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Manipulation of superconductivity in van der Waals materials and thin films

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A CHARGE TRANSPORT STUDY OF A MOLECULAR NETWORK ON GRAPHENE

In this chapter, we aim to open a band gap in graphene by imposing a larger periodic potential on the electrons via a self-assembled molecular network. To this end, we show the preliminary charge transport results on how evaporated monolayer Co-TCPP molecules affect the transport properties of exfoliated monolayer graphene. We observe a large change in the transport data before and after the deposition of molecules. However, we find no significant evidence of a side band opening. Furthermore, our atomic force microscopy measurements conducted after the transport measurements suggest the molecules did not form a close-packed network on top of the single layer graphene.

8.1. INTRODUCTION

Graphene is used as an effective decoupling layer in studying self-assembled molecular networks on a metal substrate [186]. In Scanning Tunnelling Microscopy (STM) studies, self-assembled molecules are sometimes deposited on graphene instead of directly on metal due to the fact that graphene has a low density of states at the Fermi energy, therefore, there is less hybridization of molecular states with electronic bands of the substrate. The intrinsic properties of molecules are hence better preserved [187]. However, what the molecular network on the graphene surface does to the macroscopic transport properties of the graphene is not frequently studied and discussed.

Here we look at self-assembled Cobalt(II)5,10,15,20-(Tetra-4-Cyanophenyl)-PorPhyrin (Co-TCPP) networks. Scanning Tunnelling Microscopy (STM) studies show that these molecules form a close network with a period of 1.6 nm on Graphene/Ir(111) substrate [STM results in preparation]. This is about 7 times bigger than graphene's unit cell. The network is expected to impose a dominant periodic potential for the electrons in the graphene layer either by strain or atomic distortion. If the newly imposed potential is dominant, the Brillouin zone in graphene is expected to be folded back multiple times opening up electronic bands at the edge of the Brillouin zone and creating density-of-state peaks near the Fermi level. This side band opening has been shown for a different molecule in the charge transport studies [188].

The reshaping of the electronic band structure should be reflected in the transport properties, as small sudden increases in conductance when swapping the carrier density

up and down the Fermi level. By performing temperature-dependent charge transport measurements, this effect could be studied in combination with possible Kondo physics caused by the Co atoms that are located at the centre of each network unit.

8.2. FABRICATION METHOD

Standard electron beam lithography and sputtering processes are used to create platinum contacts on top of a large flat bulk hBN flake (HQ-Graphene). The contacts are in a four-probe configuration. A single-layer graphene flake is then dry transferred on top using polycarbonate film, which is afterwards dissolved in chloroform. The sample is then annealed at 550°C for 8 hours in a high vacuum (10E-6 mbar) to achieve high surface cleanliness.

Afterwards, the sample surface is checked with AFM, if the surface is clean, a temperature-dependent gate sweeping transport measurement is performed in order to characterise individual sample properties. Next, the sample is transferred into an ultra high vacuum chamber where molecules are evaporated onto the surface. The Co-TCPP molecules (PorphyChem) were thermally sublimed at 820 K using a Knudsen cell evaporator (OmniVac), with the substrates kept at room temperature (recipe by Adam Watson, and confirmed with in-situ STM measurement from previous research). Finally, after the evaporation process, the molecules were expected to form a monolayer close-packed network on the graphene surface; the sample was then transferred to a cryostat in ambient conditions for transport measurements.

8.3. RESULTS AND DISCUSSION

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We first show the temperature-dependent resistance measurements as a function of gate voltage on our pristine graphene device in figure 8.1. The n-doped device shows conventional gate-dependent resistance [84]. As expected, near the neutrality point, the sample experiences increasing resistance with decreasing temperature. This is because the number of active carriers drops as temperature decreases. When the electric doping moves the sample in a metallic regime (far away from the neutrality point), the resistance decreases with decreasing temperature.

After the molecules were deposited on the device, the transport properties of the device changed drastically. Figure 8.2 shows the measured resistance as a function of gate voltage as a function of time after the deposition at room temperature. For all measurements shown, the gate voltages are swept from zero to the positive voltage then to the negative voltage and back to zero again.

Before the deposition, the graphene sample is n-doped with minimum hysteresis effect when sweeping the gate voltage, shown in figure 8.2 green curve. As expected, the gate-dependent resistance of the device changed dramatically after monolayer Co-TCPP was deposited on top of the graphene layer (day 1). The immediate measurement after the deposition shows that the originally n-doped sample has shifted to p-doped. The originally

