Origin of round and triangular irradiation induced pores in hexagonal boron nitride (hBN)

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For nearly two decades, it has been known that electron irradiation of hexagonal boron nitride (hBN) leads to the formation of triangular pores with nitrogen-terminated edges. The broadly accepted explanation was that boron is easier to displace than nitrogen, owing to their differing displacement cross-sections resulting from their mass difference and displacement threshold energies. It had also been speculated that the residual vacuum in the microscope column could play a role in the preferred removal of boron atoms, but this hypothesis was not tested until now.In this study [1], we used Nion UltraSTEM 100 in Vienna, which operates at the base pressure of 1e-10 mbar (which is three orders of magnitude lower than typical microscopes). Due to customization, it is also possible to introduce a controlled gas atmosphere of up to 1e-6 mbar around the sample without affecting the imaging conditions. We studied the electron-beam-induced pore growth in hBN at oxygen partial pressures from 1e-10 mbar to 3e-8 mbar with electron energies of 60 keV and 80 keV. In contrast to previous high-vacuum experiments, we show that electron irradiation in ultra-high vacuum (1e-10 mbar) leads to circular pores with no preference to either boron or nitrogen-terminated edges, whereas even small amounts of oxygen in the atmosphere during the experiment changes the pore shapes into triangles with nitrogen-terminated edges. These results hold for both 60 and 80 keV electron energies, and different sample types. Although pore growth at 60 keV is generally slower than at 80 keV, at the highest pressure, the growth rate appears independent of the electron energy. This indicates that at higher pressures, the pore growth is dominated by a beam-assisted chemical process rather than direct electron-beam damage.We turn to ab initio simulations to elucidate the underlying reasons for this observation. These show that oxygen atoms, created from O_2 by the electron beam, attach preferentially to B at pore edges. From this configuration, it is easier to remove the O and B together rather than just O with the electron beam, whereas the opposite is true for N atoms at the edge. This explains the prevalence of nitrogen edges at higher oxygen pressures, and therefore also the observed triangular pores.Our observations show that damage in hBN under electron irradiation is a combination of physical damage caused by electrons in the form of knock-on damage or radiolysis, and chemical etching caused by oxygen radicals, which affect boron significantly more than nitrogen. This opens the possibility of defect-engineering materials with desirable edges or atomic-scale defects by controlling both physical and chemical effects during particle irradiation.

[1] U. Javed et al., *arXiv* **2507**, 13180 (2025).