

## Characterization of Spin-Coated Polymer Films

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Neste trabalho a morfologia de filmes obtidos por revestimento rotacional foi explicada como sendo resultante de forças competitivas entre polímero, solvente e substrato. Lâminas de silício (superfícies polares) suportaram os filmes. Tolueno e tetrahidrofurano (THF) foram os solventes escolhidos para dissolver poliestireno (PS), poli(cloreto de vinila) (PVC) e poli(butiral vinílico) (PVB). Análises de microscopia de força atômica mostraram que filmes de PS obtidos a partir de soluções preparadas em tolueno são homogêneos e lisos, enquanto filmes de PS e PVC obtidos a partir de soluções preparadas em THF são muito rugosos e segregados. Entretanto, filmes de PVB preparados a partir de soluções em THF são contínuos e homogêneos. Quando as interações entre substrato e solvente são mais favoráveis que as interações entre substrato e polímero, o filme se torna rugoso e segrega. Contrariamente, quando as interações entre substrato e polímero são mais favoráveis que as interações entre substrato e solvente, ou quando as interações são muito fracas, os filmes obtidos são homogêneos e lisos. Os filmes homogêneos e lisos também foram caracterizados por elipsometria e medidas de ângulo de contato.

In this work the morphology of spin-coated polymer films is explained based on the competitive interactions between polymer, solvent and substrate. The films were formed on silicon wafers, a polar surface. Toluene and tetrahydrofuran (THF) were chosen for the dissolution of polystyrene (PS), poly(vinyl chloride) (PVC) and poly(vinyl butyral) (PVB). PS spin-coated films from solutions prepared in toluene were homogeneous and flat, while PS and PVC films obtained from solutions prepared in THF were very rough and presented segregation on the surface, as revealed by the atomic force microscopy. However, PVB films prepared from THF are continuous and homogeneous. When the interaction energy between substrate and solvent overcomes that between substrate and polymer, the films become rough and segregate. On the contrary, when the interaction energy between substrate and polymer is stronger than that between substrate and solvent, or when both interaction energies are weak, the films obtained are homogeneous and flat. These homogeneous and flat films were also characterized by ellipsometry and contact angle measurements.

**Keywords:** spin-coating, polymer films, atomic force microscopy, ellipsometry, wettability

### Introduction

Thin polymeric films are often used in the microelectronic industry, the development of sensors, packing industry and in the academic field. Homogeneous films with thickness varying from 2 to 5000 nm are commonly prepared by spin-coating. In this technique, polymer solution is dropped on the substrate surface, which rotates at a given angular velocity during a given period of time. The film thickness is controlled by the concentration of the polymer in solution, polymer molecular weight,<sup>1</sup> spinning velocity and solvent evaporation rate.<sup>2</sup> The films are stable at temperatures lower

than their glass temperature ( $T_g$ ) or melt temperature ( $T_m$ ). However, when the polymer films are annealed at temperatures higher than their  $T_g$  or  $T_m$ , the films may become unstable and dewetting takes place.<sup>3-5</sup> Depending on the substrate and the medium surrounding the layer, the wetting phase can form a continuous film, a single droplet or a pattern of discontinuous droplets.<sup>6</sup> If the interactions between substrate and polymer are van der Waals type, the values of the Hamaker constant  $A$  for polymer/polymer and polymer/substrate indicate the film stability. If  $A_{\text{polymer/polymer}}$  is higher than  $A_{\text{polymer/substrate}}$ , dewetting will be favored.<sup>3-5</sup>

This work is concerned with the morphology of thin polymer films obtained from spin-coating when different solvents are used. The interactions between substrate, polymer and solvent were qualitatively correlated with

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the resulting surface morphology of spin-coated films. We choose silicon wafers as substrate, the commercial polymers polystyrene, poly(vinyl chloride) and poly(vinyl butyral) dissolved in common solvents like toluene and tetrahydrofuran, due to their large industrial application. Moreover, the determination of the optical constants and wettability of the films was carried out. Such informations are important for the development of adhesives<sup>7</sup> and waveguides.<sup>8</sup>

