Measuring the Mean Inner Potential Of Bernal Graphite Using Off-axis Electron Holography

Avi Auslender[1], George Levi[2], Vladimir Ezersky[3], Semën Gorfman[4], Oswaldo Diéguez[4] and Amit Kohn[4]

[1]Department of Materials Science and Engineering, The Iby and Aladar Fleischman Faculty of Engineering, Tel Aviv University, Tel Aviv 6997801, Israel, Tel Aviv, Tel Aviv, Israel, [2]Department of Materials Science and Engineering, The Iby and Aladar Fleischman Faculty of Engineering, Tel Aviv University, Tel Aviv 6997801, Israel, Tel Aviv, Israel, [3]Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel, Beer-Sheva, HaDarom, Israel, [4]Department of Materials Science and Engineering, The Iby and Aladar Fleischman Faculty of Engineering, Tel Aviv University, Tel Aviv 6997801, Israel, United States

The mean-inner-potential (MIP) of a crystal is the average electrostatic Coulomb potential within a crystal with respect to vacuum. The MIP is a fundamental material property which reflects chemical-bonding and crystallographic surfaces [1].

We conducted off-axis electron holography experiments on highly-oriented-pyrolytic-graphite (HOPG) in a transmission-electron-microscope to measure the MIP from nanometer-scale volumes of Bernal graphite oriented with respect to the electron beam, along the principal axis or directions in the basal plane. These MIP were related to mean orbital electron radii and diamagnetic susceptibilities in perpendicular planes. Such intrinsic property measurements are challenging because of defect.induced interfaces at basal planes [2, 3]. Indeed, our structural examination of HOPG show stacking faults and planar rotations around the principal-axis, such that measuring intrinsic properties requires probing a volume of ~102102102nm3.

Experiments on individual Bernal graphite crystals with (0001) basal, or (1-100), (2-1-10) prismatic planes, resulted in MIP of 10.16±0.40V, 11.37±0.35V, 12.66±0.41V, respectively [4]. First-principles calculations from crystalline slabs [4] confirm these anisotropic measurements with 11.72V, 13.65V, 14.56 V, respectively. Additionally, these experiments enabled to measure the mean free path for inelastic scattering in graphite of 197keV electrons at a collection angle of 18mrad resulting in 150.6±2.0 nm.

These measured MIP enable to determine projected mean radii of electron orbitals and volume susceptibilities (SI), assuming spherically symmetric charge distribution, at 0.704±0.015Å, (-1.99±0.08)10-5; 0.744±0.015Å, (-2.23±0.07)10-5; 0.785±0.015Å, (-2.48±0.08)10-5.

