Localized States Influence Spin Transport in Epitaxial Graphene


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We developed a spin transport model for a diffusive channel with coupled localized states that result in an effective increase of spin precession frequencies and a reduction of spin relaxation times in the system. We apply this model to Hanle spin precession measurements obtained on monolayer epitaxial graphene on SiC(0001). Combined with newly performed measurements on quasi-free-standing monolayer epitaxial graphene on SiC(0001) our analysis shows that the different values for the diffusion coefficient measured in charge and spin transport measurements on monolayer epitaxial graphene on SiC(0001) and the high values for the spin relaxation time can be explained by the influence of localized states arising from the buffer layer at the interface between the graphene and the SiC surface.

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The spin dynamics in the diffusive transport regime are, in general, described by the Bloch equation for the spin chemical potential $\tilde{\mu}_S$ that describes the three-dimensional spin accumulation [1]:

$$\frac{d\tilde{\mu}_S}{dt} = D \nabla^2 \tilde{\mu}_S - \frac{\tilde{\mu}_S}{\tau_S} + \tilde{\omega}_L \times \tilde{\mu}_S \quad (1)$$

with the diffusion coefficient $D$, the spin relaxation time $\tau_S$, and the Larmor frequency $\tilde{\omega}_L = g\mu_B/h\tilde{B}$, that describes the spin precession in a perpendicular magnetic field $\tilde{B}$ with the gyromagnetic factor $g$ ($g$ factor, $g = 2$ for free electrons) and the Bohr magneton $\mu_B$. Experimentally, spin transport is commonly examined by Hanle spin precession measurements [Fig. 1(a)] that are fitted with the solutions of the time-independent Bloch equation (1) with $d\mu_S/dt = 0$. Those fits result in $D$, $\tau_S$, and the spin relaxation length $\lambda_S = \sqrt{D\tau_S}$. However, the fits are invariant under the transformation $D \rightarrow cD$, $\tau_S \rightarrow \tau_S/c$, $g \rightarrow cg$ leaving the scaling factor $c$ undefined. To unambiguously define the parameters, $D$ can be independently determined using the diffusion coefficient from charge transport measurements $D_C$ and the Einstein relation $D_C = [R_{sq}e^2\nu(E_F)]^{-1}$ [2]. Here $R_{sq}$ is the square resistance, $e$ the electron charge and $\nu(E_F)$ the density of states (DOS) of the diffusive channel at the Fermi energy. Spin transport in graphene has been extensively studied in recent years [3–16]. Because of weak spin-orbit coupling, $g = 2$ is commonly assumed to fit Hanle precession data (and define $c$) [3–15]. This was justified for exfoliated single layer graphene (eSLG) as it was shown that $D = D_C$ [5]. On the contrary, recent results on monolayer epitaxial graphene on SiC(0001) (MLEG) [17,18] show $D \ll D_C$ along with very high values for $\tau_S$ [11,19].

In this Letter we introduce a model that can explain an apparent difference between $D$ and $D_C$ by the increase of the effective $g$ factor caused by localized states coupled to the spin transport channel. Furthermore, we discuss how this model reinterprets the results on MLEG from Ref. [11] and, finally, we compare the results on MLEG to new Hanle precession measurements on quasi-free-standing MLEG on SiC(0001) (QFMLG) [20]. In this material the graphene-like, electrical neutral buffer layer, that is in conventional MLEG located between graphene and the SiC substrate, is absent [21,22]. The presented analysis points to the buffer layer as the origin of the localized states.

To examine the spin transport properties of graphene, usually the nonlocal measurement geometry is used, consisting of a two-dimensional channel with ferromagnetic electrodes that inject and detect electron spins in the

![FIG. 1 (color online).](image)

(a) Sketch of the Hanle precession geometry with a diffusive channel of width $W$ connected to the ferromagnetic spin injector ($F_i$) and detector ($F_d$) on distance $L$. The out-of-plane magnetic field $\tilde{B}$ causes the in-plane injected spins to precess while diffusing through the channel. (b) Extension of the Hanle precession geometry with localized states that are coupled to the channel. The spins can hop into these states and back into the channel while the states are not coupled with each other.
Here we introduce the factor $(\sim L)$ to the magnetic field in the Hanle geometry \[23\] that accounts for the different DOS in the channel $\nu$ compared to the localized states.

