

**The Role of Thermal History on Spontaneous Polarization and Phase
Transitions of Amorphous Solid Water Films Studied by Contact Potential
Difference Measurements**

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SUPPLEMENTARY MATERIAL

The following sections support the results presented in the main text, namely, the growth temperature (T_{gr}) and ASW film thickness effects on the spontaneous polarization of the growing films, as measured by the non-invasive, in-situ Kelvin probe method under UHV conditions. The following includes supplementary data regarding the Δ CPD-substrate temperature counter-correlation observed during the growth of the extra-thick ASW films, TP- Δ CPD measurements of films of varied thicknesses, and the zero-order desorption of the water multilayer molecules as reflected by correlation between the layer thickness (an indicator for the number of water molecules) and the peak's temperature (Sec. I). It further contains a more detailed analysis and calculations concerning the spontaneous polarization of the water films, in particular regarding the accumulated electric fields and dipole alignment (Sec. II).

I. Thickness effect

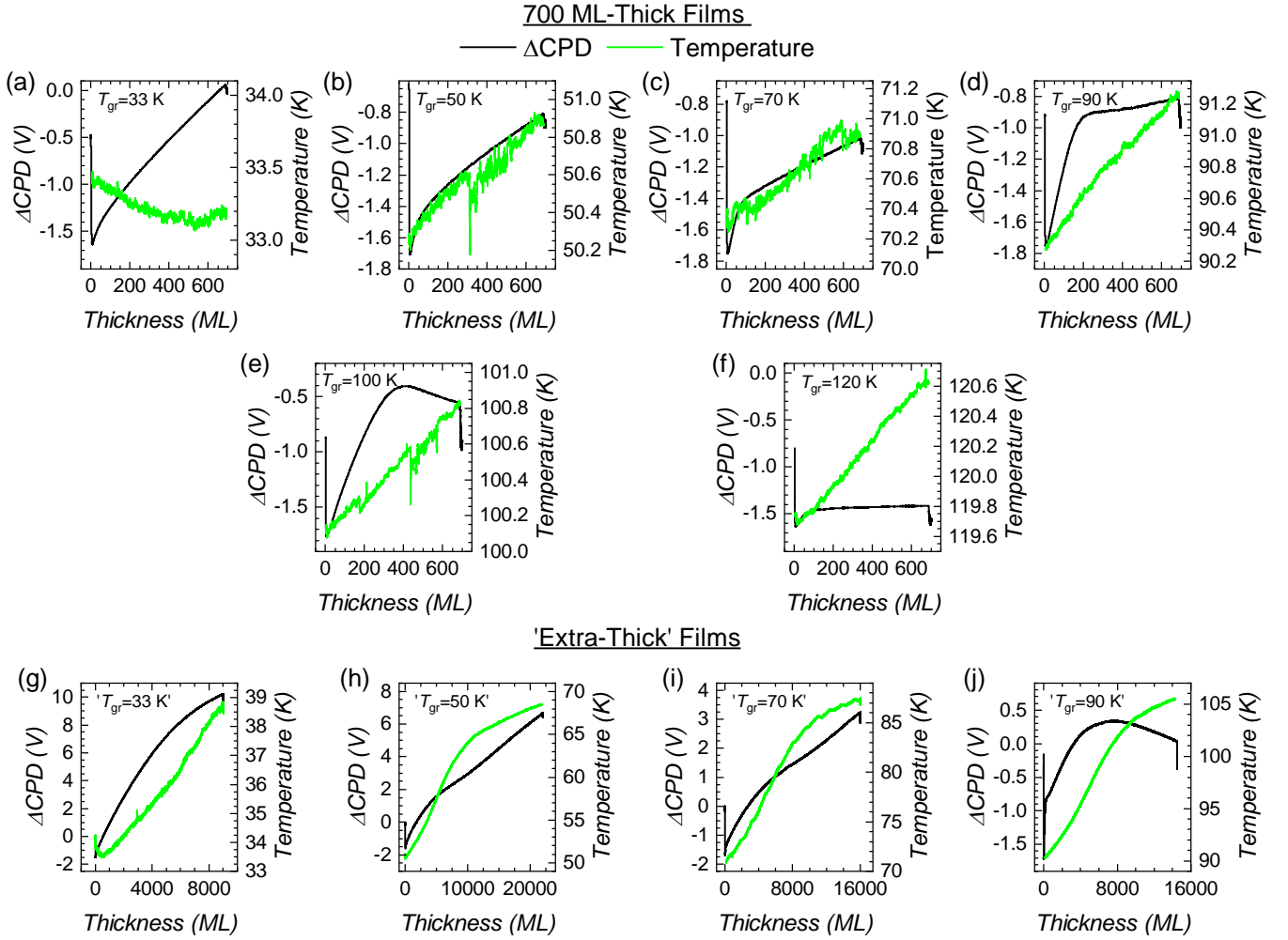


FIG. S1. Polarization and temperature change during the growth of ASW films. Δ CPD profiles versus ASW film thickness during growth at different growth temperatures (in black). Substrate temperature during growth is also depicted (in green) while the Δ CPD measurements are taken. (a)-(f) Δ CPD measurements during the growth of 700 monolayers (ML)-thick films in the growth temperature (T_{gr}) range of 33-120 K. At such thicknesses, the temperature modification is negligible, and no apparent correlation between the Δ CPD and temperature profiles can be observed. For the extra-thick films [(g)-(j)] one can observe a convexity-concavity duality; convexity of the temperature profile follows the concavity of the Δ CPD. When the temperature levels-off, the Δ CPD profile approaches linearity again.

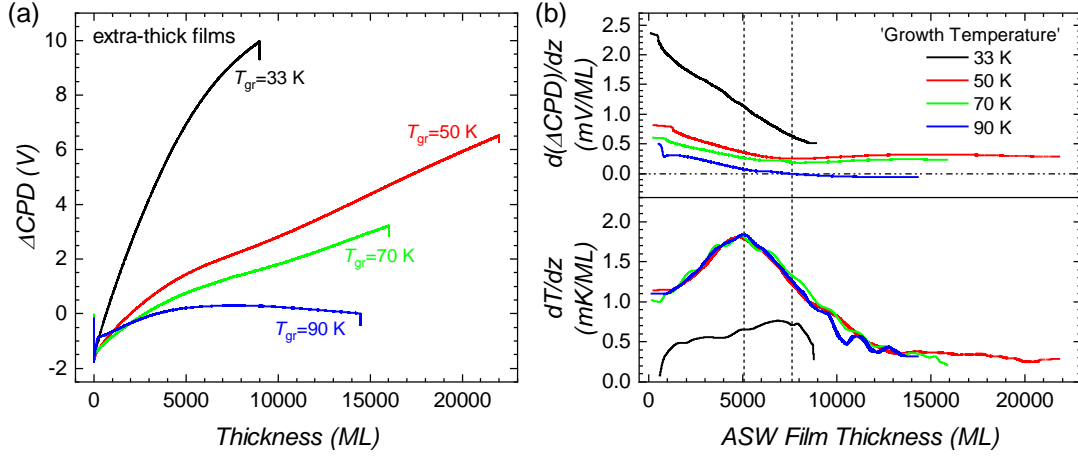


