Atomically precise semiconducto – graphene and *h*BN interfaces by Ge intercalation

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The integration of graphene and hexagonal boron nitride (*h*BN) into semiconductor technology requires their synthesis on semiconducting surfaces, which is still a challenge due to the low catalytic activity of these substrates in the chemical vapor deposition process. Here we report on the intercalation of monolayer Ge under epitaxial graphene (and *h*BN) on Ni(111). The intercalation of metals[1-4], semiconductors[5-7], oxygen[8-10] and hydrogen[11-12] under epitaxial graphene is an active topic in current graphene research due to the strong influence of the substrate on the electronic properties of graphene. The intercalant is often more than a mere buffer layer and forms a chemical bond to the substrate. This mofidifies the electronic properties of the 2D material on top. For example, H intercalation under graphene on SiC causes the formation of a SiH-graphene interface resulting in an unperturbed band structure[11], the intercalation of oxygen under graphene grown on Ni_3Al alloy causes selective oxidation of Al atoms and formation of Al_2O_3–graphene interface[13]; for graphene on Ir(111), the oxygen intercalation results in a p-doping of graphene[10]; intercalation of Si under graphene on Ni, Co and Fe results in the formation of corresponding silicides[5]. The existence of many intermetallic alloys with different stoichiometries such as M_3Si, M_2Si and MSi (M= Ni, Co, Fe) highlights the versatility of graphene/intermetallic interfaces. In particular, using ARPES, it was shown that, after a full Si intercalation, the electron energy band structure of graphene is essentially undoped and resembles that of graphene in vacuum[5]. These promising results naturally point towards the question how the interface and the electronic structure for graphene and related 2D materials is affected by the type of semiconductor intercalant. In particular, Ge is promising due to its higher charge carrier mobilities when compared to Si while it is also compatible with CMOS technology. It has been shown that graphene can be grown on Ge by MBE[14] or CVD[15] and that graphene on H-terminated Ge[16] and on Ge oxide surface[17] have superb electronic properties that can even exceed the mobilities of free-standing graphene membranes[17]. Clearly, the electronic properties of such devices will be strongly influenced by the interface structure. However, to date nothing is known about the interface structure between graphene (*h*BN) and Ge. Previous works on Ge intercalation were done for graphene on SiC for which the intercalated Ge is amorphous and no precise interface structures was reported[6,7]. Nevertheless, it was reported that Ge intercalation under graphene on SiC leads to ambipolar doping of ±0.3 eV[6,7] which is highlighting the versatility of this interface. Thus, in the present work we investigate a bottom-up method for the fabrication of atomically precise interfaces of Ge with 2D hexagonal materials such as graphene and *h*BN epitaxially grown on Ni(111). Furthermore, we present a complete structural and electronic characterisation of this interface and its theoretical description.

Intercalation of Ge monolayer results in atomically precise interfaces between these 2D materials and Ge with GeC_6 and GeB_3N_3 stoichiometry and $\sqrt{3}x\sqrt{3}$ reconstruction. Semiconductor interfaces prepared in this way decouple the 2D layer electronically from the substrate and lead to the restoration of the Dirac cone of graphene as well as the unperturbed electronic structure of *h*BN. Photoemission study of alkali-metal doped graphene shows that the intercalated Ge layer prevents charge leakage to the metal substrate, thereby allowing higher doping levels of graphene. This leads to an increase in electron-phonon coupling and thus raises the superconducti- on transition temperature. Moreover Ge intercalation leads to new adsorbate patterns, as compared to bulk GICs and graphene on metals (i.e. we have found a BaC_8 phase). Together with the application potential of Ge nanostructures this new interface is a path for the integration of graphene and *h*BN into state-of-the-art semiconductor technology.

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