Spintronics and thermoelectrics in exfoliated and epitaxial graphene
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Spin transport in epitaxial graphene on the C-terminated (000$\overline{1}$)-face of silicon carbide

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Abstract

We performed a temperature dependent study of the charge and spin transport properties of epitaxial graphene on the C-terminated (000$\overline{1}$) face of silicon carbide (SiC), a system without a carbon buffer layer between the graphene and the SiC. Using spin Hanle precession in the nonlocal geometry, we measured a spin relaxation length of $\lambda_S = 0.7$ µm at room temperature, lower than in exfoliated graphene. We show that the charge and spin diffusion coefficient, $D_C$ and $D_S$ respectively, increasingly deviate from each other during electrical measurements up to a difference of a factor 4. Thus, we show that a model of localized states that was previously used to explain $D_C \approx D_S$, can also be applied to epitaxial graphene systems without a carbon buffer layer. We attribute the effect to charge trap states in the interface between the graphene and the SiC.

9.1 Introduction

The field of spintronics studies the behavior of electron spins in solid state systems, with possible applications for post CMOS nanodevices. A current goal of this research field is to find suitable materials to transport spins over distances longer than several micrometers. Graphene is a candidate material because it offers very good spin transport properties up to room temperature (RT). Both epitaxial graphene (EG) that is grown by thermal decomposition of silicon carbide (SiC) and graphene grown by chemical vapor deposition have shown to be of good quality for spin transport devices, as well as scalable to wafer-sized device arrays. In particular, EG has received interest because of promising findings for transistors, metrology and superconductivity. Recent reports of ballistic transport and ferromagnetism in EG on SiC, in combination with the graphene properties of low spin-orbit and hyperfine interactions, show great promise for novel functionalities in spintronics.

EG grown on the silicon (Si)-terminated (0001) crystal face of SiC typically has a non-conducting carbon buffer layer between the first graphene layer and the substrate. In previous studies we showed that this buffer layer has a strong effect
Spin transport in epitaxial graphene on the C-terminated (0001)-face of silicon carbide is a common tool to quantify spin transport properties such as the spin diffusion coefficient $D$ and the spin relaxation time $\tau_S$. This effect can be explained by the effect of localized states in the buffer layer that cause a narrowing of the Hanle curve, with its width strongly correlated with $\tau_S$. Removing the buffer layer by the method of hydrogen intercalation also removes the effect of the localized states. EG on the carbon (C)-terminated (0001)-face of SiC is a system without an intrinsic buffer layer, so we expect that the system behaves more or less like exfoliated graphene. This is relevant to check, because a previous study of EG on SiC(0001) by Dlubak et al. claimed a spin relaxation length of $\lambda_S = 100 - 300 \mu m$ at 2 K, which was extracted from magnetoresistance measurements in a 2-terminal geometry. This is an order of magnitude larger than the best result obtained so far in a high quality exfoliated graphene and hexagonal boron nitride heterostructure, where $\lambda_S = 13 \mu m$ at RT and 24 $\mu m$ at 4 K.

In this work, we study the spin transport properties of a monolayer EG spin device on SiC(0001). This material is different from the material in the work of Dlubak et al. which is few-layer graphene characterized by multiple randomly oriented graphene layers that are electronically isolated due to the unconventional rotational stacking. We report a spin relaxation length of $\lambda_S \approx 0.7 \mu m$, measured by four-terminal nonlocal spin valve and Hanle precession experiments. We show a small deviation between the diffusion coefficients $D_C$ and $D_S$, that we determined by charge and spin transport measurement respectively. Despite the absence of the buffer layer we think that the Hanle curve is still slightly affected by charge trap states that are present in the interface between the EG and the substrate. Overall, we show that EG graphene on SiC(0001) has more or less similar spin transport properties as low quality exfoliated graphene, probably due to a non-uniform thickness, grain boundaries and charge doping by the interface.

For a comparison between EG on the Si-terminated and C-terminated faces of SiC (S-EG and C-EG respectively), let us look at their atomic structure. The commonly observed buffer layer of S-EG is the C-rich 6$\sqrt{3} \times 6\sqrt{3}$R30°-surface termination, which is geometrical similar to graphene, but non-conducting because of sp$^3$ bonds to the SiC substrate (Fig. 9.1(a)). The buffer layer is associated with unintentional doping due to charge interface states. In contrast, thermal decomposition of C-EG does not favor the formation of covalent bonds and the first layer that forms is graphene (Fig. 9.1(b)). Due to the relatively high growth rate of C-EG, graphene nucleates in small islands that can easily merge into a uniform graphene coverage with a thickness of one or a few layers. There have been reports of two different possible stackings orders of the graphene layers: (i) a rotationally disordered stacking sequence between subsequent layers and (ii) conventional Bernal (AB) stacking with rotational disorder only between adjacent grain orientations.

