ConceptGraphene

New Electronics Concept: Wafer-Scale Epitaxial Graphene

Small or medium-scale focused research project

WP2 Characterization and integration

Deliverable 2.1 “Report on characterization of epitaxial graphene”

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Deliverable Summary

Deliverable 2.1 "Report on characterization of epitaxial graphene"

In this deliverable we summarize three categories of results.

First we report results on the rotational order/disorder of few-layer graphene grown on the C-face of SiC at LiU. In contrast to published results of other groups, we find that the graphene grown with the LiU method does not show rotational disorder, possibly due to the higher growth temperature which leads to larger grains.

Secondly, we report results of intercalation of graphene on SiC at ERL. Our collected work allows us to compare quasi-free-standing graphene obtained by using different intercalation elements: hydrogen, fluorine, and oxygene. Hydrogen intercalation has shown to be very promising: it leaves graphene with an improved carrier mobility that is temperature independent. Fluorine intercalation was shown to lead to p-type doping of graphene on SiC. Finally, for oxygen intercalation we have observerd broadened π-bands, indicating a high degree of disorder possibly due to a large concentration of short-range defects. Comparing the three, hydrogen intercalation gave highest mobility, but transport measurements on fluorine intercalated graphene has not been carried out yet.

Third, we present preliminary results on doping of graphene. The complete report on doping and the environment of graphene is due in D2.2 at month 18. We have found a promising route to influence the doping level of graphene on SiC through photo-chemical gating. With this method we found an improved room-temperature mobility of 5100 cm^2/Vs (MS2 achieved). We have developed models of doping of graphene on SiC. We believe charge transfer appears from surface donor states in the buffer layer. We have found that this leads to linearly increasing doping with increasing magnetic field. As a consequence, the $\nu = 2$ quantum Hall state is pinned over a wide magnetic field range which results in an improved breakdown current. This means that devices made of this type of graphene, reaching a precision of 3 parts in 10^{10} in the Hall resistance quantization, are very promising for metrology.

1. **Rotational disorder between adjacent graphene layers on SiC(000-1) (LiU)**

Previous studies have reported that stacks of graphene grown on the (000-1) surface (C-face) of hexagonal SiC consist of graphene layers which are rotated against each other [see e.g. Hass et al., Phys. Rev. B 75 (2007) 214109]. We have investigated the rotational disorder between adjacent graphene layers in stacks grown on the C-face using low-energy electron microscopy (LEEM), low-energy electron diffraction (LEED), and photoelectron spectroscopy (ARPES, PEEM, XPEEM). Graphene samples were grown on nominally on-axis C-face SiC and both n-type 6H and 4H substrates were used. High temperature sublimation in an inert gas environment was applied [C. Virojanadara et al., Phys. Rev. B 78 (2008) 245403] and the temperature range 1800-2000°C, pressure range 500-850 mbar and average growth time of 15 min was used. Important information was obtained by using the capability to selectively observe the LEED pattern from small areas of the sample with a size down to 400 nm. An example is shown in figure 1. In fig. 1a) the existence of different domains is clearly visible. The extracted reflectivity curves (fig. 1b)) show that the domains consist of between 5 and 6 layers. μ-LEED patterns taken with a probing area of 400 nm from areas 1 and 2 show only one set of diffraction spots. It is obvious that the graphene lattices of regions 1 and 2 are rotated against each other. However, if the domains would consist of graphene stacks where adjacent layers in the same stack were rotated against each other, each area by itself should show more than one set of diffraction spots. Hence we have to conclude that the layers within one domain are not rotated against each other. The same information can be extracted from observed photoemission angular distribution patterns displayed in fig. 1d), which also show only one set of Dirac cones each (L. I. Johansson, S. Watcharinyanon, A. A. Zakharov, R. Yakimova and C. Virojanadara, Appl. Surf. Sci. to be published).

Equivalent observations were made for several samples (L. I. Johansson, S. Watcharinyanon, A. A. Zakharov, T. Iakimov, R. Yakimova, and C. Virojanadara, Phys. Rev. B 84 (2011) 125405). The reason we can

observe ordered grains (crystallographic domains) of multilayer graphene we suggest is due to that larger grains form at the higher growth temperature we have utilized, compared to earlier efforts where lower growth temperatures have been applied, resulting in smaller grain sizes. The results open the question as to why stacks of graphene grown on the C-face show the signature of Dirac fermions in other experiments [see P. N. First et al., MRS Bulletin 35 (2010) 296, and references therein]. These observations were explained by rotational disorder within the stack which decouples the electronic structure of the layers in the vicinity of the K-point. An alternative scenario would be a deviation from Bernal AB stacking in the form of, for example, AA stacking.

