Supporting Information for

# Probing the tightly bound layer in poly(vinyl alcohol) thin films using swelling measurements

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## Spectroscopic Ellipsometry (SE) Fit results

The SE angles $\Psi$ and $\Delta$ are shown as functions of wavelength, $\lambda$ in Fig. S1(a) for a PVA thin film of dry (unswollen) thickness of 189 nm. Note that the PVA thin films were modelled as resting on a 2 nm native $SiO_2$ layer on the Si substrate, refer Fig. S1(b). The corresponding fit parameters are summarised in Table S1. The time dependence of the MSE during the swelling process is shown in Fig. S2.

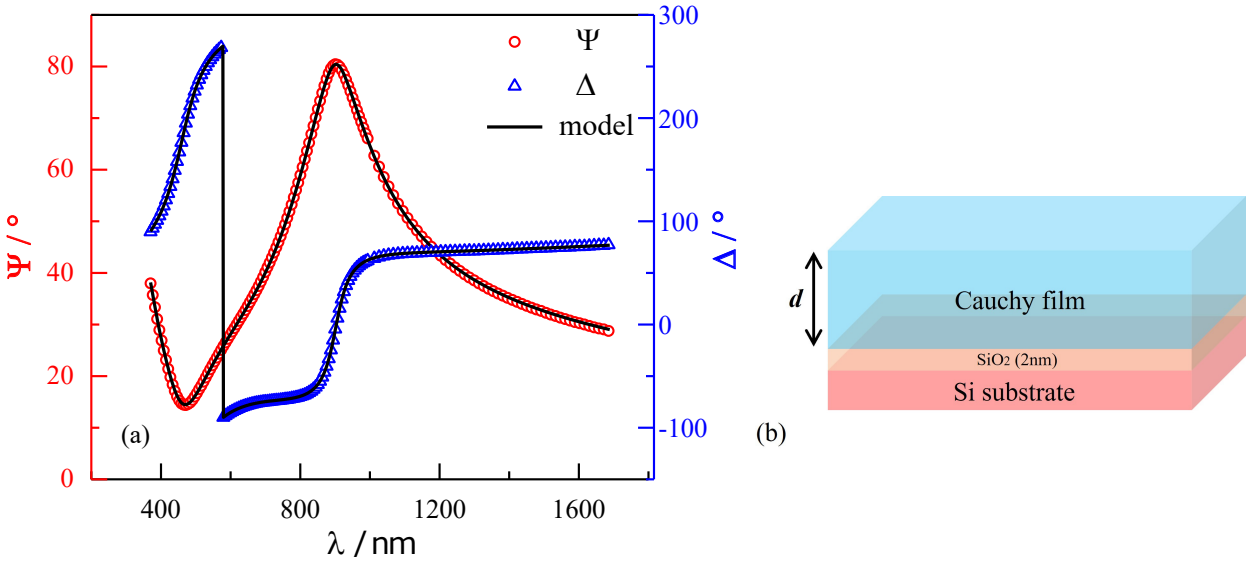


Figure S1: (a) $\Psi$ (left y-axis) and $\Delta$ (right y-axis) dependence on $\lambda$ for PVA thin film of dry (unswollen) thickness 189 nm. The measured data are indicated as symbols and the fits to the Cauchy dispersion relation with $C = 0$ are indicated as solid black curves; (b) A not-to-scale schematic of the model (Si substrate)/$SiO_2$(2nm)/(polymer film) used for the data fits.

Table S1: Cauchy model fit parameters, A and B, and the MSE corresponding to Fig. S1.

| Film Thickness (nm) | Model Parameters | | |
|---|---|---|---|
| | A | B ($\mu m^2$) | MSE |
| 189 | 1.504 | 0.005 | 2.9 |

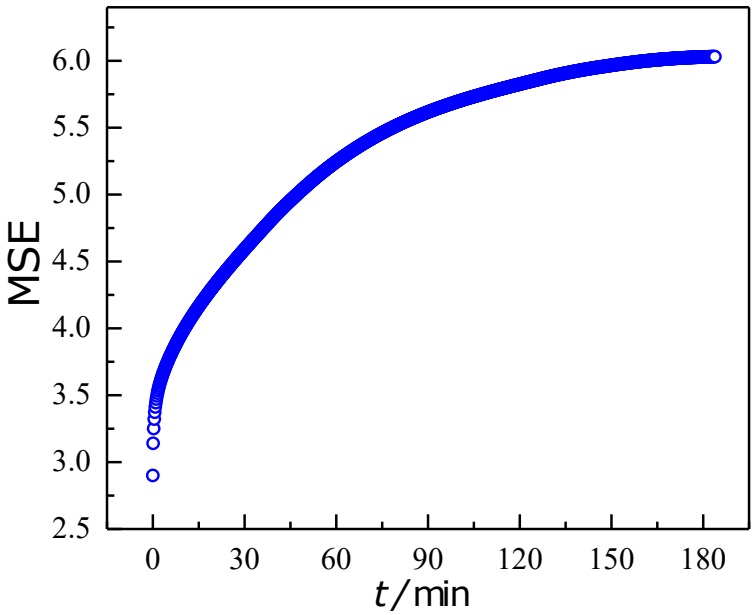


Figure S2: Dependence of the MSE values on time of exposure to $H_2O$ vapour, $t$, for 189 nm PVA thin film.