The measured orbital radii and diamagnetism in the basal plane are comparable to expected values for carbon σ-bond hybridization [5-7]. Increased MIP on prismatic planes is related to s-orbital components, which decrease due to delocalized electrons between basal planes.
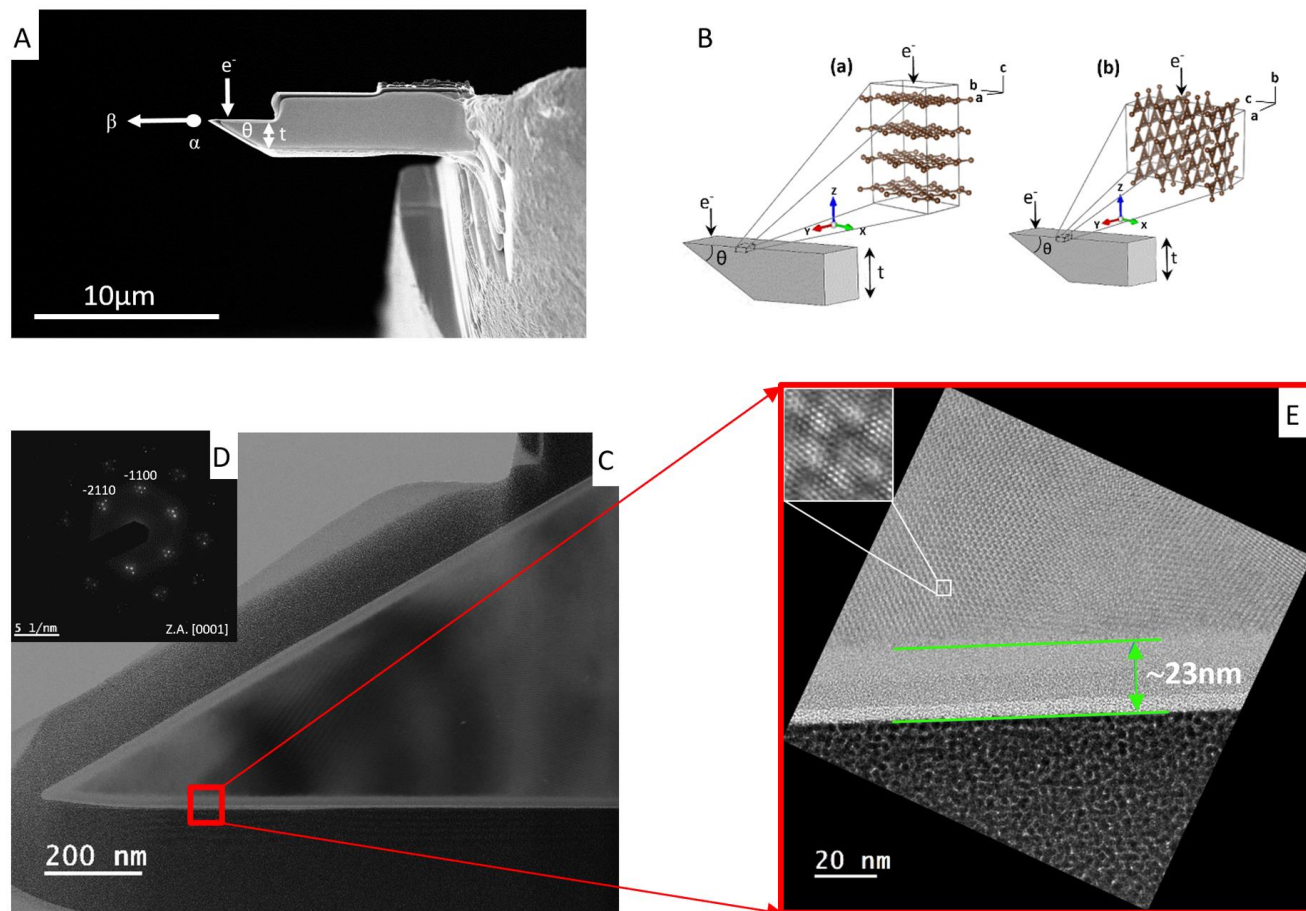
Figure 1. Fig.1 (A) Secondary electron SEM micrograph of a (0001) 30º wedge sample connected to a Cu grid and after ion milling illustrating tilt axes, α, β. t is the sample thickness, θ is the wedge angle (in this report: ~30º or ~45º). The direction of the electron beam is denoted by the arrow. (B) Schematic illustration of HOPG TEM wedge samples in two crystallographic plane orientations at the surface, where the electron beam direction is denoted by an arrow (z-direction); Electron beam perpendicular B(a) (x-y plane), and parallel B(b) (y-z plane, in