# STRUCTURAL STUDIES OF HYPER-THIN SILICON COMPOUND COATINGS ON POLYMERS

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**Abstract**

In order to investigate the first stages of Plasma-Enhanced Chemical Vapor Deposition (PECVD) of $SiO_2$ and $Si_3N_4$ on polymeric substrates, we have deposited hyper-thin coatings of these compounds on three different polymers, namely polyimide (PI, 50 µm, DuPont Kapton-H®), polyethyleneterephthalate (PET, 50 µm, DuPont Mylar®) and polypropylene (PP, 38 µm, Hercules). Rutherford Backscattering Spectroscopy (RBS) shows that the silicon surface concentration is a linear function of the deposition time, t. A layer-by-layer growth mode (Frank-van der Merwe) has been deduced from the combined results of Reactive Ion Etching (RIE) in oxygen plasma followed by Scanning Electron Microscopy (SEM), and Angle Resolved X-ray Photoelectron Spectroscopy (ARXPS). Finally, the presence of an "interphase" between the PECVD coating and Kapton® was investigated by XPS and RBS at grazing angle.

## 1. Introduction

Transparent barriers, such as $SiO_2$ and $Si_3N_4$ against oxygen and/or water vapor permeation through polymers are the object of increasing interest in the food and pharmaceutical packaging industries [1], and more recently in encapsulation of organic-based displays.

The typical evolution of the "Oxygen Transmission Rate" (OTR, in standard $cm^3/m^2/day/bar$) versus the thickness, d, of the barrier layer is characterized, in a logarithmic plot, by two "plateaus", separated by a roughly hundred-fold drop at the so-called "critical thickness", $d_c$ [2]. This value, which depends both on the coating and on the substrate, was found to be about 15 nm for $SiO_2$ on PET [2], and 12 nm for $SiO_2$ on Kapton® [3].

For $d > d_c$, the OTR value slowly decreases toward a "residual value", which is attributed to the presence of pinhole defects in the coating [2]. However, for $d < d_c$, a coated polymer possesses practically the same OTR value as the bare substrate material. This is commonly explained in the literature by a coating which is not continuous, but island-like, during the first stages of deposition [4]. Such a so-called Volmer-Weber growth mode evidently leaves part of the substrate surface uncoated, so that the layer displays no appreciable barrier effect.

In order to verify this hypothesis, we have deposited hyper-thin ($d \leq 12$ nm) $SiO_2$ and $Si_3N_4$ films on three different polymers, namely polyimide (PI, 50 µm, DuPont Kapton-H®),

polyethyleneterephthalate (PET, 50 μm, DuPont Mylar®) and polypropylene (PP, 38 μm, Hercules). The two types of silicon compounds were deposited using a radio-frequency (RF : 13.56 MHz), capacitively-coupled PECVD reactor, described in detail elsewhere [2]. To deposit $SiO_2$ layers, we used hexamethyldisiloxane (HMDSO), oxygen, and argon feed-gas mixture in the proportions 1:6:3, respectively. For the $Si_3N_4$ coatings, we used silane, ammonia and argon gas mixture, in the proportions 1:3:1, respectively. The total gas pressure was kept constant at 80 mTorr (10.6 Pa), and the RF power, P, was always adjusted so as to maintain the d.c self-bias voltage, $V_B$, at the cathode (which supports the substrate) constant at $V_B = -250$ V (i.e. : P=100 W).

## 2. Results and discussion

### 2.1. Growth Model

In order to investigate the evolution of the surface concentration of Si during film growth, we used Rutherford Backscattering Spectroscopy (RBS) [5] : 1 MeV α particles were made to impinge at normal incidence on the substrate surface; backscattered particles were collected at a scattering angle of 150° by a silicon lithium drifted [Si(Li)] detector, which had a Full-Width-at-Half-Maximum (FWHM) energy resolution of 13 keV for the $^{241}Am$ α lines. Since the RBS peak area of a given element depends on the α particle dose used to perform the measurement, and since this dose is not trivial to measure during irradiation of insulating materials like polymers, we evaluated the $A_{Si}/A_C$ ratio, $A_{Si}$ being the area under the silicon peak, and $A_C$ that of a window of constant width chosen in the carbon signal coming from the substrate. As the substrate was found not to lose any significant amount of carbon during irradiation [3], the ratio $A_{Si}/A_C$ is precisely equivalent to the number of silicon atoms per dose unit.

