Intrinsic Terahertz Plasmons and Magnetoplasmons in Large Scale Monolayer Graphene

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Abstract
We show that in graphene epitaxially grown on SiC the Drude absorption is transformed into a strong terahertz plasmonic peak due to natural nanoscale inhomogeneities, such as substrate terraces and wrinkles. The excitation of the plasmon modifies dramatically the magneto-optical response and in particular the Faraday rotation. This makes graphene a unique playground for plasmon-controlled magneto-optical phenomena thanks to a cyclotron mass 2 orders of magnitude smaller than in conventional plasmonic materials such as noble metals.

Reference

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ABSTRACT: We show that in graphene epitaxially grown on SiC the Drude absorption is transformed into a strong terahertz plasmonic peak due to natural nanoscale inhomogeneities, such as substrate terraces and wrinkles. The excitation of the plasmon modes dramatically the magneto-optical response and in particular the Faraday rotation. This makes graphene a unique playground for plasmon-controlled magneto-optical phenomena thanks to a cyclotron mass 2 orders of magnitude smaller than in conventional plasmonic materials such as noble metals.

KEYWORDS: Graphene, terahertz, magneto-optics, magnetoplasmons, Faraday rotation

Graphene attracts a lot of attention as a novel optoelectronic and plasmonic material for applications ranging from the terahertz to the visible.1−14 One expects that plasmon waves in graphene can be squeezed into a much smaller volume11,13 than in noble metals routinely used in plasmonics and, importantly, can be manipulated by external gate voltage. A Dirac-like linear electronic dispersion and zero bandgap in graphene make its electromagnetic response rather unusual compared to other known two-dimensional conductors, such as 2D electron gases (2DEGs) in semiconductor heterostructures,15 even though the basic description of the propagating plasma modes is essentially the same.1,2

In order to observe plasmonic absorption optically one generally has to break the translational invariance of the system. Typical ways to couple plasmons to electromagnetic radiation in two-dimensional systems are placing an external grid in the vicinity of the sample16 and making stripe- or dotlike periodic structures inside the system.17−19 In graphene, this coupling has recently been achieved by pattering it in the shape of ribbons10 and by using a metallic atomic force microscopy (AFM) tip in scattering-type scanning near field optical microscopy.12 However, no measurement of graphene plasmons in magnetic field was reported so far.

Graphene epitaxially grown on SiC shows a number of intrinsic uniformly distributed defects caused by the substrate terraces and thermal relaxation after the graphitization process.20−23 In this Letter, we demonstrate that these defects, usually considered a nuisance, are in fact beneficial to excite terahertz plasmons in graphene without the need for artificial structuring. Because of the small cyclotron mass of the Dirac-like charge carriers in graphene we observe a strong effect of the magnetic field on the plasma modes, reminiscent of the behavior observed in 2DEGs. This is in drastic contrast to conventional plasmonic materials like gold, where the carrier mass exceeds the free-electron mass, leading to at best a weak dependence on magnetic field.24

A layer of honeycomb carbon was grown on the silicon side of SiC by a graphitization procedure at 1450 °C in an argon atmosphere, as described in our previous work.25 Subsequent hydrogen passivation of the silicon dangling bonds transformed the so-called buffer layer into quasi freestanding graphene.26,27 X-ray photoemission spectroscopy confirmed that the thickness...
was one graphene layer and that the backside of the SiC substrate was graphene free. After hydrogenation, graphene becomes strongly p-doped; the Fermi level, $E_F = -0.34$ eV, is below the Dirac point, which corresponds to a hole concentration $n = e^2/(\pi \hbar v_F^2) \approx 8 \times 10^{12}$ cm$^{-2}$, where $v_F \approx 10^6$ m/s is the Fermi velocity. All magneto-optical measurements were done in the Faraday geometry (magnetic field and propagation of light normal to the sample) using a Fourier transform infrared spectrometer connected to a split-coil superconducting magnet. The illuminated area of several square millimeters was fully covered by graphene.

