Supporting Information for "Wavefront kinetics of plasma oxidation of polydimethylsiloxane: limits for sub-μm wrinkling"

F. Angus Bayley, Joanne Lingling Liao, Paul N. Stavrinou, Arnaud Chiche, and João T. Cabral

RSC Soft Matter, November 1, 2013

I. ADDITIONAL SCATTERING LENGTH DENSITY PROFILES FROM X-RAY REFLECTOMETRY

Figure 5 of the paper shows X-Ray Reflectometry data (XRR data) and scattering length density (SLD) profiles for PDMS coupons treated under a range of plasma doses. Figure 1 compiles all of the XRR data for plasma doses up to 37.5 kJ, alongside the corresponding SLD profiles. Prolonged plasma exposure is known to increase susceptibility to cracking and expedite hydrophobic recovery [1, 2].

Inspection of the development of SLD profiles as dose increases reveals that the gradual variation of the general shapes of both experimental XRR spectra and SLD profiles is abruptly disrupted between the 3.7 kJ and 5.8 kJ treatments, suggesting a distinct physical change in the structure of the specimen surface layer on a molecular scale. After the onset of this transition, it is evident from Fig. 1a that the rate at which the reflectivity declines at $Q > Q_c$ increases significantly, and from the SLD profile in Fig. 1b, it is also clear that for doses $>$ 3700 J, the depth, z, required for the electron density of the treated sample to reach that of unconverted PDMS ($\rho = 9.34 \times 10^{-6}$Å^{-2}) substantially increases from close to zero for mildly oxidized samples, to up to 100 Å for the heavily oxidized ones. These trends are generally associated to a spike in the air-oxide interface roughness [3]. It was also noted that the sudden change in the trends also coincided with the formation of cracks on the surface of the treated specimens that appeared after the 5800 J dose treatment, as shown in Fig. 2. Such cracks are inevitable in heavily oxidized samples where a build up of stresses, which can be attributed to volume changes in the conversion process, are naturally relieved through cracking [2, 4]. For specimens exposed to high plasma doses, we estimate the glassy skin thickness from the top surface (z=0) to the baseline PDMS SLD, according to the criteria defined earlier.

II. ALTERNATIVE CRITERIA FOR DETERMINATION OF FILM THICKNESS FROM SCATTERING LENGTH DENSITY PROFILES

Figure 5c of the paper provides a comparison between thickness data obtained from analysis of wrinkling data and XRR SLD profiles. Evidently, the profiles do not correspond to well-defined bilayers and several definitions are possible for the thickness of the skin layer.