FIG. S2. Growth of 'extra-thick' ASW films. (a) ΔCPD profiles versus ASW film thickness during the growth of 9000-22000 ML-thick films at the indicated initial growth temperatures. For all the thick films the polarization shows concavity (positive but decreasing slope) with the film thickness above 1000 ML and even a net orientation flipping for films grown at the initial growth temperature of 90 K (turn to negative slope near 7600 ML). For each initial growth temperature, at some thickness the concavity saturates, and the profile becomes linear again. This is a comparative representation of data shown in Fig. 1 of the main text and Figs. S1(g)-S1(j) above. (b) Analysis of the counter-correlation between the ΔCPD and substrate temperature observed during film growth. The initial concavity of the ΔCPD -versus-thickness curves is reflected by the decreasing polarization accumulation rate [$d(\Delta\text{CPD})/dz$ or the internal electric field; lines with markers], however, at thickness of ~ 7600 ML this trend changes and the rate increases before it stabilizes at a constant value, i.e. a linear change of the ΔCPD with film thickness (at ~ 11500 ML). Exceptions are the $T_{\text{gr}}=33$ K curve, which shows only a concave profile, and the $T_{\text{gr}}=90$ K, which reveal a maximum at thickness of 7600 ML [seen in (a)] before stabilizing at a negative polarization rate (crossing the horizontal dashed-dotted line, which denotes $d(\Delta\text{CPD})/dz=0$; polarization flipping). The temperature profile on the other hand is convex below 5000 ML (increasing rates of temperature change, dT/dz ; solid lines) and concave above (profiles descend). At 7600 ML the rate of temperature change approaches its initial value. At higher thicknesses the rate decreases furthermore. When the rate is sufficiently low (below 0.5 mK/ML) the $d(\Delta\text{CPD})/dz$ curves saturate (at ~ 11500 ML). Note the identical effect of film thickness on the rate of temperature change of the different films, with the exception of the films grown at 33 K. The $T_{\text{gr}}=33$ K rate of temperature change curve (in solid black) shows much lower rates due to the more efficient cooling of the film.

