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Time Evolution of the Free Surface of Ultrathin Copolymer Films

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ABSTRACT: Optical microscopy and X-ray reflectivity have been used to investigate the behavior of ultrathin films of a symmetric diblock poly(styrene-*b*-methyl methacrylate) (P(S-*b*-MMA)) copolymer deposited on a silicon substrate. Thick films of such a copolymer exhibit, at equilibrium, a multilayer structure where the lamellae, of thickness L, are oriented parallel to the substrate and the PS and PMMA blocks are located respectively at the air/polymer and substrate/polymer interfaces. The influence of the thickness constraints on the morphology of the free surface has been studied. For copolymer whose molecular weight M_w is 91 500, spin-coated films with thicknesses less than the lamellar period have been annealed under vacuum at 170 °C. Different morphologies are encountered depending on the annealing time and the thickness. For thin films whose thickness t_{ac} is such that $L/2 < t_{ac} < L$, either a stretched monolayer or the formation of islands is observed. When the film thickness is equal to $L/2$, a stable monolayer of low surface roughness is found, while, for thicknesses less than $L/2$, the monolayer is not stable.

Introduction

Symmetric A–B diblock copolymers are macromolecules composed of two unlike polymers A and B of the same length linked by a covalent bond. Because of the incompatibility between blocks A and B, symmetric diblock copolymers in the bulk experience a microphase separation for temperatures T between the glass transition temperatures T_g of the blocks and the order–disorder transition temperature (T_{ODT}). The ordered equilibrium morphology is lamellar and the period L corresponds to the thickness of a -ABBA- or and -BAAB- bilayer.[1]

Recently, numerous studies have focused on the behavior of block copolymers near surfaces and more especially on the influence of the external surfaces on the lamellar ordering in symmetric diblock copolymer thin films.[2-15]

In thin films where the thickness is a few times the characteristic period L in the bulk, it has been found that there is a strong orientation of the lamellae parallel to the external surfaces[3-12] since minimization of the surface energies dictates which block is located at both external surfaces. As a result, the film thickness is quantized. In the particular case of a symmetric diblock poly(styrene-*b*-methyl methacrylate) (P(S-*b*-MMA)) copolymer, when thin films are prepared by spin coating onto a silicon substrate, it has been shown[7-11] that, after annealing above T_g, the thickness of the ordered film is equal to $t_{ord} = (n + {}^1/_2)L$, where n is an integer $\geq$ 0: the PS block is preferentially located at the air/copolymer interface while the PMMA block is located at the Si substrate/copolymer interface (Figure 1). Furthermore, the free surface of the ordered copolymer thin films exhibits a morphology which depends on the thickness t_{ac} of the as-cast film.[11,12] If t_{ac} is exactly equal to $t_{ord} = (n + {}^1/_2)L$, the free surface of the ordered film is flat. Otherwise, either islands of height L or holes of depth L are formed on the surface after annealing above T_g: their existence is a direct consequence of the minimization of the surface energies and reflects the ordering of the lamellae within the film.[15]

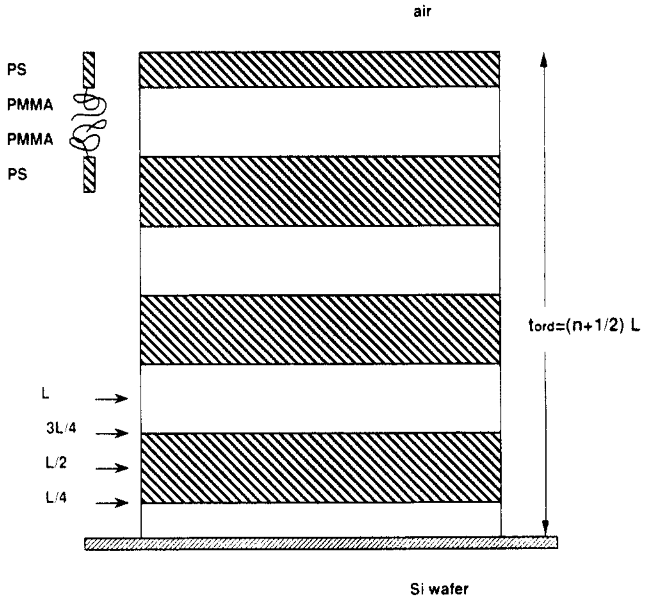

Figure 1. Schematic of the lamellar morphology found in thin films of symmetric diblock P(S-*b*-MMA) copolymer.

The question then arises as to the morphology of a film when the total thickness is less than the lamellar period L. For such very thin films, perturbations of the lamellar morphology are expected due to the strong constraints placed on copolymer molecules by the thickness of the sample. Henkee et al.[6] pointed out that, in this case, the normal microdomain structure is inhibited, but the electron microscopy technique could not establish the exact nature of the morphology: it could be either phase-mixed or microphase-separated on a small scale.

Recently, Russell et al.[14] focused on this question using neutron reflectivity on thin films of symmetric diblock P(S-*b*-MMA) copolymers of high molecular weight M_w = 300 000. They have shown that, for film thicknesses less than $3L/2$, the copolymer films are always microphase-separated. Films with approximate thicknesses of $L/4$, $L/2$, and $3L/4$ exhibit a monolayer morphology with the PS block at the air/copolymer interface and the PMMA block at the Si substrate/copolymer interface. The corresponding conformations of the copolymer chains are

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Table I
Sample Thicknesses

sample	desired thickness (Å)	thicknesses measd by X-ray reflectivity (Å)
A	91 ($L/4$)	93 ± 1
B	182 ($L/2$)	196 ± 2
C	271.5 ($3L/4$)	260 ± 2
D	271.5 ($3L/4$)	292 ± 2
E	364 (L)	325 ± 2
F	364 (L)	368 ± 2

respectively tilted (or compressed), unperturbed, and extended. For an L-thick specimen, the monolayer is covered with a mixed layer of both PS and PMMA.

Since t_{ac} is such that $L/2 < t_{ac} \leq L$, both the $3L/4$-thick and the L-thick films should exhibit islands of height L on top of a monolayer $L/2$ which are not observed in ref 14. In ref 14, it is pointed out that the surface energy required to form islands depends on the molecular weight M_w through the height L of the islands, and thus, the formation of islands is not possible when M_w is high (300 000). Previous studies[11,12] performed on a P(S-*b*-MMA) copolymer of lower molecular weight (M_w = 100 000) have shown that, for thin films whose thickness is a few times the lamellar period, the formation of islands on the free surface is easy and fast.

