Supporting Information

Sub 10 Nanometer Feature Size in Silicon Using Thermal Scanning Probe Lithography

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Yield stress and softening temperature in nanoscale experiments

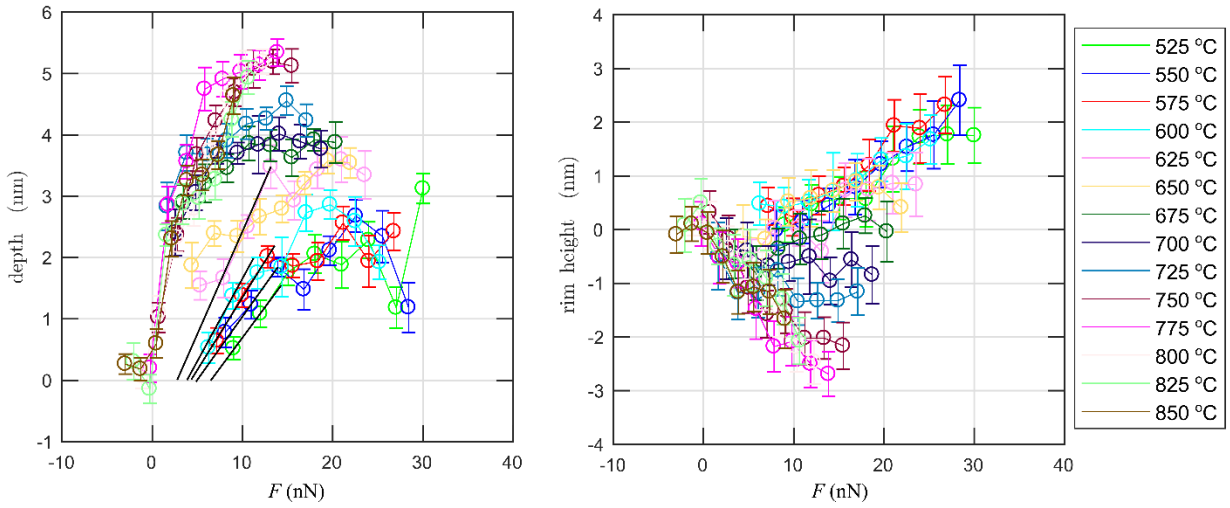

Figure S1: Average line depth *d* and rim height *h* for all measured temperatures. The black lines in the left panel are guides to the eye to indicate the finite force F_0 at $d = 0$ required to nucleate a permanent deformation in the polymer.

For low temperatures a finite force F_0 is required to nucleate the formation of the line as indicated by the black lines in figure S1. F_0 originates from a finite yield stress present in the sample. As expected, F_0 decreases with temperature and should approach zero at the glass transition temperature. At 675 °C the write behavior is similar to the one at higher temperatures, and we take this information as an indication that we have crossed the glass transition temperature. Accordingly, we observe the glass transition in the nanoscale experiments for a nominal tip-heater temperature of approximately 650-675 °C. We note that 5 nN for our 2-3 nm radius tips corresponds to normal pressures in the range of 150-400 MPa.

The rim height (right panel in figure S1) on the other hand should be of similar value as long as there is no decomposition of the material because a similar volume has to be displaced. From figure S1b we see that the rim height starts to decrease at 625 °C. For higher temperatures the rim height continues to decrease almost linearly until we reach a temperature of 775 °C, at which the effect saturates. We interpret the result in the following manner: Decomposition is a thermally activated process and at intermediate temperatures only a certain fraction of molecules is decomposed. In the range from 625 °C to 775 °C this fraction increases from 0 to 1.

These results indicate that decomposition starts at or slightly below the glass transition temperature of the polymer.

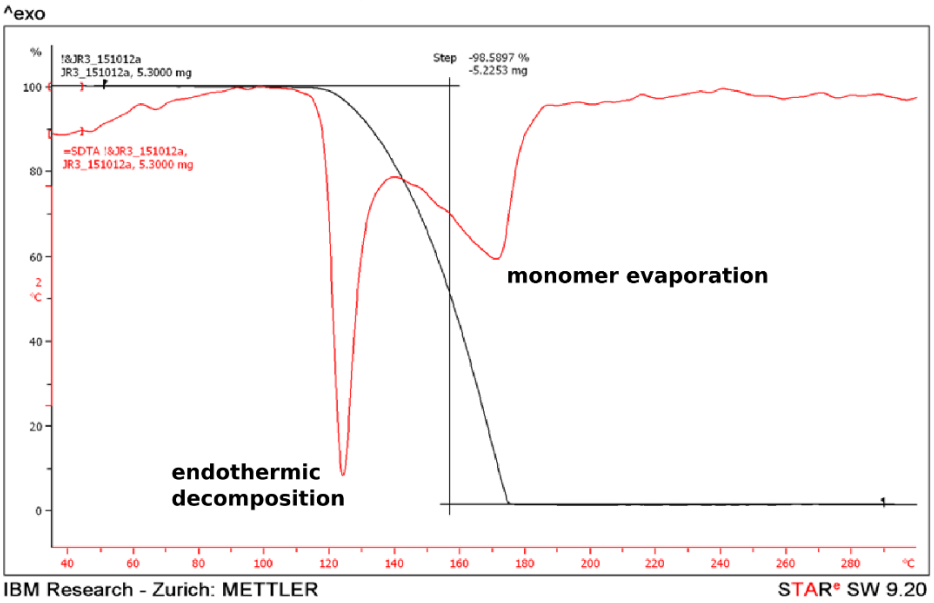

Figure S2: TGA (black) and DSC (red) traces of the PPA decomposition.

The same behavior was observed in macroscopic thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments. Figure S2 shows a combined TGA (black) and DSC (red) measurement of the polymer used. Decomposition is indicated by an endodermic peak in the DSC signal and the onset of weight loss in the TGA curve. It starts at 120 °C and is complete at approximately 135 °C. Unfortunately, the decomposition signal is much stronger than a glass transition signal occurring at the same temperature. However, using different PPA samples, we could demonstrate the onset of decomposition shifts linearly with an increasing fraction of plasticizer (monomer) towards lower temperatures (see ref. 28 of the manuscript). This behavior provides the following indication: The plasticizer lowers the glass transition temperature of the material. This causes a shift of the decomposition peak because the decomposition is linked to the softening of the material. In other words, the glassy state of the polymer prevents decomposition of the polymer because the decomposition reaction requires the activity of alpha transitions in the polymer.

We note that the difference of the transition temperatures observed in the nanoscale and macroscale experiments is due to two reasons: First, the tip temperature will be much lower than the tip heater temperature due to the high thermal resistance of the nanoscale tip. Second, the time scale of the nanoscale experiments is microseconds while the timescale of the macroscale experiments is second to minutes. For higher rates an additional shift of the transition temperatures to higher temperatures is expected.