Supporting information

Frontal vitrification of PDMS using air plasma and its impact on surface wrinkling

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A coarse grained propagation model is used to describe the oxidation of PDMS upon plasma exposure. According to our model, the thickness of the glassy layer is given by

$$h = \frac{\ln(t)}{\mu} - \frac{1}{\mu}\ln\left(\frac{1}{\overline{KI_0}}\ln\left(\frac{1}{1-\phi_c}\right)\right) \quad (1)$$

Since ϕ_c <<1, $\ln\left(\frac{1}{1-\phi_c}\right) \approx \phi_c$ leading to a simplification of equation (1)

$$h = \frac{\ln(t)}{\mu} - \frac{1}{\mu}\ln\left(\frac{\phi_c}{\overline{KI_0}}\right) \quad (2)$$

The values of *h* were calculated using the experimental wavelengths and the parameters μ and $\overline{KI_0}$ in eq. (1) computed assuming ϕ_c=0.06. Figure S1 shows the inferred *h* as a function of the plasma exposure time for different power values, and the power dependence of the model parameters.

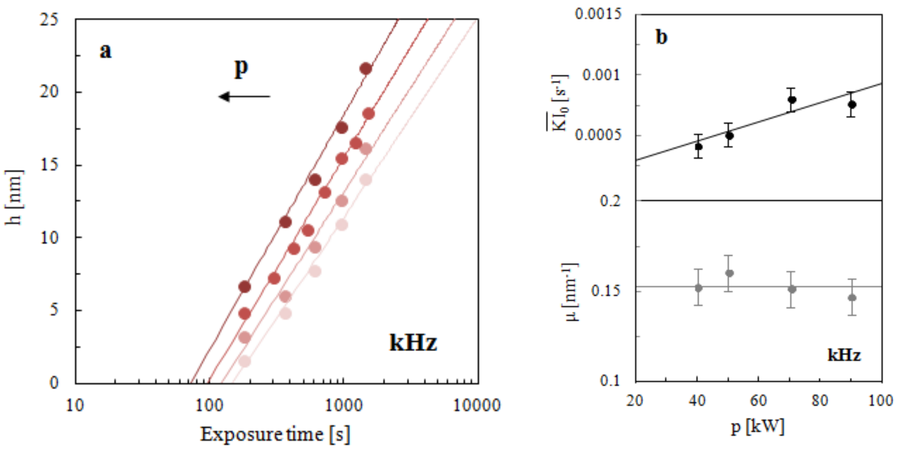

Figure S1: (a) Thickness of the plasma oxidized PDMS as a function of exposure time for different power settings. The values were calculated from the experimental wavelengths measured with $\varepsilon_{prestrain}$=20% and constant air pressure P=0.93 mbar. The lines are logarithmic fits. (b) Power dependence of model parameters μ and $\overline{KI_0}$for all exposure times. The parameters were computed using the experimental values of *h* and eq. (8), taking ϕ_c=0.06.

The curves at different power values collapse into a single master curve when the data are plotted as a function of $D \equiv p \times t$ and we thus write:

$$h = \frac{\ln(D)}{\mu} - \frac{1}{\mu}\ln\left(\frac{1}{KI_0}\ln\left(\frac{1}{1-\phi_c}\right)\right) \quad (3)$$

Moreover, the pressure P is found to influence the plasma oxidation: an increase in P leads to a slowing down of the reaction kinetics. Figure S2 shows h as a function of the plasma dose D for different pressures P, and the pressure dependence of the model parameters.

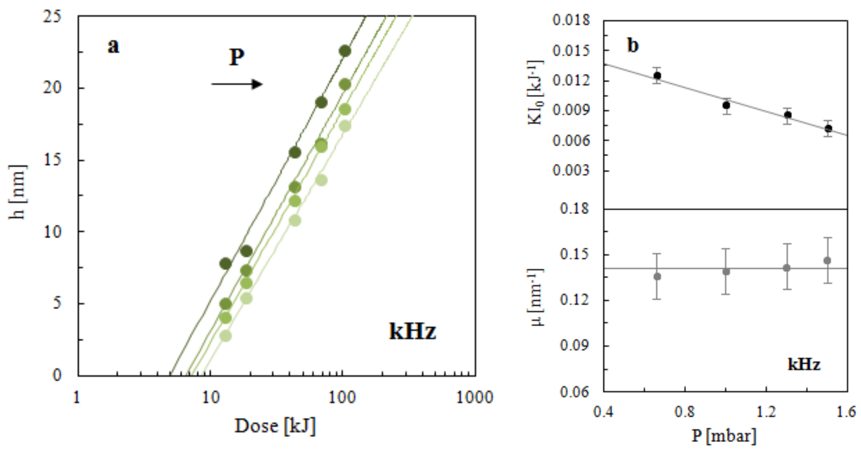

Figure S2: (a) Thickness of the plasma oxidized PDMS as a function of dose for different pressures (shown in b). The values were calculated from the experimental λ measured with $\varepsilon_{prestrain}$=20% and lines are logarithmic fits. (b) Pressure dependence of model parameters μ and KI_0 for all doses. The parameters were computed from eq. (8) taking ϕ_c=0.06.

