Electron Beam Etching Kinetics of Diamond and Graphite

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Electron Beam Induced Etching (EBIE) has recently gained increased interest as it avoids surface staining and damage characteristic of focused ion beam (FIB) milling.[1] In the EBIE process surface adsorbed precursor molecules are dissociated by electrons crossing the substrate-vacuum interface, generating reactive fragments that give rise to etching in the vicinity of an electron beam. EBIE of diamond[2] and amorphous carbon[3,4] has been investigated, but no direct comparison has been made between the etch kinetics of different C allotropes. EBIE was performed using a stationary 20 kV, 3.5 nA electron beam that was underfocused to 2 μm to produce a top-hat flux profile. EBIE was performed on ultra nano-crystalline diamond (UNCD) and highly ordered pyrolytic graphite (HOPG). Cylindrical pits were created as a function of etch time at 13 Pa of H_2O, and characterised by tapping mode atomic force microscopy (AFM). UNCD exhibits distinct initial and steady state etch rates (Figure 1). Etching was not observed in the first six minutes of electron irradiation, beyond which the etch rate increased to approximately 3.5 x 10^{-2} $Å^3$/electron. The etch rate of HOPG was found to vary across the sample surface, and was approximately one to two orders of magnitude lower than that of UNCD. Defects play a key role in EBIE of graphite, yielding localised areas of enhanced etching within electron exposure sites, such as those shown in the inset of Figure 1.
The etch rate differences reported here can be described by corresponding differences in etch efficiency, expressed as the product Nσ, where N is the H_2O adsorbate concentration at the surface [molecules/m^2] and σ is the effective cross-section for electron induced generation of reactive fragments (e.g., O* and H* radicals) that react with C to form volatile species such as CO_x and CH_y. Nσ can vary across a sample surface and is a function of local electronic surface structure and substrate composition. The difference between the etch rates of UNCD and HOPG are ascribed to the effects of sp^3 and sp^2 bond hybridisation on Nσ, while the change in etch rate of UNCD is ascribed to electron modification of the as-grown diamond. The results presented here are used to explain etch kinetics and surface roughening effects previously[4] reported to limit the spatial resolution of EBIE.

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1 I. Utke et al., J. Vac. Sci. Technol. B, **26**, 4(2008)
2 P. Hoffmann et al., Proceedings of SPIE **5925** 1 (2005)
3 D. Wang et al., J. Vac. Sci. Technol. B, **13**, 5 (1995)
4 M. Toth et al., Nano Lett., **7**, 2 (2007)

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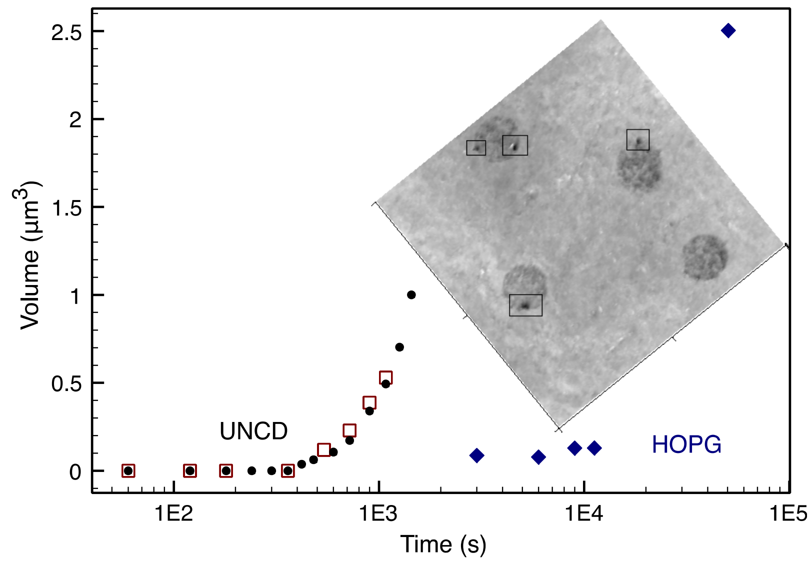

Figure 1: UNCD (• & □) and HOPG (◆) etch pit volume as a function of time under identical EBIE conditions. Inset: AFM image of HOPG etch pits (field width = 12 μm). Areas of increased etch rate highlighted.