the [2-1-10] direction) to (0001) basal plane. (C) Bright field cross-sectional TEM micrograph of the wedge sample, from which an angle of 30.5º is measured, (D) SAED pattern recorded from this sample, edge-on view with respect to the basal plane (E) High-resolution (phase contrast) TEM micrograph from the region denoted schematically by the blue square. The inset shows a magnification of the marked area.
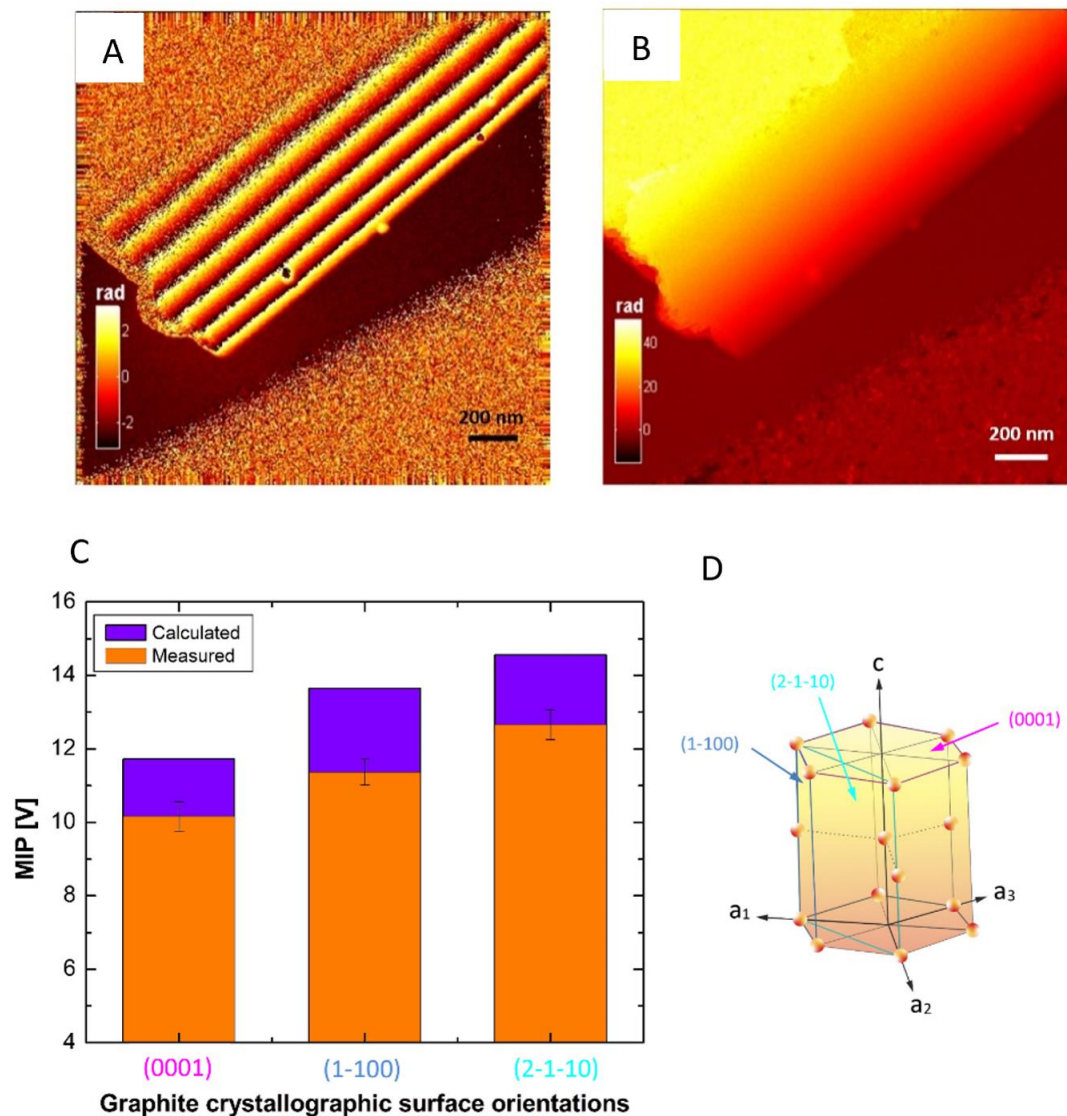
Figure 2. Fig.2 (A) Reconstructed electron phase map from the edge of the first HOPG wedge sample with the (0001) plane at base surface and nominal wedge angle of 30º (phase spacing: 2π), (B) Unwrapped phase map of (A), (C) Measured and calculated MIP of Bernal graphite for three crystallographic planes, (D) Bernal graphite structure indicating the relevant planes.

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