Graphene Nanoribbons on Hexagonal Boron Nitride: Deposition and Transport Characterization

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Chemically synthesized “cove”-type graphene nanoribbons (cGNRs) of different widths were brought into dispersion and drop-cast onto exfoliated hexagonal boron nitride (hBN) on a Si/SiO$_2$ chip. With AFM we observed that the cGNRs form ordered domains aligned along the crystallographic axes of the hBN. Using electron beam lithography and metallization, we contacted the cGNRs with NiCr/Au, or Pd contacts and measured their $J$-$V$-characteristics. The transport through the ribbons was dominated by the Schottky behavior of the contacts between the metal and the ribbon.

Confining graphene in one dimension yields graphene nanoribbons (GNRs), which have great potential for application in semiconductor technology. Depending on their width and edge configuration, GNRs can have a bandgap that, e.g., allows turning on and off the current flow in the GNR which is needed to design transistors. Initially, GNRs were obtained by top-down methods like etching structured graphene sheets or unzipping carbon nanotubes. However, these ribbons had rough edges which limit carrier transport and thus the usability of the GNRs in devices. Advances in solution chemistry opened up new routes to obtain GNRs by atomically precise bottom-up synthesis. There, GNRs are obtained by reactions of precursor molecules on catalytic metal surfaces. However, it is not possible to measure the GNRs’ transport properties on a metal surface. One way to overcome this issue is to transfer the GNRs to insulating substrates (typically Si/SiO$_2$). The disadvantage here is that the transfer process usually involves etchants that contaminate the GNRs. Instead, solution-processable GNRs can be employed. Here, GNR powder is dispersed in a solvent and then drop-cast onto an arbitrary surface. In previous experiments, SiO$_2$ substrates were used, whose rough surface and charged impurities negatively influence carrier transport. The mobility of extended graphene was shown to increase considerably when graphene was placed onto hexagonal boron nitride (hBN) instead of Si/SiO$_2$. However, to the best of our knowledge, deposition and device fabrication of GNRs on hBN has not been reported. In this work we demonstrate the deposition of GNRs onto the atomically flat surface of exfoliated hBN, showing a unique self-assembly behavior with domains of parallelly aligned GNRs over tens to hundreds of nm. We further discuss the fabrication and characteristics of GNR-based FET devices on hBN.

We investigated solution-processable “cove”-type GNRs (cGNRs) of different widths (4 and 6 carbon dimers, see Fig. 1(a), (b)). These cGNRs were predicted to have a band gap between 1.5 eV and 2.0 eV. The alkyl-side chains, which are attached for better solubility, were shown to have no substantial effect on the electronic structure. To fabricate devices, cGNR powder (see our previous reports for the syntheses of the 4-cGNRs and 6-cGNRs) was put in tetrahydrofuran (THF) for the 4-cGNRs, or in chlorobenzene for the 6-cGNRs, respectively. Hereafter, the mixture was sonicated for at least 1 hour, until the powder was mostly dispersed and the dispersion turned violet (gray) for the 4-cGNRs (6-cGNRs), as can be seen in Fig. 1(c).