When the thickness is reduced to t_{ac} such that $L/2 < t_{ac} \leq L$, the formation of islands of height L on an $L/2$-thick sublayer is expected; one aim of this paper is to study the effect of the thickness constraints on the formation and growth of these islands. On the other hand, when the film thickness is less than or equal to $L/2$, the quantization relationship ($t_{ord} = (n + {}^1/_2)L$) is of no use as regards the free surface morphology. This latter point has never been investigated to our knowledge and will be addressed in this paper.

Optical microscopy and X-ray reflectivity have been used both to detect the presence of islands and to visualize and measure the surface roughness. The evolution of the free surface with the annealing time is reported here for different film thicknesses.

Experimental Section

The symmetric diblock copolymer of polystyrene (PS) and poly(methyl methacrylate) (PMMA) we used in this study was prepared by living anionic polymerization at the Institut Charles Sadron in Strasbourg (France). Its characteristics were measured by volume exclusion chromatography coupled with light scattering and viscometry. The copolymer had a molecular weight of 91 500 and its M_w/M_n was 1.03. The fraction of PS segments (f) was 0.515.

Thin films for optical microscopy and X-ray reflectivity studies were prepared by spin coating a toluene solution of the copolymer onto a clean silicon wafer. The 2.5-cm-diameter Si wafers were cleaned by oxidation of the surface impurities by UV irradiation under an oxygen flow.[16] Wafers of 1-mm thickness were used to avoid any bowing of the wafers during the spin-coating procedure. Different film thicknesses were obtained by varying the concentration of the copolymer solution and the spinning speed (in the 2000–3000 rpm range). Copolymer thin films were then dried under vacuum for several hours to remove residual solvent. The film thicknesses were measured by X-ray reflectivity: the data are summarized in Table I. Annealing of the samples was carried out under vacuum at 170 °C, and the specimens were quenched after the following annealing times: 1, 4, 6, and 20 days. To check that there was no degradation of the copolymer, a 1-μm-thick sample was annealed under the same conditions up to 40 days, and volume exclusion chromatography was performed on this annealed sample with the result that no depolymerization was observed. All the samples were investigated by both optical microscopy and X-ray reflectivity. For all the samples, observations and measurements were done in their central area.

Optical microscopy observations were performed on a Reichert Polyvar Met microscope used under reflection conditions. The differential interference contrast technique (Nomarski layout)[17] was used to investigate the presence of steps, islands, or holes on the surface and to detect and visualize the roughness of the surface. When islands or holes were present on the surface, their surface coverage was measured by coupling interference microscopy and image processing; the procedure has been given earlier.[12]

X-ray reflectivity has been described elsewhere.[18,19] In ref 18 the derivation of the general equations for the reflection coefficient and their limitations have been discussed. We shall therefore restrict ourselves to the particular aspects which are relevant to the case of symmetric diblock copolymer thin films. Let us only recall that the ratio of reflected to incident intensity is measured as a function of the angle of incidence; fringes of equal inclination are recorded, allowing the determination of thicknesses. Since the contrast between the indices (i.e., electron densities) of PS and PMMA is very small, the interference pattern is mainly due to the interference between the beams reflected at both the silicon/polymer and polymer/air interfaces. The overall thickness is thus measured and the particular morphology of the polymer/air interface makes the specificity of the study of symmetric diblock copolymer thin films.

Indeed, this latter interface exhibits inhomogeneities, at least, at three different length scales.

(i) At the largest scale (≃mm) the spin-coating technique induces a slight curvature of the surface. The corresponding thickness variations make the analysis more difficult. This implies that one investigate only a small area of the sample during a single experiment. To achieve this goal we used a very well defined incident beam whose size was only 25 μm × 100 μm. Moreover, a sharp resolution (0.1 mrad) is required and was obtained by means of a Ge(111) or Si(111) crystal.

(ii) At an intermediate length scale (≃μm), islands or holes are eventually present at the free surface.[11,12,15] Then, the reflected intensity depends on coherence effects which are discussed in Appendix A. In the case of thick films, the existence of two different thicknesses makes the reflected intensity beat (Figure 2a).[19] For the very thin films investigated here, the two possible different expected thicknesses are $L/2$ and $3L/2$ and the peaks have the peculiar shape represented in Figure 2b; the overall periodicity corresponds to the thickness of the $L/2$ sublayer.

(iii) At small length scales, the air/copolymer interface is "rough". It is shown in Appendix A that, neglecting diffuse scattering, the measured roughness is the standard deviation $\langle z^2 \rangle^{1/2}$ of the distance z between the substrate and the free surface. The roughness is an average value over elongated areas of the film surface several microns long and only ≃1 nm wide because of the enhancement of the coherence at grazing incidences.

It is also shown that the difference between a rough surface and a surface covered with well-defined objects is a quite subtle one[19] and depends on the ratio of the object size to its height. With regard to the latter remark, the simultaneous observation of the samples by both optical microscopy and X-ray reflectivity was fruitful: for the very thin films investigated here, the differential contrast microscopy is very sensitive to the presence of sharp steps, i.e., of islands or holes, and to the surface roughness. X-ray reflectivity then allows a quantitative measurement of either the roughness or the height and the surface coverage of islands. It has to be pointed out that optical microscopy can visualize only low-frequency roughnesses while X-ray reflectivity is also sensitive to high-frequency roughnesses.

