

Letter

Analysis of X-ray reflectivity curves of non-Gaussian surfaces

G. Vignaud ^{a,*}, A. Gibaud ^a, F. Paris ^b, D. Ausserré ^b, G. Grübel ^c^a Université du Maine, URA 807 CNRS, Faculté des Sciences Le Mans Cedex 72017, France^b Université du Maine, URA 509 CNRS, Faculté des Sciences, Le Mans Cedex 72017, France^c ESRF, Experimental division, Avenue des Martyrs, BP 220, Grenoble Cedex F 38043, France

Received 30 September 1997; accepted 30 October 1997

Abstract

Surfaces of symmetric diblock copolymers thin films exhibiting non-Gaussian distribution of height are studied by X-ray reflectivity and atomic force microscopy (AFM). When deposited on a silicon substrate, the surface is essentially flat and its roughness may be described by a Gaussian distribution of height. Upon annealing, films operate a two-dimensional phase transformation and form islands at the free surface having height and size that evolve as a function of annealing time. The height probability function cannot be represented by a Gaussian distribution anymore, and the question that arises is how to take into account the morphology of such surfaces in the reflectivity calculations. In a first approach, we show that the height distribution function derived from AFM measurements is directly transferable to analyze X-ray reflectivity curves according to a formalism that we present. In a second part, we determine the height distribution function from a fit to the observed reflectivity. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: X-ray reflectometry; Thin film structure and morphology; Polymers; Elastomers and plastics

1. Introduction

X-ray and neutron reflectivity have recently been known as a veritable explosion of interest in the scientific community working on the structural characterization of thin films. Dating back to the work of Parratt [1] who initiated the recursive technique, reflectivity curves are now mainly analyzed via the matrix technique. More recently, the Born approximation and the distorted Born approximation [2–6] were used to model the diffuse scattering that is inevitably observed in off-specular directions as soon as the surface presents some kind of roughness with correlations between height fluctuations. A wide variety of surfaces and interfaces occurring in nature are well represented by a kind of roughness associated with self-affine fractal scaling, defined by Mandelbrodt [7] in terms of fractional Brownian motion. An isotropic rough surface can be described by the mean-square height difference given by:

$$G(R) = \langle [h(r) - h(O)]^2 \rangle, \quad (1)$$

where $h(r)$ stands for the height of the surface at the in-plane position r and the symbol $\langle \rangle$ denotes an ensemble

average. For any physical surface, $G(R)$ will saturate to a mean-square roughness σ at sufficiently large horizontal lengths, i.e., when R is larger than the roughness correlation length ξ [8,9]. For surfaces in which the correlation length of the fluctuations of height is smaller than the coherence length of the beam, the reflectivity measurements are frequently analyzed by means of two quantities such as: (1) the mean-square roughness σ of the surface that produces a deviation of the intensity decay from the Fresnel reflectivity in the specular direction; and (2) the height–height correlation function that is the relevant quantity intervening in the analysis of the diffuse scattering.

This simple description is only possible if the height distribution of the surface is Gaussian, or if the roughness is sufficiently weak, i.e., $q_z \sigma < 1$. In such a description, only the second moment of the distribution $\sigma = \langle (h(r) - \langle h(r) \rangle)^2 \rangle^{1/2}$, i.e., the roughness of the surface, is sufficient to model the decay of the specular reflectivity curve. Although this assumption is frequently acceptable, it happens that some surfaces can in no way be described by such a distribution. In such cases, the specular reflectivity can only be calculated by means of the probability $p(z)$ of finding some points of height z at the surface. Up to now, little work on X-ray reflectivity has been presented on the

* Corresponding author.

case of non-Gaussian surfaces mainly because it was difficult to access the height probability function $p(z)$. With the recent development of the atomic force microscope (AFM), it is now possible to extract statistical information of the surface (distribution of height, correlation function, etc.) from microscopy images and to compare with the results calculated from X-ray scattering measurements [10,11]. In particular, one can precisely define $p(z)$ and transfer it in the reflectivity calculation of non-Gaussian surfaces. It is the purpose of this work to present first, a formalism to describe the reflectivity of non-Gaussian surfaces, and second, to examine the validity of such a formalism in samples on which the probability $p(z)$ has been determined by AFM. In addition, we will show that it

is possible to deduce $p(z)$ from a fit to the measured reflectivity.