See discussion in the main text (Results and Discussion, Sec. A) regarding the effect of the temperature change on the evolution of the ΔCPD -versus-thickness curves.

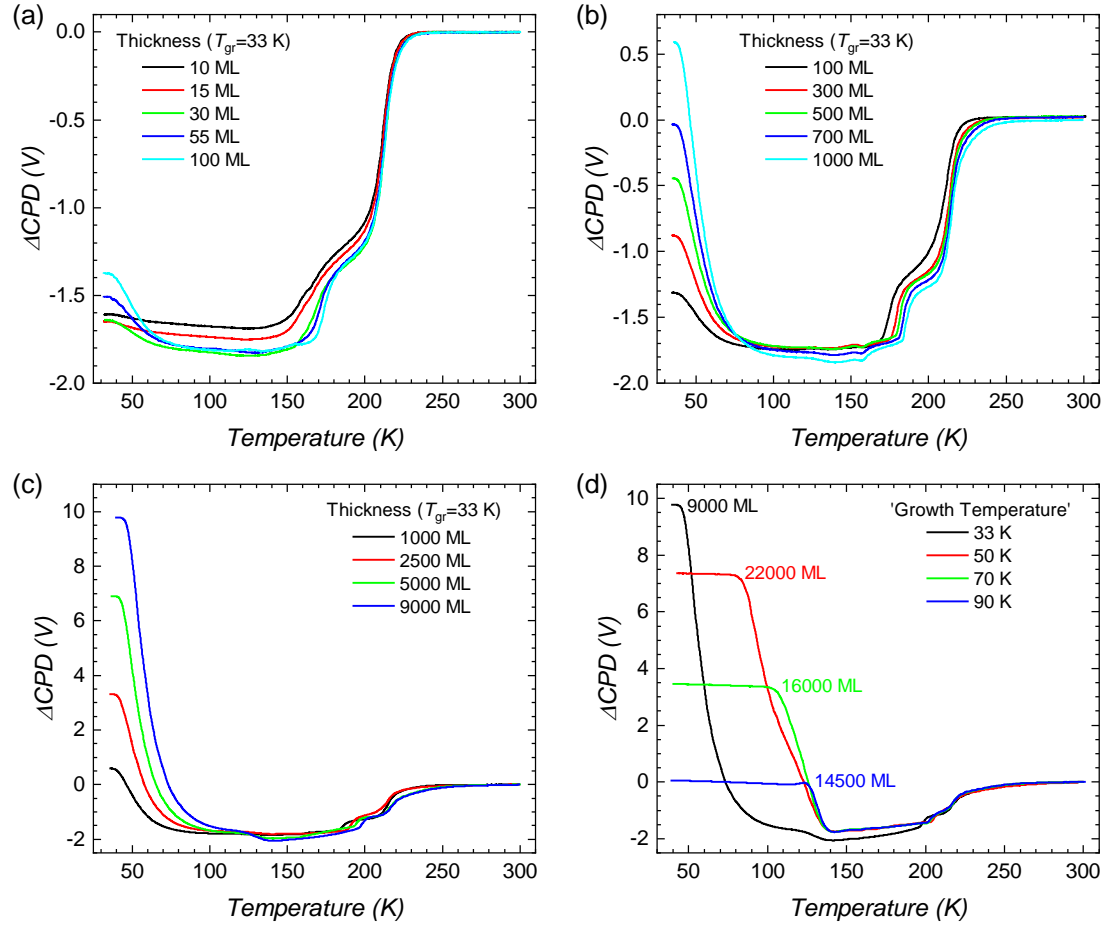


FIG. S3. Film thickness effect on the spontaneous polarization of ASW films. (a)-(c) TP- ΔCPD spectra of 10-9000 ML- thick ASW films grown at 33 K. (d) TP- ΔCPD spectra of 9000-22000 ML- thick films grown at 33-90 K (the 'extra-thick' films). The corresponding $d(\Delta\text{CPD})/dT$ spectra are presented in Fig. 5 of the main text; see discussion there.

