doi:10.1017/S1431927620016050
Microsc. Microanal. 26 (Suppl 2), 2020
© Microscopy Society of America 2020

Atomic and Electronic Structure of Black Arsenic and Ambient Stability Studied by Analytical STEM

Hwanhui Yun, Supriya Ghosh, Prafful Golani, Steven J. Koester and K. Andre Mkhoyan

University of Minnesota, Twin Cities, Minneapolis, Minnesota, United States

Two-dimensional (2D) black arsenic (BAs) is a van der Waals layered material, which has atomic structure and physical properties analogous to one of the most prominent and well-studied 2D materials, black phosphorus.[1-3] Even at the early stage of research, BAs has shown intriguing characteristics from anisotropic materials properties to the thickness-dependent electronic structures.[3-6] To better understand the new material and maximize its utility, fundamental structural and electronic characterization is essential. Here, analytical STEM is utilized to explore the nature of 2D layered BAs highlighting its layer-dependent dielectric responses and moisture-sensitive degradations at various ambient environments.

Plan-view TEM samples were prepared by the scotch tape based mechanical exfoliation[1] and cross-sectional TEM samples were made by the mechanical exfoliation of BAs onto a Si substrate, followed by the focused ion-beam lift out method. STEM experiments were carried out using aberration-corrected FEI Titan G2 60-300 (S)TEM equipped with Super-X energy dispersive X-ray spectrometer for EDX and a Gatan Enfinium ER EELS. STEM-EELS data was acquired with the monochromated electron beam. HAADF-STEM image simulations were carried out using the TEMSIM code based on the Multislice method.[7, 8]

Atomic-resolution HAADF-STEM images of BAs are acquired from five different crystalline directions and compared with simulated images, directly confirming the atomic structure and the degree of structural anisotropy of BAs (see Figure 1a). The layer number-sensitive lattice contrast of plan-view HAADF-STEM images is used to precisely determine the number of layers (see Figure 1b and 1c). The low-loss EEL spectra obtained as a function of the number of layers reveal modification of the dielectric responses at a few-layer-thick BAs (see Figure 2a). Stability of BAs is examined by using various STEM techniques including HAADF-STEM imaging, EDX elemental quantification, electron beam diffraction patterns, and EELS. Degradation behavior of exfoliated BAs flakes at various ambient conditions are detailed as shown in Figure 2b, which allows identification of key parameters affecting degradation of the material.[9]

https://doi.org/10.1017/S1431927620016050 Published online by Cambridge University Press