Temperature increase during plasma exposure and possible effect on surface wrinkling

The temperature within a plasma chamber is known to increase during exposure. Combined with glassy skin formation, the surface expansion (upon heating) and contraction (upon cooling) can result in spontaneous, generally isotropic, wrinkle formation. Since the focus of this study is on mechanically-induced wrinkling, we quantify the temperature changes within the plasma chamber and evaluate a possible impact on surface topography. The plasma chamber temperature was thus monitored as a function of air plasma frequency (kHz, MHz), power (7-100W) and duration (0-7200 s) using a calibrated thermocouple. These results are shown in Figure S3.

We find the maximum chamber temperature to be 40°C after 2h exposure at the highest MHz air plasma induction power. Similar values are observed within the kHz air plasma at 30W (which however reaches up to 90°C at 80W).

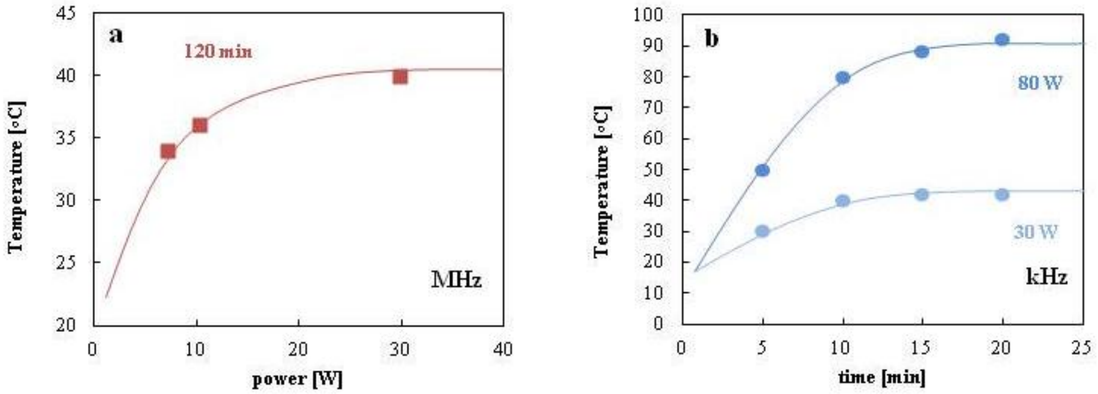

Figure S3: Plasma chamber temperature (a) within MHz air plasma chamber after 2 hours of operation as a function of the induction power; (b) within kHz air plasma chamber as a function of time for two representative induction powers. The lines are guides to the eye.

Considering the thermal expansion coefficient of PDMS, the maximum thermal strain was estimated to be $\varepsilon_{max} \approx 0.6$ % (MHz), below the critical prestrain (the largest value attained in the kHz plasma is $\varepsilon_{max} \approx 2\%$, but exposure times employed in our study at such high power are much shorter). By comparison, the uniaxial mechanical prestrain exerted throughout the paper is 20%. To confirm our expectation that thermal effects do not contribute to the topographies reported, we measure by AFM a PDMS surface (a) exposed to 2 hr 30W air MHz plasma in the absence of mechanical prestrain and (b) a fresh PDMS surface. These are confirmed to be effectively identical within measurement uncertainty, and no thermally-induced isotropic wrinkling is observed.

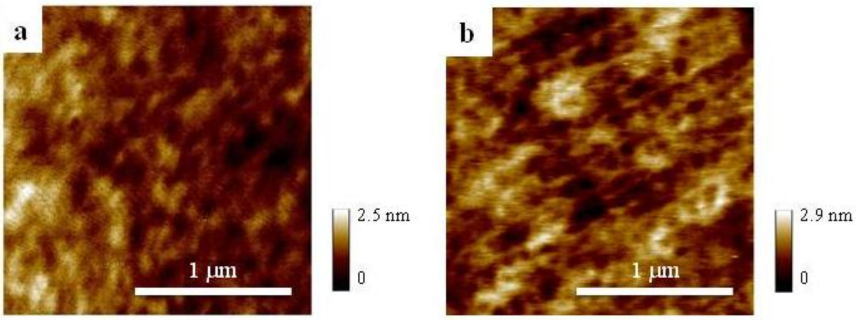

Figure S4: AFM topography images of (a) PDMS surface exposed to an air MHz plasma with induction power p=30 W for 120 min, in the absence of pre-strain and b) an unoxidised PDMS surface.

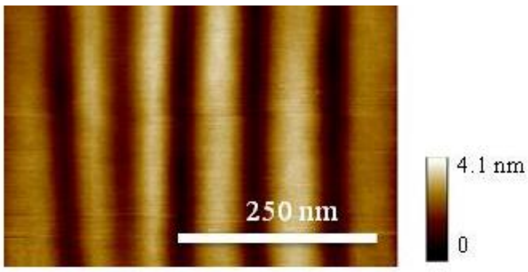

Figure S5: Illustrative AFM topography image of a 100 nm wavelength readily achieved on PDMS by MHz air plasma oxidation with $\varepsilon_{prestrain} \approx 20\%$, at P=1.2 mbar, p= 7 W, and t = 90 s.