Our C-EG is grown on $n$-type 4H-SiC at high temperatures of ~ 1850 °C in a buffer argon gas environment at a pressure of 850 mbar for 15 min. This method yields a sample covered with roughly one graphene monolayer, as confirmed by low
Figure 9.1: (a) Epitaxial graphene on the Si terminated SiC(0001), showing the non-conducting carbon buffer layer between the substrate and the graphene. (b) Epitaxial graphene on SiC(001\textbar), grown on the C terminated face of the crystal. This system does not have a buffer layer.

energy electron microscopy (LEEM). This growth method is accompanied by the formation of many growth centers, giving rise to domains with a different growth rate. Thus, it yields graphene domains with a grain size in the order of micrometers, which can have local variations in their thickness.

We followed roughly the device fabrication as described in Ref. 6. In short, we used a double resist layer LOR-3A + ZEP-520A (MicroChem) to define bonding pads and leads. To enhance adhesion we removed the graphene underneath these structures using reactive ion etching with O$_2$ plasma for 20 s at 40 Watt. We then deposited 5 nm Ti + 35 nm Au by e-beam vaporation. Next, we used standard electron beam lithography (EBL) techniques and the negative-tone resist Ma-N 2401 (MicroChem) to define a graphene strip and etched away the rest of the graphene in another O$_2$ plasma etching step (20 s at 40 Watt). We removed the negative resist in acetone for 10 min at 40 °C. We defined the smaller contacts by EBL and a dou-
ble resist layer of 120 nm PMMA 950k and the conductive polymer Aquasave (Mitsubishi Rayon) to avoid charging effects during e-beam exposure. In the final step we deposited two layers of 0.4 nm of Ti which were oxidized in situ at a pressure of $> 10^{-1}$ mbar to act as a tunnel barrier, followed by 45 nm of Co. The contact resistances $R_C > 1$ kΩ were characterized by three-probe resistance measurements, and where large enough to exclude significant contact-induced spin relaxation by conductivity mismatch (between 2.0 kΩ and 4.3 kΩ, compared to a channel resistance of $\sim 0.7$ kΩ)\cite{26,27}. The final device, depicted in Fig. 9.2(a), was glued to a chip carrier, wire bonded and loaded in a liquid helium flow cryostat with a vacuum pressure of $\sim 10^{-7}$ mbar.

This fabrication method resulted in some contamination from resist residue. Only one device showed clean and low-noise spin signals, the result of which we present here.

![Figure 9.2](image_url)

**Figure 9.2:** (a) Colored scanning electron micrograph of a typical spin transport device, showing the Co spin contacts with a TiO$_2$ tunnel barrier (turquoise), the graphene (outlined in white) and the SiC substrate (grey). The dark grey, diagonal lines are terrace steps. We performed Hall measurements with the cross structure on the left (contacts i-iv) to extract the carrier density and the charge diffusion coefficient. The contacts in the middle and right (for instance contacts 1-4), were used for nonlocal spin valve measurements, from which we extracted spin transport properties. (b) Spin transport device schematics of the nonlocal geometry. The spins are injected below contact 2 and picked up after a distance $L$ at contact 3. Due to Hanle precession, the spins rotate while applying an out-of-plane field $B_z$. The arrows in the contact show their magnetization direction (in this case parallel).
9.2 Room temperature measurements

We used the device geometry shown in Fig. 9.2 and standard ac lock-in techniques to characterize the RT properties of the graphene by charge and spin transport measurements. With the Hall cross geometry (contacts i–iv) we determined the charge carrier density \( n \), by measuring the Hall resistance \( R_H \) as a function of an applied out-of-plane field \( B_z \). For these measurements, we used an ac current of 1 \( \mu A \). Unexpectedly, our device showed strong changes in \( n \) during measurements, from hole doping to strong electron doping after subsequent traces (see Supplementary Information for an electronic characterization of the device using Hall measurements).

After a number of measurements, we observed a saturation at a charge carrier density of \( n = 2.1 \pm 0.02 \times 10^{13} \text{ cm}^{-2} \) (electron doping). Other devices showed smaller changes in \( n \) or no changes at all. These findings point to a process of charge accumulation in traps at the interface between the graphene and the SiC, happening during electrical measurements. The large variation between devices indicates that the charge carrier density is influenced by patches of bilayer or multilayer graphene, by defects or by small differences in the local structure of the interface.