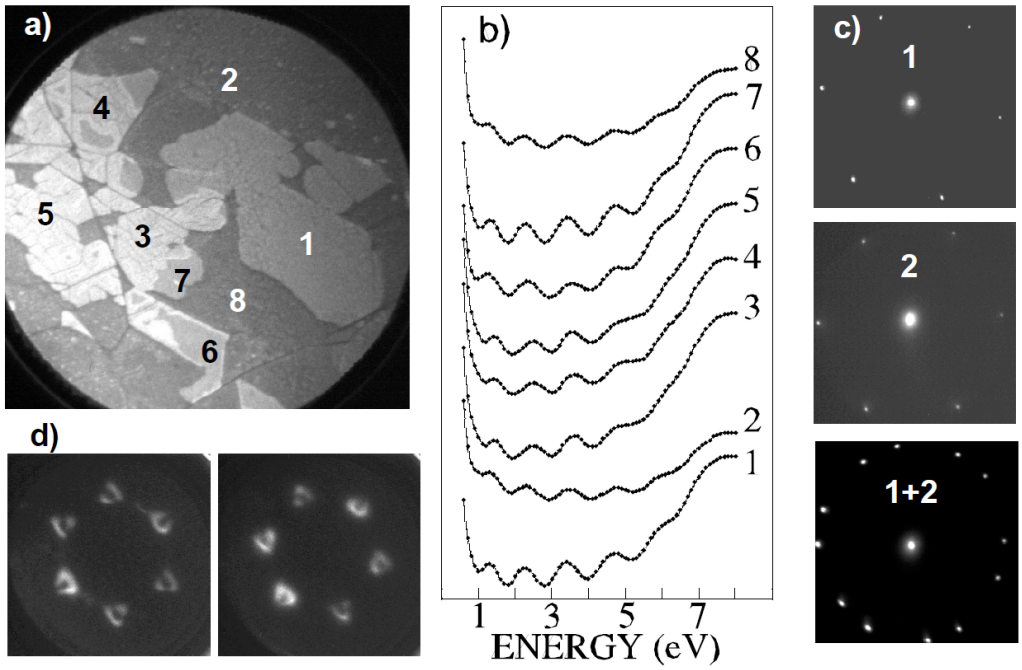

Fig. 1: a) LEEM image recorded from a sample at 2.7 eV and a field of view of 10 µm. b) Electron reflectivity curves extracted from the different areas labeled 1-8. c) The two upper panels show µ-LEED patterns collected at 45 eV using a probing area of 400 nm from the positions labeled 1 and 2 in Fig. 1a). The lower panel shows the LEED pattern collected using a 5 µm aperture and sampling domains 1 and 2. d) Shows two constant energy photoelectron angular distribution patterns (E_i,k_x,k_y) of the π-band collected using a probing area of 800 nm, a photon energy of 45 eV and at an energy of about 2 eV below the Fermi. One Dirac cone centered around each of the six K-points in the Brillouin zone is clearly observed.

2. Characterization of quasi-free-standing graphene obtained by intercalation (ERL)

We have continued our studies on quasi-free-standing graphene obtained by intercalation of different elements under the so-called buffer layer on SiC(0001) (Si-face). Different elements have been used.

Hydrogen intercalation has previously been shown to transform the buffer layer into a quasi-free-standing graphene monolayer. We have characterized these layers by Raman spectroscopy, photoelectron spectroscopy, infrared absorption spectroscopy and Hall effect measurements. The graphene monolayers on the hydrogen saturated SiC surface show an improved carrier mobility (3000 cm^2/Vs at a hole concentration of $5 \ 6\times10^{-2} \ cm^{-2}$) and a strongly reduced temperature dependence of the carrier mobility. The work has led to a manuscript which was accepted for publication in Applied Physics Letters.

Fluorine intercalation was studied in our longstanding collaboration with the group of Eli Rotenberg, Advanced Light Source, Berkeley, USA. The quasi-free-standing graphene layers on fluorinated SiC surface show a very high p-type doping. Transport measurements have not yet been carried out. The work was published in Applied Physics Letters (A.L. Walter, K.-J. Jeon, A. Bostwick, F. Speck, M. Ostler, Th. Seyller, L. Moreschini, Y.S. Kim, Y.J. Chang, K. Horn, E. Rotenberg , *Highly p-doped graphene obtained by fluorine intercalation*, Appl. Phys. Lett. 98 (2011) 184102).

