

Band gap engineering graphene on Ir(111) by hydrogenation and controlled patterning of graphene by hydrogen desorption

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The interest in graphene on metal substrates has been increasing over the last decade due to overwhelming prospects in numerous applications such as, nano-sized electrical components. Graphene has remarkable electronic properties, in particular, ballistic transport of the charge carriers leads to the highest electronic conductivity of known substrates at room temperature [1]. This high conductivity is desirable for high speed transistors; however the on/off ratio for intrinsic graphene is too low for using it in real applications [2]. Opening a tunable band gap in the graphene band structure is a means of overcoming this problem, but this is a challenging task.

We present measurements showing how patterned hydrogenation mediated by the Moiré structure of graphene on Ir(111) opens a band gap. This is explained by confinement effects and breaking the translational symmetry of the real, as well as, the reciprocal sublattices of the graphene [3]. The band structure was investigated by angle-resolved photoemission spectroscopy (ARPES) and the electronic density of both graphene on Ir(111) and hydrogenated graphene on Ir(111) was studied by scanning tunneling spectroscopy (STS) and the results agreed with density functional theory (DFT) calculations [3].

The patterned hydrogenation of graphene leads to a band gap opening around the Fermi level of at least 450 meV which is seen in the ARPES measurements presented in Figure 1. The size of the band gap increases with coverage (see Figures 1b and 1c). If one assumes that the band gap is symmetric around the Fermi level, the patterned hydrogenation has given rise to a band gap of approximately 900 meV. For comparison silicon has a band gap of 1.1eV. Thus patterned hydrogenation is a way of functionalizing graphene to optimize its usefulness in device applications.

STM images of hydrogenated graphene on Ir(111) are shown in Figure 2 imaged at different sample bias voltages at absolute values greater than 0.5V. The hydrogen clusters are imaged as donut shapes following the honeycomb Moiré pattern of the graphene. Here we measure the change in the electronic structure of the hydrogenated graphene by imaging the same area with different biases. The fact that the middle of the hydrogen clusters shift from dark to bright with increasing bias voltage, could indicate the presence of a gap in these areas. An estimate of the band gap is 1000 meV as measured at the centers of the hydrogenated regions. The presence of localized states, due to e.g. hydrogen vacancies, makes the evaluation of the size of the gap uncertain. However, investigations by STS will be carried out in order to confirm the size of the local band gap opening. Furthermore we plan to evaluate the size of the gap in the areas between the hydrogenated regions. These regions will be accessible by STS and we expect interesting electronic properties due to lateral confinement effects imposed by the hydrogenated and non-hydrogenated regions [3].

Finally we performed controlled hydrogen desorption using the scanning tunneling microscope tip. In Figure 3a it is clearly seen that a well-defined patch of clean graphene has been revealed. This allows us to directly measure both the hydrogen terminated and clean graphene regions on the sample with the same tip. Moreover, this method demonstrates STM as a strong tool for the direct patterning of devices in graphene at the nanoscale [4].

1. Geim, A.K. and K.S. Novoselov, *The rise of graphene*. Nature Materials, 2007. **6**(3): p. 183-191.
2. Novoselov, K.S., et al., *Electric field effect in atomically thin carbon films*. Science, 2004. **306**(5696): p. 666-669.
3. Balog, R., et al., *Bandgap opening in graphene induced by patterned hydrogen adsorption*. Nature Materials, 2010. **9**(4): p. 315-319.
4. Fuechsle, M., et al., *A single-atom transistor*. Nature Nanotechnology, 2012. **7**(4): p. 242-246.

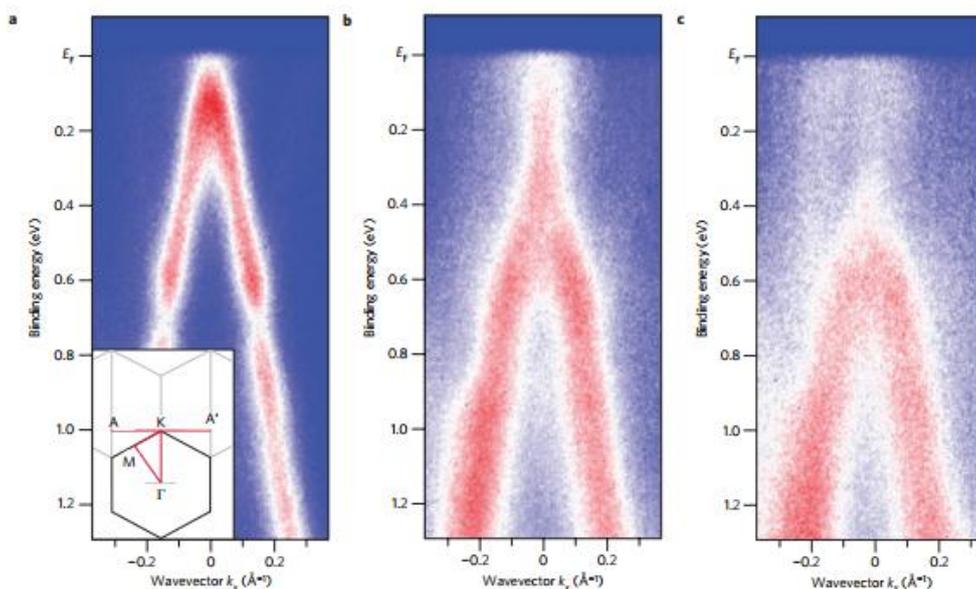


Figure 1 π -band images of graphene obtained by ARPES a) clean graphene on Ir(111) b) graphene on Ir(111) exposed to 30s dose of atomic hydrogen c) graphene on Ir(111) exposed to 50 s dose of atomic hydrogen [3].

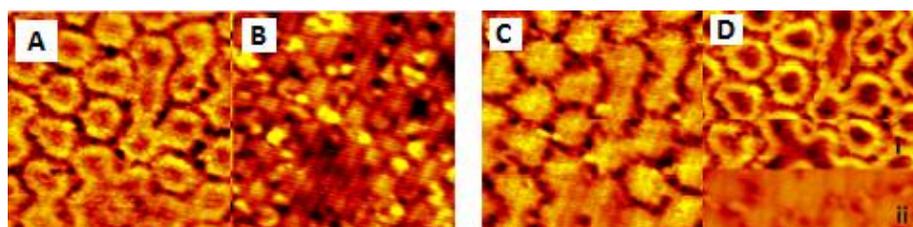


Figure 2 Full coverage of hydrogen on graphene on Ir(111) 100Åx100Å A) +657.2mV, +0.370nA B) +1314.4mV, +0.370nA C) -657mV, -0.370nA, D) 100Åx100Å i: -423mV, -0.360nA ii: -1314.4mV, -0.350nA

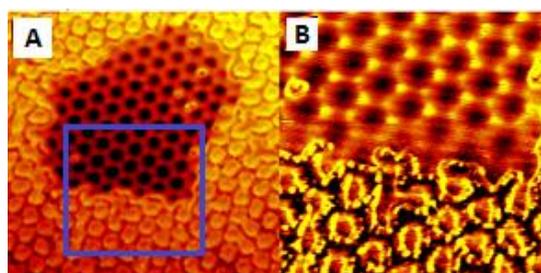


Figure 3 Desorption of hydrogen on graphene on Ir(111) A) 300Åx300Å, -449mV, -0.490nA B) 150Åx150Å, -449mV, -0.470nA, a high resolution image of the area marked with blue in A).