Supporting information

Bilayer sample preparation

Bilayer samples of itraconazole glasses were prepared by physical vapor deposition as shown below in Figure S1a. A portion of the sample was covered while performing the first deposition at the set temperature, illustrated in Figure S1a for a $T_{substrate,\,1}$ = 270 K. This portion of the sample was uncovered and a second position was covered during the second deposition at $T_{substrate,\,2}$ = 325 K as shown in Figure S1b. Ellipsometry measurements on the three regions of the resulting sample provided a critical test of the hypothesis that substrate temperature controls orientation in the vapor-deposited glass.

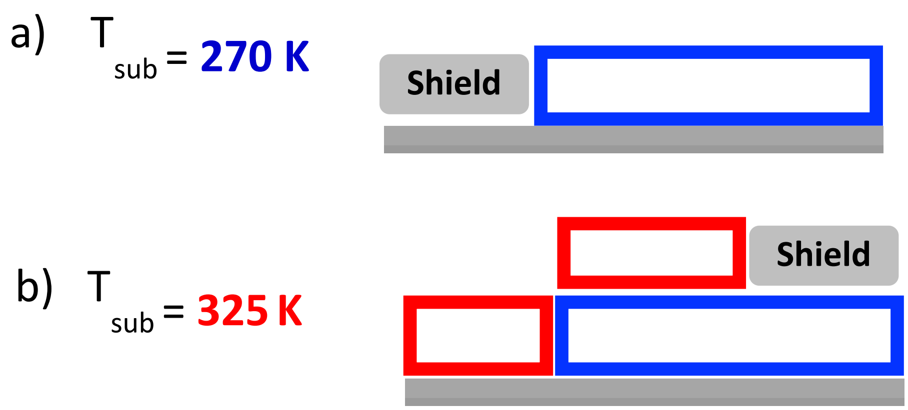

Figure S1: Schematic of the deposition of the bilayer samples. After deposition of the first layer, illustrated in a) for T_{sub} = 270 K as the first layer, the temperature as adjusted and the shield moved. b) deposition at the second substrate temperature T_{sub} = 325 K.

Ellipsometry and modeling of bilayer samples

Ellipsometry data was modeled using CompleteEASE™ software (Version 5.08, J.A. Woollam Co.) using four layers to describe the bilayer samples: the silicon substrate, 2 nm of native oxide and two anisotropic Cauchy layers. For each anisotropic Cauchy layer, the refractive index as a function of wavelength is given by $n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$, where A, B, and C are fitting parameters; the birefringence was described as a wavelength-independent constant where $\Delta n = n_z - n_{xy}$. The single layer portions of the samples were modeled using only one anisotropic Cauchy model. For all these fits, the initial fitting parameters were determined by typical values obtained by fitting single layer samples deposited over a wide range of substrate temperatures: $A_{xy=z}$ = 1.6, $B_{xy=z}$ = 0.01, $C_{xy=z}$ = 0.001.

Several methods were used to obtain the final fit result presented in Figure 4 of the main text and to assure that our models accurately represented the bilayer samples. The first fitting method started with two isotropic layers with the thicknesses indicated by the single layer portions of the sample shown in Figure S1. The model was allowed to optimize the thickness, the fitting parameters A, B, and C, and the birefringence for both layers in order to minimize the mean square error (MSE). Excellent fits were obtained as shown in Figure S2. The birefringence values obtained were those shown in Figure 4 of the main text. The thicknesses of the two layers as determined by the fitting were within 3% of the values of the outer portions of the sample. The MSE values for these fits were 3 – 5, consistent with an excellent fit to the data. The birefringence values that resulted for each layer from this fit were within 0.003 of the birefringence in the single layer portions of the sample. The fitted thickness and birefringence results strongly support our conclusion that molecular orientation is controlled by substrate temperature and is not affected by the orientation of the underlying layer.

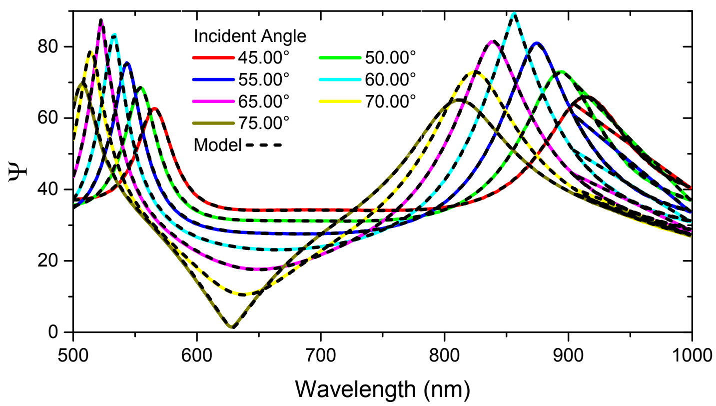

Figure S2: Ellipsometry parameter Ψ measured at different incident angles (solid lines) show a good fit to the model (dashed lines) used to describe the film shown in the center portion of Figure S1. This result indicates that two anisotropic Cauchy layers with different birefringences, as shown in Figure 4 in the main text, accurately describe the sample.

A second method was used in an attempt to fit the data shown in Figure S2. Here we tested the idea that the orientation of the second layer was slaved to the orientation of the first layer in a manner that would be expected for an epitaxial process. For the fitting, we constrained the birefringence of the second layer to be equal to that of the first layer. The resulting fit was very poor (not shown) with an MSE greater than 100.

For completeness, we note that a second bilayer sample was deposited with the order of the substrate temperatures reversed relative to Figure S1. Using the first procedure described above, excellent fits to the data were obtained with MSE values less than 5. The resulting birefringence values for the two layers are shown in Figure 4 of the main text. The second approach, which used the birefringence of the initial layer to describe the entire film, resulted in very poor fits with MSE values greater than 100.