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Correlated AFM/STEM Study on the Mechanical Stiffness of Defect-Engineered Graphene

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The first isolation of a single layer graphene sheet from graphite via the adhesive tape method in 2004 [1] triggered an avalanche of experiments studying this two-dimensional (2D) material, including investigations on the unique electronic as well as mechanical properties. The latter have been consistently demonstrated to be superior to other materials despite its extremely low weight [2,3,4]. Since these macroscopically observed properties are a result of elemental composition and atomic structure, the 2D nature of graphene allows for a direct correlation by linking atomic resolution scanning transmission electron microscopy (STEM) images to the observed macroscopic properties. Moreover, this structure-to-property correlation permits investigations on alterations of material properties through defect-engineering. In this study, the in-plane mechanical stiffness of graphene in its pristine state is compared to a defective state in the form of vacancies by correlating atomic force microscopy (AFM) nano-indentation measurements to atomic resolution STEM images.

In order to maintain direct correlation, the experiment is executed in a clean and controlled ultra-high vacuum (UHV) environment, which prevents unwanted external influences from affecting the fundamental physical properties of the material. The main microscopes used for this study are part of the Controlled Alteration of Nano-materials in Vacuum down to the Atomic Scale (CANVAS) system at the University of Vienna, which is an interconnected UHV apparatus containing an AFM module, a STEM module and an alteration unit used for defect-engineering. The AFM module consists of a GETec AFSEM device from the Quantum Design company in a vacuum chamber with a pressure in the order of 10^{-8} mbar. Atomic resolution imaging is permitted by a Nion Ultra STEM 100, which is an aberration corrected STEM device. Furthermore, the STEM module includes an in-situ cleaning laser used for removing surface contamination from 2D materials. Lastly, the alteration unit provides a target chamber, which allows the introduction of vacancies through low energy Ar plasma irradiation. All of the mentioned devices are connected via UHV vacuum tubes allowing safe transport without any exposure to ambient conditions throughout the measurement procedure.

The sample consists of CVD-grown graphene supported by a SiN TEM chip with circular perforations of 3 µm diameter. Appropriate graphene drumheads have been individually selected by means of Raman spectroscopy, with the criterion being a single layer of pristine quality. Each drumhead is evaluated in terms of layer number and defect density using the I_G/I_{2D} ratio and I_D value, respectively [5]. The Raman pre-characterized sample is then inserted into the CANVAS system where the experiment is executed solely on the pristine monolayer drumheads. This includes an initial set of AFM nano-indentation measurements of graphene in its pristine state as a reference value. After that, the sample surface is prepared for the irradiation by removing surface contaminants using the in-situ cleaning laser of the STEM unit. The irradiation is performed by singly charged Ar ions with kinetic energies below 200 eV. The irradiation is followed by the determination of the atomic structure and corresponding vacancy density via atomic resolution STEM images. Here, the vacancy density is precisely determined by 2D scan maps, which combine individual small FOV atomic resolution images into one large area, followed by processing of the data set by a convolutional neural network [6]. Lastly, a second set of nano-indentation measurements is performed on the drumheads with known vacancy density.

The nano-indentation measurements of pristine graphene return a 2D elastic modulus of 288 ± 27 N/m, which decreases to 156 ± 26 N/m with a vacancy density of approximately 1×10^{13} cm^{-2}. Fig. 2 illustrates this decrease of E^{2D} observed on drumhead number 129. Fig. 1a and 1b reveal the atomic structure of the suspended graphene drumhead after the irradiation. The former shows prominent surface corrugation as a result of the relaxation mechanism due to local strain introduced by the vacancies [7], which might be a significant factor for the weakening mechanism.

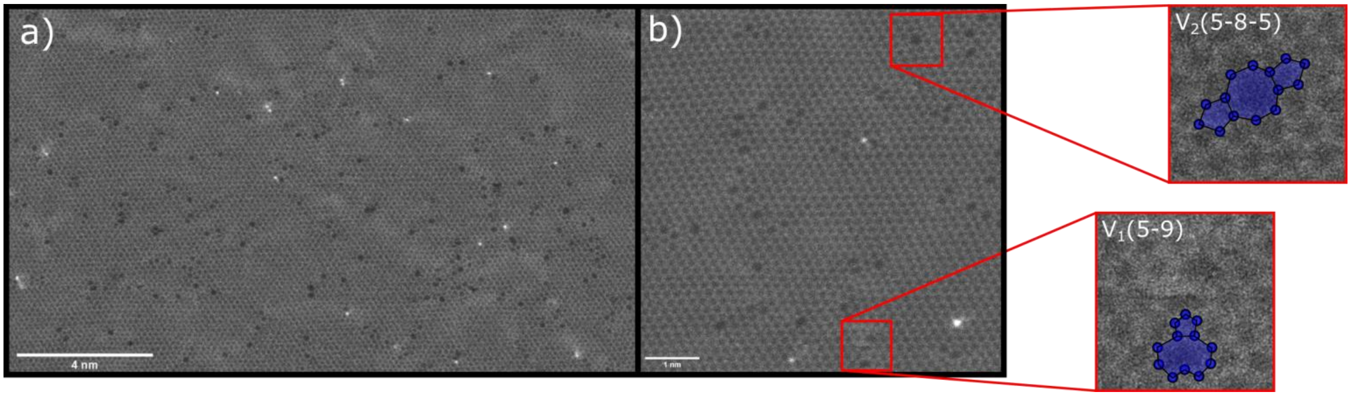

Figure 1. Atomic resolution STEM image of graphene after irradiation (a) and corresponding magnification (b) showing the single- and double-vacancies introduced into the structure.

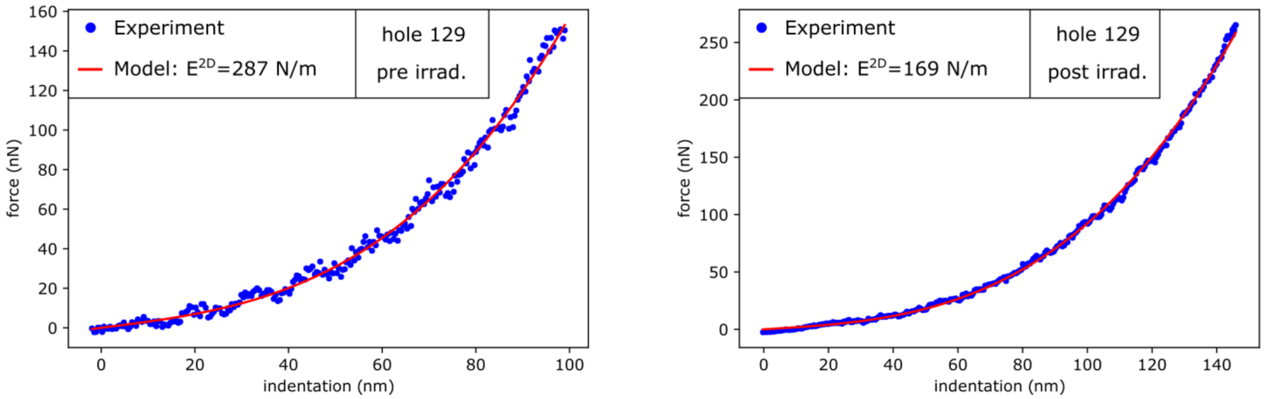

Figure 2. AFM nano-indentation measurement of the same drumhead before and after irradiation, with an introduced vacancy density of 1×10^{13} cm^{-2}.

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