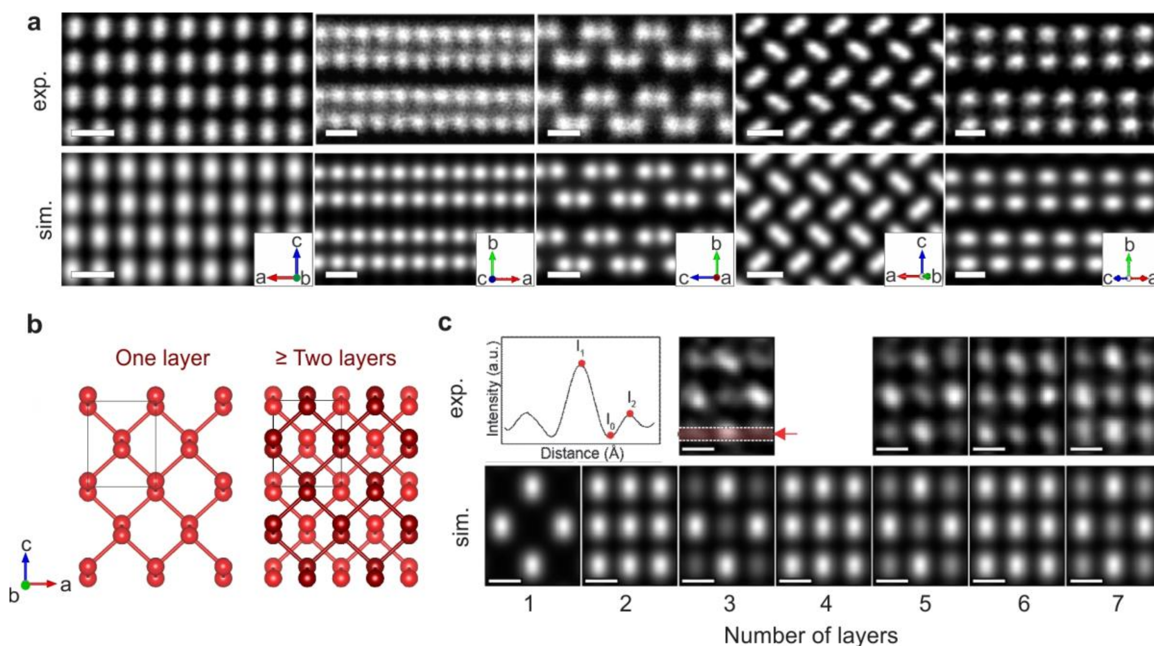

Figure 1. HAADF-STEM images of BAs. (a) Experimental and simulated HAADF-STEM images in five crystallographic orientations. Scale bars are 0.2 nm. (b) Atomic model of BAs in the plan-view (010) direction. Half-unit cell shifted alternating layers are highlighted using different color code. (c) Comparison of experimental and simulated HAADF-STEM images at different layer numbers. Scale bars are 0.2 nm. Line profile extracted from the region indicated with a red arrow is shown on the top-left panel.

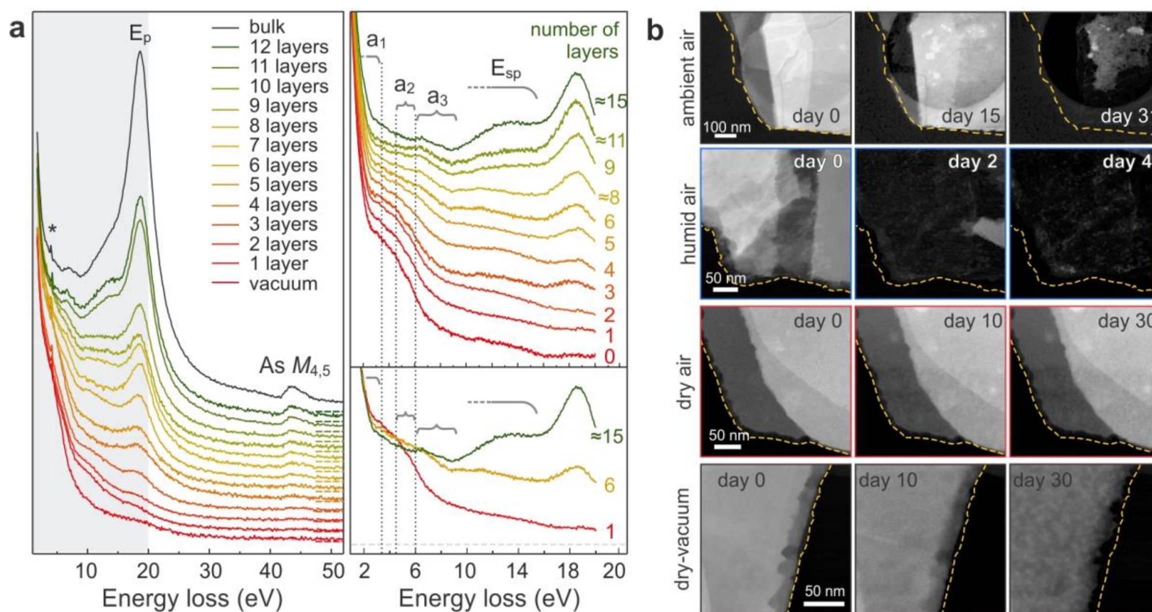

Figure 2. (a) Low-loss EELS as a function of the number of layers. EEL spectra on the right column were obtained with the higher energy resolution from the shaded region in the left column: stacked with (top) and without (bottom) vertical shift. (b) Time-series HAADF-STEM images of BAs flakes under different environments. The initial shape of the flakes are marked with dashed lines.

https://doi.org/10.1017/S1431927620016050 Published online by Cambridge University Press

References

1. L. Li et al., Nat. Nanotechnol. **2014,** *9* (5), 372-377.
2. Z. Hu et al., Nanoscale **2018,** *10* (46), 21575-21603.
3. Y. Xu et al., Nanoscale **2019,** *11* (31), 14491-14527.
4. Y. Chen et al., Adv. Mater. **2018,** *30* (30), 1800754.
5. M. Zhong et al., Adv. Funct. Mater. **2018,** *28* (43), 1802581.
6. A. Kandemir et al., J. Mater. Chem. C **2019,** *7* (5), 1228-1236.
7. J. M. Cowley et al., Acta Crystallogr. **1957,** *10* (10).
8. AJ Kirkland, "Advanced Computing in Electron Microscopy" (Springer, New York).
9. The project was partially supported by UMN MRSEC program DMR-1420013. P.G. and S.J.K. were supported by the NSF under Award No. ECCS-1708769.

https://doi.org/10.1017/S1431927620016050 Published online by Cambridge University Press