1	2.0	98	2.0
50 min in LPD method 1 solution	88.8	9.7	1.5	96.1 ^a	3.9
50 min in LPD method 2 solution	92.4	7.0	0.6	100 ^a	0.0

^a Includes traces of Ti–O.

We contrasted these results with the milder LPD route, method 1. This showed (Table 2) evidence for a smaller amount of hydrolysis based on the smaller reduction of the carbonyl peaks and of the shake-up peaks compared to method 2. This suggests that the PMR-15 surface is less altered by the conditions of method 1.

Two additional control experiments are reported in Table 2. In one case, a PMR sample was placed in aqueous HCl at 50 °C, and in the second case, the PMR was treated with 0.3 M boric acid at room temperature (pH = 4.65). These solutions included some of the LPD components, and both showed signs of hydrolysis. It is interesting to note that although the boric acid solution was less acidic, the hydrolysis, based on the XPS data in Table 2, seems to have been more extensive than in HCl. This suggests that boron-based Lewis acids may assist imide hydrolysis.

Discussion

It is clear that titania films can be attached to polyimide polymers using LPD. XPS data show that the PMR-15 surface after exposure to the deposition solution is not simply an array of imides but rather that surface hydrolysis liberates carboxylic acids and amides on the surface. Since sulfonation is done under acidic conditions, sulfonated PMR-15 is also likely to have surface carboxylic acids and amides from imide hydrolysis. Thus, the sulfonated PMR-15 and the PMR-15 that has only been exposed to the LPD solution both have surface acid groups that apparently facilitate titania attachment. The PS substrates used by Dutschke et al.^{20,21} in contrast, would not form such groups in the deposition solutions used here since no imide hydrolysis is possible. Correspondingly, the resulting LPD films were adherent only after separate treatments that activated the PS surface.

Under the deposition conditions used here, titania nanoparticles are present in the solutions. This allows for the possibility of film formation either by attachment of such particles or by heterogeneous nucleation on the substrate. Although electrostatic interactions have been invoked to account for oxide film depositions on functionalized surfaces, the present results and those of other groups indicate that more detailed considerations may be needed. Masuda et al.³³ reported that the titania particles that form in a solution similar to those used here have a slightly negative ζ potential at the pH of deposition (-14 mV at pH = 2.8; approximately -20 mV at pH = 3.8). This would result in an electrostatic repulsion with the sulfonated surfaces used here and by Dutschke et al.,²⁰ which are expected to have substantial

negative ζ potentials under the deposition conditions (based on measurements on sulfonated SAMs on silicon).⁴⁶

Using the method 2 solution, Masuda et al. reported good adhesion and the highest growth rate of LPD titania films on (positive) amine surfaces, with peak growth rates only 10–35% lower on other SAM surfaces (methyl > phenyl > hydroxyl). As the ζ potential of methyl-terminated SAM surfaces is near zero at pH 3,⁴⁶ the electrostatic interaction would be negligible for this substrate, so additional interactions must be considered. The concentration of the LPD solution would give a Debye layer thickness of less than a nanometer. If the range of the van der Waals interaction (which is expected to be attractive) between the particles and the substrate is longer than this, it may lead to a secondary minimum in the net interaction, allowing deposition of films in the absence of an attractive electrostatic interaction. A systematic study of the ζ potentials under deposition conditions using substrates with both positive and negative ζ potentials, combined with film growth rate and adhesion measurements and atomic force microscopy (AFM) measurements of particle–substrate forces, may elucidate the relative importance of electrostatic, van der Waals, and other interactions in the deposition of LPD films from particulate suspensions.

It should also be noted that the success of method 1 on sulfonated PMR-15 reported herein is (at first glance) at odds with previous work^{18,45} in which method 1 did not produce a titania film on a sulfonated SAM or on a sulfonated polyelectrolyte, each on a silicon wafer. For the deposition of LPD titania on untreated PMR using either solution, the answer may lie in the specific interactions of titania with carboxylic acids. In the early 1990s O'Regan and Grätzel⁴⁷ developed a solar cell which contained a dye that was attached to TiO₂ nanoparticles via a benzoic acid moiety. This strong chemisorption of benzoic acid to TiO₂ led to a series of papers dealing with the interaction of various carboxylic acids and TiO₂.^{48,49} Weisz et al.⁵⁰ found a linear correlation between the pK_a of the acid and the chemisorption stability constant (K_L). For example, oxalic acid with pK_a 1.25 has $\log K_L = 9.0$, while acetic acid with pK_a 4.75 has $\log K_L = 2.3$. Benzoic acid with pK_a = 4.2 has \log

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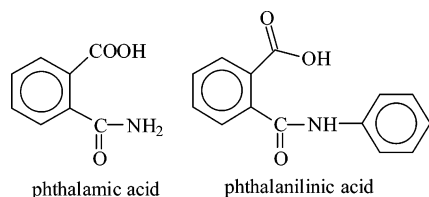


Figure 10. Model compounds for the polyamic acid that is produced by partial hydrolysis of PMR-15.