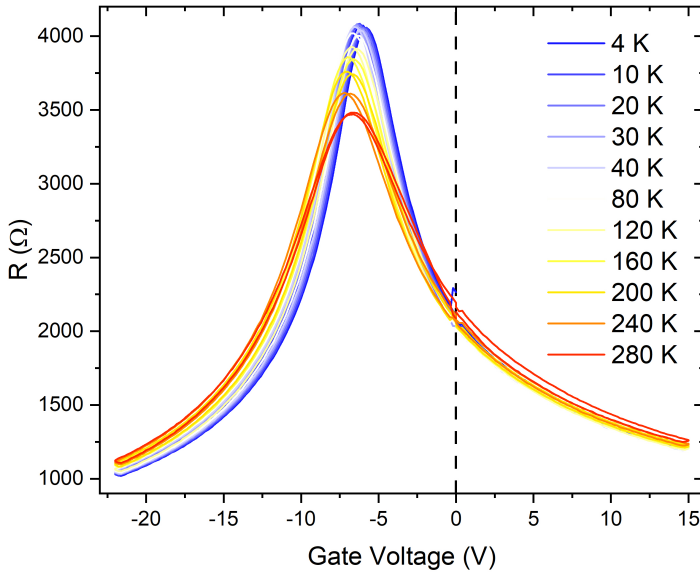


Figure 8.1: Gate dependent 4-probe transport measurement for pristine graphene at different temperatures down to 4K.

homogeneous sample with one dominant charge neutrality point is now exhibiting two separate peaks in resistance during the gate sweep. The hysteresis effect is also much more pronounced with a negative shift where the shift direction is opposite of the sweeping direction. This is a strong indication of an extra capacitive coupling for the graphene layer, normally induced by an added capacitor between the graphene and the back gate. It is possible that during the deposition or the sample transportation process, there were non-conductive molecules (or other hydrocarbons) inhomogeneously getting trapped between the graphene and the hBN, especially during the period when the sample was exposed to air. Another feature is the dramatic drop in the resistance. Suggesting there are potentially additional charge carriers contributing to the system.

Throughout the measurements the data collected with the same method changes drastically, as shown in Figure 8.2 Day 1 to Day 4. In this measurement period, during the 4 days, the sample has not been removed from the cryostat. During each day, a cool-down (to 4 K) and warm-up (to 300 K) cycle was performed.

As can be seen, at the end of the second measurement day, the two separate charge neutrality points have merged into one closer to the zero gate voltage. The hysteresis effect still presents a negative shift indicating there is still a screening effect from the back gate. After leaving the sample in the cryostat overnight, the negative shift in the hysteresis is still pronounced but with a smaller amplitude than before (day 3), suggesting

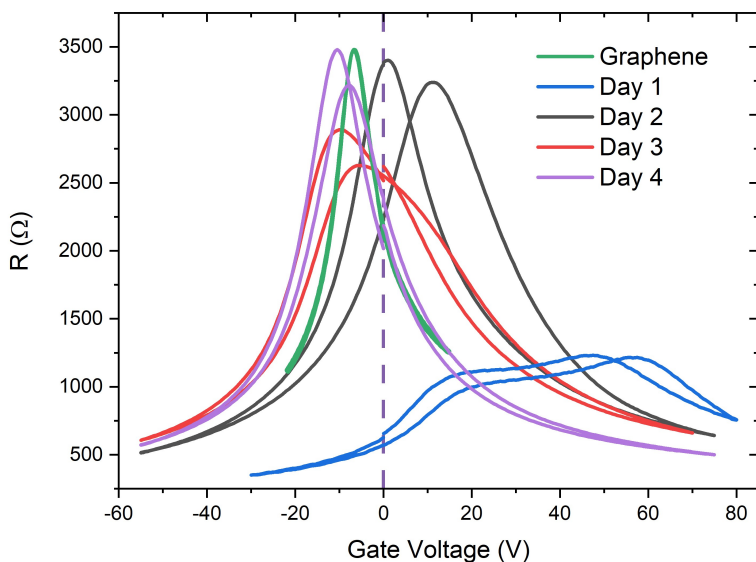


Figure 8.2: 4-probe transport measurements of a graphene sample with and without deposition of Co-TCPP at room temperature. Data was collected on the same sample on 4 different days after the Co-TCPP was deposited on the graphene; day 1 being the first day after the deposition. All measurements were performed in the vacuum ($1\text{E-}7$ mbar), between measurements the sample stayed in the vacuum. No annealing process was done during the data collection. For all measurements, the sweeping direction goes from zero to the positive voltage then to the negative voltage and to zero again.

a decrease in the capacitive effect for graphene. However, the device has reverted back to having the n-doped nature where the neutrality point lies on the negative side of the gate voltage. This indicates that the sample is highly unstable. The sample again shows different behaviour at the end of the experiments (day 4).

The sample also shows interesting behaviours during the temperature-dependent gate sweep, as shown in figure 8.3, where we plot the measured resistance as a function of gate voltage for different temperatures down to 4.1 K. For each step of the temperature variation, the sample seems to go through a gradual change, without any abrupt discontinuity. The resistivity of the metallic part (at high negative/positive gate voltage) of the graphene in the voltage sweep seems to decrease with decreasing temperature as expected. However, the resistivity around the neutrality points also seems to decrease with decreasing temperature. This strongly suggests that the sample still behaves quite metallic even around the neutrality point, with the lowest resistance observed at 4.1 K. This could result from charge transfer from the molecular layer to the graphene sheet. The other possibility is that there are newly generated surface states which had hybridised with the sharp Dirac point in the electronic band of graphene. Thus, even near the neutrality point, the sample exhibits metallic properties.