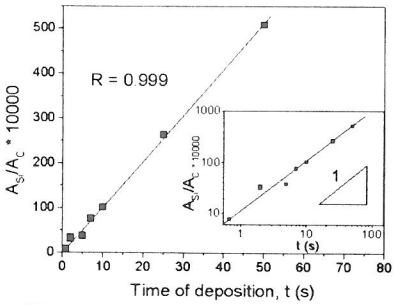


Figure 1. $A_{Si}/A_C$ (see text) versus deposition time, t, evaluated by RBS, in the case of $SiO_2$ deposition on Kapton®.

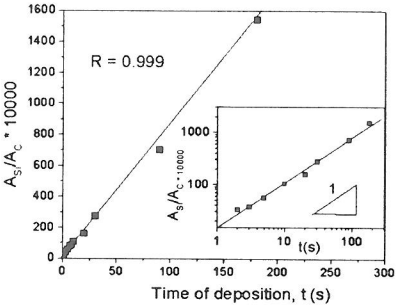


Figure 2. $A_{Si}/A_C$ (see text) versus deposition time, t, evaluated by RBS, in the case of $Si_3N_4$ deposition on Kapton®.

Figure 1 shows the evolution of $A_{Si}/A_C$ versus the PECVD deposition time, t, for the case of $SiO_2$ on Kapton.®. The surface concentration of Si is seen to be a linear function of t, for 0.5 s < t < 100 s. Since the separately-measured $SiO_2$ deposition rate was 1 nm/s, we can affirm that the sticking coefficient of Si precursors was constant during the entire growth process (0.5 nm < d < 100 nm). Figure 2 shows the results for the same experiment in the case

of $Si_3N_4$ on Kapton®; the same linear evolution of the surface concentration of Si is observed for 2 s < t < 180 s, that is, 0.6 nm < d < 60 nm (the measured deposition rate of $Si_3N_4$ having been 0.3 nm/s).

In previous articles [6,7], we have described a new method to detect and characterize sub-µm breaches in $SiO_2$ coatings on polymers. This technique, based on reactive ion etching (RIE) in oxygen plasma, was performed in the same reactor that served for deposition, at a pressure of 100 mTorr (13 Pa), with $V_B = -200$ V. Since $SiO_2$ and $Si_3N_4$ coatings are both inert towards Atomic Oxygen (AO), while polymers are rapidly etched, the latter occurs on portions of the substrate which are not coated. The surface topography is then greatly enhanced, which can readily be observed by Scanning Electron Microscopy (SEM).

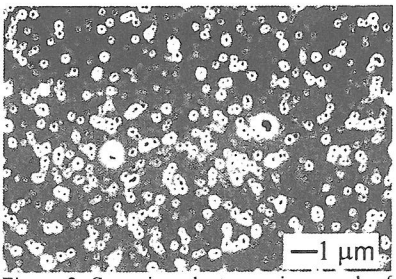


Figure 3. Scanning electron micrograph of a 2 nm thin $SiO_2$ coating on PET, following 10 minutes of exposure to oxygen plasma.

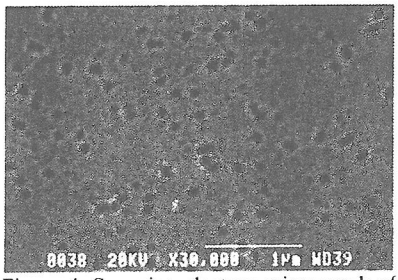


Figure 4. Scanning electron micrograph of a 1 nm thin $Si_3N_4$ coating on Kapton®, following 5 minutes of exposure to oxygen plasma.

Figure 3 is a SEM image of a 2 nm thin $SiO_2$ coating on PET, after the sample had been exposed to oxygen plasma for 10 minutes. Clearly, no evidence for island-like surface coverage is observable, the bright round spots being free-standing $SiO_2$ film over cavities etched in the polymer. The tiny black points in the center of each bright zone are the primary "pinhole" defects in the coating, through which the AO penetrated to the polymer substrate [6,7]. Figure 4 is also a SEM image of a 1 nm $Si_3N_4$ coating on Kapton® after 5 minutes of etching.

These two images bear witness to the exact opposite of island structures resulting from Volmer-Weber growth: the fact that we observe free-standing films over cavities and discrete pinholes allows us to definitively state that this 2 nm $SiO_2$ on PET (also observed for PP and PI substrates, but not presented here for a lack of space) and 1 nm $Si_3N_4$ on Kapton® coatings are continuous, albeit with many small holes.