Results and Discussion

Films with approximate thicknesses of $L/4$, $L/2$, $3L/4$, and L were investigated in this study. L is the mean value of the lamellar period as measured by interference microscopy[11,12] in thicker films (≃15 lamellae): L = 364 ± 10 Å. The thicknesses of the as-cast films deduced from X-ray reflectivity measurements are shown in Table I. The thickness is very sensitive to slight changes in both the spinning speed and the concentration of the copolymer solution; it is, thus, most tricky to get accurate values of

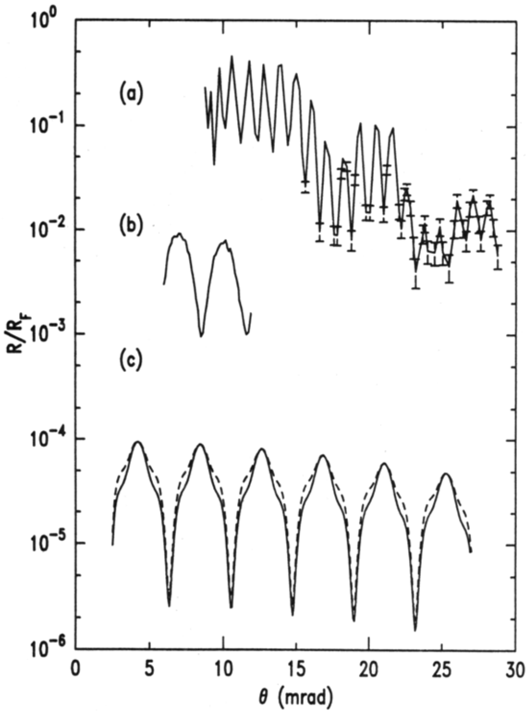

Figure 2. (a) X-ray reflectivity profile for a symmetric diblock P(S-*b*-MMA) copolymer film annealed for 1 day at 170 °C. The beating is due to interference between beams reflected on $3L/2$ and $5L/2$ thick areas. (b) For islands of height L over an $L/2$ sublayer, the intensity does not beat but the profile of the peaks is not a simple cosine. (c) Theoretical X-ray reflectivity curves for a system of islands of height L (surface coverage $\simeq$ 20%) on an $L/2$ sublayer, assuming either coherent interferences between the beams (solid line) or incoherent ones (dashed line).

Table II
X-ray Photoelectron Data[a]

sample	annealing time (days)	depth d (Å)	x (mol % PMMA)
A	1	15	<3
		75	12
	40	15	15
		75	30
B	1	15	<3
		75	4
	40	15	<3
		75	5
C	40	15	<3
		75	<3
E	40	15	<3
		75	<3

[a] The relative composition of the PMMA and PS blocks has been determined from the analysis of the O_{1s} and C_{1s} signals. The penetration depth d corresponds to the depth where 95% of the signal is observed, and x is the molar concentration of PMMA at the air/polymer interface, integrated either over the first 15 Å or the first 75 Å of the sample.

the film thicknesses. However, those shown in Table I are suitable for the present study.

It has to be pointed out that, for all the as-cast samples, the root-mean-square (rms) roughness of the free surface, as measured by X-ray reflectivity, is equal to $R \simeq 5$ Å, which is close to the rms roughness of the silicon wafer.

The evolution of the annealed thin films has been followed by optical microscopy, X-ray reflectivity, and X-ray photoelectron spectroscopy (XPS). The results of the XPS measurements are given in Table II.

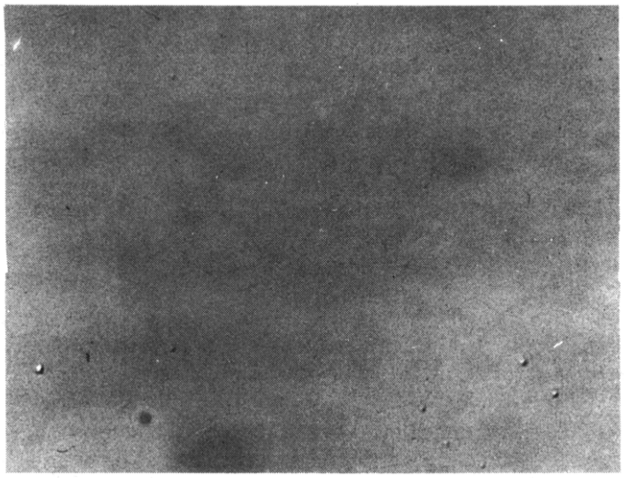

Figure 3. Optical micrograph of the free surface of sample B annealed for 1 day at 170 °C. The free surface is flat as it is also observed after 20 days of annealing at 170 °C. The full, long dimension of the micrograph is 100 μm.

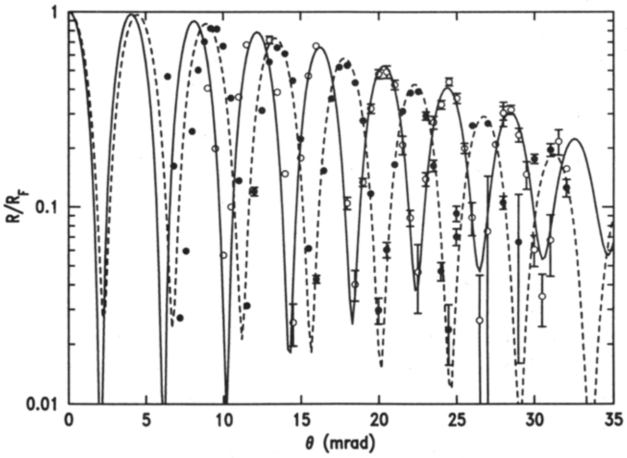

Figure 4. X-ray reflectivity curves obtained for sample B: (dashed line) as cast (thickness = 196 Å and roughness = 7 Å); (solid line) annealed for 20 days at 170 °C (thickness = 172 Å and roughness = 3.4 Å).

Let us first consider the case of sample B ($L/2$). After 1 day of annealing, optical microscopy observations of the free surface do not reveal any roughness, any step, or island (Figure 3). As evidenced by X-ray reflectivity measurements, the 1-day annealing procedure induces a drastic decrease of the rms roughness (R = 3.4 Å), while XPS measurements show unambiguously that the free surface consists of pure PS. All these data suggest that the copolymer film is microphase-separated and adopts a monolayer morphology with the PMMA block at the Si/polymer interface and the PS block at the air/polymer interface. The characteristics of the copolymer film do not change after 20 days of annealing (Table II, Figures 3 and 4); whereas the contrast between PS and PMMA is low, it thus appeared possible by using X-ray reflectivity to demonstrate that the copolymer film is microphase-separated with PS and PMMA layers of roughly equal thickness located respectively at both air/polymer and substrate/polymer interfaces. The roughness, measured by X-ray reflectivity, was found to be low whatever the annealing time and only to fluctuate slightly (4 ± 1 Å). The reason for this random fluctuation is that the X-ray scan was not performed exactly at the same place of the sample for the different annealing times. Thus, after 20 days of annealing, the monolayer morphology is stable. This behavior was expected since the monolayer morphology is consistent with the preferential segregation of the PS and PMMA blocks to the two interfaces (Figure 1). It has to be pointed out that the monolayer thickness