## Materials

Silicon (100) wafers purchased from Crystec (Berlin, Germany) with a native SiO<sub>2</sub> layer approximately 2 nm thick were used as substrates. Polystyrene, PS, (M<sub>w</sub> ~ 200.000 g mol<sup>-1</sup>) was kindly supplied by BASF (Ludwigshafen, Germany). Poly(vinyl chloride), PVC, (M<sub>w</sub> ~ 80.000 g mol<sup>-1</sup>) and poly(vinyl butyral), PVB, (M<sub>w</sub> ~ 40.000 g mol<sup>-1</sup>) were kindly supplied by Trikem (São Paulo, Brazil) and Monsanto (São Paulo, Brazil), respectively. Analytical grade toluene and THF were used to prepare the solutions at the polymer concentration of 10 mg mL<sup>-1</sup>. The polymers were dissolved only in good solvents, where no phase separation takes place.

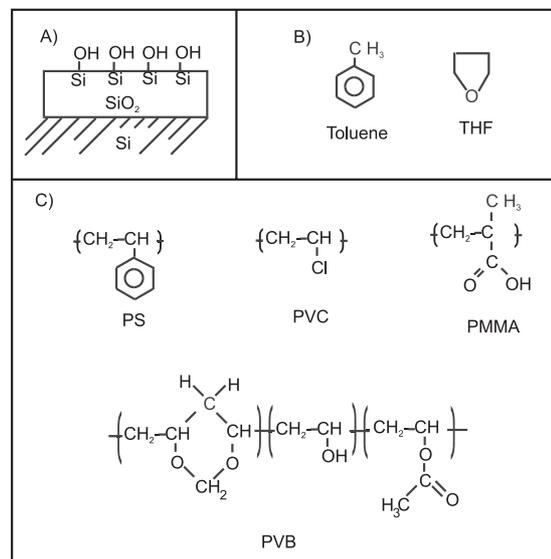
The chemical structure of substrate, solvents and polymers are schematically represented in Figure 1.

## Methods

**Spin-coating.** The polymer films were prepared by spin-coating on Si wafers with a Headway PWM32-PS-R790 spinner (Garland, USA). The wafers with dimensions of 1.5 cm x 1.5 cm were previously rinsed in a standard manner<sup>9</sup> and dried under a stream of N<sub>2</sub>. All coatings were performed with the spinning velocity of 3000 rpm and the spinning time of 30 seconds.

**Ellipsometry.** The mean thickness and index of refraction (n) of the films were determined by means of ellipsometry<sup>10</sup> in a DRE-X02 Ellipsometer (Ratzeburg, Germany), equipped with a He-Ne laser (632.8 nm). The samples characteristics are shown in Table 1.

**Contact angle.** Measurements were performed in a home-built apparatus<sup>11</sup> equipped with a Casio QV-10



**Figure 1.** Schematic representation of the chemical structures of substrate, solvents and polymers used in the experiments.

digital camera, which is connected to a computer. Sessile water drops of 4 μL and 2 μL were used for the advancing ( $\theta_A$ ) and the receding contact angle ( $\theta_R$ ), respectively. At least five samples of the same composition were analyzed at different spots.

**Atomic Force Microscopy (AFM).** Measurements were carried out with an instrument from Park Scientific (Sunnyvale, CA, USA) equipped with a homebuilt head with a laser deflection detection system in the contact mode in air at room temperature. V-shaped silicon nitride cantilevers with sharpened pyramidal tips and force constants between 0.03 and 0.1 N/m were applied. All AFM images represent unfiltered original data and are displayed in a linear gray scale. At least three samples of the same composition were analyzed at different areas of the surface.