Finally, we have confirmed the layer-by-layer Frank-van der Merwe growth mode using ARXPS. The measurements were performed on a VG ESCALAB MKII instrument, using Mg Kα X-rays (1254 eV), at Take Off Angles (TOA), θ, varying from 0 to 80°. We observed that, in the case of a 2 nm thin $SiO_2$ layer on Kapton®, the carbonyl component (-288.6 eV) of the C1s signal coming from the substrate is detectable at $\theta = 0$, 40, and 60°, but not at $\theta = 80°$ [8]. This latter observation, too, confirms that the 2 nm thin $SiO_2$ coating totally covers the substrate surface [3, 8].

The fact that the same statement can be made for three different polymers, which posses different (and low) surface energies (γ), at first appears surprising. However, a simple

explanation can be found in work published by Bichler et al. [9] : these authors have observed that $O_2$ plasma exposure of PP lasting a few tens of milliseconds is enough to increase $\gamma$ very significantly. We believe that our plasmas contain certain active species (AO in the case of $SiO_2$, and N in the case of $Si_3N_4$), which "pretreat" the substrate immediately after plasma ignition, that is, before deposition occurs. Moreover, the vacuum ultraviolet (VUV) emission from the excited gas may also play an important photochemical role in this increase of surface "wettability", before appreciable deposition can occur [10].

The observation of layer-by-layer growth now clearly justifies the use of RBS as a very precise means for measuring hyper-thin film thicknesses : since the Si surface concentration is a perfectly linear function of t, the deposition time, one only needs to calibrate this linear plot versus thickness, d, using other precise means to measure d. Figure 5 comprises data evaluated by Variable Angle Spectroscopic Ellipsometry (VASE), X-Ray Fluorescence (XRF) and RBS, which are all seen to align perfectly after normalization.

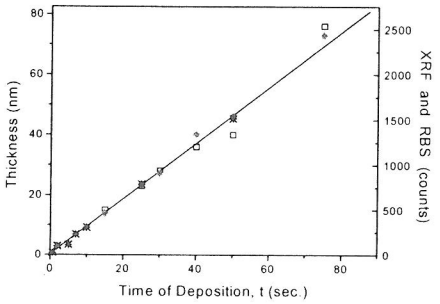


Figure 5. Superposition of (◆) XRF and (✳) RBS ($A_{Si}/A_C$ multiplied by 16400 to match the scale of this plot) signals and ( ) thicknesses evaluated by VASE directly on the polymer versus time of deposition, t (in seconds).

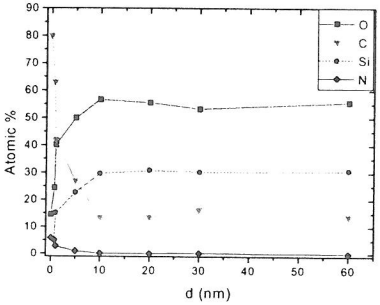


Figure 6. Chemical composition evaluated by XPS (TOA = 0 °) versus the thickness, d, of the $SiO_2$ layer deposited on Kapton® polyimide.

## 2.2. The interphase

Previous work performed in our laboratories has demonstrated the presence of an "interphase" between PECVD films and polymeric substrates : this region, sometimes exceeding 50 nm (for example in the cases of PET [11] and PC [12]), was found to consist of a cross-linked polymer with an "organosilicon" overlayer of varying chemical composition. This interphase is thought to result from chemical modifications of the substrate surface and ablation / re-deposition of volatile organic fragments induced by VUV radiation [10], energetic ions and active species (such as AO) [9] coming from the plasma phase. In the study presented here, we have used two new approaches to investigate the presence of an interphase in the case of $SiO_2$ deposited on Kapton®.

Figure 6 is a plot of Si, O, C and N atomic percentages evaluated by XPS (TOA, $\theta = 0°$) for different $SiO_2$ thicknesses (evaluated by RBS). The coating composition is seen to be constant for $d \geq 10$ nm. However, for $\theta = 0°$, using the Mg K$\alpha$ source, the depth analyzed is about 10 nm. The data of Fig. 6 therefore imply that the coating composition is constant starting with the very first layers deposited.

In order to verify the possible presence of an interphase beneath the coating, we performed RBS measurements at a grazing angle. A so-called IBM geometry was chosen, in which 1.5 MeV α particles impinged at normal incidence on the sample surface, but exiting particles were collected at a scattering angle of 95°. In this way, the (emerging) latter particles lose more energy per unit of depth, and the depth resolution is greatly enhanced [5].