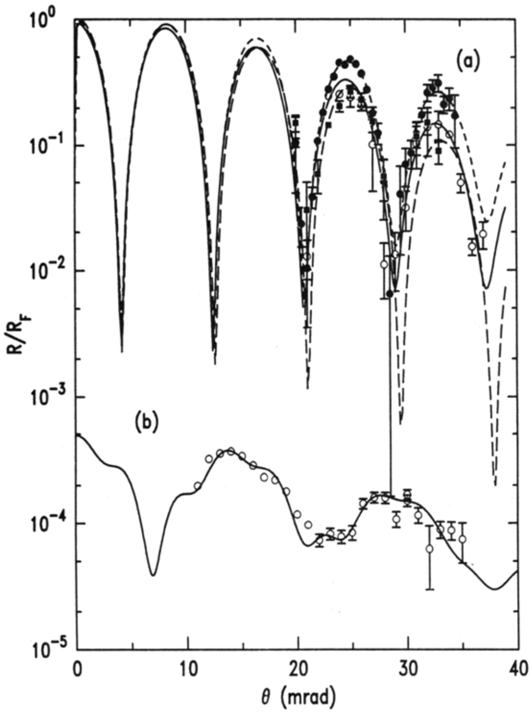

Figure 5. (a) X-ray reflectivity profiles obtained for sample A: (solid line, empty circles) as cast; (short-dashed lines, filled circles) after 1 day of annealing; (long-dashed line, filled squares) after 4 days of annealing. The film thickness is 93 Å. The roughness induces an attenuation of the reflected intensity and its affect is clearly seen on the last interference peak. The roughnesses are respectively equal to 4.5, 3.4, and 5.5 Å. (b) X-ray reflectivity profile obtained for sample A annealed for 20 days. The best fit corresponds to a model of 110-Å-thick bumps (surface coverage ≃ 20%) on a 50-Å-thick layer.

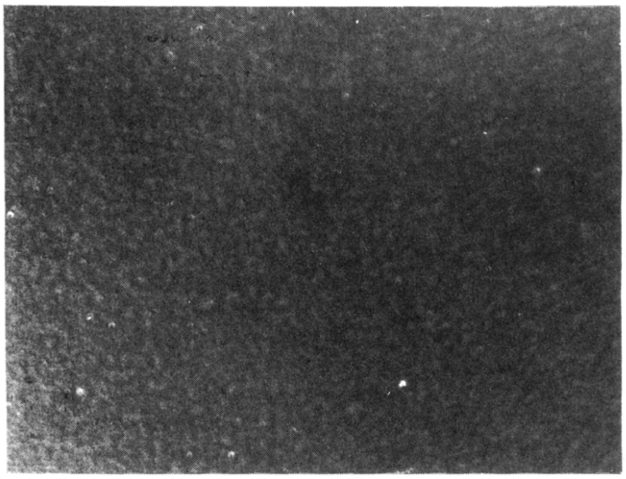

Figure 6. Optical micrograph of the free surface of sample A annealed for 20 days at 170 °C. Light patches are seen on a darker background. The full, long dimension of the micrograph is 85 μm.

is equal to 172 Å, i.e., 10 Å less than the $L/2$ value in a multilayer stacking.

After 1 day of annealing, sample A ($L/4$) has the same characteristics as sample B ($L/2$): it shows a low rms roughness ($R = 3$ Å) (Figure 5a), there are neither islands nor holes on the free surface, and pure PS is located at the air/polymer interface (Table II). These data allow us to conclude that the copolymer is microphase-separated and forms a monolayer on top of the silicon substrate. The XPS data support a monolayer structure with an interface whose width is about 50 Å, in agreement with neutron reflectivity measurements.[10]

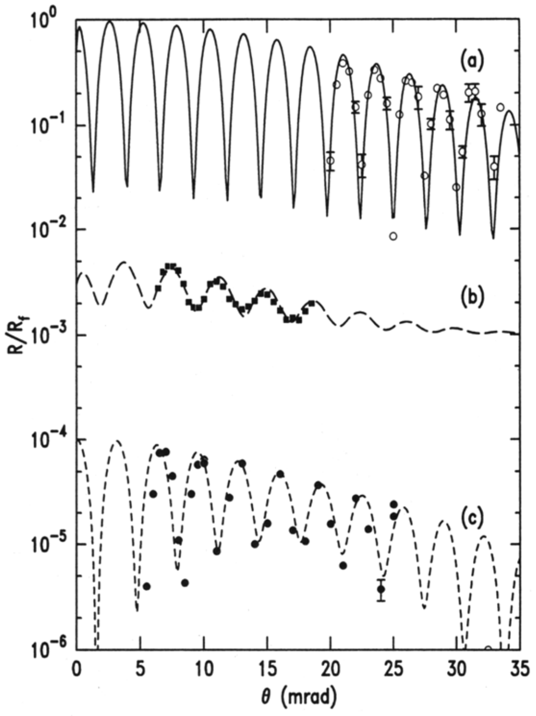

Figure 7. (a) X-ray reflectivity curve obtained for the as-cast, 293-Å-thick sample D. (b) X-ray reflectivity curve obtained for sample D annealed at 170 °C for 20 days. The existence of islands leads to a lowering of the contrast. (c) X-ray reflectivity curve obtained for sample C annealed at 170 °C for 20 days. The long-period beating corresponds to 20-Å-high bumps on a 240-Å layer.

In contrast with the $L/2$-thick sample, X-ray reflectivity shows that the rms roughness R increases continuously for annealing times greater than 4 days (Figure 5a), while a surface roughness is seen by optical microscopy after 6 days of annealing. There is a drastic change in all the data after 20 days of annealing. At high magnification (×125), interference microscopy observations[11,12] show clearly the existence of light blue patches on a darker blue background (Figure 6). The perimeters of the patches do not correspond to sharp steps; i.e., the patches are not islands. Indeed, the X-ray reflectivity curve shows the existence of at least two periods corresponding to $t = 50$ Å (which represents about 80% of the sample area) and $t = 160$ Å (20% of the sample area) (Figure 5b). The surface coverages are deduced from the relative intensity of both peaks. However, this model includes only two characteristic thicknesses, which is a crude approximation. Complementary atomic force microscopy measurements show clearly that the thickness distribution near 160 Å is wide whereas the thickness distribution near 50 Å is quite narrow. Finally, XPS data (Table II) are clearly inconsistent with a fully phase-mixed model. The actual surface concentration of PMMA must be intermediate between (1) 15% over the whole surface and (2) 100% on the bumps' surface and 0% on the 50-Å-thick layer. At large take-off angles, the 160-Å-thick bump contribution is not significant, and the measurements do not allow discrimination between the two above-mentioned possibilities since, apart from the bumps, the film thickness is less than the penetration depth. We have no definite explanation for the inner structure of the copolymer film. Furthermore, we do not have any evidence that the morphology of the free surface after 20 days of annealing is an equilibrium state. To go further in understanding the equilibrium state, additional experiments must be done with copolymers of lower molecular weight, thus evolving in a shorter time. However, the bumps' thickness is only about 10 Å

