Graphene on SiO_2 under ultrahigh pressure

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Since the first isolation of graphene [1], silicon dioxide (SiO_2) has been one of the most used supporting substrate, due to its insulating properties and its easy integration in silicon based electronics. Interestingly enough, theoretical predictions still give controversial results on the binding mechanism of graphene on SiO_2; some works indicate strong chemisorption[2], other authors [3] suggest weak physisorption; finally, other works [4] suggest that both chemisorption and physisorption on SiO_2 are possible, depending on the surface cut.

Atomic Force Microscopy experiments on graphene placed on an amorphous SiO_2 surface shows a dramatic irreversioble change in graphene's height profile, after the application of high pressure (tens of GPa) to the system by means of a diamond tip. These finding seem to suggest that both chemisorption and physisorption of graphene are possible on the very same surface of SiO_2, with the transition triggered by the high pressure.

To clarify this rich scenario, we investigated the binding mechanism of graphene on different SiO_2 surfaces by means of Density Functional Theory (DFT) calculations. We found that a stable configuration always exists in which graphene is physisorbed to the SiO_2 substrate, i.e. it is bound by weak dispersion forces at a distance of ~3Å. Furthermore, we found that, depending on the particular surface cut, several stable arrangements of C atoms exist on the SiO_2 surface, in which one or more C atoms are chemically bound to either the Si or the O atoms of the surface. Among these configurations, we focused on the ones retaining the honeycomb lattice, characteristic of freestanding graphene. With the aim of clarifying whether the application of high pressure could induce the transition from the weakly bound physisorbed graphene to the strongly interacting chemisorbed one, we run DFT calculations on coordinate paths connecting the chemisorbed and physisorbed configurations. Our calculations (Figure 1) show that the chemisorption and the physisorption are two possible energy minima in the configuration space, separated by a energy barrier and, more itnerestingly, by a pressure barrier of the order of 10-20 GPa, confirming the experimental findings.

References

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Figures

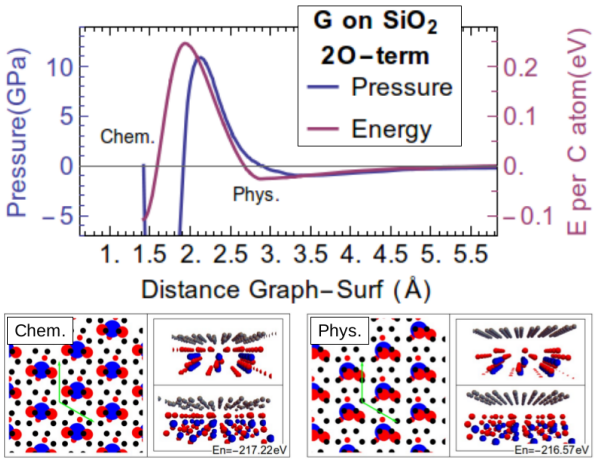

Figure 1. (Top) Pressure and energy barriers separating the chemisorbed configuration (bottom left) and the physisorbed one (bottom right) for graphene on a 2O terminated SiO_2 slab.