The spin accumulation in the localized states is represented by $\tilde{\mu}_S^*$ and its dynamics can be described by a Bloch equation similar to Eq. (1) that does not include a diffusive term but a term for the coupling to the channel.

$$\frac{d\tilde{\mu}_S^*}{dt} = -\frac{\tilde{\mu}_S^*}{\tau_s} + \tilde{\omega}_L^* \times \tilde{\mu}_S^* - \Gamma(\tilde{\mu}_S^* - \tilde{\mu}_S). \quad (2)$$

The Lamor frequency in the localized states $\tilde{\omega}_L^* = \omega_L^* \hat{z} = \alpha \omega_L \hat{z}$ can be different from $\tilde{\omega}_L$ due to a possibly different factor $g^*$ defined, $\tau_s^* \equiv \beta \tau_s$ is the spin relaxation time of the localized states and the term $-\Gamma(\tilde{\mu}_S^* - \tilde{\mu}_S)$ describes the flow of spins from the localized states to the channel and vice versa with the coupling rate $\Gamma = (R e^2 / \lambda_s)^{-1}$, where $1/R$ is the conductance per unit area between the localized states and the channel and $\nu_{LS}$ the density of localized states \[24,25\].

To describe the spin dynamics in the channel we also have to add on the right side of the Bloch equation (1) a coupling term

$$\frac{d\tilde{\mu}_S}{dt} = D \nabla^2 \tilde{\mu}_S - \frac{\tilde{\mu}_S}{\tau_S} + \tilde{\omega}_L \times \tilde{\mu}_S - \eta \Gamma(\tilde{\mu}_S - \tilde{\mu}_S^*). \quad (3)$$

Here we introduce the factor $\eta = \nu_{LS}/\nu$ that accounts for the different DOS in the channel $\nu$ compared to the localized states.

The two coupled equations (2) and (3) can be reduced to one effective Bloch equation. For this purpose we consider the system to be in a stationary state with $\frac{d\tilde{\mu}_S^*}{dt} = 0$, rewriting Eq. (2) to $\tilde{\mu}_S^* = q \cdot \tilde{\mu}_S$ with

$$q = \frac{\tau_s^* \Gamma}{(\tau_s^* \Gamma + 1)^2 + (\tau_s^* \omega_L^*)^2} \times \begin{pmatrix} (\tau_s^* \omega_L^*)^2 & 0 & 0 \\ 0 & (\tau_s^* \Gamma + 1) & 0 \\ 0 & 0 & (\tau_s^* \Gamma + 1 + (\tau_s^* \omega_L^*)^2 / \Gamma) \end{pmatrix}. \quad (4)$$

As the spin accumulation is purely perpendicular to the magnetic field in the Hanle geometry \[23\] ($\tilde{\omega}_L \parallel \tilde{\omega}_L \parallel \tilde{B} \parallel \tilde{\mu}_S$) we get the effective Bloch equation

$$0 = D \nabla^2 \tilde{\mu}_S - \frac{\tilde{\mu}_S}{\tau_s^*} + \tilde{\omega}_L^* \times \tilde{\mu}_S. \quad (5)$$

Here we introduce the effective spin relaxation time $\tau_s^{ef}$ and the effective precession frequency of the system $\tilde{\omega}_L^{ef} = \omega_L^{ef} \hat{z}$ defined by

$$\frac{1}{\tau_s^{ef}} = \frac{1}{\tau_s} + \eta \Gamma \frac{(\tau_s^* \omega_L^*)^2}{(1+\tau_s^* \Gamma)^2 + (\tau_s^* \omega_L^*)^2}. \quad (6)$$

The expressions for $\tau_s^{ef}$ and $\omega_L^{ef}$ are plotted in Fig. 2 as a function of the coupling rate $\Gamma$ (black solid curves). Note that independent from the value of $\Gamma$ (or the value of $\eta$, $\tau_s^*$, or $\alpha$) the model shows a decrease of $\tau_s^{ef}$ and an increased $\omega_L^{ef}$.

For weak coupling, $\Gamma \ll 1/\tau_s^*$ (Fig. 2, blue dash dotted curves), we have long dwell times for the spins in the localized states and therefore $\tau_d \gg \tau_s^*$. As a consequence all the spins that hop into the localized states will relax before returning into the channel and are therefore "lost" for the spin transport. We get $1/\tau_s^{ef} = 1/\tau_s + \eta \Gamma$, while $\omega_s^{ef} = \omega_L + \Theta((\tau_s^* \Gamma)^2)$. This is due to the fact that spins dwelling in the localized states account for additional precession and relaxation, but they do not contribute to diffusion.

