Calibrating an Ellipsometer Using X-ray Reflectivity

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Introduction

Ellipsometry is a nondestructive method for determining the thickness and refractive index of various thin films and has been widely used in the semiconductor industry as a major metrology measurement. Since ellipsometry measures both the phase and the amplitude of visible, polarized light reflected off a surface, rather than just the intensity, theoretically both the film thickness and an isotropic value for the index of refraction can be found. However, in practice, it is not possible to unambiguously determine both values for ultrathin films, and therefore the thickness values can be quite unreliable. Comparatively, x-ray reflectivity (XRR) can reliably measure the thickness of a large range of film thicknesses, ranging from a few to several thousand angstroms, with sub-angstrom resolution and without explicit assumptions about optical properties of the material. The thickness can be easily calculated from the destructive interference period. More complete structural information can also be obtained using XRR, including the electron density as a function of distance from the substrate and the roughness of the film interfaces; however, these structural parameters can only be determined by modeling the electron density and fitting the model parameters to the data. Since both ellipsometry and reflectivity measure similar film properties, a comparison between the values obtained using each would be useful. We describe in this report the use of XRR to calibrate and test an ellipsometer for measuring the thickness of spun-cast poly(tert-butyl acrylate) (PtBA) films of varying thickness. Doing so allows us to ensure an accurate thickness characterization of ultrathin polymer films using the ellipsometer and to vary the deposition conditions and reliably determine the effect on film thickness.

Experimental Aspects

The PtBA thin films were prepared by spin coating, using solutions of PtBA in butanol with various concentrations at 2000 rpm spin speed. The film thickness in this study ranges from about 100 Å to well above 1000 Å. The ellipsometer we used was a Stokes Ellipsometer LSE (Gaertner Scientific), which uses a novel method for determining the polarization state of reflected light, and therefore the film thickness and index of refraction, almost instantaneously. A helium-neon laser, with a wavelength of 6328 Å, is set at a fixed angle of incidence of 70° with a sample. More detailed information about the ellipsometer can be viewed at http://www.gaertnerscientific.com/ellipsometers/lse.htm. X-ray reflectivity measurements were taken at beamline 1-BM, the bending magnet line of SRI-CAT sector 1at the APS. The x-rays were monochromated to an energy of 9.659 keV using a Si(111) double-crystal monochromator with sagittal focusing in the horizontal direction. The incident beam was defined by slits to measure 0.3 mm vertically by 1 mm horizontally.

Results and Discussion

The calibration of the ellipsometer was done in two steps: find the optical refractive index for PtBA and then test this value using PtBA films of varying thicknesses. The first and most important step was done by examining a previously made spun-cast PtBA film using XRR. The reflectivity data for this sample was fit to a model that indicated a film thickness of 493.4 Å and a silicon oxide thickness of 9.1 Å. This same sample with the known thickness was then examined with the ellipsometer. The optical index was found to be 1.456 (±0.002). This value was then fixed for all other measurements on PtBA films.

In order to test this refractive index calibration, a series of five PtBA films were made with different film thickness values. The analysis of the XRR data was done in two ways. The simplest method is to find the positions of the minima, due to the destructive interference, in the reflectivity curves and determine the film thickness directly from them. The more complete method is to fit the data to a model of the electron density. Both should ideally give the same information, but the first method is much easier and does not rely on model assumptions. Since we are interested in comparing thickness measurements between the ellipsometry method and the XRR method, only the thickness of the films is of interest here. The film thickness can be found from the minima positions using the following procedure. From simple arguments about optical path length difference and Snell's law, we can write an equation that relates the thickness of a single, uniform slab of material on a substrate to the position of an interference minimum in the reflectivity,

$$\frac{(2n-1)\pi}{T} = \sqrt{q_n^2 - q_c^2} \qquad (1)$$

Here, T is the film thickness, n is a positive integer index numbering the minima, q_n is the momentum transfer value at the minimum numbered n, and q_c is the critical momentum transfer for total external reflection. Figure 1 shows a plot of the minima positions for one of the samples.

A rigorous fit to the reflectivity data was also performed. It was found that a simple, single film layer did not adequately fit

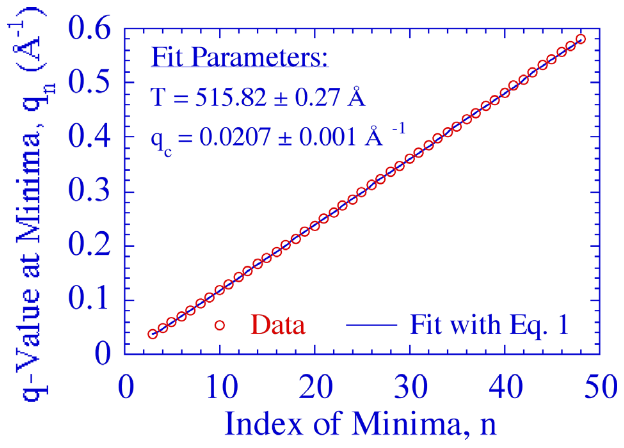

FIG. 1. A plot of minimum position versus minimum number. The solid line is a fit to the data, giving a film thickness of 515.82 ± 0.27 Å.