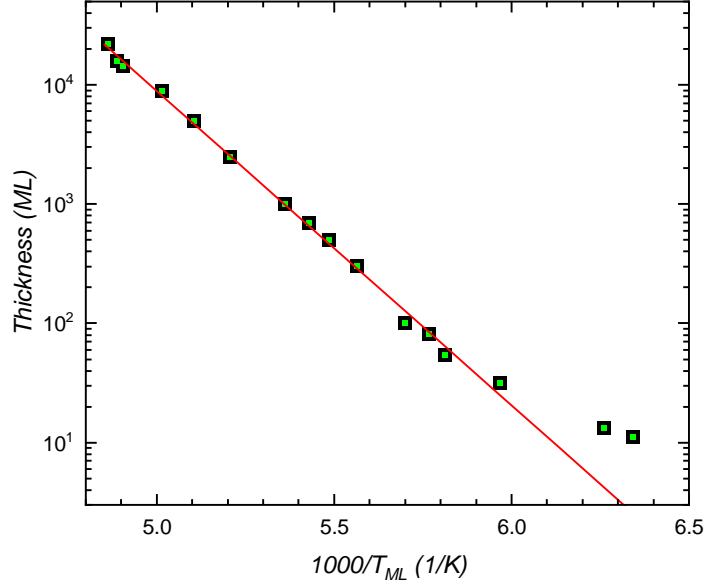


FIG. S4. Demonstration of the zero-order kinetics of ASW multilayer desorption. The $d(\Delta\text{CPD})/dT$ multilayer peak shifts to higher temperatures (T_{ML} is the temperature of the multilayer desorption peak) with film coverage (represented by the layer thickness; y-axis, semi-logarithmic scale). Taken from the thickness dependent $d(\Delta\text{CPD})/dT$ spectra (Fig. 5 in the main text) for up to 9000 ML-thick films grown at 33 K and those of the extra-thick films grown at T_{gr} in the range of 33-90 K (14500-22000 ML). In the multilayer regime, the coverage (thickness) is proportional to $\int_{T_0}^{T_{\text{ML}}} \exp(-E_a/kT) dT$, where E_a is the desorption activation energy, k is the Boltzmann constant, and T_0 is the onset temperature for the multilayer desorption. Because of the narrow range of T_{ML} at high coverages, the integration can be approximated to $A_0 \exp(-E_a/kT_{\text{ML}})$. Fitting the data yields an apparent activation energy of 4.7 ± 0.5 kcal/mol, relatively close to the water hydrogen bond strength of 5.5 kcal/mol.

II. Deriving the electric field and the dipole alignment of polarized ASW Films

The average contribution of a single molecule to the observed polarization P_{obs} is given by

$$P_{\text{obs}} = P_z = \frac{\bar{\mu}_z}{\Omega}, \quad (\text{S1})$$

where Ω is the molecular volume and $\bar{\mu}_z$ is the z -direction component of the dipole moment of a single molecule in the ASW film. Here Ω is taken as the van der Waals volume (see Table SI). The polarization can also be associated with the electric field by the following relation:⁹

$$P_z = \varepsilon_0 E_z, \quad (\text{S2})$$

We consider the film polarization according to the ΔCPD measured beyond the coverage (θ) of 10 ML, where the ΔCPD increases with layer thickness. Other studies, including the work of Bu et al. (Ref. 14), present only negative and decreasing surface potentials (V_{film}). The sign of the surface potential is a matter of convention. In most works it is defined to be negative when negative charges are placed upon the surface. In Ref. 10 for example, the notation is opposite to that presented here and the measured polarization is in accordance (in sign) to measurements of Bu. *et al.* in Ref. 14. From the definition of the ΔCPD , this measurement is relative to CPD of the bare substrate (thus to its work function), and is calculated here by:

$$\text{CPD} = \Phi_{\text{sample}} - \Phi_{\text{probe}}, \quad (\text{S3})$$

where Φ is the work function of either the substrate or the probe, which are typically not determined/unknown (at least that of the probe), however are also not required.