Figures 1a,b shows the optical transmission and Faraday rotation spectra measured at 5 K in fields $B$ up to 7 T. The diagonal conductivity $\sigma_{xx}(\omega)$, normalized to the universal conductivity $\sigma_0 = e^2/4\hbar^2$, shown in Figure 1c is obtained from the optical transmission, as described in the Supporting Information. At zero magnetic field, we observe a strong maximum centered around 6.5 meV (1.6 THz) instead of the normally expected Drude peak at zero frequency due to free carriers. As we demonstrate below, the deviation from the Drude behavior is associated with the presence of a confinement potential acting on free carriers and the corresponding plasmonic absorption. A similar resonance was observed recently in graphene microribbons in the polarization perpendicular to the ribbons.10

When a magnetic field is applied, the plasma resonance splits into two modes, one of which increases and the other decreases with $B$ (Figure 1c). In order to get further insight into the origin of these modes we extracted the Hall conductivity $\sigma_{xy}(\omega)$ from the Faraday rotation spectra (Figure 1d) and obtained the optical conductivity for left and right circularly polarized radiation, $\sigma_{xy}(\omega) = \sigma_{xx} \pm i \sigma_{yy}$ (Figure 1e,f), as described in the Supporting Information. One can clearly see that each of the modes is excited only in one circular polarization. The peak positions in $\sigma_{xy}(\omega)$ and $\sigma_{xx}(\omega)$ we denote $\omega_+$ and $\omega_-$ respectively, since the former increases and the latter decreases with magnetic field. The inset of Figure 1f shows the field dependence of $\omega_+$ and $\omega_-$. The field-induced splitting of the plasmon peak resembles strikingly the appearance of collective resonances observed previously in disk-shaped quantum dots of two-dimensional electron gases based on GaAs heterostructures7,19 and in bound 2D electrons on the surface of liquid helium.28,30 In both cases, the upper and lower branches were attributed to the so-called bulk and edge magnetoplasmons, respectively, with the frequencies

$$\omega _ \pm = \sqrt{\frac{\omega _c^2}{4} + \omega _e^2} \pm \frac{|\omega _0|}{2}$$

where $\omega_c$ is the plasmon frequency at zero field, $\omega_e = \pm eB/mc$ is the cyclotron frequency, defined as positive for electrons and negative for holes, $m$ is the cyclotron mass, and $c$ the speed of light. At high fields ($|\omega_0| \gg \omega_c$), the upper branch becomes essentially the usual cyclotron resonance with a linear dependence on magnetic field, while the lower branch represents a collective mode confined to the edges31 with the energy inversely proportional to the field.

In order to clarify the origin of the confinement that causes the plasmonic resonance, we performed vibrating cantilever AFM imaging, allowing us to extract topographic and phase information. In Figure 2a, a topographical height image of a 10 $\times$ 10 $\mu$m$^2$ area of the sample is presented. The dominating structures are the terraces due to the miscut angle of SiC. Their irregular shape as compared to morphologies observed earlier23 is related to the specific graphitization temperature used in our work. Importantly, the terraces are oriented in the same direction across the entire sample. Figure 2b presents the map of the oscillation phase of the cantilever on the same area. The dark spots in the phase correspond to regions without graphene, as was determined by Raman spectroscopy. Closer inspection of the AFM images also reveals numerous wrinkles such as the ones indicated by the arrows in Figure 2c,d. The wrinkles are formed due to the relaxation of strain in graphene during the cooling down after the graphitization.20 Figure 2e shows height profiles for the lines marked in Figure 2a. Profiles 1 to 3 correspond to steps in the SiC substrate, while traces 4 to
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Lorentz formula for the optical conductivity\textsuperscript{17,32}
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And we also plot the magnetoplasmon frequencies
plasmonic contribution was not taken into account. In Figure 3,
developed

different polarizations with respect to the zero direction
indicated by the white arrow in (a).

Figure 2. Topographic height (a) and phase (b) of a $10 \times 10 \mu m^2$ region of epitaxial graphene on SiC used for optical experiments. (c,d) Close-ups of the regions in (a) and (b) marked by dashed rectangles. Arrows point to graphene wrinkles. Height profiles (e) along selected lines marked in (a), corresponding to terraces (1–3) and wrinkles (4–7). Terahertz transmission (f) for different polarizations with respect to the zero direction.

7 are taken across the wrinkles on the terraces and show that
these wrinkles have a height of less than 1 nm, which is in
agreement with previous work.\textsuperscript{10} The regions of homogeneous
graphene have a typical size of about one micrometer
throughout the whole sample.