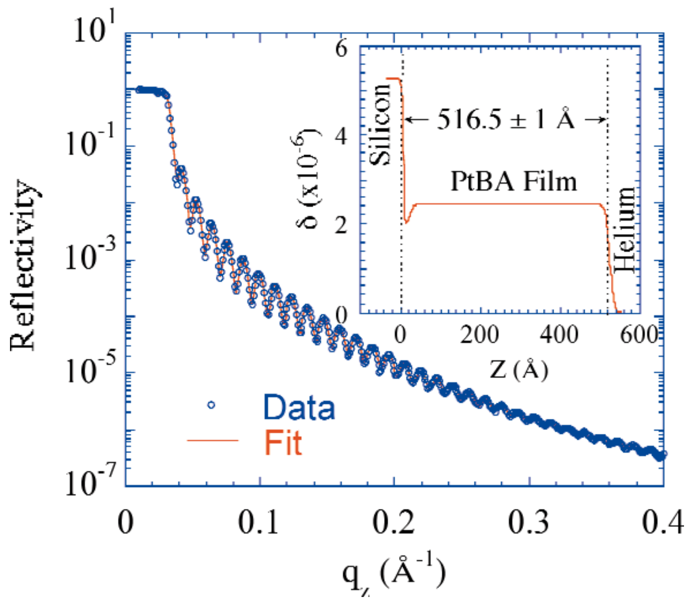

FIG. 2. A fit to x-ray reflectivity data for the same sample as analyzed in Fig. 1. The solid line is a fit to the data, which gives a film thickness of 516.5 ± 1 Å. The inset is a plot of the real part of the index of refraction of the film, d, which is directly related to the electron density, as a function of distance from the substrate.

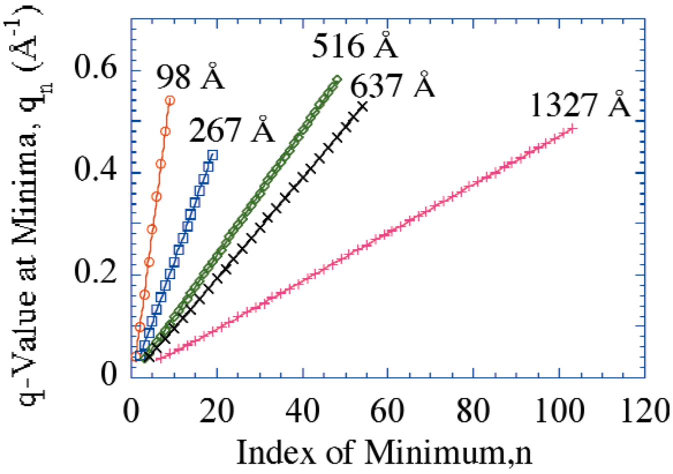

FIG. 3. A plot of minimum position versus minimum index for the five PtBA samples. The solid lines are fits using Eq. (1) in the text.

the data, so a two-layer "Gaussian-step" model was used. Figure 2 shows the reflectivity data and fit for the same sample as in Fig. 1. The inset shows the real part of the index of refraction, which is related to the electron density, as determined from the model parameters. From the fit, we get a thickness value for the film, including the lower density region near the substrate, of 516.5 (± 1) Å, which agrees extremely well with the value found using the simpler minima position method. Since this is the case and since we only are interested in the thickness of the film, we therefore relied on the simpler method for analysis of the rest of the samples with thickness ranging from ca. 100 Å to above 1000 Å. Figure 3 shows the minima position plots for all of the samples and their respective fits.

Table 1. Thickness measurements from ellipsometry and reflectivity.

Sample Number	Ellipsometry (Å)	Reflectivity (Å)
1	94.7	98.42 (± 0.21)
2	267.5	267.26 (± 0.27)
3	516.0	515.82 (± 0.27)
4	637	637.12 (± 0.22)
5	1324	1327.62 (± 0.26)

Table 1 lists the film thickness values as determined by ellipsometry and XRR. All the thickness values found by ellipsometry and reflectivity are extremely similar. The lowest and largest thicknesses were outside the reflectivity error but were still within 4 Å of each other. Ellipsometry typically gives the largest error for extremely thin films, which may explain the discrepancy for sample 1. The probable cause, perhaps also for the thinnest film, is that there will be variation in film thickness across the sample. These variations are averaged within the x-ray footprint for the reflectivity results, but they are not averaged in the ellipsometry results, beyond the 1 mm spot size of the probing laser light. Typical variations for these PtBA films, as measured by ellipsometry for the 516 Å sample, are on the order of ±2 Å near the center of the sample. Near the edges, surface-tension causes more significant changes in the thickness during the film deposition. Determining the optical refractive index using XRR is particularly useful for films with film thicknesses below 50 Å, such as in the case of organic monolayers.

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