doi:10.1017/S1431927620015822
Microsc. Microanal. 26 (Suppl 2), 2020

Electron Irradiation of Two-dimensional MoS2: Insights into the Influence of Electronic Excitations from First-principle Calculations

Silvan Kretschmer and Arkady Krasheninnikov

Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Sachsen, Germany

Two-dimensional (2D) materials are routinely characterized nowadays in the transmission electron microscope (TEM). The high-energy electron beam in TEM can create defects in the target, and as the influence of defects on materials properties is expected to be stronger in systems with reduced dimensionalities, understanding defect production in 2D materials is of particular importance. Irradiation-induced defects can appear through three mechanisms, namely ballistic or knock-on damage (1), ionization and electronic excitations (2) and beam-induced chemical etching (3). Only the first channel is well understood, while numerous observations of defects formation in 2D transition metal dichalcogenides below the knock-on threshold point out that other mechanism should be important [1,2]. Here we investigate the role of electronic excitations in defect production by using advanced first-principles simulation techniques based on the Ehrenfest dynamics combined with time-dependent density-functional theory and demonstrate that a combination of excitations and knock-on damage in 2D MoS_2 under electron beam can give rise to the formation of vacancies and explain the experimental observations of defects production far below the knock-on threshold. As our first-principles calculations show, electronic excitations will quickly delocalize in an otherwise unperturbed periodic structure. The situation changes dramatically then the translational symmetry is broken, as is the case for the displacement of one target atom upon momentum transfer from an impinging electron. We propose a possible mechanism for the observed sub-knock-on threshold damage which involves the localization of the excitation at an emergent vacancy site. According to our calculations, this localized electronic excitation then gives rise to a decrease in the displacement threshold as anti-bonding states are occupied at the emergent defect site. Consequently, beam damage may be expected for voltages below the knock-on threshold as observed by the Sub Angstrom Low Voltage Electron (SALVE) microscope operated by our collaborators at Ulm University.

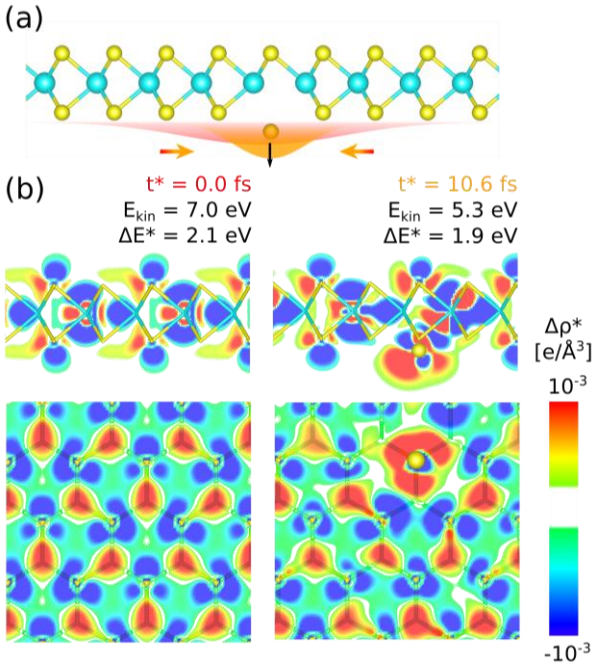

Figure 1. (a) Sketch of the Ehrenfest Dynamics simulation setup with a delocalized excitation, which localizes at the incipient vacancy when initial kinetic energy is assigned to the recoil S atom. (b) Evolution of the

excitation in MoS2 sheet, side and top views, illustrating the charge density difference for the excitation, which localizes at the emerging vacancy.