$K_L = 3.4$. Even nicotinic acid (pK_a 2.03) interacts strongly with TiO_2 ($\log K_L = 7.8$), although there is electrostatic repulsion between these two positively charged species. The explanation suggested by Weisz is that the pyridine nitrogen in fact strengthens the chemisorption by hydrogen bonding with the titania surface.

The benzoic acid SAM on a silicon surface, though likely having little charge at the pH values of our deposition solutions,²⁶ serves as a chelating ligand for the metal of the oxide. The pK_a of the polyamic acid produced by PMR-15 imide hydrolysis is 3.7.⁵¹ It too, like benzoic acid (pK_a 4.2), can chelate to the titania.

Although direct data on the chelation ability or pK_a of the product of PMR-15 hydrolysis (polyamic acid) are not available, we can use phthalanilinic acid as a model for the PMR-15 polyamic acid (Figure 10). Phthalanilinic acid is known as a ligand for various metal ions,⁵² including titanium.^{53,54} Complexation through its carboxylic acid is assisted by the amide nitrogen⁵⁴ (Figure 10). Acid and amide groups liberated during the acidic sulfonation or in the LPD deposition solution seem to chelate titanium ions and initiate titania growth on the surface, even without electrostatic attraction. This would also explain the reported titania deposition on polyamide microcapsules.²²

Finally, we note that even the uncharged benzoic acid and amic acid groups would still have attractive van der Waals interactions with the titania, favoring film formation.⁵⁵ It must further be kept in mind that the electrostatic and van der Waals effects of the SAM will be felt directly only during the initial stages of film growth. Any influence beyond the first few nanometers is expected to be indirect, perhaps e.g. in establishing a denser or more adherent inner film on which subsequent oxide can deposit (presumably via the attractive oxide–oxide van der Waals interaction dominating over a now much weaker oxide–oxide electrostatic repulsion). In this context, it is relevant that an initial thin amorphous titania

layer was found to accelerate subsequent deposition of anatase from method 2 solutions compared to phenyl, methyl, amine, and hydroxyl surfaces.⁵⁶

Conclusion

This study sought ways to form an adherent TiO_2 film on PMR-15. The sulfonate group is known to promote oxide film growth, and several direct PMR-15 sulfonation methods gave sufficient sulfonate groups on the surface to be detected by EDAX. The least destructive method that still gave sufficient amounts of sulfonate group on the surface was using a mixture of chlorosulfonic acid and sulfuric acid. Two LPD solutions were tested, and both produced adherent titania films on the PMR-15 surface. Method 1 gave a 450 nm amorphous TiO_2 film after 48 h, with or without prior sulfonation. Method 2 gave 660–750 nm of a highly oriented (004) crystalline anatase film in 22 h on chlorosulfonic acid-activated PMR-15. Comparable thicknesses (520 nm, 630 nm) were obtained on unsulfonated PMR-15.

The XPS spectrum of a bare PMR-15 sample after 50 min in the deposition solution showed signs of hydrolysis. This hydrolysis exposed benzoic acid groups that chelated the titanium ions to anchor the formation of a film. In a separate experiment, we compared sulfonate and benzoic acid active group monolayers on silicon; with respect to film thickness and orientation, regardless of the source of the surface functionalization (SAM or acid treatment), the results were almost the same. This leads to the suggestion that three mechanisms can promote film growth under the appropriate conditions: electrostatic attraction, as with amine surfaces for negatively charged LPD anatase particles (as reported by Masuda et al.^{33,56}); van der Waals attractions in the presence of small or no electrostatic attraction, as with the sulfonate surfaces used here and by Dutschke et al.,^{20,21} and chelation when surface benzoic acid groups are present.

An important lesson of this work is that while controlled preconditioning of a polymer surface to promote oxide attachment may be an important part of such methodologies, in the specific system (LPD titania on PMR-15) studied herein an explicit sulfonation step proved unnecessary to promote formation of an adherent film. The interaction of the polyimide with the deposition solution was sufficient to provide anchoring sites for the oxide.

Acknowledgment. The authors thank Professor Arthur Heuer for helpful discussions during the course of the work and for comments on the manuscript. Support from the U. S. National Science Foundation (Grant Nos. DMR 9803851 and DMR 0203655) and the Minerva Center for Microscale and Nanoscale Particles and Films as Tailored Biomaterial Interfaces (BIU) is gratefully acknowledged.

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