## Results and Discussion

The spin-coating process can be visualized in 3 steps. In the first step, the substrate is covered by the polymer solution in the steady state. Here 2 cases will be considered. If the interactions between polymer and substrate are stronger than those between substrate and solvent, the

**Table 1.** Characteristic of polymers used for spin-coating. Films of PS and PVC prepared from THF were too rough for the ellipsometric measurements as well as for the contact angle measurements. All measurements were performed at (23 ± 1) °C

Sample	Solvent	Thickness (nm)	n <sup>632.8</sup>	$\theta_A$ (°)	$\theta_R$ (°)	$\Delta\theta$ (°)
SiO <sub>2</sub>	-	1.70 ± 0.05	1.462	5 ± 1	-	-
PS	Toluene	50 ± 2	1.585 ± 0.005	90 ± 2	88 ± 2	2
PVB	THF	99 ± 5	1.51 ± 0.02	60 ± 1	34 ± 3	26

chains will preferentially wet the substrate. On the contrary, if the interactions between solvent molecules and substrate are stronger than those between substrate and polymer chains, the chains will be driven away from the substrate. This kind of competition controls the adsorption of polymers from solution onto inorganic surfaces,<sup>12-14</sup> as first described by Silberberg:<sup>15</sup>

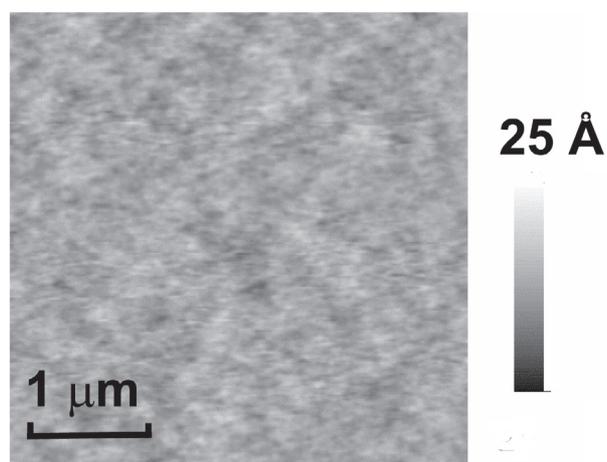
$$\chi_s^{po} = [f_{ps} - f_{os} + \frac{1}{2}(f_{pp} - f_{oo})] / kT \quad (1)$$

where  $\chi_s^{po}$  is the adsorption energy involved in the adsorption of a polymer segment from solution onto a substrate;  $f_{ps}$ ,  $f_{os}$ ,  $f_{pp}$ ,  $f_{oo}$  represent the interaction energies polymer/substrate, solvent/substrate, polymer/polymer and solvent/solvent, respectively;  $k$  is the Boltzmann constant and  $T$  is the temperature. When  $f_{ps}$  is larger than  $f_{os}$  the polymer adsorption takes place.

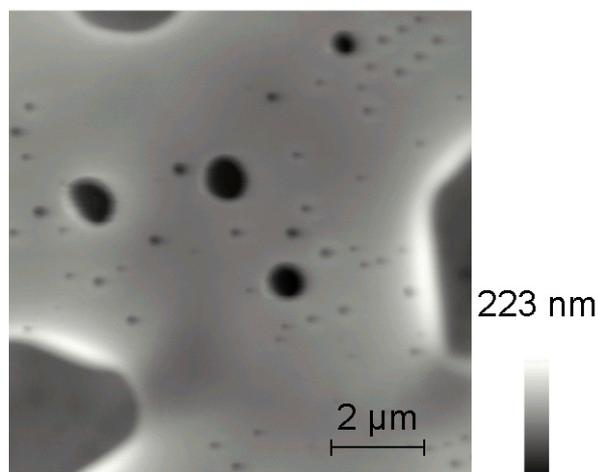
In the first spinning moments the solvent begins to evaporate, increasing the solution concentration. As a consequence, the solution viscosity increases and the chains mobility decreases. If the interactions between substrate and polymer are repulsive, the chains tend to aggregate to minimize the contact with the surface. On the contrary, if the interactions between substrate and polymer are attractive, the polymer chains tend to wet the substrate. After complete solvent evaporation the film adopts the structure corresponding to the lowest free energy of the system. It is important to remember that the resulting structure in this case might not be the equilibrium one.