Subsequently, we exfoliated hBN on a Si/SiO$_2$ chip, drop-cast the cGNR dispersion onto the chip, and evaporated the solvent by placing the chip onto a hot plate. Afterwards, we investigated the flakes with an atomic force microscope (AFM). Fig. 1(d) and (h) show AFM phase images of 4- and 6-cGNRs, respectively, on hBN flakes. In contrast to previous studies on SiO$_2$, which had to be carefully functionalized to allow cGNR adsorption, we found that cGNRs adsorb readily to the atomically flat hBN surfaces and form well-ordered domains with domain sizes ranging from 60 nm to over 1 µm and ribbon lengths of up to 350 nm. The situation is similar to adsorption on highly-oriented pyrolitic graphite (HOPG) surfaces, but with an important difference. While cGNRs on HOPG form arrays of straight ribbons, here we find that individual GNRs have a wiggled structure. Although we cannot offer a clear explanation for this observation, a possible reason could be the slight lattice mismatch between hBN and the graphene backbone of the cGNRs. This was shown in molecular dynamics simulations to lead to lateral buckling and snake-like motion of GNR. Alternatively, non-planar adsorption of the alkyl-side chains on the hBN could play a role. We note that, although we assume that the cGNRs form monolayers on the hBN flakes, given the z-resolution of our AFM we cannot rule out that more than one layer of cGNRs is adsorbed on the hBN. The ordered domains of cGNRs on...
hBN are found to be rotated by 60° with respect to each other. The angles between the domains become especially clear when we plot a two dimensional Fast Fourier Transformation (2D-FFT) of the AFM phase image (Fig. 1 (e)). The broadening of the 2D-FFT is mainly due to the wiggled structure of the cGNRs.

Fig. 1 (f) shows an optical microscope image of an exfoliated hBN flake on Si/SiO\textsubscript{2} before deposition of 6-cGNRs. When exfoliating hBN onto SiO\textsubscript{2}, it often cleaves along its crystallographic axes. Considering the hexagonal lattice structure of hBN consisting of alternating B and N atoms\textsuperscript{22}, this yields cleaving axes in multiples of 30°. Two of those axes are indicated with black dashed lines in Fig. 1 (f). Fig. 1 (g) is an AFM phase image of the area enclosed by the black square in Fig. 1 (f) after drop-casting the 6-cGNRs onto the chip. When comparing the orientation of the cGNRs in Fig. 1 (g) and the edges of the hBN flake in Fig. 1 (f), it becomes apparent that the cGNR domains are aligned along the crystallographic axes of the hBN.

Next, we contacted the cGNRs by performing electron beam lithography and evaporating metals (thermally and e-beam). NiCr/Au or Pd served as contact materials.

We contacted multiple cGNRs at once, using interdigitated comb-like structures (see lower inset of Fig. 2). The orientation of the contact combs was chosen in such a way that the contacts were perpendicular to some of the cGNR domains. Fig. 2 shows an optical microscope image of one device with 15 nm thick Pd contacts.

The schematics of the measurement setup is sketched in the upper inset of Fig. 2. With a probe station at ambient conditions, a source drain voltage $V_{sd}$ was applied across the ribbons and the drain current $I_d$ was measured. The heavily p-doped Si substrate could be used as a back gate electrode by applying a back gate voltage $V_{BG}$. The SiO\textsubscript{2} layer was 285 nm thick, the thickness of the used hBN flakes varied between 10-40 nm and the spacing of the contacts between 70-120 nm.

Fig. 3 shows $I$-$V$-measurements of 4- and 6-cGNRs contacted with NiCr/Au and Pd. The NiCr/Au contacted 4-cGNRs (black squares) show a current onset for the lowest source drain voltages. We note that all curves are asymmetric with respect to $V_{sd} = 0$.

The Pd contacted 4- and 6-cGNRs look very similar on the negative voltage side and differ only slightly on the positive side. This is quite surprising since their different band gap should be reflected in the $I$-$V$-curves. Further, when measuring contact pairs of further devices (of the same kind of cGNR and the same contact metal) the shape of the $I$-$V$-curves deviated from the curves shown in Fig. 3 and also the drain currents varied even by orders of magnitudes (see, e.g., inset of Fig. 4). Taking all these effects into account, it seems likely that the measurements are dominated by the Schottky behavior of the contacts between the semiconducting cGNRs and the metallic electrodes. The transition from the metal to the cGNR and back to the metal can be seen as two
FIG. 3. I-V-curves. I-V-measurements of 4- and 6-cGNRs contacted with NiCr/Au and Pd (dots) and fits for the negative and positive voltage regions (lines). Inset: Schematics for two Schottky contacts connected back-to-back over a cGNR.