Polarized optical transmission (Figure 2f) provides a hint
that the terahertz resonance peak is related to the
morphological structures seen by AFM. A significant anisotropy
is found, which correlates with the orientation of the terraces.
In particular, the absorption maximum is at about 1.7 times
higher energy for the electric field perpendicular to the terraces
than for the parallel orientation. Note that the peak position
remains at finite energy for every polarization. The excitation of
the plasmon parallel to the terraces is likely due to the rough
shape of the SiC step edges. One cannot exclude that the
wrinkles, which are randomly oriented, might also play a role in
confining the carriers. Because of the anisotropy, the curves and
the plasmon energy in Figure 1 are effective averages over all
polarizations.

It is worthwhile to notice that the terahertz transmission of
multilayer graphene epitaxially grown on the carbon side of SiC
also reveals an absorption peak, although at a somewhat lower
energy, with a strong polarization dependence as shown in the
Supporting Information. Although it might have a similar
plasmon origin as in the case of monolayer graphene on the
silicon face of SiC, the presence of many layers with different
doping levels makes this interpretation less straightforward.

We found that it is possible to describe quantitatively the
plasmon structure and its splitting in magnetic field by a Drude-
Lorentz formula for the optical conductivity\textsuperscript{17,32}

$$\sigma_\parallel(\omega) = \frac{2D}{\pi} \frac{i}{\omega \mp \omega_0 + i\gamma - \omega_0^2/\omega}$$

where $D$ is the plasmon spectral weight and $\gamma$ is the scattering
rate. In the present case, this equation should be regarded as
purely phenomenological, although it can be rigorously derived
for certain types of inhomogeneous media, such as disk-shaped
quantum dots, using the effective medium Maxwell-Garnett
approach (the relevant details are given in the Supporting
Information). Equation 2 is the simplest analytical expression
which reduces to a Lorentzian shape in the limit of zero field
($\omega_0 = 0$) and describes the usual Drude cyclotron resonance
when the plasmon energy is vanishing ($\omega_0 = 0$). For small
values of $\gamma$, it indeed has resonances $\omega_\pm$ at frequencies given by
eq 1. We fitted the experimental spectra of both $\sigma_\parallel = (\sigma_+ + \sigma_-)/2$ and $\sigma_\perp = (\sigma_+ - \sigma_-)/2i$ at every magnetic field to eq 2,
treating $\omega_0$, $\omega_0^2/\gamma$, and $D$ as adjustable parameters. We also
added a small frequency independent background term $\sigma_0$ to the real part of the diagonal optical conductivity, which
may have various origins, as discussed in the Supporting
Information. The fits are shown as dashed lines in Figure 1c,d.

The experimental data including all important spectral features
are well reproduced, which, given the complexity of the sample,
comes as an encouraging surprise to be explained in future
studies. However, the noticeable deviations, especially in $\sigma_\perp(\omega)$, demonstrate the limitations of this simple model with
respect to our sample.

Figure 3 shows the field dependence of $\omega_0$ and $\omega_\pm$ extracted
from the fitting procedure. The bare plasmon frequency is
essentially constant, while the cyclotron frequency demonstrates
a perfectly linear growth with a slope $h\omega_c/|B| = 2.1$ meV/T corresponding to a cyclotron mass of 5.5% of the free
electron mass $m_e$. Note that in our previous work\textsuperscript{25} an apparent
deviation from the linear dependence was reported because the
plasmonic contribution was not taken into account. In Figure 3,
we also plot the magnetoplasmon frequencies $\omega_\pm$ calculated
using eq 1 and the experimental values of $\omega_\parallel$ and $\omega_\perp$. They are
very close to the peak positions in $\sigma_\parallel$ (Figure 1e,f). The
spectral weight of the plasmon peak shows only a small, if any,
magnetic field dependence. The value of $h\Delta/\omega_0$ extracted from
the fitting is about 0.52 eV. Taken alone, it is somewhat smaller
than the expected value of $2|e_j|=0.68$ eV. The difference might be related to a noncomplete coverage of the substrate by graphene (see Figure 2b), however can also be due to the presence of the background $n_0$. The broadening, $h\gamma_c$ of the peak is about $10-12$ meV, which is more than two times smaller than observed in a similar sample by another group.33 It might still be larger than the intrinsic electron scattering, since the spectral feature is additionally broadened by the distribution of sizes and shapes of the homogeneous regions. A more detailed discussion of the spectral weight, background, and scattering is given in the Supporting Information.