For strong coupling, $\Gamma \gg 1/\tau_s^*$ (Fig. 2, red dashed curves), we have to distinguish two cases. For $\omega_s^* \gg \Gamma$, we get the same result for $\tau_s^{ef}$ and $\omega_s^{ef}$ as for weak coupling. The strong precession in the localized states dephases all spins that hop into these states and they are lost.

The most interesting is the case of strong coupling, $\Gamma \gg 1/\tau_s^*$, and low precession frequencies, $\omega_s^* \ll \Gamma$, corresponding to the measurements in MLEG (see below). We get: $1/\tau_s^{ef} = 1/\tau_s + \eta \Gamma$ and $\omega_s^{ef} = \omega_L + \eta \omega_L^*$. Both values are in this limit independent from the coupling rate $\Gamma$ (Fig. 2). Note that we get an increased $\omega_s^{ef}$ also for $\omega_s = \omega_s^* (g = g')$. This is due to the fact that spins dwelling in the localized states account for additional precession and relaxation, but they do not contribute to diffusion.

How does this model relate to the results on spin transport in MLEG on SiC(0001) reported in Ref. \[11\]? Here an increased $\tau_s$ and a strongly reduced diffusion coefficient ($D \ll D_C$) were observed. As mentioned before, $g = 2$ was assumed in Ref. \[11\] as there was no reason to assume a change of the $g$ factor for the graphene channel itself.

$$\omega_s^{ef} = \omega_L + \eta \Gamma \frac{(\tau_s^* \omega_L^*)^2}{(1+\tau_s^* \Gamma)^2 + (\tau_s^* \omega_L^*)^2}. \quad (7)$$

FIG. 2 (color online). The effective spin relaxation time $\tau_s^{ef}$ (a) and Lamor precession frequency $\omega_s^{ef}$ (b) as a function of the coupling rate $\Gamma$ (black solid curves). The asymptotic values in the limit of strong (red, dashed curves) and weak coupling (blue, dash dotted curves). In the graphs we keep $\tau_s = 150$ ps [gray dotted curve in panel (a)], $\tau_s^* = 5$ ns, $\omega_L = 10$ GHz [for a magnetic field of $B \approx 50$ mT, gray dotted curve in panel (b)] and $\eta = 50$ constant.
e.g., a changed spin-orbit coupling. But in graphene combined with localized states, with $\omega_L^g \equiv \xi \omega_L > \omega_L$ and hence $g_{\text{eff}}^g \equiv \xi g$, this assumption presents itself wrong. The values that are obtained by fitting assuming $g = 2$ are described by a modified Bloch equation that we receive by dividing Eq. (5) by the scaling factor $\xi$:

$$0 = D_{\text{mod}}^{\dagger} \vec{\nabla}^2 \vec{\mu}_S - \frac{\vec{\mu}_S}{\tau_{\text{mod}}^{\dagger}} + \vec{\omega}_L \times \vec{\mu}_S$$

(8)

with $D_{\text{mod}}^\dagger = D/\xi$ and $\tau_{\text{mod}}^{\dagger} = \xi \tau_{\text{mod}}^{\dagger}$. The effective spin relaxation time of the system including the localized states can be obtained by either assuming $D = D_C$ for the fit or assuming $g = 2$ and correcting the spin relaxation time with $\tau_{S}^{\dagger} = \tau_{\text{mod}}^{\dagger}/\xi$. The enhanced $\tau_{S}$ value in Ref. [11] is therefore not an intrinsic property of MLEG on SiC(0001) but is based on assuming a Bloch equation to fit the data which does not take the localized states into account.

Note that the measured spin relaxation length does not change when assuming a different $g$ factor as $\lambda_{S}^{\dagger} = (D_{\text{mod}}^\dagger \tau_{\text{mod}}^{\dagger})^{1/2} = (D_{\text{mod}} \tau_{\text{mod}})^{1/2} = \lambda_{S}^{\dagger} < \lambda_{S}$.