The X-ray reflectivity experiments were made at the Troika Beam line of the ESRF on diblock copolymer thin films of PS-PBMA, which were annealed at 150°C for 6 min and 4 h. The samples that we have studied were made by spin-coating a toluene solution of the diblock copolymer on the surface of a flat silicon wafer. Upon annealing, such materials undergo a two-dimensional phase transformation in which the surface of the film presents either holes or islands depending on the initial value of its thickness [12–14]. In this case, the initial thickness of the film which was 400 Å, led to the formation of islands, the height and the size of which were evolving upon the

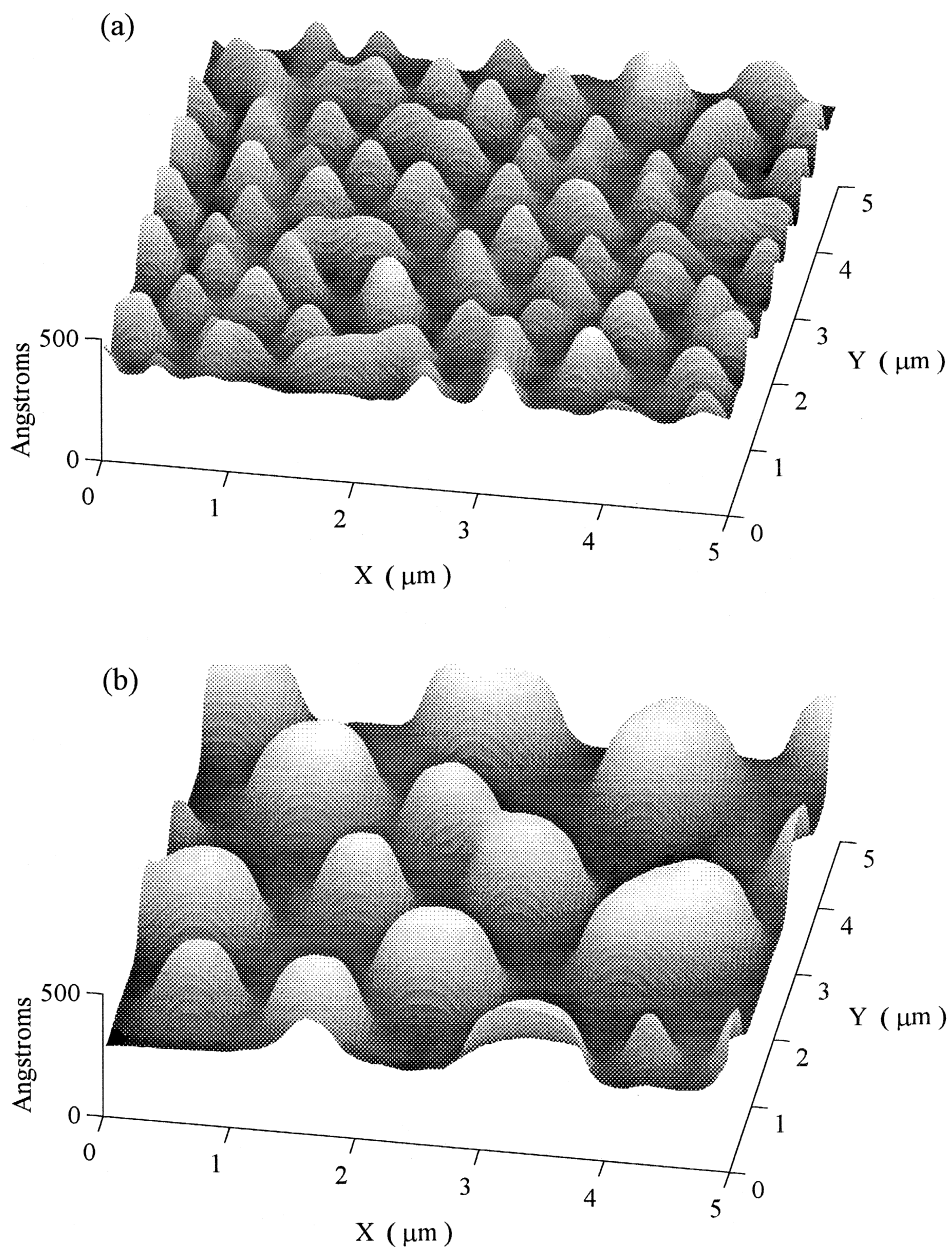


Fig. 1. AFM image of relief domains at the free surface of PS/PBMA diblock copolymer films annealed for 6 min (a) and 4 h (b) at 150°C.

annealing time. Fig. 1 shows the morphology of the film surface measured by AFM over a square surface of $5 \times 5 \mu\text{m}^2$ and clearly evidences a huge difference in the statistical properties of the two surfaces. The height probability function $p(z)$ of these two surfaces is presented in Fig. 2. It is clear on this figure that, in both cases, the probability $p(z)$ cannot be represented by a Gaussian distribution.

In the Born approximation, the differential scattering cross-section is the Fourier transform of the correlation function density–density. For a thin film of a diblock copolymer presenting a corrugated surface as shown in Fig. 1, assuming that the material is homogenous, except for the presence of the surface, the differential cross-section restricted to the specular direction becomes [14]:

$$\frac{d\sigma}{d\Omega} = r_e^2 \left| \frac{\rho_{\text{si}} - \rho_{\text{cp}}}{iq_z} e^{-\frac{1}{2}q_z^2 \sigma_{\text{si}}^2} + \frac{\rho_{\text{cp}}}{iq_z} \frac{1}{S} \iint_S dx dy e^{-iq_z z(x,y)} \right|^2, \quad (2)$$

where r_e is the classical radius of the electron, S is the coherently illuminated area of the sample, and ρ is the electron density of either the silicon wafer or the diblock copolymer. $z(x, y)$ defines the height of the surface of the