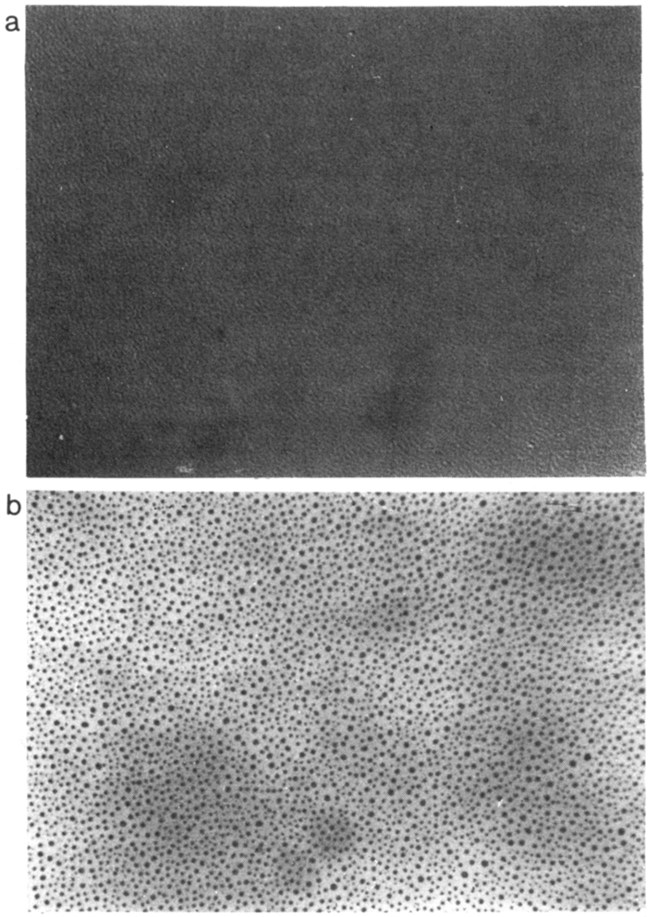

Figure 8. Optical micrographs of the free surface of sample D: (a) annealed for 1 day at 170 °C; (b) annealed for 20 days at 170 °C. Islands appear as dark patches on a lighter background. The full, long dimension of micrographs a and b are respectively 100 and 160 μm.

less than the equilibrium thickness of a monolayer at the air/silicon interface. Hence, a tentative picture is as follows: bumps are in a monolayer-like structure and the morphology of the 50-Å-thick layer is characterized by a smooth concentration gradient with PS at the free surface.

The data obtained in the $L/2$-thick film and $L/4$-thick film cases indicate strongly that a low surface roughness (3 Å) could be correlated with the existence of a monolayer morphology.

Two samples (C and D), the thicknesses of which are close to $3L/4$, have been investigated: $t_{ac}{}^{C} = 260$ Å $= 0.71L$ and $t_{ac}{}^{D} = 293$ Å $= 0.80L$ (Table I) (Figure 7a). As mentioned in the Introduction, the total thickness at any point of the surface of an ordered film is given by $(n + {}^{1}/_{2})L$, where n is an integer and L is the period of the lamellar stacking in thick films. Since the thickness t_{ac} of the film is here close to $3L/4$, i.e., such that $L/2 < t_{ac} < 3L/2$, the formation of islands of height L on the free surface is expected.[11,12] Their surface coverage $\%\ S$ is given by $\%\ S = (t_{ac} - L/2)/L$ and should be equal to about 20% for sample C and 30% for sample D.

After 1 day of annealing, for both samples the rms roughness is too high to be measured by X-ray reflectivity. The observation of the free surface by optical microscopy (Figure 8a) shows that the surface of sample D is rough, while no roughness is visible in the case of sample C (Figure 9a). Obviously, in the case of sample C, the frequency of the roughness measured by X-ray reflectivity is too high to be detected by optical microscopy.

After 4 days of annealing, as revealed by optical microscopy, elevations are present on the free surface of sample D. They appear as very thin elongated patches, more or less connected. As time progresses, this network splits into long, thin segments which themselves split again into shorter ones and so on.

After 20 days of annealing, the free surface of sample D is covered by round-shaped islands and their surface coverage is 15 ± 5% (Figure 8b). Complementary atomic force microscopy experiments have shown that the islands are not completely formed; i.e., their height is less than the expected value and their edge profile is smooth. The X-ray reflectivity curves (Figure 7b) were analyzed using a model of islands; only one thickness (sublayer thickness) could be extracted, 204 [illegible] 5 Å, and the overall thickness was inferred: 612 ± 61 Å (see Appendix A). It has to be noted that the sublayer thickness is higher than the expected value $L/2$; this higher thickness is consistent with the incomplete formation of islands. Thus, after 20 days of annealing, the copolymer film has almost built up a multilayer structure as is encountered in thicker films (Figure 1).

In the case of a t_{ac}-thick copolymer film with $L < t_{ac} < 3L/2$, we found, after 20 days annealing, perfectly formed holes in the $(L/2, 3L/2)$ top layer (Figure 10). Their depth (369 Å), obtained by X-ray reflectivity, was found to be exactly equal to L.

The evolution with annealing time of sample C is quite different. Up to 20 days of annealing, its free surface does not exhibit the presence of any island (Figure 9). After 1 day of annealing, the X-ray reflectivity profile is too much disturbed to be exploitable, proving that the roughness is very high. For longer annealing times, the reflectivity curves are still disturbed but it has been possible to extract approximate values of the roughness: it is equal to 10 Å after 4 days of annealing and decreases to 8.5 Å after 6 days of annealing. Figure 7c shows that, after 20 days of annealing, the reflectivity curve becomes well structured and exhibits a long-period beating which indicates the existence of 20-Å-high bumps (surface coverage $\simeq$ 10%) on a 240-Å-thick layer. XPS measurements performed on this sample after 20 days of annealing (Table II) show that there is pure PS at the free surface. The conformation of the copolymer film is thus a monolayer where the molecules are extended; the thickness of the monolayer is equal to 240 Å. The very low bumps detected by X-ray reflectivity are not visible by optical microscopy. Let us note that these bumps correspond only to a 3-Å rms roughness.

