Accessing kinetics of structural rearrangements in graphene via direct atomic imaging

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The raise of nanoscience and nanotechnology and necessity to characterize the structure of individual objects consisting of a countable number of atoms determined the shift of structure characterization paradigm from bulk methods like X-ray diffractometry to local high resolution methods like electron microscopy. The similar shift in paradigm is urging now in chemistry – chemical processes defining structure and properties of nanoscale and low dimensional objects often constitute a negligible part of the total volume of the material, and thus their assessment by experimental bulk chemical methods if often impossible. The new concept is provided by the time resolved electron microscopy allowing for direct observation of atomic rearrangements.

We are developing the methodology to apply the formalism and approaches of the classical chemical kinetics for the quantitative description of atomistic processes observable in the microscope. We show that a proper statistical treatment of the data obtained in a range of experimental conditions allows determining the threshold energies for radiation induced reactions. But not only that: we show that true activation energies for thermally activated reaction pathways for individual defects can be estimated as well.

We apply this methodology for reactions of point defects in graphene. The cross-sections and threshold energies of irreversible (atom emission) and reversible (bond rotation, see Fig.1) processes are measured. Observation of statistically significant number of events at variable experimental conditions allows decoupling

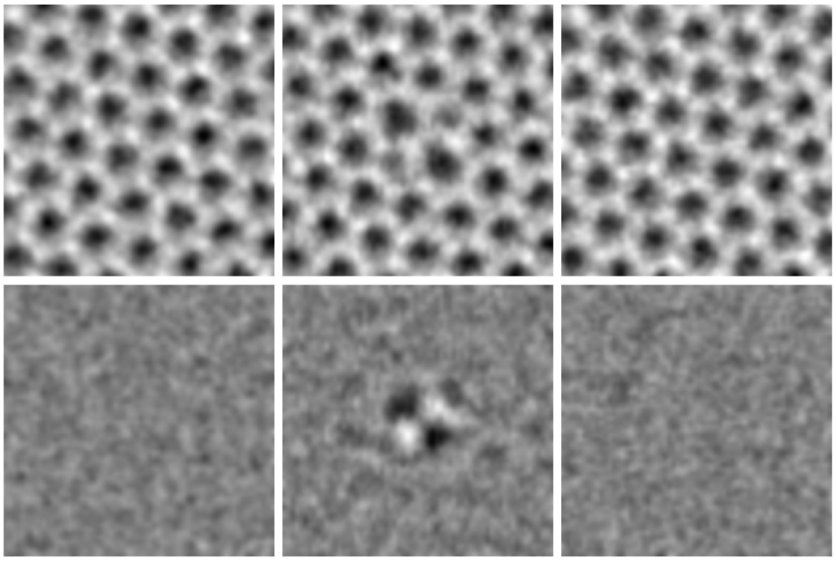

Fig. 1. Sequence of electron microscopy images showing the bond rotation reaction in graphene. The upper row – unprocessed images of the graphene lattice separated by time slices of 1s. The lower row – the same images filtered in order to remove the pattern of the lattice.

of radiation induced and thermal reaction pathways and obtaining independent estimations of cross-sections and activation energies for direct and backwards rotations. The cross-sections of direct rotation were found to be in a decent agreement with theoretical estimations. Interestingly the backwards rotation is characterized by very high cross-section exceeding theoretical values by 3-4 orders of magnitude. The values obtained rule out electron-nucleus collision as the main mechanism of energy transfer from electron beam to the sample. We speculate that the energy is transferred through electron-electron interactions via strong coupling of excited electron states with the phonon modes localized around the defect.

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