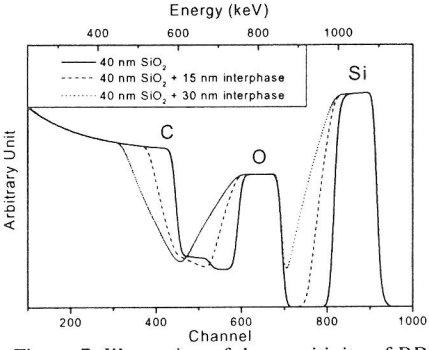


Figure 7. Illustration of the sensitivity of RBS at the geometry chosen : spectra produced using the RUMP software.

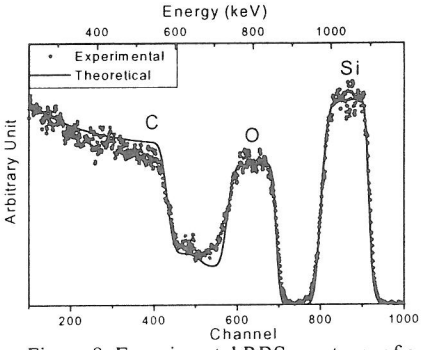


Figure 8. Experimental RBS spectrum of a 51 nm $SiO_2$ coating on Kapton® fitted with RUMP (see text).

Figure 7 illustrates the sensitivity of the method : using RUMP software [13], we have simulated the RBS spectra of $SiO_2$ coatings on Kapton® for three different cases, namely 40 nm of $SiO_2$ films without an interphase, and with two different interphase thicknesses, 15 nm and 30 nm respectively. The interphases were simulated here by a layer of composition which evolves linearly from that of Kapton® to that of $SiO_2$. One notes that the slopes of the low energy (low channel number) edges of the Si and O peaks change, as does the high energy edge of the C peak. We estimate that this method is sensitive enough to detect an interphase thickness of less than 5 nanometers. Figure 8 shows the experimental RBS spectrum of a 51 nm (evaluated by VASE) $SiO_2$ coating on Kapton®, and the corresponding RUMP simulation : the best fit was obtained for the case of a 40 nm $SiO_2$ film and a 7 nm thick interphase, the latter value being close to the above-mentioned sensitivity limit.

We can therefore conclude that the interphase of PECVD $SiO_2$ on Kapton® is much thinner than in the cases of PET or PC substrates, which suggests that PI is much less susceptible to form volatile fragments than PET and PC. This latter statement appears to be confirmed by our recent mass-spectrometric investigations [14].

### 3. Conclusion

In order to test the hypothesis proposed in the literature regarding nucleation during the first stages of PECVD growth of silicon compounds on polymeric substrates [4], we have deposited hyper-thin silica and silicon nitride films using RF plasma-enhanced CVD. RBS measurements have shown that, in the case of a Kapton® PI substrate, the surface concentration of Si is proportional to the time of deposition, t. For the case of $SiO_2$ films, the study was performed for $0.5\ s \leq t \leq 100\ s$, which corresponds to thicknesses $0.5\ nm \leq d \leq 100\ nm$ ; for $Si_3N_4$, $2\ s \leq t \leq 180\ s$, corresponds to thicknesses $0.6\ nm \leq d \leq 60\ nm$. This result also shows that the sticking coefficient of precursor species is constant during the growth process.

Using oxygen plasma RIE, followed by SEM of the etched surface, we observed that the coating is continuous, not island-like, even for $d \approx 2$ nm, for the case of all three polymeric substrates studied, namely PI, PP and PET. This combination of experimental data proves that the growth occurs in a layer-by-layer (Frank-van der Merwe) mode, rather than in an island-coalescence (Volmer-Weber) mode.

Nevertheless, such thin coatings contain very large number densities, n, of tiny pinhole defects ($n \approx 10^9$ $cm^{-2}$, for 2 nm $SiO_2$ on PET) of radii estimated to be $\leq 25$ nm . Despite the fact that < 1 % of the substrate surface is uncoated, lateral diffusion of gaseous permeant [15] explains why coatings with $d \leq d_c$ possess no barrier properties.

Finally, RBS measurements performed at grazing angle have allowed us to investigate the possible presence of an interphase in the case of $SiO_2$ deposited on Kapton®. If at all present, it was found to be only about 5 nm in thickness, that is, much thinner than in the cases of PET or PC substrates.

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