The behavior of sample C does not correspond to the one observed in thicker films (few lamellae) and is different from the one of sample D; a better understanding of the time evolution of sample C needs to recall recent data we obtained in thicker films.

Previous studies of the kinetics of formation of islands (or holes) on the free surface of thicker films[15] have shown that two kinds of behavior can be encountered depending on the excess of copolymer in the incomplete top layer. If the quantization of the ordered film is such that $t_{ord} = (n + {}^{1}/_{2})L$, islands are expected to be formed on the free surface when the thickness t_{ac} of the as-cast film verifies $(n + {}^{1}/_{2})L < t_{ac} < (n + {}^{3}/_{2})L$. The excess of copolymer in the incomplete top layer (and thus the surface coverage $\%\ S$ of the islands) is directly related to the quantity $\delta t = t_{ac} - (n + {}^{1}/_{2})L$.

It has been shown that, for small values of δt (i.e., low values of $\%\ S$), the formation of islands is slow and that they form individually as in a "nucleation–growth" mechanism.[20] In contrast, for large values of δt (i.e., for high values of $\%\ S$), there are isotropic spatial correlations

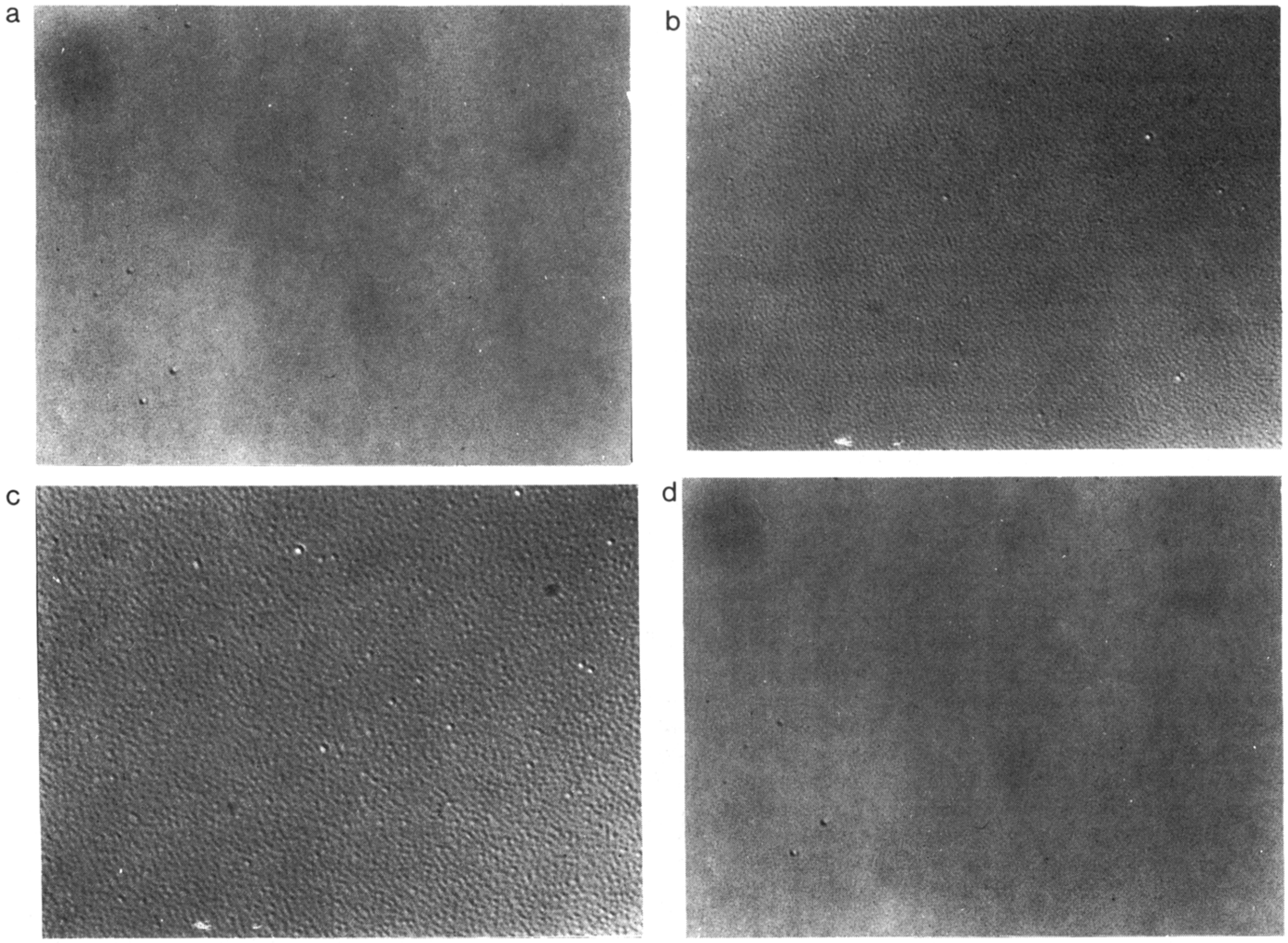

Figure 9. Optical micrographs of the free surface of sample C annealed at 170 °C for 1 (a), 4 (b), 6 (c), and 20 days (d). The full, long dimension of the micrographs is 100 μm.