film at the coordinates (x, y) taking the origin of the z axis on the surface of the substrate. σ_{si} represents the roughness at the film–substrate interface assuming that the distribution of height is Gaussian at this interface. The roughness and the electronic density of the substrate have been determined on the non-annealed film $\sigma_{\text{si}} = 3 \text{ \AA}$, $\rho_{\text{si}} = 0.73 e^{-\text{ \AA}^{-3}}$ and these values were kept fixed for the annealed films. Keeping only the specular part, the above equation can be written as:

$$\frac{d\sigma}{d\Omega_{\text{spec.}}} = r_e^2 \left| \frac{\rho_{\text{si}} - \rho_{\text{cp}}}{iq_z} e^{-\frac{1}{2}q_z^2 \sigma_{\text{si}}^2} + \frac{\rho_{\text{cp}}}{iq_z} \int dz p(z) e^{-iq_z z} \right|^2, \quad (3)$$

where $p(z)$ is the probability density function of the surface heights of the film. It is clear from Eq. (3) that the measured reflectivity is only dependent on the Fourier transform of the height probability $p(z)$. However, note that the diffuse scattering integrated in the specular direction is not considered in this calculation. It appears from the AFM images (Fig. 1) that since the averaged distance between the islands and the size of the islands are small, we do not expect diffuse scattering to peak in the specular direction and it is possible to neglect this quantity (such is not always the case [3]). As shown by Eq. (3), the calculation of the specular reflectivity can be made if one can measure the probability function $p(z)$, or if one has a sufficient knowledge of the surface properties, allowing a close guess of its analytical form. As presented above, the measurement of $p(z)$ is made possible with an AFM that measures the relative height of the points in a surface. From the heights measured by AFM, it is straightforward to determine $p(z)$. Another alternative consists in modeling $p(z)$ by an analytical form. This is easy for example, in the case of a grating, in which one knows that the surface presents two dominating heights (the heights of the grooves and of the steps) to adjust $p(z)$ to the X-ray reflectivity data [15]. It is, in principle, also possible to develop the characteristic function $w(q_z)$ (which is the Fourier transform of $p(z)$) as the following series expansion:

$$w(q_z) = \int dz p(z) e^{-iq_z z} = 1 - iq_z \langle z \rangle - \frac{q_z^2}{2!} \langle z^2 \rangle + \dots + \frac{i^n}{n!} \langle z^n \rangle k^n. \quad (4)$$

