Metal Atomic Permeability Across Graphene Vacancies: a First Principle Study

F. Munoz[1,2], J. Mella[1,2], R.I. Gonzalez[1,2], A.H. Romero[3], M. Kiwi[1,2]*

[1] Departamento de Fisica, Facultad de Ciencias, Universidad de Chile, Santiago, Chile.
[2] Centro para el Desarrollo de la Nanociencia y la Nanotecnologia CEDENNA, Santiago, Chile.
[3] Physics Department, West Virginia University, West Virginia, USA.
[*]fvmunoz@gmail.com

In the last years, much work has been devoted to understand many unconventional properties of graphene sheets, such a large thermal conductivity, anomalous quantum Hall effect, Klein tunneling, very large electron mobility, optical transparency, etc [1]. However, the possibility of atomic diffusion from an electrode on one side to the other side of a graphene layer, and how it becomes manifest in electronic measurements, has received little attention. However, if the graphene sheet has defects or vacancies this situation can vary significantly [2].

We studied, by means of first principles calculations, how the presence of vacancies and defects modifies the energy barrier needed for atomic diffusion of a metal, from one side of a graphene sheet to the other side. We consider the effect of a Stone-Wales defect, a single vacancy and a pristine graphene sheet, see Figure 1. The selected metal species were Co, Cu and Au.

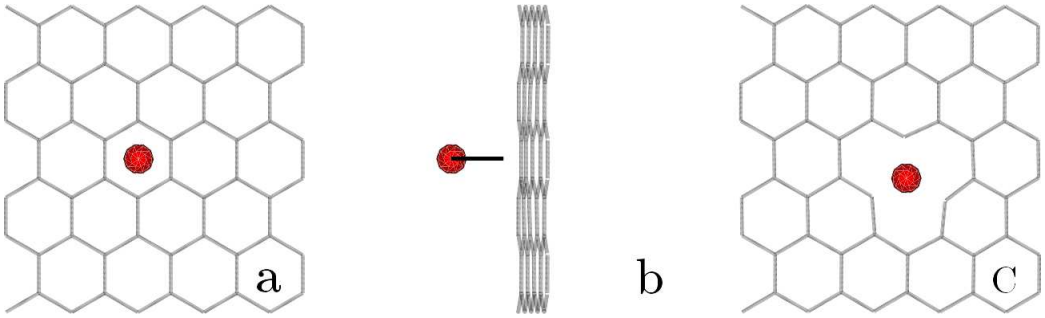

Figure 1: (a), (b) frontal and side view of the setup for a single metal atom crossing graphene. (c) frontal setup used to study a defective graphene sheet.

In the case of the diffusion of a single atom across pristine graphene the energy barriers are quite large, and the breaking of carbon-carbon bonds is necessary for atomic tunneling. However, a single vacancy defect can decrease this barrier by more than 85%. An Stone-Wales defect also can decrease this barrier, see Figure 2.

References

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We also studied the permeability of an atom belonging to a metal cluster. In this context, for pristine graphene, the energy barriers are larger than for a single metal atom. This seems intuitive, since an additional metal-metal interaction hinders the permeation across the graphene sheet. However, a vacancy can have important consequences for a Co atom: the barrier is remarkably smaller, and the permeation is energetically favorable. This permeated Co atom will attach to the vacancy very strongly, sealing it from further Co diffusion. Our conclusions indicate that resistivity and conductivity measurements of defective graphene need to be carefully interpreted, independently of the electrodes used, if vacancies are present in the sample.

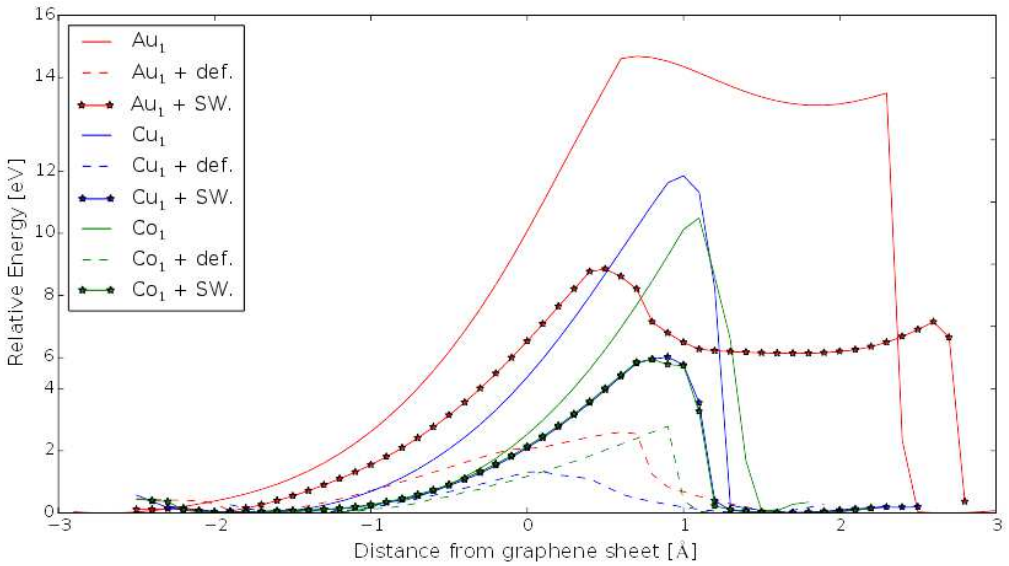

Figure 2: Energy barrier when a single metallic atom crosses through graphene. The x-axis denotes the position of the metal atom crossing the graphene sheet (x=0). The y-axis is adjusted to be zero at the beginning of each curve. The metal atom approaches from the negative values of the x axis, this dynamical dependence is evident in the asymmetry of the curves. The curves using defective graphene have a dashed line, the curves using a Stone-Wales defect have star symbols.