Oxygen intercalation was recently proposed to be a viable route for engineering the interface between SiC(0001) and graphene [S. Oida, et al., Phys. Rev. B 82 (2010) 041411]. We have investigated this system. To that end, samples covered with the buffer layer were exposed to oxygen at different pressures and temperatures. An example is shown in fig. 2, which display the C1s core level before (a) and after (b) oxygen intercalation. The conversion of the buffer layer is evident from the changes observed in the spectra. Fig. 2(c) displays the corresponding Si2p core level spectra, which indicate the oxidation of the SiC substrate. ARPES spectra of the π-bands (fig. 3) were also recorded. A strong broadening of the π-bands was observed

which indicates a high degree of disorder. Fig. 4 compares Raman spectra of quasi-free-standing graphene obtained by oxygen intercalation and hydrogen intercalation. Evidently, oxygen intercalation leads to the formation of numerous short range defects, which cause a large D band signal. The amount of defects introduced by interface oxidation is much higher than that caused by hydrogenation. In view of the large defect density, an electrical characterization by Hall effect measurements has not been attempted. The work was presented at the International Conference on Silicon Carbide and Related materials, Cleveland, Ohio, USA.

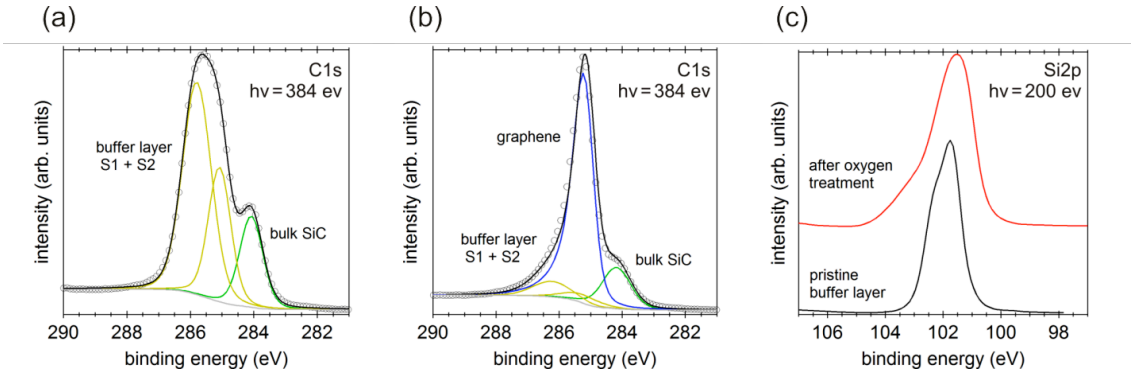

Fig. 2: C1s core level spectra of (a) pristine buffer layer, (b) after oxygen treatment. (c) Si2p core level spectrum before and after oxygen treatment.

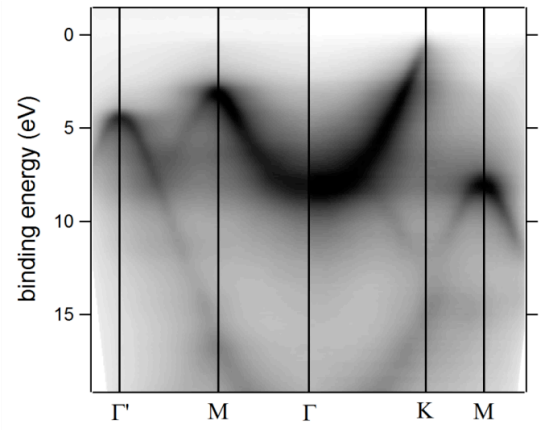

Fig. 3: Band structure measured by ARPES at hv = 65 eV after in situ oxygen treatment.

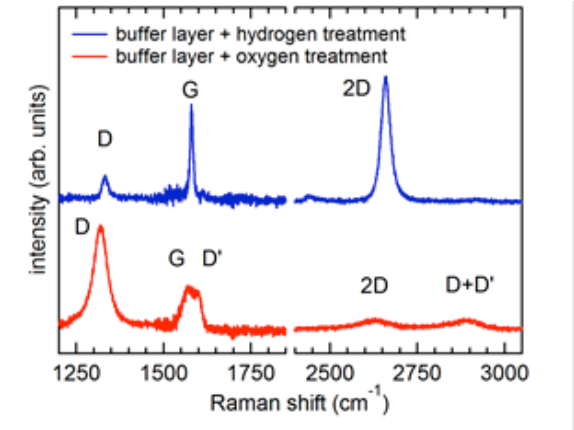

Fig. 4: Back-ground corrected Raman spectra of an oxygen treated sample (lower spectrum) and a hydrogen intercalated sample (upper spectrum).