back-to-back connected Schottky diodes with a resistor (one or many cGNRs) in between (see inset of Fig. 3). Since the detected current is limited by the current leaking through the Schottky diode in reverse direction, we fitted the Schottky barriers separately for negative and positive voltage regions (for the reverse direction of the Schottky diode). Using the thermionic emission model, the fit formula for the current density of our setup is

\[ J = A T^2 \exp \left( \frac{-\Phi}{k_B T} \right) \exp \left( \frac{qV}{nk_B T} \right) \left[ 1 - \exp \left( \frac{-qV}{k_B T} \right) \right] \]

(1)

Here, \( A \) is the Richardson constant, \( T \) the temperature, \( \Phi \) the height of the Schottky barrier, \( k_B \) the Boltzmann constant, \( q \) the charge, \( V \) the voltage applied across the barrier and \( n \) the ideality factor, which describes how the barrier height changes when applying a voltage across it. Fixing \( T = 300 \) K and \( q = e \) (the elementary charge), we extracted the following values for \( \Phi \) and \( n \) by fitting our data to the formula above: For the NiCr/Au contacted 4-cGNRs we obtained \( \Phi = (1.243 \pm 0.014) \) eV (\( (1.186 \pm 0.002) \) eV) and \( n = 1.145 \pm 0.010 \) (\( n = 1.089 \pm 0.001 \)) for the positive (negative) voltage side, for the Pd contacted 4-cGNRs \( \Phi = (1.128 \pm 0.003) \) eV (\( (1.180 \pm 0.004) \) eV) and \( n = 1.033 \pm 0.001 \) (\( n = 1.037 \pm 0.001 \)) for the positive (negative) voltage side, and for the Pd contacted 6-cGNRs \( \Phi = (1.171 \pm 0.002) \) eV (\( (1.175 \pm 0.002) \) eV) and \( n = 1.039 \pm 0.001 \) (\( n = 1.038 \pm 0.001 \)) for the positive (negative) voltage side.

It can be seen that the NiCr/Au contacts yield a higher ideality factor which means the I-V-curves deviate more from the ideal behavior. Additionally, they show slightly higher barriers than the Pd contacts. Furthermore, Pd contacts worked more reliably than NiCr/Au contacts which is why no data is shown for NiCr/Au contacted 6-cGNRs. Taking these facts into account, Pd seems to be the better contact material. The above numbers, however, have to be considered with care. Strictly speaking, the Richardson constant \( A \) is only valid for the free electron mass, but has to be modified using the electron effective mass\( ^{25,24} \), which is unknown for our contact configuration. Using a modified \( A \) can have the same effect as changing the height of the Schottky barrier. Since we have no possibility to determine the effective mass in the region between cGNR and metal, we used the unmodified formula as an estimate for the Schottky barrier height.

Additionally we studied the stability of our fabricated devices in air. Fig. 4 shows Pd contacted 6-cGNRs measured directly after fabrication (black squares) and two weeks later (red squares). The decreased drain current could be due to degradation of the cGNRs or contamination of the cGNRs by particles in the air.

Finally, we studied the gate response of our devices. As can be seen in the inset of Fig. 4 the devices showed (almost) no back gate dependence which could be due to Fermi level pinning at the Schottky contacts. Also, we note that the distance to the Si back gate is much larger than the separation of the metal electrodes. Therefore, we expect the gate coupling to be greatly reduced due to screening.

In summary, we dispersed chemically synthesized 4- and 6-cGNRs in THF or chlorobenzene. The dispersion was drop-cast onto exfoliated hBN. cGNRs adsorb readily to the flat hBN surfaces and form ordered domains aligned along the crystallographic axes of the hBN, showing the potential of hBN as a substrate for GNR-based devices. We contacted the cGNRs with NiCr/Au, or Pd contacts. The I-V-characteristics of the devices are dom-
inated by the Schottky behavior of the contacts between metal and ribbon.

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