Chapter 16
Entropy of Nanostructures: Topological Effects on Schottky Vacancies Concentration in Graphenic Bidimensional *HC(N)* Lattices

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ABSTRACT

Recent advances in graphene studies deal with the influence of structural defects on graphene chemical, electrical, magnetic and mechanical properties. Here the complex mechanisms leading to the formation of clusters of vacancies in 2D honeycomb HD lattices are described by a pure topological point of view, aiming to correlate the variation of specific topological invariants, sensible to vacancy concentration, to the structural evolution of the defective networks driven by the topo-thermodynamical Gibbs free energy. Interesting predictions on defect formation mechanisms add details on the topological mechanisms featured by the graphenic structures with defects. Future roles of bondonic particles in defective HD materials are also envisaged.

INTRODUCTION

The graphene basal plane, which is made by sp^2 carbon atoms chemically bonded through π-π orbital interactions, is definitely a *stable* 2D network, with high in-plane stiffness, where vacancy defects spontaneously occur at quite low concentration. Vacancies formation in a honeycomb lattice made of *N* atoms *HC(N)* in fact is normally achieved by ion bombardment (Cataldo et al. 2002; 2003; 2009), neutron

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bombardment (Cataldo et al. 2013; 2014a; 2014b), high energy processing (Cataldo, 2000a; 2000b) or after reaction with oxygen gas (this latter method is preferred for its relative simplicity). Such an imperfection of the atom network due to vacancy is known as *Schottky defect*. It is created by transferring an atom/ion from the original correct site normally to the surface of the sample.

The possibility to use atomic-scale defects to tailor graphene properties finds its ground in the defect-induced modifications of graphene band structure, such as for example the appearance of sharp peaks in the density of states (localized states) near the Dirac point in the case of vacancies.

Irradiation with high-energy ions creates defects in the honeycomb system whose atomic structure (as well the electronic structure) remains debated. Some observations on the magnetic behavior of proton-irradiated graphene suggest that the majority of irradiation defects consist in reconstructed monovacancies (via Jahn-Teller mechanisms) rather than divacancies or other more complex defects. On the contrary, in case the dangling bonds remain unsaturated, monovacancies are generally believed to group and evolve into divacancies or more complex 555-777 defects. Experimentally, graphene layers show in fact various types of structural (vacancies, grain boundaries, dislocations) and topological (Stone-Wales, dislocation dipoles) defects which vary graphene electronic, magnetic and mechanical properties, vacancies being the most common defects. Typical defective regions with diameters of 20 nm are generated in fact in the graphene basal plane exposed to oxygen/argon flow at 723 K, being the threshold temperature for the reaction of graphene with oxygen gas in the range 473 - 573 K (Liu et al, 2008). A related investigation (Yamada et al. 2010), still using Raman spectroscopy, has shown the existence of temperature-related size effect on vacancy density, suggesting that the size of the vacancy defects becomes smaller when the oxidation temperature lowers. Therefore, a graphene oxidation temperature in the onset region favors the creation of *subnanometer vacancy* defects in the graphenic mesh. Recently and for the very first time a Japanese-North American team (Yamada et al. 2014), by adopting various oxidation temperatures in the 493 - 573 K interval, has directly observed subnanometer vacancies in graphenic layers detected by High-resolution TEM microscopy (HRTEM) and those defective structures were simulated ab-initio to determine their relative stabilities by density functional theory (DFT) computations. Direct observations of the structures of the vacancy defects in the basal plane including functional groups have been obtained via HRTEM images that show the tendency of graphene oxidized at 533 K to form subnanometer vacancy stable defects with an average density of 1 defect/100 nm^2. The presence of C=O bonds, proven by XPS spectroscopy, demonstrates that the vacancy defects introduced in the basal plane of graphene were generated by oxygen gas upon heating. Typical defective structure involve a few hexagonal rings in different configurations with 0.5 nm size (see next section). Moreover, according to the authors the experimental observation of subnanometer vacancies underline the stabilization role played by oxygen-containing functional groups such as C=O and C−O−C.

In recent paper (Lehtinen et al. 2014) aberration-corrected transmission electron microscopy (AC-HRTEM) demonstrated that the encapsulation of defective graphene between two other graphene layers (ABA stacked trilayer graphene) permit the identification of vacancy-type defects created by proton irradiation. This sort of graphene-sandwich acts like a "protective coating" around the dangling bonds of defective graphene and may be filtered from the experimental images by a specific Fourier post-processing. Filtered HRTEM images unambiguously show that proton irradiation produces the distinctive patterns of reconstructed and unreconstructed divacancies (respectively described as 5|8|5 and 555-777 defects) and reconstructed and unreconstructed monovacancies, the last showing a triangular symmetric shape. Excellent agreement between experimental and simulation results characterize the mentioned study (Lehtinen et al. 2014) that supports previous theoretical investigation (Nanda et al. 2012) *correlating*