3. Preliminary report on graphene doping.

As-grown epitaxial graphene is always strongly n-doped. In (S. Kopylov, A. Tzalenchuk, S. Kubatkin and V. I. Fal'ko, Appl Phys Lett **97** (11), 112109 (2010)) we explored the origin of this doping and presented a theoretical model of charge transfer from the SiC substrate to monolayer or bilayer graphene at zero magnetic field. We analysed doping of graphene grown on SiC in two models, which differ by the source of charge transferred to graphene, namely, from SiC surface and from bulk donors. For each of the two models, we found the maximum electron density induced in monolayer and bilayer graphene, which is determined by the difference between the work function for electrons in pristine graphene and donor states on/in SiC, and analyzed the responsivity of graphene to the density variation by means of electrostatic gates. The model gives the saturation carrier density of 10^{13} cm^{-2} for realistic values of the workfunction difference – close to the densities normally observed in as-grown graphene on SiC. Such initial carrier densities impose constraints on various applications of graphene, such as in transistors or metrology. For the former, the tunability transport with electrostatic gating becomes impossible, whereas for the latter application, the range of quantising magnetic field becomes impractical. However, we noted that particular growth processes developed by Linköping and Erlangen produce SiC/G with a much lower doping level (A. Tzalenchuk et al., Nature Nanotechnol **5** (3), 186-189 (2010); S. Weingart et al., Appl Phys Lett **95** (26), 262101 (2009)) indicating that efficient annealing of donors on and near the SiC surface is possible.

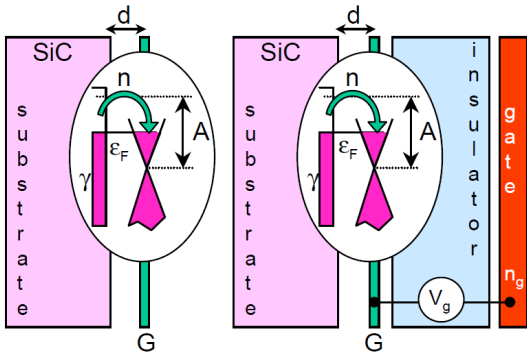

Fig. 5 : Charge transfer between SiC and bare/gated graphene.

Once the carrier density in the as-grown graphene is made relatively low (compared to the saturation value of 10^{13} cm^{-2}), it can be efficiently tuned by gating. Normally this is done by application of a voltage between an isolated metal gate and graphene. In (S. Lara-Avila, K. Moth-Poulsen, R. Yakimova, T. Bjornholm, V. Fal'ko, A. Tzalenchuk and S. Kubatkin, Adv Mater **23** (7), 878-882 (2011)) we demonstrated a novel technology – photochemical gating. The technology is based on generation of potent acceptors in a specially chosen polymer heterostructure covering graphene subjected to deep UV light. With this method we were able to reduce the electron density in graphene by a factor of 50. Importantly, this change in the carrier density resulted in a fivefold increase in carrier mobility up to 16 000 cm^2/Vs at the liquid helium temperature. At room temperature we have demonstrated the mobility of 5100 cm^2/Vs, thus achieving milestone MS2.

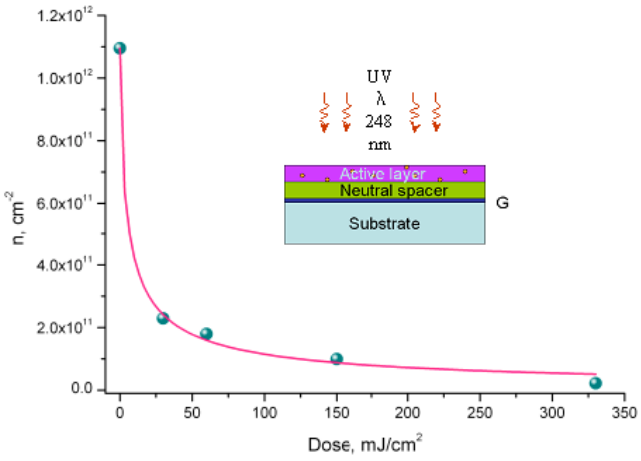

Fig. 6: Photochemical gating of graphene.

