Supporting Information

Thermal Degradation in Ultrathin Films Outperforms Dose Control of n-Type Polymeric Dopants for Silicon

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Figure S1. Thickness (H) of the brush layer of the PSn-SG1 samples grafted in RTP at 250 ºC as a function of annealing time in logarithm scale. The same figure reports the evolution of brush thickness as function of annealing time in logarithm scale for the PS14.2 sample (open symbols).
**Figure S2.** Structures of DFT PSn-SG1 and PSn-P models comprising two or six PS units.

**Figure S3.** DEP-MS evolution profiles as a function of temperature for PS$_{4.3}$-SG1 (black curve) and PS$_{5.3}$-P (red curve) samples heated to 800 °C at 20 °C·s$^{-1}$. The curves were acquired in selected ion monitoring (SIM) mode at $m/z=137$ uma for diethoxyphosphinoyl fragment (dashed black curve), $m/z=110$ uma for monoethoxyphosphinoyl fragment (dashed red curve) and $m/z=104$ for styrene (continuous curves).

Data reported in Figure S3 show that PS$_{4.3}$-SG1 starts loosing diethoxyphosphinoyl fragment ($m/z=137$ uma) at approximately 300°C. As this temperature is well below to the temperature of the first loss of PS$_{5.3}$-P, namely the loss of monoethoxyphosphinoyl fragment ($m/z=110$ uma), that occurs at approximately 400 °C, the DEP-MS analysis clearly indicates that the thermal stability of PSn-SG1 is definitely lower than PSn-P samples.