The spin transport properties were determined using the nonlocal spin valve geometry shown in Fig. 9.2(b). In this geometry, an ac current \( I \) is applied between ferromagnetic contact 2 and 1, creating a non-equilibrium spin accumulation \( \vec{\mu}_S \) underneath injection contact 2. If placed within a distance in the order of \( \lambda_S \) away from the injector, the detector (contact 3) picks up a nonlocal voltage response with respect to a reference (contact 4), caused by the spins diffusing through the channel. Due to their different coercive fields, each contact can be switched individually by applying an in-plane \( B \)-field. The spin-dependent signal can then be made visible in a spin valve measurement (Fig. 9.3(a)), where the nonlocal resistance \( R_{nl} = V_{nl}/I \) switches between two levels, depending on the relative orientation of the injector and detector being parallel (\( \uparrow \uparrow \)) or anti-parallel (\( \uparrow \downarrow \)).

To characterize the graphene spin transport properties, we measured \( R_{nl} \) while inducing Hanle spin precession by applying an out-of-plane \( B \)-field. The result is shown in Fig. 9.3(b) and is commonly called a Hanle curve. The spin transport properties \( D_S \) and \( \tau_S \) can then be determined by fitting the Hanle curve with the solution to the Bloch equation:

\[
\frac{d\vec{\mu}_S}{dt} = D_S \nabla^2 \vec{\mu}_S - \frac{\vec{\mu}_S}{\tau_S} + \vec{\omega}_L \times \vec{\mu}_S, \tag{9.1}
\]

Here, \( \vec{\omega}_L = \mu_B g \vec{B} / h \) is the Larmor frequency, with \( \mu_B \) the Bohr magneton, \( g \) the Lande \( g \)-factor and \( h \) the reduced Planck’s constant. Any background signal that is not spin dependent can be accounted for by applying the fitting procedure on the symmetrized (spin) signal \( (R_{nl,\uparrow\downarrow} - R_{nl,\uparrow\uparrow})/2 \).

The fit (solid line) shown in Fig. 9.3(b) gave the following spin transport properties: \( D_S = 137 \pm 9 \text{ cm}^2 \text{s}^{-1} \), \( \tau_S = 37 \pm 1.4 \text{ ps} \), and \( \lambda_S = \sqrt{D\tau_S} = 0.72 \pm 0.03 \mu m \). Using
Figure 9.3: RT charge and spin transport measurements showing: (a) A two-level spin valve that switches between the inner electrodes being parallel (↑↑) and anti-parallel (↑↓). (b) Hanle precession measurements (black circles) and curve fit (solid red line) of the spin-dependent signal \( R_{nl,\uparrow\downarrow} - R_{nl,\uparrow\uparrow}/2 \). The inset shows the measurement data of the ↑↑ and the ↑↓ states. The length of the spin channel was \( L = 1 \mu m \).

The independently measured charge transport measurements described earlier, we found for the charge diffusion coefficient \( D_C = \sqrt{\frac{1}{n\pi} \frac{h v_F}{4 e R_{sq}^2}} = 117 \text{ cm}^2 \text{ s}^{-1} \), with \( h \) Planck’s constant and \( v_F = 10^6 \text{ m s}^{-1} \) the Fermi velocity. The difference between \( D_S \) and \( D_C \) of \( \approx 15\% \) can be explained by the fact that we measured charge and spin transport at different locations and measurements of \( n \) indicate significant variations in the local graphene transport properties.

9.3 Temperature dependence of the spin transport properties

Figure 9.4 shows the temperature dependence of the measured spin transport properties \( D_S, \tau_S \) and \( \lambda_S \), indicated by the black circles. First, we performed a Hanle
measurement at RT, indicated by the black arrow. Then, we cooled down the device to 4.2 K and performed the same Hanle measurements at a set of increasing temperatures up to RT. At each temperature, we also measured $D_C$, shown as red triangles in Fig. 9.4(a). The blue squares in this figures are the experimental results for $D_S$ of S-EG from Ref. [6].

We observed a slight increase of both $D_C$ and $D_S$ after the initial cool-down of the sample. However, after subsequent measurements at increasing temperatures $D_S$ rapidly dropped to below its RT value and, strikingly, deviated from $D_C$ to the point that they differed by a factor of $\xi = D_C/D_S \approx 4$ at 8 K. During the rest of the measurements we further increased the temperature back to RT, but observed only small variations in $D_S$ and $\xi$.

![Figure 9.4](image_url)

**Figure 9.4:** Temperature dependent spin transport properties of C-EG (black circles). The arrows indicate the initial measurement performed before cooling down to 4.2 K. The rest of the measurements are done at gradually increased temperatures up to RT. For comparison the properties of S-EG from Ref. [6] are included in the figure (blue squares). (a) The spin diffusion coefficient $D_S$ of C-EG, compared with $D_S$ of S-EG and with the charge diffusion coefficient $D_C$ of C-EG (red triangles). (b) The spin relaxation time $\tau_S$. (c) The spin relaxation length $\lambda_S = \sqrt{D_C \tau_S}$. Only the error bars that are larger than the symbols are shown.