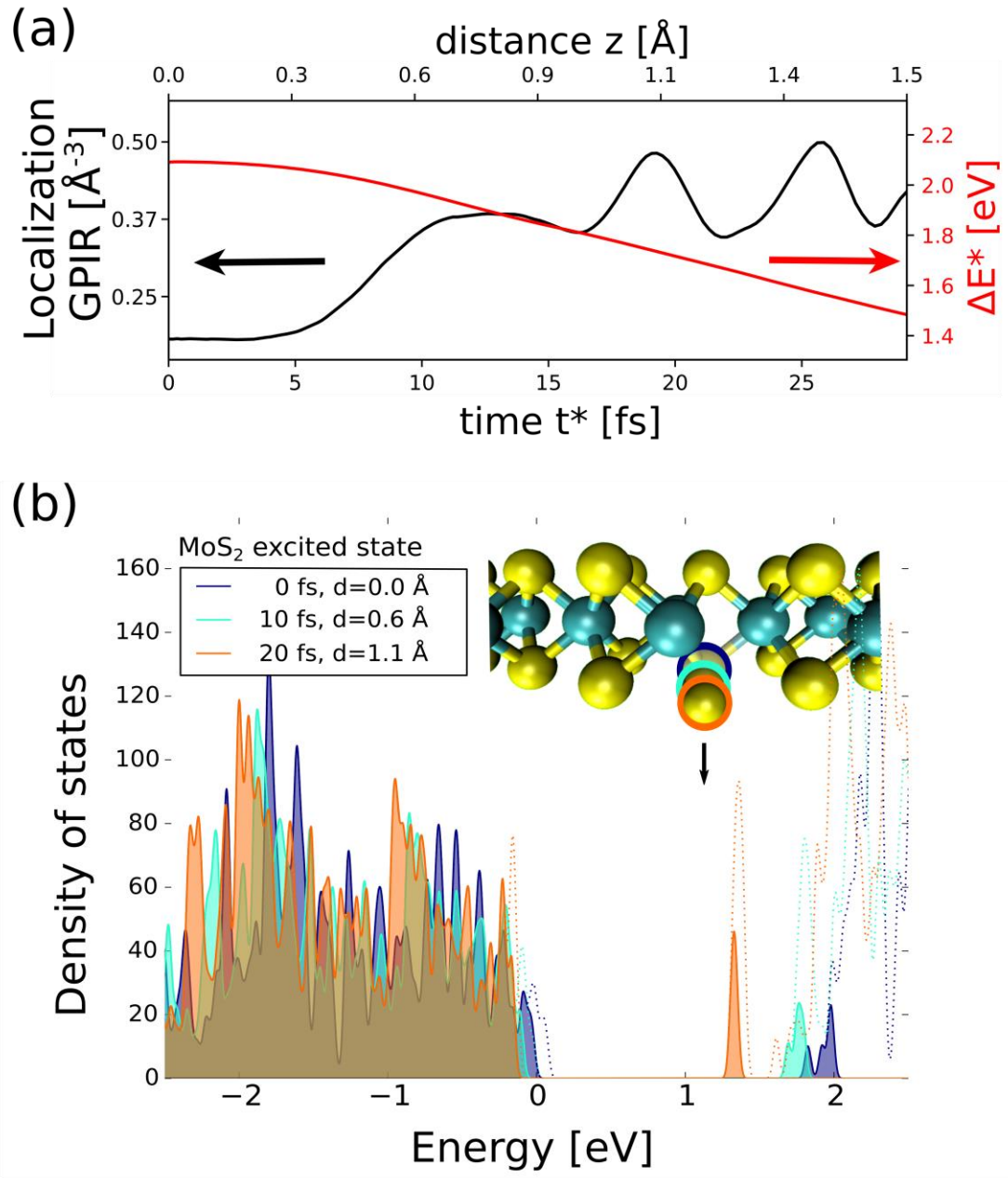

Figure 2. (a) Quantification of the excitation localization by means of the generalized inverse partition ratio (GPIR). The panel also shows the change in the excitation energy. (b) The static electronic structure of MoS2 sheet with emerging S vacancy for several positions of the recoil atom with d being its displacement from the original position, as calculated by constraint-DFT. The occupied defect state localized at the vacancy splits off from the conduction band minimum.

References

[1] Y.Lin, T.Björkman, H.Komsa et al. Nature Communications **6** (2015) 6736
[2] G. Algara-Siller, S. Kurasch et al. Appl. Phys. Lett., **103** (2013) 203107

https://doi.org/10.1017/S1431927620015822 Published online by Cambridge University Press