

Supporting Information

Supplement 1

In order to investigate the influence of redeposition effects, the milling depths and side wall angles (derived from top and base widths) are investigated via SEM and AFM in the relevant dose range for this study. As can be seen by the circles and triangles in Fig. S 1, the milling depths and side wall angles (with respect to the surface normal) are practically behaving linearly. If redeposition effects are of relevance, the milling depths show a decreasing behavior for higher doses, based on the fact that milled material cannot escape from the relevant areas, which reduces the effective removal rate.²⁵⁻²⁹ Furthermore, the side wall angles show a tendency towards higher angles, relative to the surface normal, which is also not found for the relevant dose range. These results hence confirm that unavoidable redeposition effects are present, but of minor relevance to the used geometries with final aspect ratios of less than 0.5.

Please note that even if redeposition events were influencing the results, this would lead to an underestimation of the relevant ranges with a high removal rate, but not to a modification of the basic result (see high dwell time ranges in Fig. 1).

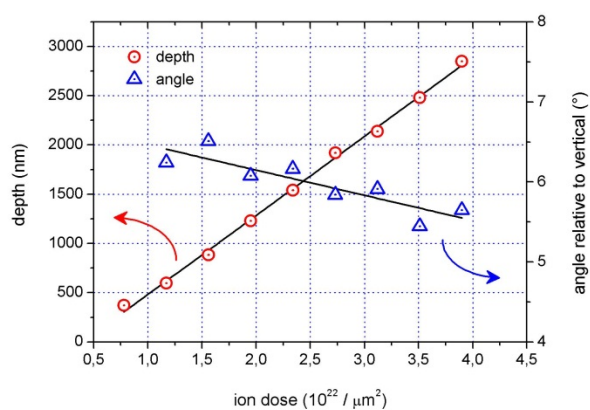


Fig. S 1: Milling depth (circles) and side wall angle (triangles; values are given vs. the surface normal) via regular patterning as a function of total ion doses on PP1. The relevant ion beam dose in this study ranged from 1.5×10^{22} to 3.2×10^{22} ions / μm^2 .

Supplement 2

To exclude the possibility that the observed effects are related to the special chemistry of polypropylene, high-density polyethylene (HDPE) has been used for verification experiments due to its simple chemistry. Fig. S2 shows a direct comparison of PP and HDPE for dwell time experiments with a PoP of 20 nm (top) as well as PoP experiments for different dwell times (bottom). As it can be seen the behaviour is very similar except the absolute RR values and the RR increase for increasing dwell times. The lower RR starting values are attributed to the more dense packing of HDPE and the higher thermal conductivity ($0.543 \text{ W.m}^{-1} \text{ K}^{-1}$)³⁴ whereas the delayed RR increase compared to PP is a result of the higher volatilizing threshold of HDPE of about 400°C .³⁵ The PoP experiments reveal also very similar behaviour for different dwell times and suggest strongly that the observed effects of technically induced heating is closely related to the thermal conductivities and less by specific chemical peculiarities.

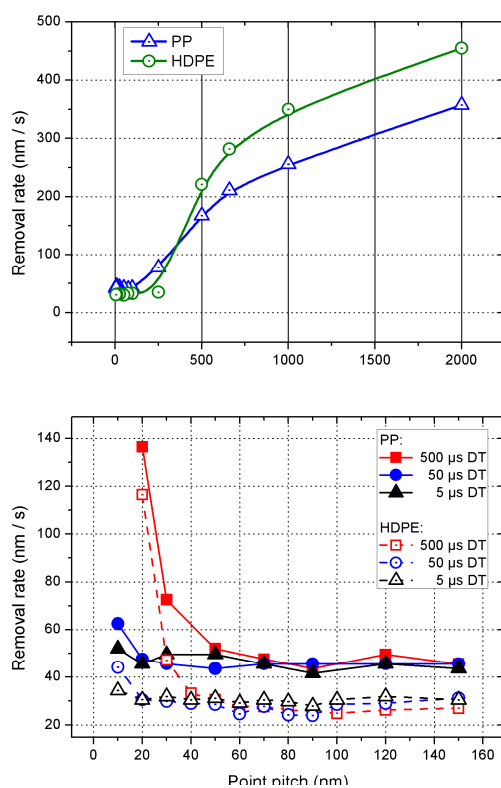


Fig. S 2: Removal rate versus dwell time (top) and point pitch (bottom) in direct comparison for PP and HDPE.

Supplement 3

Fig. S 3 shows alternative patterning shift sequences in order to maximize the point distance between subsequent IL frame patterning points. Currently, a fully flexible patterning sequence is being developed which takes into account temperature decay at each individual point in order to find the point with the lowest temperature for the subsequent beam pulse.

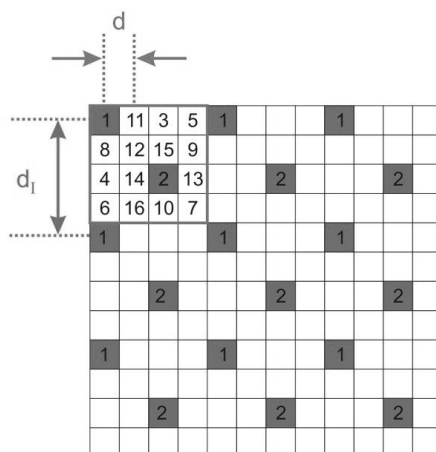


Fig. S 3: Alternative patterning shift sequences (frame top left).

Supplement 4

Representative Raman spectra for pristine polypropylene before patterning (circles) and after structuring with highly degrading parameters (squares; room temperature, 2000 μs dwell time, 20 nm point pitch, regular patterning).

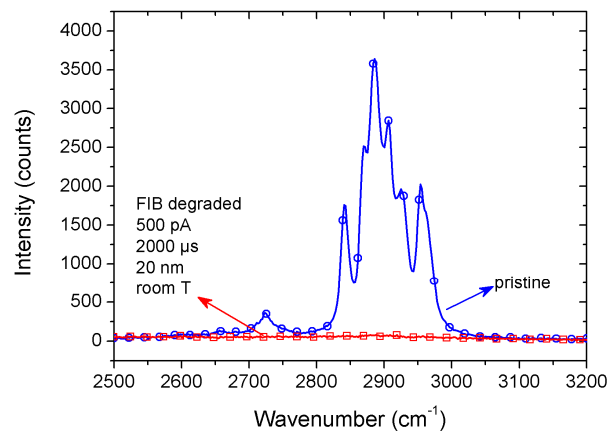


Fig. S 4: Raman spectra for pristine polypropylene (circles) and after highly degrading FIB structuring

References

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35. Q. Zhao, B. Zhang, H. Quan, R.C.M. Yam, R. K.K. Yuen, R.K.Y. Li, *Comp. Sci. Techn.* 2009, 69, 15-16, 2675 – 2681.