MICROSCOPIC STUDY OF QUASI-FREE STANDING EPITAXIAL GRAPHENE AND GRAPHENE P-N JUNCTIONS FORMED ON SiC BY ATOMIC INTERCALATION OF GERMANIUM

K. Emtsev[a*], **A. Zakharov**[b], **C. Coletti**[a]
S. Forti[a] and **U.Starke**[a]

[a]Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany
[b]MAX-Lab, Lund University, Lund, S-22100, Sweden
*Corresponding author: *k.emtsev@fkf.mpg.de*

Epitaxial graphene (EG) grown on SiC single crystal wafers appear to be suitable candidate for graphene based electronics [1-3]. For further implementations it is, however, required to be able to control the electronic and structural properties of EG which are predominantly governed by the heterointerface with the substrate. Generally, solid heterointerfaces are quite difficult to influence since they remain inaccessible after growth. The heterointerface graphene-SiC(0001) is unique as its electronic properties can be manipulated on atomic scale. For example, hydrogen can be used to passivate interface states [4]. From previous photoemission measurements [5] we know that as-grown epitaxial graphene on SiC(0001) resides on top of the so-called buffer layer (also referred to as $6\sqrt{3}$ reconstruction according to its LEED pattern, see Fig. 1(a)). The latter consists of a carbon layer with graphene-like topology and bond lengths but with strong covalent bonds to the SiC substrate.
In this contribution we show that the electrically inactive $6\sqrt{3}$ buffer layer can be structurally and electronically decoupled from the SiC substrate by intercalating an atomic layer of germanium at the interface with the substrate. This results in the formation of a quasifree standing graphene film that is separated from the substrate by a Ge buffer layer.
The initial samples were prepared by annealing the SiC(0001) wafer in argon atmosphere at T=1400°C in our home CVD reactor [3]. Fig. 1 presents the LEED patterns and high resolution C1s core level spectra before and after deposition of several monolayers of Ge followed by subsequent annealing at T=720°C. As evident from the LEED patterns in Fig.1(a, c) such a treatment result in a complete disappearance of the initial $6\sqrt{3}$ reconstruction. Only graphene related spots remain visible. Further strong changes can be seen in the C1s core level spectra in Fig. 1(b, d). Two broad components (s_1 and s_2) of the buffer layer which reflect different chemical bonding of carbon atoms within the buffer layer (see Ref. [5]) are now converged into a single sharp graphene-like peak. Note also that the signal of the SiC substrate is significantly damped in comparison to the initial surface. The above observations can be reconciled in a model where Ge atoms diffuse underneath the buffer layer, break its covalent bonds to the substrate and hence structurally decouple the graphene from the SiC substrate.
ARPES valence band maps in the vicinity of the K-point of graphenes Brillouin zone in Fig. 2(a-d) demonstrate a complete recovery of the electronic structure expected for quasi-free standing graphene after the Ge intercalation process. Furthermore, depending on the

preparation conditions graphene shows moderate p- or n-doping.
The microstructure of the surface before and after decoupling of the buffer layer from the SiC surface was investigated by means of low energy electron microscopy (LEEM). Corresponding LEEM micrographs are presented in Fig. 3. As can be seen the domains of the decoupled graphene film are of the same size as on the initial samples. Details of the intercalation process will be presented at the conference.