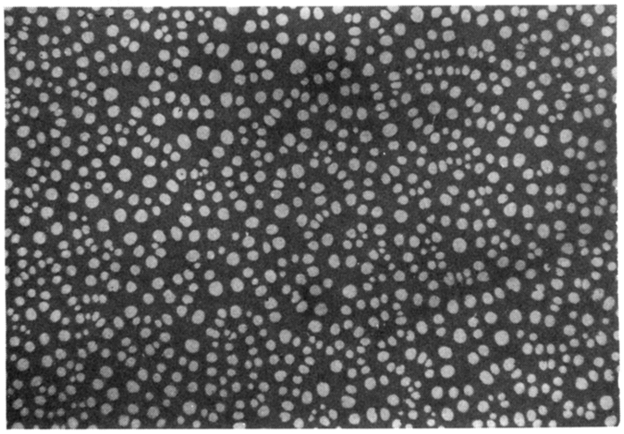

Figure 10. Optical micrograph of the free surface of a thin copolymer film, the thickness of which is $L < t < 3L/2$. The film was annealed at 170 °C for 20 days. Holes appear as light patches on a dark background. The full, long dimension of the micrograph is 400 μm.

between islands, and their formation is fast and collective as in a "spinodal" transition.[20] In the particular case of an 82K poly(styrene-*b*-butyl methacrylate) (P(S-*b*-BMA)) diblock copolymer, we have shown[15] that the transition between the two processes of formation occurs for a surface coverage of about 20%. This value should depend on both the characteristics of the copolymer and the interaction with the silicon substrate.

We think that, here, samples C and D correspond respectively to the two different above-mentioned situations. For sample C, which is the thinnest film (i.e., the excess of copolymer is the smallest), the formation of islands, if they form, should be slow and individual. The X-ray reflectivity data show clearly that the evolution of sample C exhibits a transient, disturbed stage where the roughness is high (the copolymer film "tries" to form islands). But, finally the copolymer film adopts a monolayer configuration where the molecules are extended with very few (10%) and very low (20 Å) bumps on top of the monolayer. The final conformation depends on four parameters: the surface energy (segregation of the PS block at the free surface), the line tension induced by the formation of islands, the elastic energy of the molecular chains, and the interaction with the silicon substrate. Either in the monolayer conformation or when islands of height L are formed on the $L/2$ sublayer, the PS block is located at the free surface. In the case of thick samples, i.e., when the interaction between the two external surfaces is weak, the copolymer system creates islands and does not extend its chains.[11,12] In the present case, where the interaction between the silicon substrate and the free surface is greater, the copolymer system chooses the inverse solution.

In the case of sample D, the excess of copolymer is larger: it should induce a severe stretching of the molecules in the case of a monolayer morphology. On the other hand, the formation of islands is expected to be fast and collective. These combined features are sufficient to force the copolymer to create islands at its free surface. Indeed, after 4 days of annealing, elevations are formed in a collective way. Our data show that sample D behaves like thick films; however, the size of the elevations is very small

($\leq 1\ \mu m$) even after 20 days of annealing at 170 °C (Figure 8b) while for thicker films,[12] the size distribution function of the islands exhibits a maximum at 6 μm after only 6 days of annealing at 170 °C. The formation of islands is obviously slowed down. For such very thin films, indeed, each copolymer molecule is in strong interaction with the Si substrate through its PMMA block.

Let us consider finally the L-thick films. After annealing, samples E and F should exhibit islands on their free surface with a surface coverage respectively equal to 39% and 51%. When sample E is annealed, optical microscopy observations of the free surface reveal the presence of a very slight roughness for annealing times less than 4 days; the roughness is more pronounced for annealing times ranging from 6 to 20 days. Islands are visible after 40 days of annealing. For annealing times $\leq$ 4 days, the rms roughness, measured by X-ray reflectivity, is so high that it cannot be extracted from the reflectivity curves. Obviously, the frequency of the roughness detected by X-ray reflectivity is too high to be seen by optical microscopy. After 6 days of annealing, the rms roughness decreases to 8 Å while after 20 days of annealing, the X-ray reflectivity curves clearly show the existence of two oscillations which are very close. On the other hand, XPS data show that there is pure PS on the free surface after 40 days of annealing. Thus, XPS data and optical microscopy observations suggest strongly that the two beatings (t = 260 Å and t = 280 Å) detected by X-ray reflectivity after 20 days of annealing announce the formation of the islands which are seen after 40 days of annealing. It has to be noticed that, in the present case, the formation stage of islands is a little longer than for the D sample; but the global behaviors of samples D and E are similar.

Sample F, the thickness of which is equal to the theoretical period L, behaves in a different way with annealing. Islands with a surface coverage of 51% should form on the free surface. However, after 20 days of annealing, there are no islands on the free surface; only a uniform roughness is visible by optical microscopy. On the other hand, the analysis of the X-ray reflectivity curves is not possible due to the too high value of the rms roughness. Unfortunately, we do not have XPS data for this sample and we do not know what block is located at the free surface. However, the data obtained by both optical microscopy and X-ray reflectivity show that the copolymer film did not reach a multilayer structure.

Previous optical microscopy observations on thicker films of the same copolymer have shown that 2 or 3 days of annealing at 170 °C is sufficient to order over more than 10 layers.[7,11] However, we often noticed that when the thickness of the as-cast sample was close to nL (n = 2 or 3), islands formed after times much longer than 3 days.[22] Indeed, in this case, the formation of islands requires a high amount of line energy.

When the free surface of the copolymer film is not structured, the time evolution of the film thickness can be studied. As shown in Figure 11, the thickness of sample A remains constant and equal to that of the as-cast film, which is consistent with the results of ref 14. In contrast, the thickness of film B decreases during the first 6 days of annealing down to a plateau value t = 172 Å (Figure 11). This decrease in thickness cannot be attributed to the evaporation of retained solvent molecules with regard to the behavior of sample A. The plateau value t = 172 Å is therefore the equilibrium thickness of a monolayer at the air/SiO$_2$ interface. This thickness is lower than that of an inner monolayer inside a multilayer. The decrease in the thickness has also been recently observed for M_w = 300 000 and 10 days of annealing at 170 °C by Russell et al.[14] However, in the latter case, the thickness measured after annealing was exactly the expected ideal value (L/2).

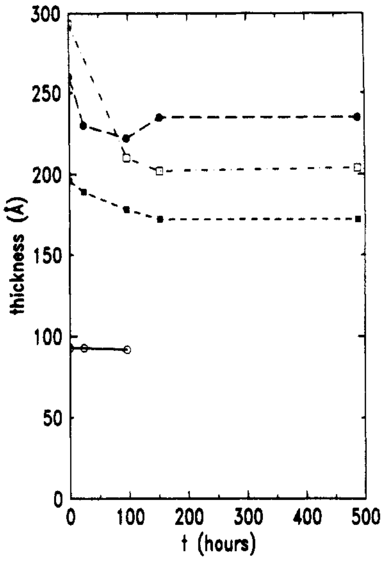

Figure 11. Time evolution of the thickness of L/4-thick sample A (solid line), L/2-thick sample B (short-dashed line), and 0.7L-thick sample C (dash-dotted line). The long-dashed line shows the time evolution of the sublayer thickness of 0.8L-thick sample D.

