First-Principles Study on Oxidative Etching of Diamond (100) Surface

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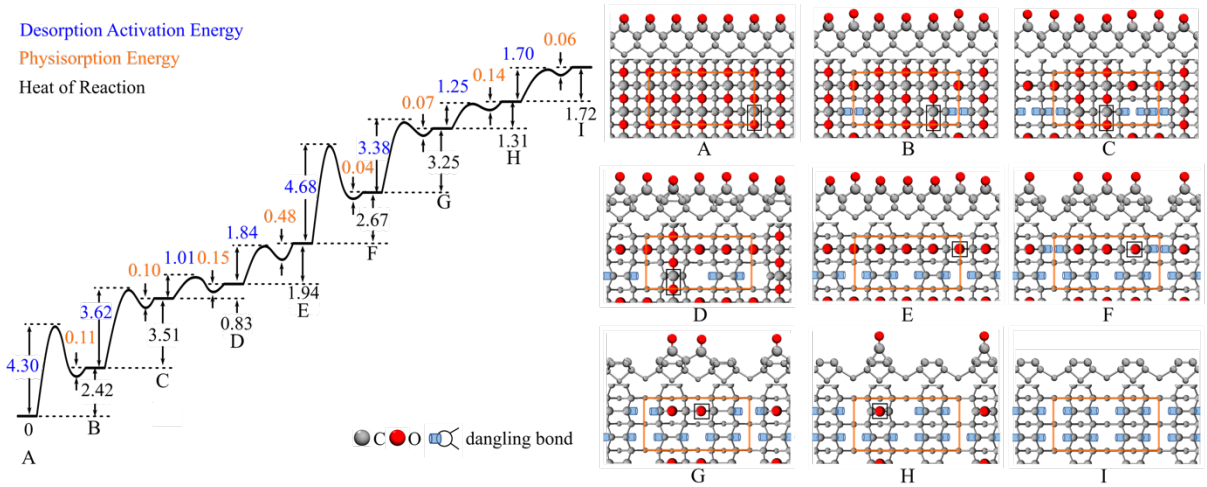
Precision engineering of diamond is a major technological hurdle in its use as a material for micro-mechanical and micro-electromechanical systems (MEMS), power electronics, radio frequency (RF) power devices, and quantum technology. Traditional methods used in semiconductor industry have been proven to be ineffective because of diamond's hardness and chemical inertness. While several micro and nanoscale devices and structures have been fabricated using reactive ion etching and thermochemical etching, the quality and etching rates still falls short of the required standards for practical applications. One of the ways to improve these methods is to gain an atomic-level understanding of the mechanism of diamond oxidation of which several aspects still remains elusive as of this writing. In this study, we performed first-principles density functional simulations to develop a comprehensive theory of the oxidation of diamond (100) surface, from the adsorption of O_2 to the etching of entire surface layer. Gas-phase triplet O_2 can be metastably adsorbed before undergoing intersystem crossing to singlet state and form carbonyl and epoxide groups. The more stable ether chain forms on defect-free surfaces at higher surface coverage. The desorption activation energy of CO is lesser than CO_2 for both atomically smooth surface and various defective surfaces. Preferential etching has been found along the rows perpendicular to the direction of C-dimers which are caused by the vacancy left by desorbed CO. The desorption activation energy of isolated CO agrees reasonably with existing experiment and theoretical studies. In addition, we report for the first time a wide range of activation energies caused by vacancy nucleation and surface reconstruction resulting from subsequent CO desorption which explains the unusually broad peak of the thermal desorption spectra. Single-atom-high etched trough is stabilized by dimerization and adsorption of O_2, which gives theoretical support for the observed features of diamond (100) surfaces thermally etched with dry oxygen. This study will contribute to the fundamental science of the interaction of diamond surface and oxygen and could lead to insights that will accelerate the development of diamond fabrication tools.



Etching of the top-layer atoms of diamond (100) surface through successive CO desorption