Thus,

$$\begin{aligned} \Delta\text{CPD}(\theta) &= \text{CPD}(\theta) - \text{CPD}_0 = \Phi_{\text{sample}}(\theta) - \Phi_{\text{bare sample}} \\ &= \Delta\Phi_{\text{substrate/film interface}} - V_{\text{film}}(\theta). \end{aligned} \quad (\text{S4})$$

The ΔCPD is thus defined in the framework of the substrate. Moreover, when we charge our films with electrons, we detect positive ΔCPD values, and oppositely in the case of cations charging.^{13,35} The film surface voltage, therefore, is offset and shows an opposite trend (sign of the slope) than the ΔCPD .

According to the definition of the observed ΔCPD , its derivative with respect to distance (in the z -direction, normal to substrate) equals the z -direction component of P

$$P_z = \varepsilon_0 \frac{d(\Delta\text{CPD})}{dz}. \quad (\text{S5})$$

Therefore, we can correlate between the measured voltage and $\bar{\mu}_z$ by

$$\bar{\mu}_z = \varepsilon_0 \Omega \frac{d(\Delta\text{CPD})}{dz}. \quad (\text{S6})$$

Based on these relations we can calculate the z -direction component of the electric field, E_z and the degree of dipole alignment $\bar{\mu}_z/\mu$. Yet, in order to obtain the field, one must translate the adsorbed mass, in terms of monolayers (ML) to the actual film thickness in length scales. In order to perform this conversion, we need to know both the porosity and the thickness of a compact monolayer, s . Since all the films consist of an equal number of molecules to that contained in 700 ML compact ASW film, their mass is equal- to

$$m = \rho V = \rho AL, \quad (\text{S7})$$

where m is the film mass (can be calculated, however not required), ρ is the film density in g/cm^3 , V is the film volume, A is the area of the substrate, and L is the film thickness.

For compact films the thickness, L_c , is:

$$L_c = (\#ML)s. \quad (\text{S8})$$

From here we can calculate the thickness of any film, according to

$$\rho L = \rho_c L_c, \quad (\text{S9})$$

where ρ_c is the density of the compact film. Thus

$$L = L_c \frac{\rho_c}{\rho} = (\#ML)s \frac{\rho_c}{\rho}. \quad (\text{S10})$$

In Table SI are the values required for the calculation of the electric field and the dipole alignment. In Table SII are the T_{gr} dependent densities of ASW films, the derived z -direction component of the electric field, and the degree of dipole alignment.

TABLE SI. Water molecular parameters that are required to derive the electric field and the dipole alignment in ASW films. μ is the total dipole moment, s is the interlayer spacing (the monolayer thickness), and Ω is the molecular van der Waals volume.

μ (D) ^(a)	s (Å) ^(b)	Ω (Å ³) ^(c)
3.0	3.7	17.35

^(a) See Results and Discussion, Sec. B of the main text.

^(b) Taken from Refs. 49 and 50.

^(c) Calculated according to Ref. 51.

TABLE SII. ASW film densities, calculated values of the electric field, and dipole alignment (calculated based on Table SI).

	T_{gr} (K)	Density (g cm ⁻³) ^(a)	E_z ($\times 10^6$ V m ⁻¹)	$\bar{\mu}_z/\bar{\mu}$ ($\times 10^{-5}$)
$\rho_c=0.93$ g cm ⁻³	31	0.70	5.57	8.57
	33	0.72	4.46	6.86
	35	0.74	4.26	6.55
	40	0.74	3.18	4.90
	45	0.75	2.59	3.99
	50	0.76	2.03	3.13
	60	0.78	1.64	2.53
	70	0.79	1.45	2.23
	80	0.81	1.20	1.85
	90	0.82	0.50	0.77
	100	0.86	-1.52	-2.35

^(a) ASW densities were taken from or calculated according to Ref. 21.