Thin films of polystyrene (PS) were spin-coated onto silicon wafers from solutions prepared in toluene or in THF. The films were analyzed by means of AFM. Figure 2 and Figure 3, show the surface structure of PS films from solutions prepared in toluene and THF, respectively. In the former, the PS film is continuous and smooth with a root mean square (r.m.s.) roughness of 1.9 Å, while in the latter, the film is discontinuous with r.m.s. of  $55 \pm 5$  nm. Ellipsometry and contact angle measurements easily characterized the PS film prepared from toluene. The hysteresis in the contact angle ( $\Delta\theta$ ) is very low (Table 1), confirming the very smooth surface observed by AFM. On the contrary, PS films obtained from THF were too rough for ellipsometry, as revealed by the very low intensity of reflected light. The interaction energy between polymer and substrate,  $f_{ps}$ , is weak in both cases. PS is very hydrophobic, while  $\text{SiO}_2$  is a very hydrophilic surface (Table 1). For instance, PS films are easily detached from silicon wafers or glass slides, when immersed in a water bath, because water wets  $\text{SiO}_2$  much better than PS and the interaction between PS and  $\text{SiO}_2$  is weak.<sup>16</sup> Toluene and THF are good solvents for PS<sup>17</sup> with different polarities.

The interaction between toluene and  $\text{SiO}_2$  is very unfavorable. The acid-base interactions between them are very weak.<sup>18,19</sup> Therefore, there is no competition between polymer and solvent for the substrate. However, THF is an organic base, which shows stronger acid-base interactions with  $\text{SiO}_2$  than toluene, turning the interaction energy solvent/substrate,  $f_{os}$ , strong.<sup>18</sup> In this case, the polymer chains dry in the form of aggregates to minimize surface energy. Bolger<sup>19</sup> observed that a Brønsted-type acid-base interaction plays a very important role in the adhesion of polymer coatings from organic solvent to metal oxides. The free energy of such acid-base reaction was calculated for  $\text{SiO}_2$ /toluene and  $\text{SiO}_2$ /THF as + 35 RT and + 4.2 RT, respectively, evidencing the preferential interaction between  $\text{SiO}_2$  and THF. Similar results were found by Fowkes<sup>12</sup> for the adsorption of poly(methyl methacrylate) (PMMA) from organic solvents onto inorganic surfaces. He showed that the adsorption of PMMA, a basic polymer



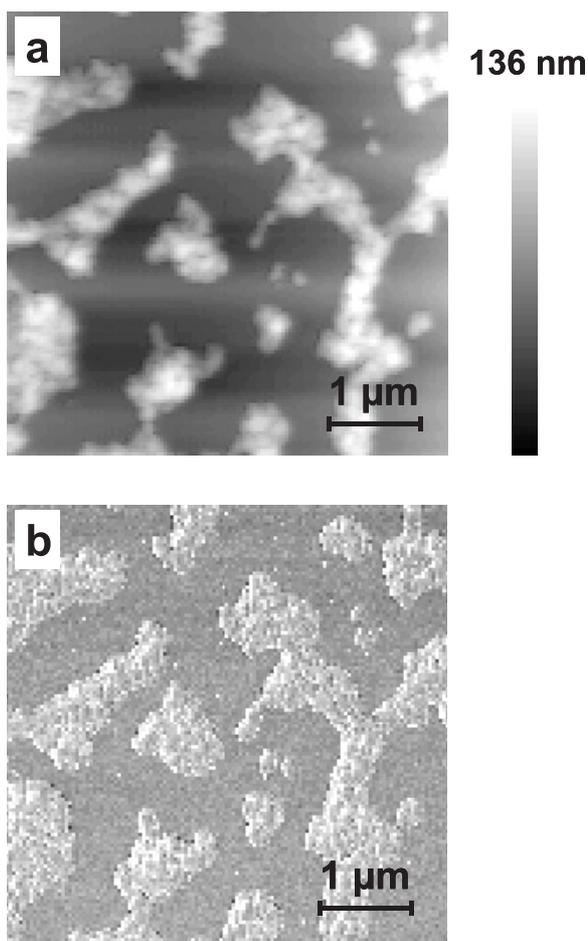
**Figure 2.** AFM topographic image of PS spin-coated film from toluene.