The coefficients of the polynomial $\langle z^n \rangle$, which can be fitted to the data, are the moments of the distribution, and once these coefficients determined a Fourier inversion of $w(q_z)$ yields $p(z)$. The major drawback of such a calculation is that one generally needs many coefficients to correctly describe a reflectivity curve, and that these coefficients are unknown. We show now on an example how

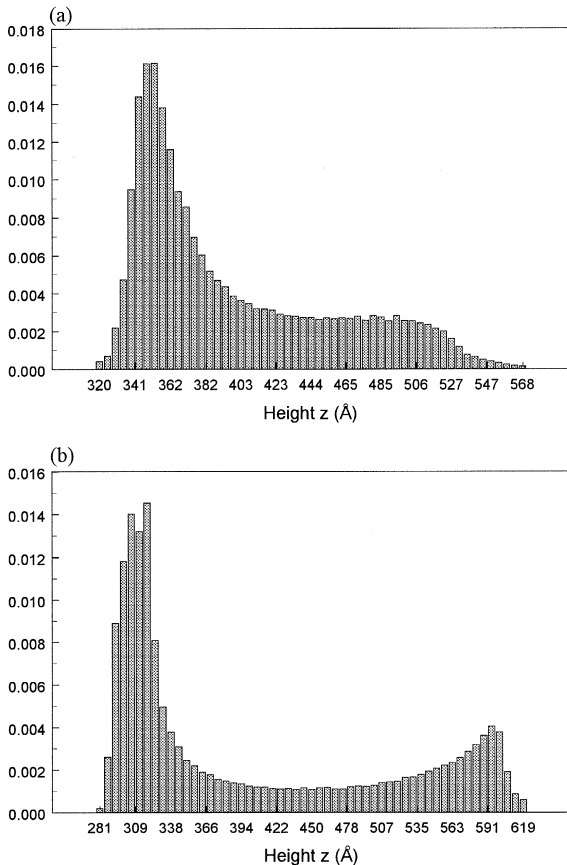


Fig. 2. Height probability function extracted from the AFM measurements on PS/PBMA copolymer films annealed for 6 min (a) and for 4 h (b) at 150°C . Note the appearance of the peak at 600 \AA after 4 h of annealing.

we have analyzed our reflectivity curves with help of the height distribution function.

To ascertain the validity of this method, we have first measured the height probability of the surface of the diblock copolymer annealed for 6 min. In such case, it is somewhat difficult to predict the functional shape of $p(z)$, since the surface of the film that was essentially flat before the annealing is undergoing deep modifications with the onset of the island growth. The reflectivity curve presented in Fig. 3a clearly shows some oscillations that would have been difficult to interpret in an ab initio calculation. With the help of the AFM measurements, $p(z)$ is introduced in the calculation, and a good agreement is immediately obtained between the calculated and the observed reflectivities. The calculation begins at $Q_z = 0.05 \text{ \AA}^{-1}$ because of the limitation imposed by the Born approximation. Resolution effects have been considered by convolving the calcu-