Finally, sample D ($t \simeq 3L/4$) exhibits a more complex thickness evolution; however, a clear decrease in thickness is observed until a plateau at 235 Å is reached after 6 days annealing, i.e., 25 Å below the as-cast thickness. This 10% decrease in thickness is again similar to that observed in ref 14.

The thickness evolution observed for all these different samples is due to a balance between the chain elastic energy, the thickness constraints, and the excess of material above $t = (n + {}^1/_2)L$. At present, no definite conclusion can be drawn. Whatever it may be, a systematic study of the thickness evolution should be of great interest.

Concluding Remarks

In summary, it has been shown that, for a P(S-*b*-MMA) copolymer with $M_w \simeq$ 100 000 and with film thicknesses such that $L/2 < t_{ac} < L$, two situations are encountered depending on the film thickness: either a stretched monolayer morphology or islands in formation on top of a sublayer. In the latter case, the kinetics of formation of the islands is slowed down compared to the one observed in thicker samples. The first case has been evidenced in the case of a 0.7L-thick film while the latter one was found to occur for thicknesses ranging from 0.8L to 0.9L. For very thin films ($t_{ac} < L/2$), the preferential affinity of the blocks to the external surfaces is predominant but the monolayer morphology is not stable after long annealing times.

In light of our results, some questions showed up which cannot be answered in the case of the P(S-*b*-MMA) copolymer of $M_w \simeq$ 100 000. The time evolution of the free surface is actually too slow to study the effect of thickness constraints on the growth of islands and to check whether our picture of the structure of L/4 -thick films is correct or not. These points will be examined in the near future using lower molecular weight P(S-*b*-MMA) copolymer. Another unresolved question is the time variation of the film thickness. Work is in progress to understand

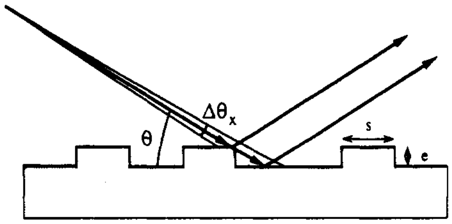

Figure 12. Schematic view of an X-ray experiment on a surface covered with islands.

this point in the simpler case of PS and PMMA homopolymers.

The lowest value of the roughness measured by X-ray reflectivity was found in the case of the $L/4$-thick film after 1 day of annealing, i.e., when the copolymer film adopts a monolayer morphology. The same value of the roughness (3.4 Å) was measured in the case of the $L/2$ monolayer as well. It is thus an open question whether a low roughness is related to the microphase-separated monolayer structure. One way to answer this is to investigate the behavior of a polymeric system which is always in a disordered state. In addition to the thickness determination, we are studying the evolution of the surface roughness of PS and PMMA homopolymers thin films with annealing time. By using atomic force microscopy and off-specular X-ray scattering, we expect to reach the Fourier spectrum of the roughness.

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Appendix A. Coherence for Inhomogeneous Systems Studied by X-ray Reflectivity

Provided that the time coherence length $\lambda^2/\Delta\lambda$ ($\simeq 1.5$ μm) is larger than all path differences (on the order of the film thickness), it can be shown that, for an extended source of size ρ, a region of coherence $\rho d/\lambda$ can be defined near each point a distance d from the source. For our system, the apparent angular size of the source is limited by the divergence of the beam, and the surface is illuminated at incidence θ. Thus the coherence area on the sample surface extends over $\lambda/(\theta\Delta\theta_x)$ parallel to the beam direction and over $\lambda/\Delta\theta_y$ normal to it.

As an example, let us consider the case of a single layer of thickness t; then the interference pattern is due to the interference between beams reflected t/θ apart along x. This implies that interference fringes will be visible if $t/\theta \ll \lambda/(\theta\Delta\theta_x)$, i.e., $\Delta\theta_x \ll \lambda/t$, implying, as expected, that the divergence of the beam should be much smaller than the interfringe. Let us now discuss the case of islands on a sublayer (Figure 12). Three different characteristic lengths are available: t/θ, $\lambda/(\theta\Delta\theta_x)$, and s, the size of the islands. Three cases can then be encountered:

$s \ll t/\theta \ll \lambda/(\theta\Delta\theta_x)$: the layer is experienced as a (very) rough transition layer with an index varying as the average density at a given z. For such a rough layer, phase differences between beams reflected at different places are iqz, where z is the local thickness. Hence the reflected beam is proportional to $\langle e^{iqz}\rangle \simeq e^{-1/2q^2\langle z^2\rangle}$, leading to a Gaussian attenuation.

$t/\theta \ll s \ll \lambda/(\theta\Delta\theta_x)$: the beams reflected by the island surface and the sublayer are coherent and electric fields do interfere. In the simplest case of smooth interfaces, one can write for the reflectivity R

$$R = R_F/\rho_s^2\Big\{\rho^2 + (\rho_s-\rho)^2[1 - 2\alpha(1-\alpha)\cos qL] + 2\rho(\rho_s-\rho)\Big[\alpha\cos\frac{qL}{2} + (1-\alpha)\cos\frac{3qL}{2}\Big]\Big\} \quad (1)$$

where R_F is the Fresnel reflectivity of the substrate of electron density ρ_s,[18] ρ is the electron density of the copolymer, and α is the fraction of the surface covered with islands.

$s \gg \lambda/(\theta\Delta\theta_x)$: there is no coherence between beams reflected by the interfaces, and the reflectivity is the average of the reflectivities for the islands and the sublayer:

$$R = R_F/\rho_s^2\Big\{\rho^2 + (\rho_s-\rho)^2 + 2\rho(\rho_s-\rho)\Big[\alpha\cos\frac{qL}{2} + (1-\alpha)\cos\frac{3qL}{2}\Big]\Big\} \quad (2)$$

The examination of eqs 1 and 2 shows that the only difference in the reflectivity curve $R(\theta)$ for a fraction α of islands of the order of 30% or less is in the shape of the interference peaks but not in the periodicity of the interference pattern (Figure 2c). This occurs because all thicknesses are multiples of the fundamental period $L/2$, to which the interfringe corresponds. In our case all distances are close together ($\simeq 10$ μm). Indeed, this does not prevent one from measuring the sublayer thickness (Figure 7).

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