

## Grain boundaries in graphene: atomic structure and electronic properties from Scanning Probe Microscopy investigations

L. Tapasztó<sup>1</sup>, P. Nemes-Incze<sup>1</sup>, S.J. Kim<sup>2</sup>, G. Dobrik<sup>1</sup>, P. Vancsó<sup>1</sup>, G. I. Márk<sup>1</sup>, C. Hwang<sup>2</sup>, L.P. Biró<sup>1</sup>

1. *Institute for Technical Physics and Materials Science, Centre for Natural Sciences, 1525 Budapest, PO Box 49, Hungary (<http://www.nanotechnology.hu/>)*
2. *Center for Advanced Instrumentation, Division of Industrial Metrology, Korea Research Institute of Standards and Science, Yuseong, Daejeon 305-340, Republic of Korea*

Email: [tapaszto@mfa.kfki.hu](mailto:tapaszto@mfa.kfki.hu)

Large area graphene sheets are essential for the majority of applications. The most promising method for their production is the CVD synthesis of graphene on metal surfaces<sup>1</sup>. However, the electronic quality of the CVD grown films is clearly inferior to the mechanically exfoliated samples, which is largely attributed to the polycrystalline nature of the CVD graphene. Therefore, to understand and ultimately control the electronic transport in polycrystalline graphene it is of fundamental importance to: (1) reveal the grain structure of the polycrystalline samples, and (2) experimentally explore the electronic properties of individual graphene grain boundaries of different types, given the large variety of their predicted electronic behavior<sup>2</sup>.

Here we present a quick and easy method for revealing the grain structure of polycrystalline graphene samples based on Atomic Force Microscopy. The basic idea is that a simple annealing step at 500 C in air selectively etches the grain boundaries of graphene rendering them easily detectable by AFM. The grain size distribution together with grain boundary angle statistics (Fig. 1) can be readily obtained from such measurements<sup>3</sup>.

Furthermore, we have also investigated the electronic properties of individual graphene grain boundaries by atomic resolution scanning tunneling microscopy and spatially resolved tunneling spectroscopy measurements<sup>4</sup>. Our findings reveal that the available local density of electronic states inside the boundaries is significantly suppressed for both electrons and holes (Fig. 2). Consequently the grain boundaries act as resistive interfaces between the highly conductive single graphene grains. We compare these findings to the results of wave packet dynamical simulations on the charge carrier propagation and scattering across graphene grain boundaries<sup>5</sup>. Moreover, we found that graphene grain boundaries can also give rise to n-type inversion channels within the overall p-doped graphene sheets, providing p-n junctions with sharp interfaces on the nanometer scale. Surprisingly, the observed electronic behavior of the grain boundaries were found to be almost independent from their angles (atomic configuration), indicating that the atomic structure of grain boundaries in CVD graphene is highly disordered leading to the observed universal electronic behavior.

## References

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## Figures

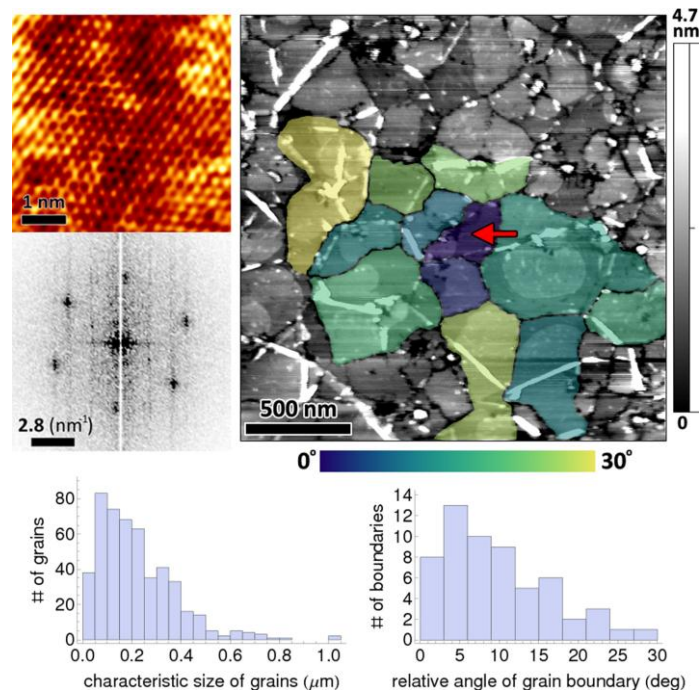


Figure 1 .AFM image revealing the grain structure of a polycrystalline CVD graphene sheet. The colors encode grains of different orientations. Grain size as well as grain angle distribution diagrams are shown in the bottom row.

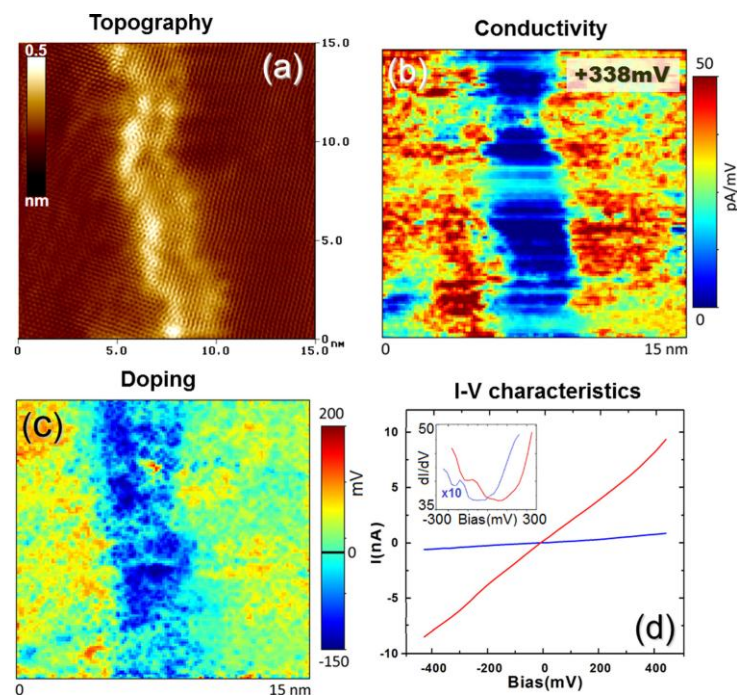


Figure 2. a) Atomic resolution STM image of a  $29^\circ$  graphene grain boundary. Spatially resolved tunneling conductivity map (b) and local doping map (c) revealing strikingly different electronic characteristics of grain boundaries as compared to the defect free graphene regions. d) Representative, individual tunneling current-voltage characteristics and their numerical derivatives (inset).