The narrow room temperature (RT) Hanle precession measurements on MLEG on SiC(0001) [11] in the center of Fig. 3 illustrate the effect of a modified $g$ factor. The fit to this data (assuming $g = 2$) gives $\tau_{S}^{\dagger} = 1.3$ ns and $D_{\text{mod}}^\dagger = 2.4$ cm$^2$/s, resulting in $\lambda_{S}^{\dagger} = 0.56 \mu$m. Compared to values obtained on eSLG [5] $\tau_{S}^{\dagger}$ is increased and $D_{\text{mod}}^\dagger$ is strongly reduced in contrast to the value of $D_C \approx 190$ cm$^2$/s obtained in charge transport measurements on the same sample and compared to $D \sim 200$ cm$^2$/s typically measured on eSLG [5,26]. At RT this discrepancy between $D_{\text{mod}}^\dagger$ and $D_C$ is resolved using a scaling factor of $\xi = D_C/D_{\text{mod}}^\dagger = 190/2.4 = 80$, which yields a spin relaxation time of $\tau_{S}^{\dagger} = 1.3$ ns/80 = 16 ps and an effective $g$ factor of $g_{\text{eff}}^{S} = 80g$. Note that these values for $\tau_{S}^{\dagger}$ and $g_{\text{eff}}^{S}$ are not describing only the graphene layer but the overall system, including the localized states.

To find out where the predicted localized states originate from, we prepared and measured spin transport samples on quasi-free-standing MLEG (QFMLG) as in Ref. [11]. QFMLG is obtained by only growing the electrical neutral buffer layer and no graphene on SiC(0001) and then intercalating the sample by hydrogen as described in Refs. [21,22]. Then we are left with a single graphene layer directly on the passivated SiC(0001) surface.

Fig. 3 shows Hanle precession curves measured on a QFMLG strip at RT next to the measurements on MLEG from Ref. [11]. The nonlocal resistance [3,11] changes slower with $B$ [27], comparable to measurements performed on eSLG [5]. The fit (assuming $g = 2$) gives $\tau_{S}^{\dagger} = 33.6 \pm 0.9$ ps and $D = 75 \pm 2$ cm$^2$/s and, therefore, $\lambda_{S}^{\dagger} = 0.50 \pm 0.01 \mu$m. These values are similar to low quality eSLG samples as $\tau_{S}$ is reduced by about a factor 4 and $D$ by a factor of approximately 3 compared to typical eSLG values [5]. Compared to MLEG we see an increase of $D$ by a factor of $\sim 30$ and a decrease of $\tau_{S}$ by about 40 times. In contrast to the MLEG data we see in charge transport measurements on similar QFMLG samples a diffusion coefficient of $D_C \approx 45$ cm$^2$/s $\sim D$ [28]. To obtain $D_C$ we use $R_{sq} \approx 3.5$ kΩ and a hole charge carrier density of $p = 6 \times 10^{12}$ cm$^{-2}$ from Hall measurements consistent with results from Ref. [22]. Comparing the results on the two graphene types on SiC(0001) it is interesting to see the striking difference of the spin relaxation times and diffusion coefficients obtained in spin transport measurements but even more important that $D_C \approx D$ in QFMLG, as expected for graphene [5]. Hence, there is no effect of the localized states. Accordingly, they have their origin in the interface between the graphene layer and the SiC substrate as this is the only structural property that is altered between conventional MLEG and QFMLG. Hence, the states could be in the dangling bonds or in the buffer layer. The strong difference of $D$ vs $D_C$ (and change in $\omega_L$) reported in Ref. [11] points to a strong coupling of the localized states to the channel [see Eq. (7) and Fig. 2(b)]. The coupling is strongest if the localized states are located in the buffer layer as this one is closest to the channel. If we assume comparable coupling of these states to the channel and between adjacent layers in graphite and considering $\eta \sim 50$ (see below), we get $\Gamma \sim 2 \times 10^{13}$ s$^{-1}$ [25], justifying the strong coupling limit (see Fig. 2).