The Dirac-like charge carriers in graphene at high doping are expected to show a classical cyclotron resonance with a linear field dependence on magnetic field,28 which perfectly agrees with our data. The cyclotron mass depends on doping according to the relation $m=|e_j|/v_F^2$. Using $|e_j|=0.34$ eV, and $m_0=0.055$ $m_e$, we find that $v_F=1.04 \times 10^6$ m/s, which matches remarkably well the Fermi velocity obtained by other methods.34

The plasmon frequency, $\omega_0=6.5$ meV, contains important information about the intrinsic properties of the electron gas and the confinement causing the plasmon excitation. It is instructive to compare the value of $\omega_0$ found in this work with the resonant frequency for the reference case of a point disk-shaped quantum dot, for which the effective medium model predicts:35,32

$$\omega_0^2 = \frac{3\pi^2n^2e^2}{2md^2} \tag{3}$$

where $\kappa = (1+\varepsilon_{SiC})/2 \approx 5$ is the average dielectric constant of the surrounding media and $d$ is the dot diameter. For $d=1 \mu m$, which roughly corresponds to the mean size of homogeneous regions in our sample, and for the same charge density $n = 8 \times 10^{12}$ cm$^{-2}$, the expected plasmon frequency would be 15.2 meV. This is more than twice the experimentally observed value. Lacking a rigorous quantitative model for the present sample, we ascribe this difference to the fact that the defect lines that separate homogeneous graphene regions are very narrow, and that the electromagnetic coupling between neighboring regions therefore plays an important role. Such a coupling causes a redshift32,56–58 of the plasmon energy as compared to the case of noncoupled particles, which is commonly observed in plasmonic nanostructures.

Important for terahertz applications is the question to what extent the presence of a plasmon affects the Faraday rotation in graphene. The simulations in Figure 4a demonstrate that the Faraday angle is at maximum close to the magnetoplasmon resonance and therefore can be controlled not only by magnetic field but also by $\omega_0$. Here we compare the calculated Faraday rotation of homogeneous graphene ($\omega_0=0$) and the rotation in the presence of plasmons such as the one observed in our sample (6.5 meV) and for higher plasmon energies (20 and 40 meV). A way to increase the plasmon frequency is to decrease the size of the homogeneous regions, which could be done, for example, by varying the miscut angle of the substrate. Notice that a route to increase the Faraday rotation for a given plasmon frequency is to use samples with reduced electronic scattering as demonstrated in Figure 4b. Rotations above 0.1 radians by just one atomic layer at a modest field of 1 T do not seem to be out of experimental reach.

Similarly, in more conventional plasmonic materials the Faraday and Kerr angles are enhanced close to the plasma resonance.24,39 For example, in a recent work a Kerr rotation on the order of $10^{-4}$ to $10^{-3}$ radians was detected in an array of Au disks.24 Thus, graphene shows more than 2 orders of magnitude larger rotation, which is a direct consequence of a much smaller cyclotron mass even though the carrier density per unit cell is also much lower than in noble metals. The measurements presented in this Letter were performed at low temperature to maximally resolve the magnetoplasmonic spectral structures. We do believe, though, that the magnetoplasmonic phenomena described here will persist up to room temperature, based on our temperature dependent experimental study of the cyclotron resonance in epitaxial graphene on the carbon face of SiC.40

In conclusion, we found that morphological defects on the nanoscale such as atomic steps in SiC and wrinkles in epitaxial graphene produce a remarkably strong plasmon resonance. This resonance has essentially the same origin as the plasmon peak observed in two-dimensional electron gases and in nanostructured graphene. The important difference, however, is that the confinement potential in epitaxial graphene is natural and does not require special lithographic patterning, which risks reducing the carrier mobility. Instead, one can think of controlling the plasmon frequency by varying the preparation of the substrate and the graphitization process. The presence of the plasmon dramatically changes the cyclotron resonance and Faraday rotation. Graphene appears to be a unique material, where one finds simultaneously a small effective mass giving rise to strong magneto-optical effects and excellent plasmonic...
properties. This combination opens pathways toward plasmon-controlled terahertz magneto-optics.

**ASSOCIATED CONTENT**

Supporting Information

details of the extraction of the magneto-optical conductivity, effective medium approach, magnetic field dependence of some fitting parameters, and terahertz transmission spectra of multilayer graphene at the C-side. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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