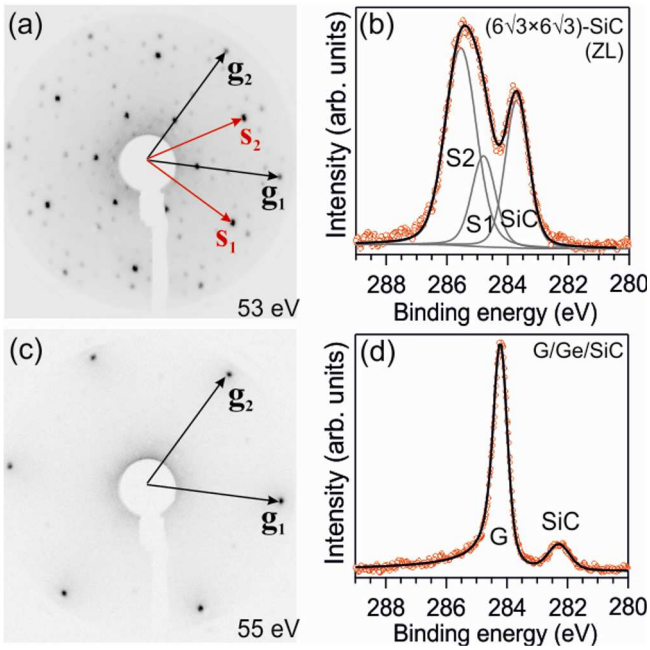

Figure 1: LEED patterns (a, c) and C1s core level spectra (b, d) taken from the initial $6\sqrt{3}$ reconstructed surface (upper panel) and after germanium deposition followed by vacuum annealing at T=720°C (lower panel). Vectors (s_1, s_2) and (g_1, g_2) correspond to reciprocal lattice vectors of graphene and the SiC lattice, respectively.

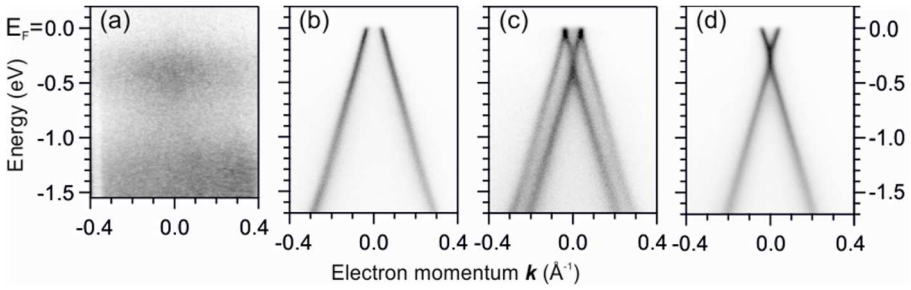

Figure 2: Photoemission valence band maps vs energy and electron momentum in the vicinity of the Kpoint ($k = 0$) of the graphene Brillouin zone taken from: (a) the initial $(6\sqrt{3} \times 6\sqrt{3})$R30° surface and after deposition of 5 ML of Ge followed by vacuum annealing at (b) T=720°C, (c) 820°C, and (d) 920°C. The photon energy was 90 eV.

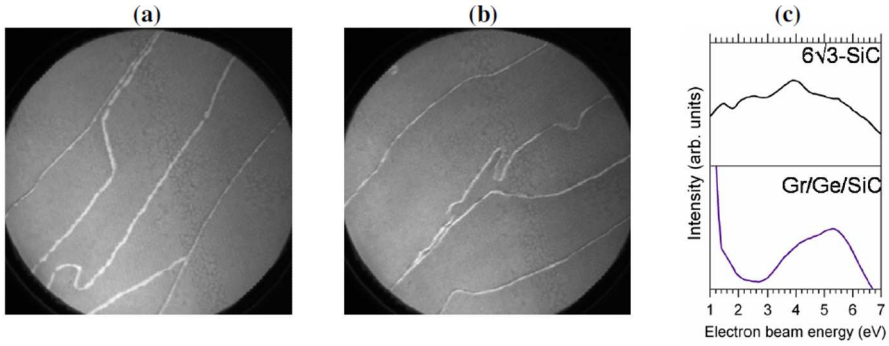

Figure 3: LEEM micrographs of the initial $6\sqrt{3}$ reconstruction (a) and of the quasi-free standing graphene obtained by intercalation of Ge atoms at the interface with SiC (b) as well as their corresponding reflectivity LEEM I-V spectra (c). Field of view is 15 μm.

References

[1] P.N. First *et al.*, MRS Bulletin, 35 (2010) 296.
[2] Y.-M- Lin *et al.*, Science, 327 (2010) 662.
[3] K.V. Emtsev, A. Bostwick, K. Horn, *et al.*, Nature Materials, 8 (2009) 203-207.
[4] C. Riedl, C. Coletti, T. Iwasaki, *et al.*, Phys. Rev. Lett., 103 (2009) 246804.
[5] K.V. Emtsev, F. Speck, Th. Seyller, L. Ley, J.D. Riley, Phys. Rev. B, 77 (2008) 155303.