Real time observation of exfoliated black phosphorus sublimation

Matthieu Fortin-Deschênes,[1] Etienne Bouthillier,[1] Pierre Levesque,[2] Alexandre Favron,[2] Richard Martel,[2] Oussama Moutanabbir[1]

[1] Department of Engineering Physics, Polytechnique Montréal, 2900 boulevard Edouard Montpetit, Montréal, Canada

[2] Département de Chimie, Université de Montréal, 2900 boulevard Edouard Montpetit, Montréal, Canada

matthieu.fortin-deschenes@polymtl.ca

Abstract

Few-layer black phosphorus (BP) is an emerging two-dimensional material which attracts a great deal of interest due to its interesting properties including tunable direct band gap, relatively high hole mobility, significant thermoelectric figure of merit of 2.5, highly anisotropic properties and many other interesting characteristics. This makes BP highly attractive for applications in electronics, optoelectronics, and energy conversion. Developing these technologies requires an atomistic-level understanding of structural and morphological properties of BP both under ambient conditions and throughout thermal treatments. With this perspective, this work describes the dynamics of thermal decomposition of exfoliated BP layers during thermal annealing using low energy electron microscopy (LEEM). The ability to probe *in situ* the behavior of BP as a function of temperature provides unprecedented insights into its thermal stability as well as into the basic mechanisms underlying its decomposition.

The investigated samples consist of exfoliated BP of variable thickness transferred onto host silicon substrates. Thermal annealing was conducted under ultrahigh vacuum (10^{-10}-10^{-9} mbar) in LEEM chamber. Figure 1 exhibits a representative set of LEEM bright field snapshots of BP layers during thermal annealing. The data indicate that the sublimation takes place at 385°C following two simultaneous but distinct pathways at the edges and on the surface. Through the latter, the sublimation of BP proceeds layer by layer through ellipsoidal holes along [001] direction. These cracks grow at a velocity of 1.25nm/s along the short axis and 1.98nm/s along the long axis at 400°C. On the other hand, the decomposition at the edge seems to take place multilayer by multilayer at around 1.1nm/s without following significantly a preferential crystallographic direction. This dynamics of BP sublimation will be discussed and elucidated by combining LEEM, thermal desorption spectrometry, DFT calculations, and kinetic Monte Carlo simulations.

The quantitative description of these mechanisms will be useful to define the optimal experimental parameters for fabrication of BP-based materials and devices.

Figures

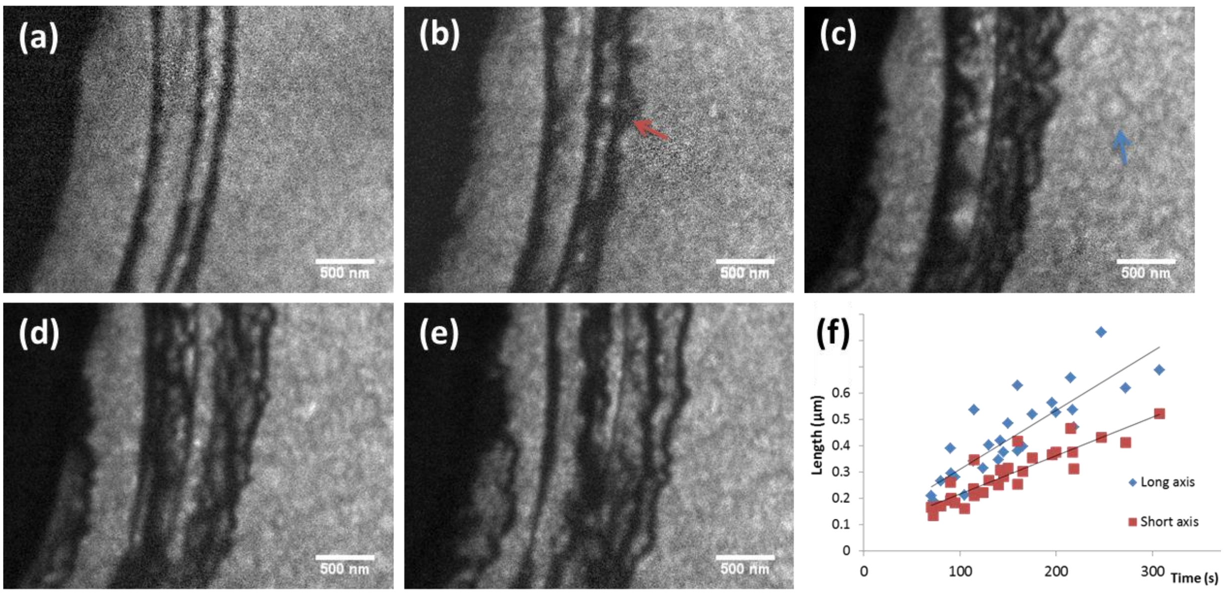

Figure 1: LEEM images taken at 400°C showing the sublimation of BP (a-e). Red arrow: edge sublimation. Blue arrow: ellipsoidal cracks. Plot of holes size evolution showing short and long axis velocities (f)