**Figure 3.** AFM topographic image of PS spin-coated film from THF.

onto acidic silica is maximum in the presence of a neutral solvent (carbon tetrachloride, for instance) and it decreases when the solvent competes with either the polymer or the substrate, as in the case of THF or chloroform. Fowkes also proposed that the adhesion of polymers onto inorganic surfaces is mainly driven by acid-base interactions.

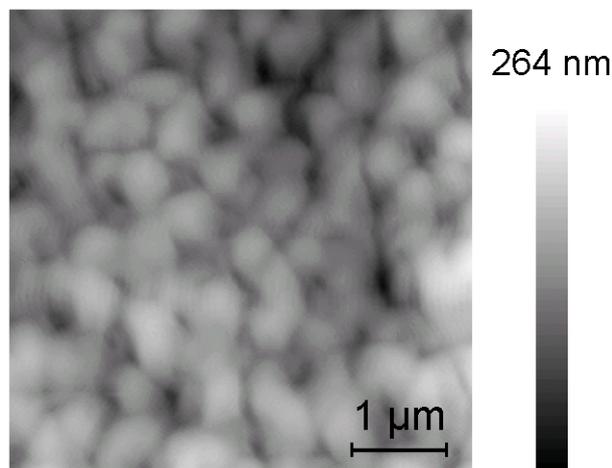
Poly(vinyl chloride) (PVC) (Figure 4a) films spin-coated from THF present regions covered by polymer aggregates and regions of bare substrate. The aggregates present a mean peak-to-valley distance of  $80 \pm 10$  nm. The acid-base interaction between  $\text{SiO}_2$  and PVC is repulsive, since both present acid character. THF is a good solvent for PVC, but the interaction energy  $f_{os}$  is strong and the PVC chains are pushed away from the substrate, drying in an aggregated form. In Figure 4b the lateral force was measured on the surface. A material contrast is evident. The light part corresponds to a softer material, whereas the darker region to a harder material. Therefore, the soft material was attributed to the PVC region and the hard one to the bare Si wafer. The PVC films could not be characterized by ellipsometry and



**Figure 4.** AFM image of PVC film spin-coated from THF. (a) topography and (b) lateral force measurement.

contact angle measurements because of the high roughness ( $r.m.s. = 32 \pm 5$  nm).

Films of poly(vinyl butyral) (PVB) were spin-coated from THF, a good solvent. Although the solvent used is the same as that used in the PVC films, the surface morphology is completely different, as shown in Figure 5. The film covering the surface is rough ( $r.m.s. = 24 \pm 2$  nm), but the substrate is not exposed. The film is formed by spherical islands with a mean diameter of  $300 \pm 30$  nm. Ellipsometry and contact angle measurements were performed. The thickness and index of refraction were obtained independently. Although the value of the index of refraction agrees well with the literature<sup>20</sup> value, its accuracy is lower than the usual because of the roughness, as indicated by the high value of hysteresis in the contact angle. PVB films are more hydrophilic than the PS films. PVB has been largely used for safety laminations. It is pressed between glass layers under heat and pressure. The excellent properties of transparency and good adhesion to glass make this polymer appropriate for the automobile windshield fabrication.<sup>20</sup> The chemical structure of PVB monomers (Figure 1) provides sites able to form H bonding with the  $\text{SiO}_2$  surface, turning the interaction energy between polymer and substrate,  $f_{ps}$ , strong. In this case, there is competition between polymer and solvent for the substrate. Since PVB covers the substrate completely, we can consider qualitatively that PVB wets the substrate even better than THF ( $f_{ps} > f_{os}$ ), driving the polymer chains towards the surface. When THF evaporates the PVB chains are already oriented to the substrate and form a continuous film.



**Figure 5.** AFM topographic image of PVB spin-coated film from THF.

## Conclusions

The morphology of spin-coated polymeric films is determined by the interaction energy polymer/substrate

and solvent/substrate. When the solvent wets the substrate preferentially, the polymer chains are driven away from the substrate and dry in the form of aggregates. Homogeneous films are obtained when there is no preferential interaction or when the polymer interacts more strongly with the substrate than the solvent.

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