

Multiscale Simulation of Epoxide Adsorbate Functionalization on Graphene Nanoribbons:

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Chemical functionalization of graphene has retained much attention of late, because of its promise to open a gap as needed for transistor operation [1,2]. Determining the impact of specific surface adsorbed molecules is also very relevant for bio or chemical sensing applications for which graphene excellent properties have been demonstrated [3]. Among the studied groups, epoxide adsorbates, easily produced by ozone decomposition on graphene surface, have shown interesting properties [1,2] and will be considered here as a case of study. At the device level, simulating the possibilities offered by functionalization require to innovatively combine traditional ab initio material property methods with tools used for charge transport such as NEGF (Non Equilibrium Green's Functions). Here, we investigate the possibility to use such a multi-scale approach by simulating a full graphene nanoribbon (GNR)-FET using a Self-Consistent NEGF code and a Tight-Binding (TB) Hamiltonian model with local perturbation parameters related to the local epoxide surface functionalization fitted to match DFT ab initio results.

N=12 armchair (12-a)-GNRs with $2 \times 10^{13} \text{cm}^{-2}$ N-doped source and drain contacts with and without chemical functionalization were simulated using our 3D self-consistent NEGF solver. A real space (RS) TB Hamiltonian based on a set of orthogonal p_z orbitals, one for each atom, a first nearest neighbor (1N) interactions and including edge perturbation was used [4]. Locally, the ozone decomposition resulting in epoxide surface functionalization consists in an oxygen atom covalently bound to two carbons atoms. Here we have used a renormalized version of the accurate TB Hamiltonian model fitted to DFT results presented in [2] that yields band structure in good agreement with DFT results obtained using the

SIESTA package [5] in the energy range relevant for transport (Fig. 1).

Fig. 2 shows the resulting $I_D(V_G)$ characteristics with 0 and 1 functionalized oxygen atom at various positions in the central slab of the channel. The device properties are changed and depend on bound position. To explain this behavior, the conduction (E_C) and valence (E_V) energy subbands profile versus channel direction x were extracted by solving a transversal Schrödinger equation for each slab Hamiltonian [6]. 1st E_C and E_V are shown together with a plot of the current spectrum in Fig. 3. As can be seen, a local barrier in the central slab, stronger for E_V than for E_C , is created when the functionalization happens at the upper edge of the slab ($y=y_6$). In this case the highest barrier, hence the lowest current, is observed for the oxygen atom bound to the $x=2$ and $x=3$ atoms of the slab (x - position), while the barrier is lower when bounded to the $x=3$ and $x=4$ atoms (x') (see Fig. 1 for slab positioning notations). When functionalization happens closer to the center ($y=y_4$), the barrier height decreases, hence an increasing current. In the case of the x - position a localized potential well is observed instead of a barrier. This moves the transition from p-type to n-type conduction to lower V_G and increases the minimum off-current.

As a conclusion, the multi-scale approach on surface functionalization we propose here seems promising for simulating the impact of innovative nanoscale material layers or defects on device performances. The simple device analysis obtained here on band edges and current performances corroborates and translates to the device level material results such as n and p-type conductance asymmetry and position related variability observed by DFT simulation at low epoxide defect concentration [1,2].

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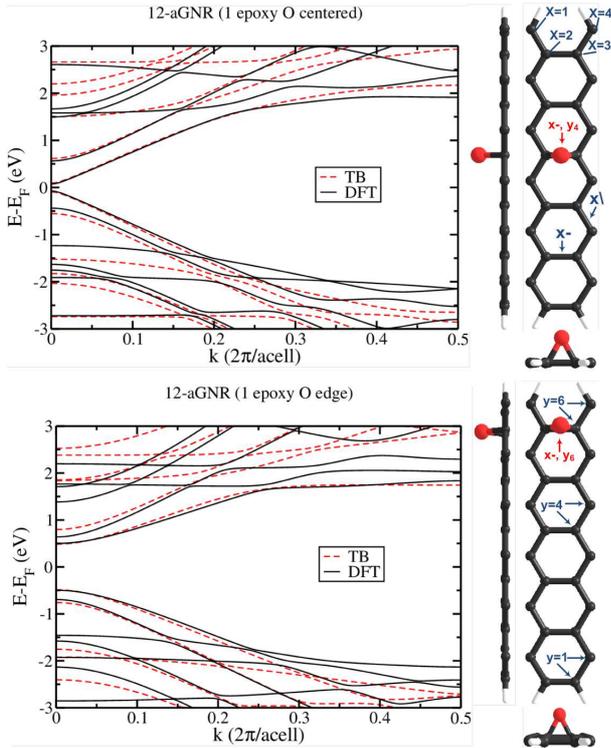