A difference in $D_C$ and $D_S$ up to RT can in general be explained by the localized states model from Ref. [17] This model predicts modified results for the standard Hanle analysis in the presence of localized states. Specifically, this results in a signif-
significant decrease of $D_S$ that also deviates from $D_C$, and an overestimation of $\tau_S$. This effect was not seen in Ref.17 for epitaxial graphene on SiC(0001) after removal of the buffer layer by hydrogen intercalation. Thus, our result is surprising, because our device does not have a buffer layer either and we expect no effect of the localized states. Note that the effect is still one order of magnitude weaker when comparing with graphene on S-EG (data from Ref 6), where we measured $\xi \approx 50$. We also observe (Fig. 9.4(b)) that $\tau \approx 27\text{ ps} - 42\text{ ps}$ remains relatively low, instead of the increased values one would obtain due to the effect of localized states.

The decrease of $D_S$ could be caused by the same charge transfer process that has such a large influence on $n$ in our Hall measurements. Even though $D_C$ was at the saturated value throughout the experimental data of Fig. 9.4, this does not have to be the case for $D_S$ because of two possible reasons. First, $D_S$ was measured on a different location then $D_C$ (contacts 1–4 and contacts i–iv respectively). Second, the charge transfer rate from the channel to localized states for the spin transport measurements might be different than for the charge transport measurement, because the spin transport measurements were nonlocal, which means that a charge current was only sent through part of the measurement configuration.

If the observed deviation of $D_S$ from $D_C$ is caused by the described charge transfer process, it is likely that the effect of localized states as described in references 17 and 18 could be accounted for by charge trap states that are present at the interface between graphene and the substrate. A mechanism describing the charge transfer from the substrate to graphene was previously given for both S-EG and C-EG28. In C-EG, interface defects such as missing C-atoms can induce electronic states in the graphene. Another possibility would be the presence of Si-oxides at the interface, which are commonly found to form during the growth process of C-EG. The strength of the induced doping in the graphene depends on the density of these defects and can be similar to the doping level in S-EG, caused by the dangling bonds in the buffer layer. For exfoliated graphene, there have been no previous reports of spin transport being influenced by charge transfer between the graphene and the SiO$_2$ substrate in a similar way (i.e. resulting in a measured difference between $D_C$ and $D_S$). This indicates that the nature of the doping in the two systems might be different and that the coupling between the spin channel and localized states in the underlying substrate in EG might be stronger than in exfoliated graphene on SiO$_2$. In the C-EG studied here, we observed a high doping of $n \sim 10^{13}\text{ cm}^{-2}$, which is similar to S-EG, while the effect on $D_S$ deviating from $D_C$ was significantly weaker. This can be caused by localized states with a high ratio $\eta$ between the localized states and the density of states in the graphene, but with a weaker coupling rate $\Gamma$. 
9.4 Conclusions

In conclusion, we report here the spin transport properties of an EG device on SiC(000\textbar{}1). Our measurements show a lower quality than for exfoliated graphene, which could be related to the structure and local variations in our sample material. We observed strong changes in the charge carrier density which we attribute to charge accumulation in traps, that happens during electrical measurements. Our results indicate that the process causes a gradual deviation of $D_C$ from $D_S$, but the effect is an order of magnitude weaker than in EG on SiC(0001) that has a buffer layer. This can be explained by a localized states that have a lower coupling rate to the C-EG when compared to S-EG that has a buffer layer.

We conclude that the model of localized states can also be applied to a graphene spin channel in the case where there is no buffer layer present, indicating that the effect in general can be related to charge traps at the interface between the graphene channel and the substrate.

References

9. Spin transport in epitaxial graphene on the C-terminated (0001)-face of silicon carbide


Supplementary information

Figure 9.5 shows the Hall measurements performed on the device described in the main text using contacts i–iv. The charge carrier density is calculated from the slope of the Hall resistance $R_H$ using $n = 1/\left(\frac{e}{\hbar} \frac{dR_H}{dB_z}\right)$. Subsequent measurements show a change in the doping level, which can point to charge transfer to the interface when sending an electric current through the graphene.
Figure 9.5: Hall resistance $R_H$ versus out-of-plane field $B_z$. All traces were done directly after each other in the same measurement configuration. The order of the measured data was: cyan circles, red triangles, green horizontal lines, purple vertical lines, black triangles. In the first few measurements there is a clear change in the carrier density from slight $p$-doping to strong $n$-doping. The final carrier density saturates at $n = 2.1 \pm 0.02 \times 10^{13}$ cm$^{-2}$, given by the slope of the black solid line.