Now we can evaluate the model and characterize the localized states by comparing the fitting results on MLEG on SiC(0001) [11] with data obtained on other types of monolayer graphene. To compensate for different $D_C$ values obtained in charge transport measurements on QFMLG
and conventional MLEG, we use data on eSLG [5] to compare with results on conventional MLEG [11]. In the limit of strong coupling we get based on Eq. (8): \(\xi = 1 + \alpha \eta\). Using the typical eSLG values, \(\tau_S = 150\) ps and \(D_C = D = 200\) cm\(^2\)/s, as the graphene values in the absence of localized states and the MLEG values as \(D^{\text{mod}}\) and \(\tau_S^{\text{mod}}\) we get \(\xi = 1 + \alpha \eta\) at RT, assuming \(g^\prime = g (\alpha = 1)\). Together with \(\tau_S^{\text{mod}}/\tau_S = 9\) we obtain \(\tau_S^{\text{mod}} = 9\) \(\tau_S = 15.0\) ns about 10 times slower than in the graphene channel. This enhanced value is very reasonable for a confined state in a material with low spin-orbit coupling.

The presence of localized states can also explain the temperature dependence of spin transport in Ref. [11] in contrast to negligible change for eSLG [3]. By assuming the same values as before for \(D\) and \(\tau_S\) in the absence of localized states, we get with the data for MLEG at 4 K \(\eta = 45\) and \(\beta = 22 (\tau_S = 3.3\) ns). These results imply less accessible localized states with longer spin relaxation times at low temperature. By assuming a Boltzmann distribution we get from the change in \(\eta\) an activation energy of \(E_a = 15\) meV.

Within our analysis, \(\eta\) describes the ratio of the DOS in the localized states and the channel. With \(\eta\) up to 80 we need a high density of localized states in our system. In MLEG with an electron charge carrier density of \(n = 3 \times 10^{12}\) cm\(^{-2}\) [11] we have a DOS of \(\nu = 3 \times 10^{13}\) eV\(^{-1}\) cm\(^{-2}\). With a density of carbon atoms in the graphenelike buffer layer of \(3.8 \times 10^{15}\) cm\(^{-2}\) and assuming that every carbon atom contributes one localized state, we get \(\eta = 80\) if these states are e.g., uniformly distributed over an energy range of \(\sim 1\) eV. Those localized states can be the origin of the strong doping observed in MLEG on SiC(0001) [29].

The observed increase of \(g\) in MLEG could in principle also be related to magnetic moments induced by the buffer layer or dangling bonds on the surface of SiC(0001) as described for hydrogenated graphene in Ref. [14]. We argue that this does not apply here since: (i) The effect in MLEG is stronger at RT than at 4 K in contrast to only low temperature effects in hydrogenated graphene. (ii) We do not see any effects resulting from randomized magnetic moments at low magnetic fields like the “dip” in the spin-valve measurements in Ref. [14]. (iii) The increase of \(g\) in MLEG is much bigger than in hydrogenated graphene.

To summarize, we developed a spin transport model for a diffusive channel with coupled localized states that results in an increased effective \(g\) factor and a reduced spin relaxation time for the transported spins. This model can be applied to any nanoscale systems, where spin transport occurs via extended states which are coupled to localized states. We use it to reinterpret the data from Ref. [11] where an enhanced spin relaxation time and a reduced spin diffusion coefficient were observed. By comparing the data from Ref. [11] to new measurements on QFMLG and typical values on eSLG we identified the buffer layer as possible source for the localized states and the measurements can be related to a \(g\) factor of \(g_{\text{eff}} = (45-80)\). Finally, we use the model to characterize the spin properties of the localized states in the buffer layer of MLEG on SiC(0001).

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[19] The results for MLEG from Ref. [11] using 4H-SiC have been reproduced in our lab for 6H-SiC.
[23] The spins are injected in the plane for small magnetic fields that do not tilt the magnetization of the electrodes out-of-plane.
[24] We assume that the spin orientation is conserved in the coupling process.
[26] With comparable $D_C$ in both systems, the transport is still dominated by impurity scattering.
[27] In the two measurements $L$ is slightly different (1.2 μm vs 1.5 μm) which has a minor influences on the width of the curve (FWHM ~ 1/L). The difference in the amplitude is not related to $\lambda_S$, which is comparable, but to a different contact polarization. There is no evidence that the minor change in $W$ (0.7 vs 1 μm) has a significant influence on the measurements.
[28] The difference between $D$ and $D_C$ (and $D_C < D$) can be explained by the low contact resistances of the measurements $R_C \approx 1.5$ kΩ and the influence on the spin transport measurements as described in the publication on contact induced spin relaxation by T. Maassen, I. J. Vera-Marun, M. H. D. Guimarães, and B. J. van Wees, Phys. Rev. B 86, 235408 (2012).