Unfortunately, in the transport measurements, there is no obvious evidence of band folding or extra super periodicity. These observations are consistent with a lack of peri-

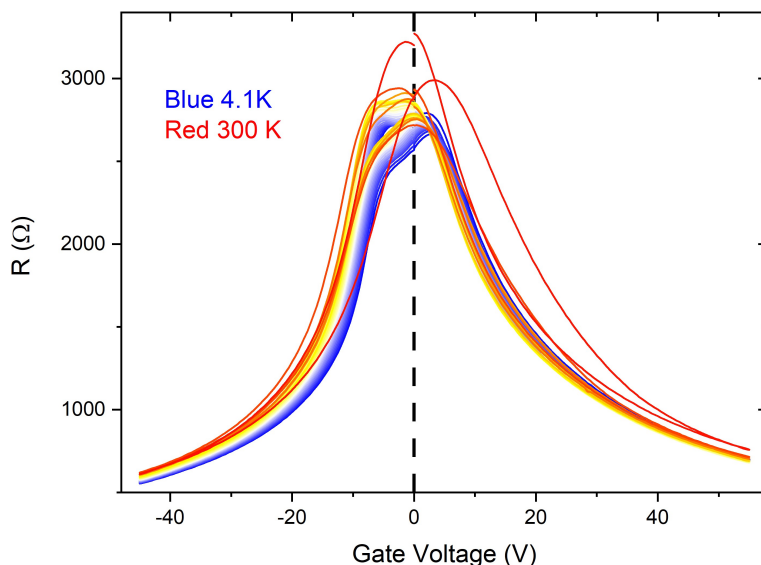


Figure 8.3: Transport measurements of the same sample with Co-TCP molecules as a function of gate voltage and temperature from room temperature down to 4.1 K with 5 K intervals between each measurement. The measurements were taken on day 2. The inset shows the same measurements on the pristine graphene sample. For all measurements, the sweeping direction goes from zero to the positive voltage then to the negative voltage and to zero again.

odicity in AFM measurements (Figure 8.4) after all transport data was collected, where the previously relatively flat and clean surface has now become rough with patches of particles that seem to be both below and above the graphene layer.

The surface height variation on the graphene with Co-TCP molecules after transport measurements is still within 2 nm at the local scale. However, this is already substantially larger than that of the pristine graphene sample prior to the Co-TCP molecules deposition (sub-nm). Furthermore, when comparing the topography of the sample (Figure 8.4 a) with the lock-in phase contrast diagram of the same measurement (b), the changes in the AFM tip phase signal that there are multiple materials with different surface forces. There is also a discrepancy between the topography and the phase diagram, which indicates the height variation measured contains contributions from both materials above and under the sheet of graphene.

8.4. CONCLUSION AND OUTLOOK

The transport properties of monolayer graphene were largely altered when Co-TCP molecules were deposited onto the surface. However, we show the deposited molecules did not form a stable close-packed network structure on the surface of graphene with the expected periodicity. This is indicated both in the transport and AFM measurements. It

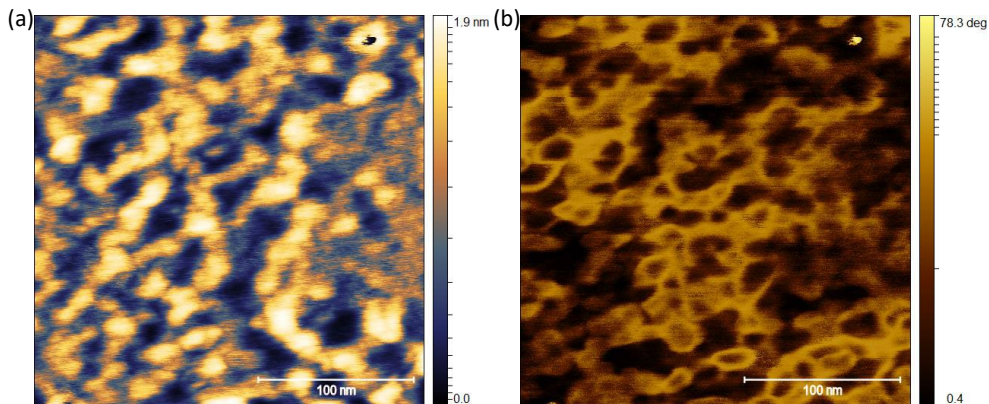


Figure 8.4: The ambient AFM measurements of graphene sample with Co-TCPP after the transport measurements. The topography is shown in (a) and the phase contrast diagram of the same region is shown in (b).

is possible that the self-assembled molecular network is not air-stable, or can be easily disturbed by the environment, supported by the dynamic transport results. There could have been defects or cracks on the pristine exfoliated graphene sample that acted as nucleation centres which encouraged the molecules to slip on and under the graphene layer

Further experiments should focus on studying Co-TCPP molecules on exfoliated graphene surfaces in air. It should be tested whether the molecules on 2D material are stable in the air. If this is not the case, all experiments need to be performed in-situ which presents several technological challenges to implement charge transport measurements that are beyond the scope of this chapter.