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Effect of spatial confinement on the chemical damage induced by ion bombardment on ultrathin polymer films

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In this work, the influence of spatial confinement in one dimension on the chemical effects induced by 2.2 GeV Bi and 2 MeV H ions in ultrathin PMMA films was investigated, by quantifying bond breaking rates as a function of the thickness h of the polymer layers (2<h<200 nm). Our data indicate that for both beams damage cross-sections for carbon-oxygen bonds, do not show substantial difference down to the smallest thickness accessible to XPS analysis (h~5 nm). The damage cross-sections estimated are ~1.5x10-13 cm2 (for O-C-O bonds) and ~2.3x10-13 cm2 (for C=O bonds) for the Bi irradiation, whilst for proton irradiation the values are ~2.7x10-16 cm2 and ~4.4x10-16 cm2, for O-C-O and C=O bonds, respectively. Variation of the cross-sections among samples of different thicknesses were within error bars. Films thinner than ~5 nm become difficult to analyse, because of the non-negligible signal of the omnipresent carbon on the substrate and because of beam-induced surface roughening and sputtering. The absence of a decrease in the damage cross section in ultrathin layers is surprising, considering the high velocity of the ions and the long range of the emitted secondary electrons, which may escape the sensitive volume before thermalization and thus lowering the effective dose. Our observations are also in contrast to recent findings of a strong thickness dependence of cratering and mass transport induced by swift heavy ions in ultrathin polymer layers, indicating that at least the chemistry probed by XPS is related to short-range events close to the track core, while in sputtering, long-range, cooperative effects along the track are of greater importance.

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