Atomistic dynamics and electronic transport in hydrogenated Graphene

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The electronic structure of graphene can be greatly modified by hydrogen (H) absorption, leading to different electronic transport properties with respect to the bare material. However, the electron transport features of hydrogenated graphene could be significantly affected by the atomistic configurations dynamically formed during the hydrogenation and the eventual subsequent annealing processes, and this dynamics is, in general, modified by the process parameters. We have simulated the dynamics of hydrogen adatoms absorbed on top of graphene, using the Kinetic Lattice Monte Carlo (KLMC) approach, which allows us to stochastically study large time and space scales. The obtained structures are discussed and their quantum transport properties are investigated using Non-equilibrium Green Function (NEGF) calculations.

The hydrogenation process of graphene is simulated by a statistically ordered sequence of events modelling the local time dependent modifications of the system during the processes. These modifications include H adsorption/desorption and surface diffusion of H adatoms adsorbed on top of graphene. We model diffusion, as a thermally activated process, which needs to overcame an energy barrier given by the sum of a migration energy and a short-ranged H-H adatoms interaction energy, accounting for the stability of the local configurations. As a consequence the event rate is given, according the transition state theory, by the Boltzmann weight

$$\nu_i = \nu_0 \exp\left[- E_i / k_b T \right] \qquad (1)$$

where E_i is the the activation energy barrier and ν_0 the frequency pre-factor. E_i is evaluated using an interaction energy model which depends only on the coordination of the adatoms extending up to third nearest neighbours

$$E_i = E(n_1, n_2, n_3) \qquad (2)$$

and it is tested against Density Function Theory (DFT). Atomic and associative desorption of hydrogen adatoms are also considered and corresponding energy barriers are also estimated with the aid of ab-initio computations (for similar approaches applied to different systems see Refs [1,2]), while atomic absorption occurs at a constant rate, fixed by an effective external atomic flux.

We model the quantum electron transport in the hydrogenated configurations simulated by KLMC considering a two terminal resistor geometry including contacts. The electron hamiltonian H_0 is approximated by the tight-binding model of graphene where the hopping integrals to the sites occupied by the H adatoms is set to zero [3]. The transport characteristics are calculated after the evaluation of the Green function $G(E)$ from the matrix equation

$$G(E)\left[E\,I - H_{tot} \right] = I \qquad (3)$$

where E is the energy H_{tot} is total effective hamiltonian of the device including the two self-energy terms due to the contacts [4].

The main results of our combined KMLC-NEGF methodology for the atomic (electronic) structure based process (device) simulations can be outlined as it follows:

- H atoms reorganize in complex structures after the deposition and (eventual) annealing due the effective H-H interaction (fig.1);

- The final configurations critically depend on the accuracy of the H-H model implemented to recover DFT calculated energetics;

The conductance calculated by NEGF (fig. 2) is generally larger with respect that obtained with a random distribution of H or using less accurate H-H interaction model [3].

In conclusion, ab-inito calibrated KLMC-NEGF simulations are used to predict the results of manipulation processes in hydrogenated graphene. This fully atomistic approach to the device and process simulation demonstrates its great potential when applied to two dimensional materials.

References

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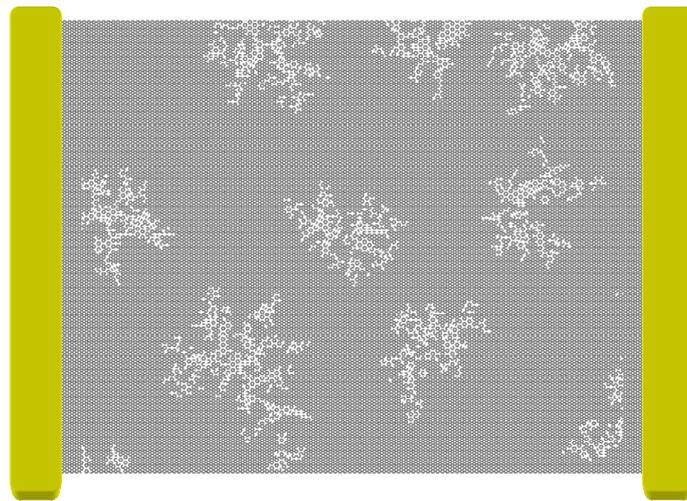
Figure 1: Example of hydrogenated graphene configuration obtained after a deposition process at T=575K and impinging flux of 10^{15} atoms/cm^{2}s. The deposition is stopped when the coverage reaches the 4% of the available sites.
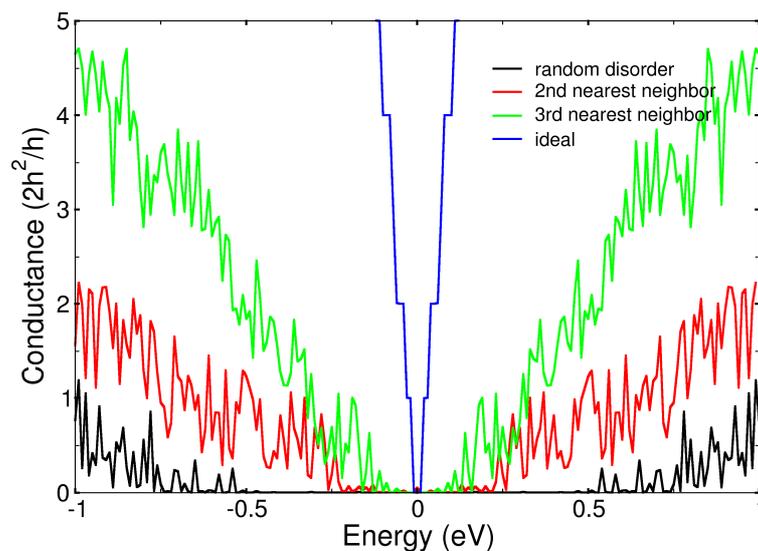
Figure 2: Conductance of a graphene ribbon with width W=40 nm, length L=50 nm and an H-concentration of ~4% calculated when the H configuration is random (black line), or the system kinetics have evolved according to a second-nearest-neighbor (red line) or a third-nearest-neighbor (green line) KMC model.