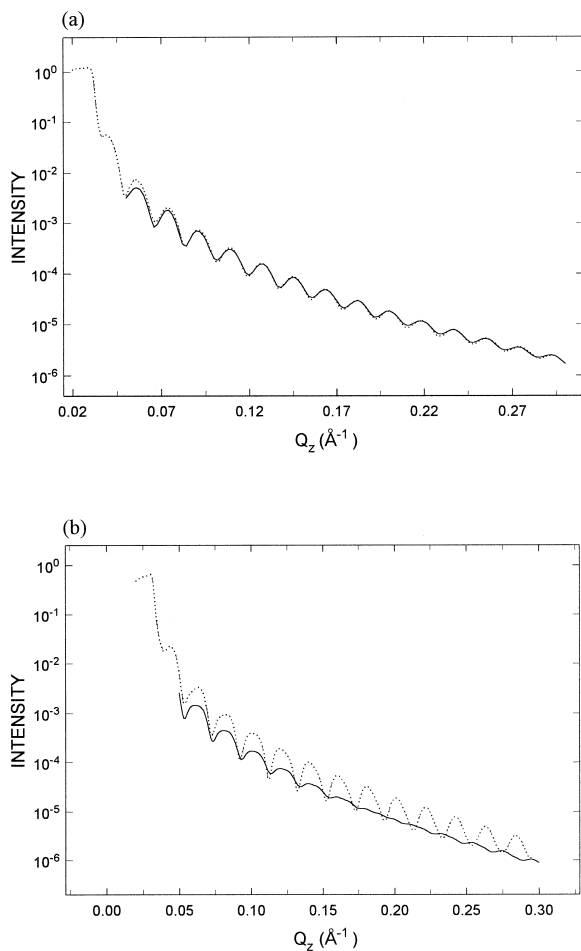


Fig. 3. Calculated (solid line) and observed reflectivities (dotted line) of PS/PBMA copolymer film annealed for 6 min (a) and for 4 h (b) at 150°C . The calculated curves begin at $Q_z = 0.05 \text{ \AA}^{-1}$ because of the limitation fixed by the Born approximation. The calculations have been done by entering the height probability extract from the AFM measurements shown in Fig. 2.

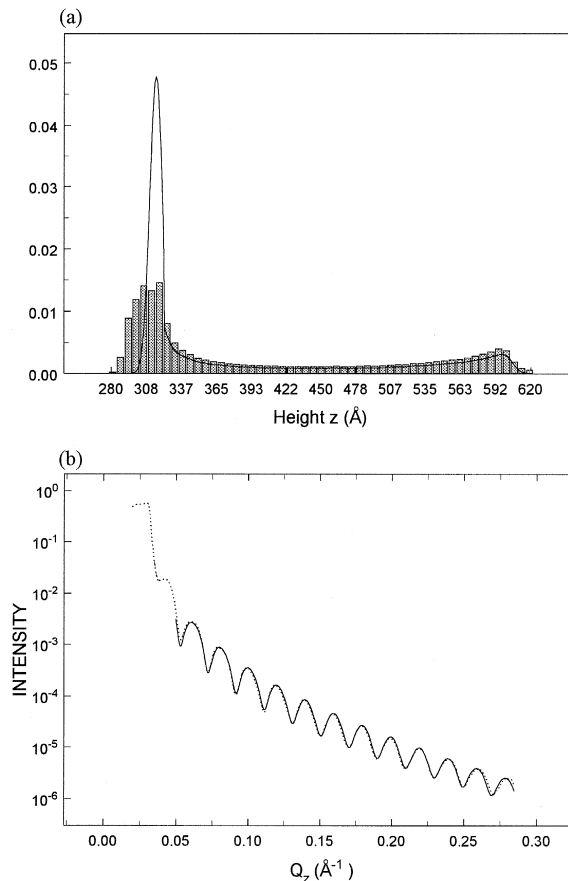


Fig. 4. (a) Height probabilities extracted from the AFM measurement compared to the functional form (solid line) used in the calculation. (b) Calculated (solid line) and observed reflectivities (dotted line) of a PS/PBMA copolymer film annealed for 4 h at 150°C (compare Fig. 4b and Fig. 3b).