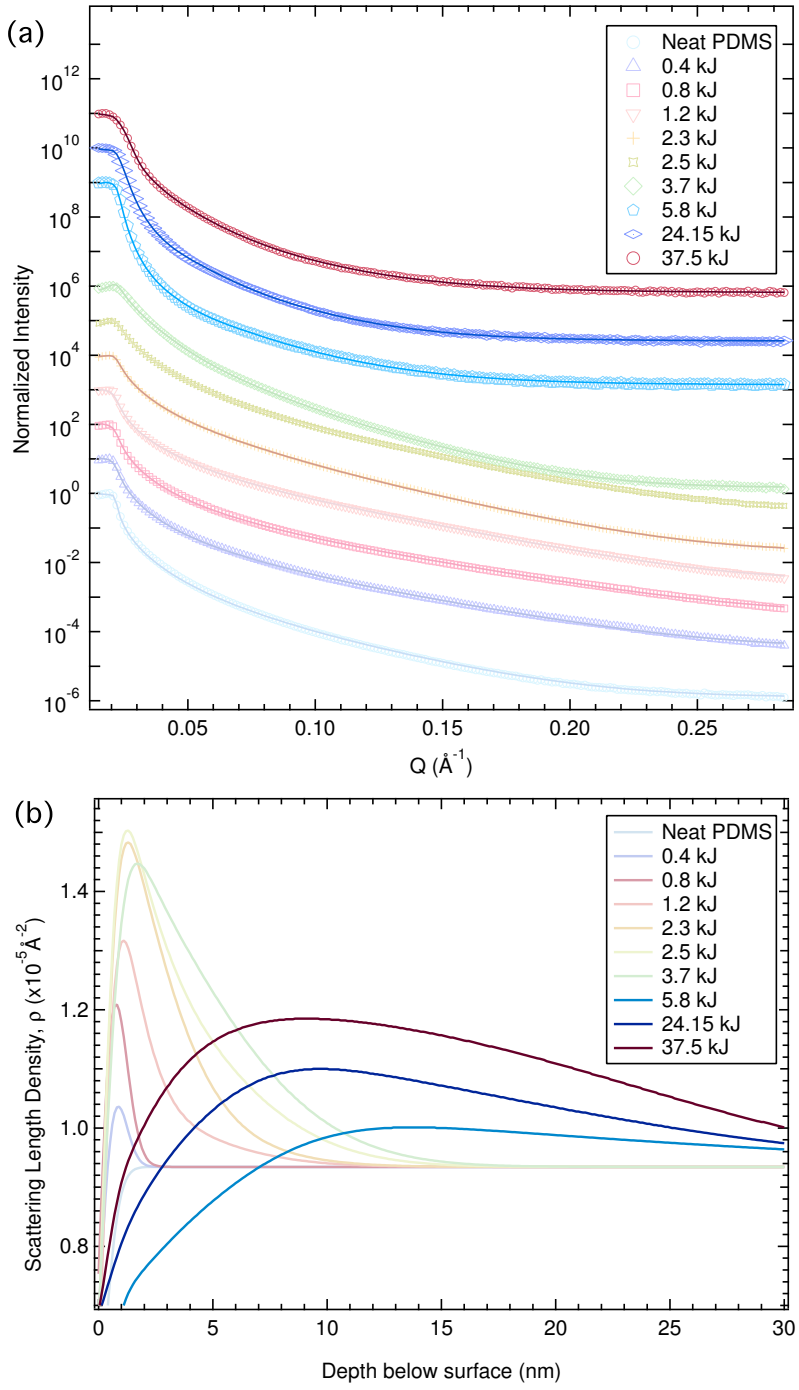

FIG. 1: X-ray reflectometry data and fits for plasma oxidised PDMS coupons treated under various levels of plasma dose. This figure shows data for all of the samples shown in Fig. 5 of the main report (light, faint colours), plus three extra at high doses 5.8 kJ, 24.15 kJ and 37.5 kJ (dark, rich colours). Scattering length density profiles resolved from the data in (a) are displayed in (b).

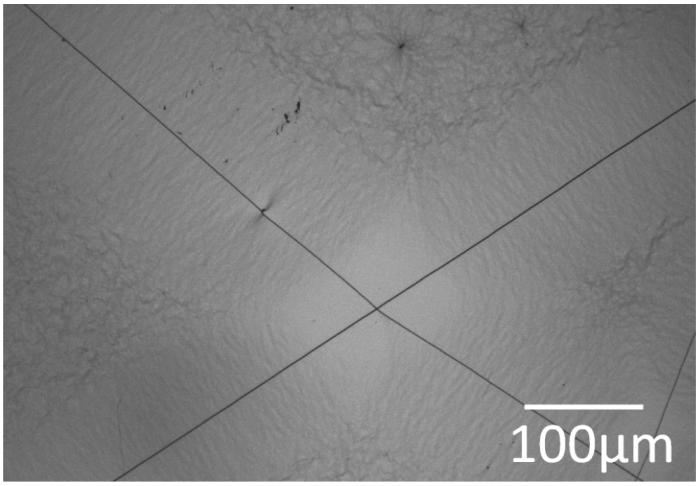

FIG. 2: Reflection mode OM image depicting the appearance of cracks in the surface of heavily oxidized PDMS on Si wafer, treated with a plasma dose $D > 3.7$ kJ.

One such definition is obtained by measuring the base width of the SLD profiles, defined as the depth range of the sample for which:

$$SLD_D > (SLD_{neatPDMS} + 0.05 \times [SLD_{D_{max}} - SLD_{neatPDMS}]) \quad (1)$$

Clearly, this criterion provides good agreement between wrinkling and XRR data. Other criteria include the width at half maximum, and distance from z=0 to the maximum SLD or subsequent inflexion point. Figure 3 displays alternative values of film thickness extracted from XRR SLD profiles by two such criteria. Thickness values represented by red squares correspond to the width at half maximum relative to the baseline, while pink triangles correspond to the thickness defined by the intersection with the SLD of PDMS and the half maximum towards the bulk material. The lines in the Fig. 5 of the paper enclose the various plausible criteria to define h_f.

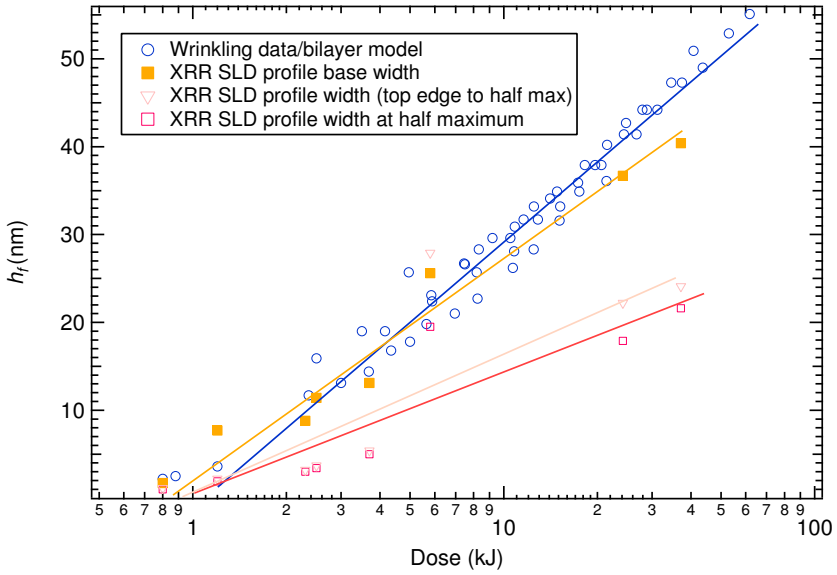

FIG. 3: Film thickness values obtained from the ideal bilayer model using measured values of wrinkle λ to those obtained by inspection of the X-ray reflectometry SLD profile data, based on several different criteria. The solid lines are guides to the eye.

[1] H. Hillborg and U. Gedde, *Polymer*, 1998, **39**, 1991.

[2] M. J. Owen and P. J. Smith, *J. Adh. Sci. Tech.*, 1994, **8**, 1063.

[3] M. Foster, *Critical Reviews In Analytical Chemistry*, 1993, **24**, 179–241.

[4] H. Hillborg, J. F. Ankner, U. Gedde, G. Smith, H. Yasuda and K. Wikstrm, *Polymer*, 2000, **41**, 6851.