Van der Waals epitaxy of graphene on hexagonal boron nitride: a process controlled by defects and impurities

J. Dabrowski[1] G. Lippert[1] G. Lupina[1]

[1]IHP, Im Technologiepark 25, 15-236 Frankfurt (Oder)

Hexagonal boron nitride (h-BN) considered to be an attractive substrate for graphene, because the interaction between h-BN and graphene is weak enough for high carrier mobility to be retained in graphene but strong enough to allow for some epitaxial relationship. The purpose of this study is to elucidate by experimental and theoretical means the role, which defects in the h-BN substrate play in the nucleation and growth of graphene.

We deposited C atoms by molecular beam epitaxy (MBE) on exfoliated h-BN and evaluated the resulting films by Raman spectroscopy and by atomic force microscopy (AFM). The deposition resulted in the formation of nanocrystalline graphene with average domain size up to several dozen nanometres. Thereafter, we analysed the atomistic details of the deposition process by ab initio density functional theory (DFT) and we linked the DFT and MBE data by random walk theory.

Graphene appears to nucleate around extended defects in virgin h-BN. The DFT analysis reveals that sticking of carbon to perfect h-BN is strongly reduced by desorption, so that pre-existing seeds are needed for the nucleation.

We argue that B_2O_3 inclusions in the virgin substrate belong to such seeds. The incoming C efficiently reduces and converts them to B_2C_4 coherent C inclusions. B_2C_4 is a good trap: C ad-atoms are trapped one by one and not released back.

This is in contrast to the behaviour of superficially similar defects that are expected as well to be found in the h-BN substrates, namely, the C_NO_N donor-acceptor pairs. The first C ad-atom trapped by such a pair is released relatively easy back to the mobile state, and the probability that it reduces the trap by CO emission is negligible due to high energy barrier for this process. The barrier is high because, in contrast to the B_2O_3 case, the O atom in C_NO_N has three neighbours, while in B_2O_3 each O atom has only two neighbours. Still, The life time of C trapped by C_NO_N is long enough for nucleation to proceed.

As for C_NC_B donor-acceptor pairs, they may act as graphene seeds. C sticks also to some larger patches of graphene embedded in the h-BN lattice, but the concentration of such patches is expected to be low due to low dissociation energy of such patches into isolated C_NC_B pairs.

Nucleation of graphene on C_N and C_B substitutional carbon would be in principle possible, but formation of such seeds during deposition is a relatively rare event due to relatively high barriers on the reaction path, and BN itself is hard to dope. Moreover, strong inhomogeneity in the distribution of graphene nano-crystals observed by AFM indicates that the role of this process is not dominant.

Finally, growth of graphene stripes from substrate steps of monatomic height is hindered by small energy difference between the barriers for desorption and diffusion of carbon on h-BN (and also on graphene). For example, random walk theory predicts that in order to grow a 1 μ wide graphene stripe extending from a monatomic step, one must expose the substrate (held at a typical growth temperature) to more than 100 monolayers of atomic carbon.

Deposition of C atoms of graphene is thus an example of a process in which film growth is dominated by defects in the substrate. Given the AFM images, results of DFT calculations, analysis by random walk theory, and the chemical data provided by the hBN supplier, one can show that the observed morphology of the graphene film is predominantly due to reactions beginning with CO emission from B_2O_3 inclusions and on C_NO_N and C_NC_B donor-acceptor pairs, while efficient step flow from monatomic steps in the substrate requires high exposure to C.

Financial support from the European Commission through STREP GRADE, No. 317839 and computing time support from John von Neumann Institute for Computing (NIC) through project hfo06 are gratefully acknowledged.