lated intensity with a Gaussian resolution function. This result unambiguously shows that AFM profiles can give, under certain conditions that we will presume, the same statistical information as an X-ray reflectivity curve. There is indeed a restriction that clearly appears in the second example that we have chosen, i.e., the case of the surface of a diblock copolymer annealed for 4 h (see Fig. 3b). In such case, the islands are well formed and have grown bigger. With our AFM, the size of the image was $5 \times 5 \mu\text{m}^2$ so that only a few islands were present in this image. As a result, the shape of $p(z)$ was determined only on a limited number of islands so that the transfer of $p(z)$ in Eq. (3) did not give a good agreement between the observed and calculated reflectivities. This shows that AFM and X-ray measurements give the same statistical information, provided that the size of the AFM image is large enough to produce a stationary condition on $p(z)$. In this case, the main reason of the discrepancy between the two curves was found in the poor determination of the bottom height of the film by AFM. As we know, with enough confidence, the morphology of our film, we have tried to include in the calculation a simple functional form $p(z)$

shown in Fig. 4a, consisting of a truncated Lorentzian to describe the top part of the film, and of a Maxwellian to describe the bottom part. The observed data are fit into the model, which leads to an excellent agreement between the observed and calculated reflectivities as shown in Fig. 4b.

2. Conclusion

In conclusion, we have shown in this letter that the statistical properties of a surface that are completely contained in the height probability distribution $p(z)$ are essential to describe X-ray reflectivity curves. As a general rule, we believe that instead of assuming Gaussian distributions, as is the case in most of the literature, it would be more suitable to determine the height probability distribution, either by AFM for simple surfaces, or by assuming some simple functional forms in more complex systems. We have indeed evidenced in this study that AFM images that verify the stationary condition are in full agreement with X-ray reflectivity curves. However, except if one is interested in only one interface for which AFM is the ideal tool, it is frequent that interfaces are buried inside the material. Then $p(z)$ at each interface can only be determined via a model. This is how it is done when one tries to define the profile of electron density by using the representation of interface in terms of slabs. However, in such a

case, the usual methodology is to assume Gaussian distributions which, to our viewpoint, are too restrictive.

References

- [1] L.G. Parrat, *Phys. Rev.* 95 (1954) 359.
- [2] S.K. Sinha, E.B. Sirota, S. Garoff, H.B. Stanley, *Phys. Rev. B* 38 (1988) 2297.
- [3] P.Z. Wong, A. Bray, *Phys. Rev. B* 37 (1989) 7751.
- [4] J. Daillant, K. Quinn, C. Gourier, F. Rieutord, *J. Chem. Soc., Faraday Trans.* 92 (1996) 505.
- [5] A. Gibaud, N. Cowlam, G. Vignaud, T. Richardson, *Phys. Rev. Lett.* 74 (1995) 3205.
- [6] R. Pynn, *Phys. Rev. B* 45 (1992) 602.
- [7] B.B. Mandelbrodt, *The Fractal Geometry of Nature*, Freeman, NY, 1982.
- [8] P.P. Swaddling, D.F. McMorrow, R.A. Cowley, R.C.C. Ward, M.R. Wells, *Phys. Rev. Lett.* 68 (1992) 1575.
- [9] G. Palasantzas, J. Krim, *Phys. Rev. B* 48 (1993) 2873.
- [10] Z. Cai, K. Huang, P.A. Montano, J.M. Bai, G.W. Zajac, *J. Chem. Phys.* 98 (1993) 2376.
- [11] J. Stettner, L. Schwalowsky, O.H. Seek, M. Tolan, W. Press, C. Schwarz, H.v. Känel, *Phys. Rev. B* 53 (1996) 1398.
- [12] G. Coulon, D. Ausserré, T.P. Russell, *J. Physiol. (Paris)* 51 (1990) 777.
- [13] D. Ausserré, D. Chatenay, G. Coulon, B. Collin, *J. Physiol. (Paris)* 51 (1990) 2557.
- [14] G. Vignaud, A. Gibaud, J. Wang, S.K. Sinha, J. Daillant, G. Grübel, Y. Gallot, *J. Phys. Condens. Matter* 9 (1997) L125.
- [15] M. Tolan, G. Vacca, S.K. Sinha, Z. Li, M. Rafailovich, J. Sokolov, H. Lorenz, J.P. Kotthaus, *J. Phys. D* 28 (1995) A231.