Fig. 1. 12-a-GNRs band structure extracted from DFT and a renormalized simpler version of the accurately fitted TB Hamiltonian model proposed in [2] for an epoxy oxygen atom in 2D graphene. This simpler version consists in renormalizing the on-site energy terms of both covalently bound carbon atoms by a shift of +15.597eV. The unit cell used for the band structure calculation (see atomic structure of the slab in the right panel, with C-atoms in black and O-atom in red) is repeated periodically along the transport (x)

direction. Two different positions for the O-atom (top: $x-, y_4$, bottom: $x-, y_6$) are shown. Band structures obtained by the simplified TB model show a reasonably good agreement with DFT results in the energy range relevant for transport.

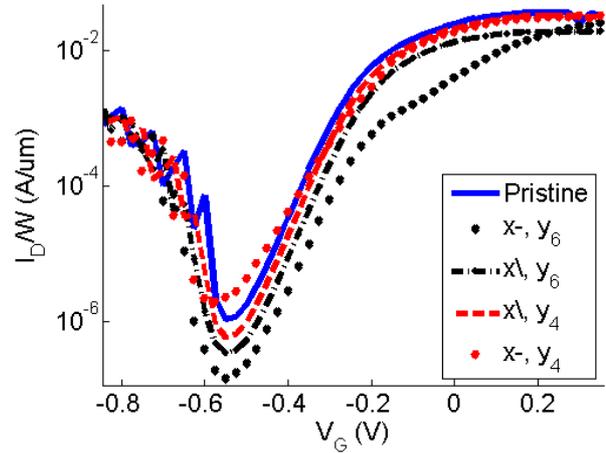


Fig. 2. Simulated $I_D(V_G)$ curves of a 12-a-GNRs with and without chemical functionalization. Source (S) and drain (D): $2 \times 10^{13} \text{cm}^{-2}$ N-doped, 60 C-atoms long each. Channel: intrinsic doping, 120 C-atoms long. A bottom gate with an equivalent oxide thickness of 0.5nm was assumed. On top and side of the GNR a 25nm air layer is simulated. D voltage $V_D=0.3\text{V}$.

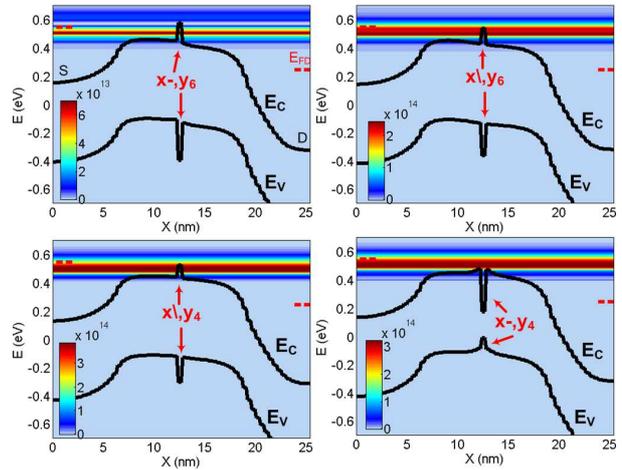


Fig. 3. First conduction and valence subband minima $E_C(x)$ and $E_V(x)$ respectively (black line) and current spectrum $J(x,E)$ in A/J (surface plot) along the channel for the 4 different epoxide functionalization cases of Fig. 2 . $V_G=-0.125\text{V}$. The positions of S and D Fermi levels are also indicated by a red dashed line at S and D side.