The donor states, which are responsible for the strong initial n-doping of graphene, are probably localised in the “dead layer” of carbon atoms, just underneath graphene. This layer is characterized by a $6\sqrt{3} \times 6\sqrt{3}$ supercell of the reconstructed surface of sublimated SiC. Missing or substituted carbon atoms in various positions of such a huge supercell in the dead layer create localized surface states with a broad distribution of energies within the bandgap of SiC. In (T. J. B. M. Janssen, A. Tzalenchuk, R. Yakimova, S. Kubatkin, S. Lara-Avila, S. Kopylov and V. I. Fal'ko, Phys Rev B **83** (23), 233402 (2011)) we have shown that that the carrier density in graphene

varies with magnetic field due to the charge transfer between surface-donor states in SiC and graphene. In high magnetic fields the carrier density saturates at a value up to 30% higher than the zero-field carrier density. Most importantly, we found magnetic field intervals of several Tesla, where the carrier density in graphene increases linearly with the magnetic field, resulting in the pinning of $\nu = 2$ quantum Hall state with electrons at the chemical potential occupying SiC surface donor states half-way between the $N = 0$ and $N = 1$ LLs in graphene. The pinned filling factor manifests itself in a continuously increasing breakdown current toward the upper magnetic field end of the $\nu = 2$ state far beyond the nominal value of $B_{\nu=2}$ calculated from the zero-field carrier density. Facilitated by the high breakdown current in excess of 500 μA at 14 T, we have achieved a precision of 3 parts in 10^{10} in the Hall resistance quantization measurements of photochemically gated graphene heterostructures.

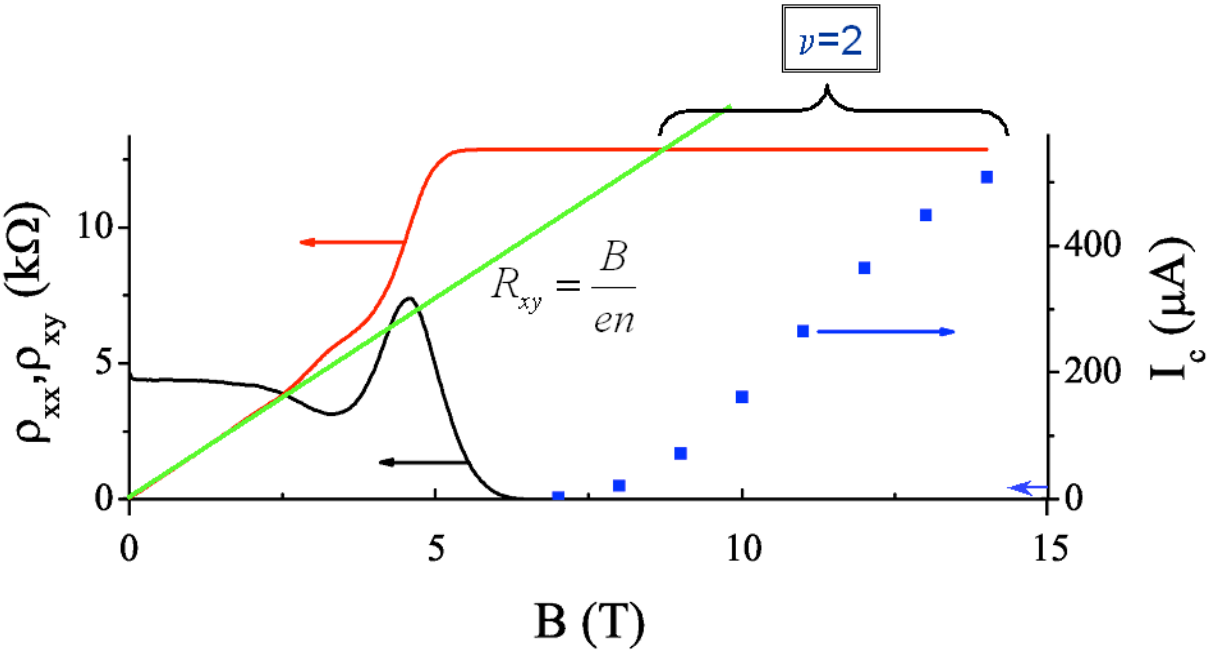

Fig. 7: Pinning of the $\nu = 2$ filling factor. I_c – breakdown current – the maximum non-dissipative current, which the quantum Hall state can sustain.