Hot carrier diffusion in graphene

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We report an optical study of charge transport in graphene. Diffusion of hot carriers in epitaxial graphene and reduced graphene-oxide samples are studied using an ultrafast pump-probe technique with a high spatial resolution. Spatiotemporal dynamics of hot carriers after a pointlike excitation are monitored. Carrier-diffusion coefficients of 11 000 and 5500 cm² s⁻¹ are measured in epitaxial graphene and reduced graphene-oxide samples, respectively, with a carrier temperature on the order of 3600 K. The demonstrated optical techniques can be used for noncontact and noninvasive in situ detection of transport properties of graphene.

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I. INTRODUCTION

Graphene, a single layer of carbon atoms, has superior charge transport,1–3 thermal transport,4 and mechanical properties.5 These make graphene a very attractive candidate for applications such as transistors,1,6 solar cells,7 electromechanical resonators,8 ultracapacitors,9 and composite materials.10 Among these properties, charge transport is the most extensively studied one since it is the foundation of most applications.1–3,6,11–20 Significant progress has been made in these studies with demonstrations of ultrahigh mobilities at room temperature,1–3,12 anomalous quantum Hall effects,2,3,21,22 and a conductivity without charge carriers.2

One important aspect of charge transport in graphene is the role played by hot carriers. It has been shown that the mean free path of carriers in graphene is several 100 nm even at room temperature.1,11 Therefore, even in devices with a channel length as long as of 1 μm, injected carriers only undergo few or even no phonon scattering events during the transport. In transport measurements performed with an applied voltage on the order of a fraction of 1 V, the carriers can have a temperature of several thousand kelvins.20 To develop nanoscale devices of graphene, it is necessary to understand and control hot carrier dynamics.

Ultrafast laser techniques are standard tools to study hot carrier dynamics in semiconductors.23 Over the past two years, significant progress has been made on using these techniques to study hot carriers in graphene.24–34 In these experiments, hot carriers with well-defined energy distributions are quasi-instantaneously injected by interband absorption of an ultrafast laser pulse. The hot carrier dynamics is probed by time resolving the change in the transmission or reflection of a probe pulse in near infrared or terahertz spectral ranges. Carrier thermalization, energy relaxation, and recombination have been studied in several types of graphene samples, including epitaxial graphene,24–31 mechanically exfoliated graphene on Si/SiO₂ substrates,32 graphene thin films grown by chemical-vapor deposition,30 reduced graphene-oxide suspensions,33 and reduced graphene oxide thin films.34 However, due to the limited spatial resolution of these experiments, transport of hot carriers has not been studied.

In this paper, we report a high-spatial-resolution ultrafast pump-probe study of hot carrier transport in epitaxial graphene and reduced graphene-oxide samples. In contrast to the previous transport studies by electric techniques, where mobilities of carriers under an externally applied electric field were measured,1–3,6,11–19 we study diffusion of hot carriers driven by the density gradient without applying an electric field. Carriers with a pointlike spatial-density profile are excited with an excess energy of more than 800 meV by a tightly focused ultrafast laser pulse through interband excitation. Expansion of the carrier profile is monitored by measuring differential transmission of a time-delayed and spatially scanned probe pulse. Carrier diffusion coefficients of 11 000 and 5500 cm² s⁻¹ are measured in epitaxial graphene and reduced graphene-oxide samples, respectively, with a carrier temperature on the order of 3600 K. The measured diffusion coefficients are compared with previously reported mobilities, by using the Einstein relation. It is quite encouraging that the hot carrier transport properties of the reduced graphene-oxide sample is only a factor of two worse than the epitaxial graphene, since the fabrication of this type of graphene is low cost. The demonstrated optical techniques can be used for noncontact and noninvasive in situ detection of transport properties of graphene.

II. EXPERIMENTAL TECHNIQUES AND PROCEDURES

We choose two types of graphene samples for our study that are both of great technological relevance, epitaxial graphene and reduced graphene oxide. The former has great potential to be used in semiconductor industry since it can be produced on large scales with a high degree of repeatability on an insulating substrate11 while the latter can be produced with low cost.15 The epitaxial graphene samples are prepared on a Si-terminated 6H-SiC (0001) crystalline wafer surface by solid-state graphitization.35,36 The reduced graphene-oxide samples are fabricated by spin-coating graphene-oxide flakes on quartz substrates to form thin films, which are then transformed to graphene films by thermal reduction at 1000 °C. By using an atomic force microscope and a scanning tunneling microscope, we determine that the epitaxial samples have one or two layers of graphene, and the reduced oxide graphene samples contain about 50 layers.34

The experimental approach for the optical study of carrier transport is rather straightforward. Carriers are first excited...
with a pump laser pulse that is incident normal to the graphene layer, with a central wavelength of 750 nm and a pulse width of 100 fs, as illustrated in Fig. 1(A). The pump pulse is obtained by frequency doubling the signal output of an optical parametric oscillator pumped by a Ti:sapphire laser. From the pump photon energy, we estimate that the initial carrier temperature \( T_e \approx 4300 \text{ K} \). The pump pulse is focused to a spot size of \( w_0 = 1.6 \mu \text{m} \) at full width at half maximum by using a microscope objective lens with a high numerical aperture. The spatial density profile of excited carriers is initially thin, but after a short time, the carriers diffuse out of the excitation spot, which results in a broadening of the profile [Fig. 1(B)]. In this process, electrons \( e \) and holes \( h \) move as pairs due to the Coulomb attraction between them.

Such a classical diffusion process is described by the diffusion equation,

\[
\frac{\partial n}{\partial t} = D \nabla^2 n - \frac{n}{\tau_e},
\]

where \( D \) is the diffusion coefficient and \( \tau_e \) is the lifetime of the carriers. Since the pump laser spot has a Gaussian shape, the injected carriers have a Gaussian spatial profile within the graphene layer, \( n(r,0) = N e^{-2 \ln(2) r^2 / w_0^2} \), where \( N \) is the peak carrier density. With this initial condition, the solution to the diffusion equations gives the density at a later time to be

\[
n(r,t) = N \left( \frac{w_0^2}{w^2(t)} \right) e^{-2 \ln(2) r^2 / w^2(t) - t / \tau_e},
\]

where

\[
w^2(t) = w_0^2 + 16 \ln(2) D t.
\]
the results of such scans. At each x, the \( \Delta T/T_0 \) decays rapidly with time. The red(gray) curve in Fig. 2(B) (left axis) shows a cross section of Fig. 2(A) at x=0. Such a fast decay is consistent with the following picture of the carrier dynamics that has been established by previous pump-probe experiments. After excitation, the carriers quickly reach a hot distribution via carrier-carrier scattering within a time scale shorter than 0.1 ps.\(^{24-26,32,33} \) Then, the carriers cool through carrier-phonon scattering on a time scale on the order of 1 ps.\(^{30} \) The decay of \( \Delta T/T_0 \) in Fig. 2(B) is mainly caused by carriers moving out of the detection window of the probe pulse in energy space. Since \( \Delta T/T_0 \) is proportional to the density of carriers at the probing energy, we can calculate how \( T_c \) changes over time using the measured \( \Delta T/T_0 \). The result is shown as the blue/dark line in Fig. 2(B) (right axis).

At all probe delays, the spatial profiles of \( \Delta T/T_0 \) along x retain a Gaussian shape with a few examples shown in Fig. 2(C). By a Gaussian fit to the profile measured at each probe delay in the range from 0.08 to 0.24 ps [indicated as the box in Fig. 2(B)], we deduce the expansion in the squared width, \( w^2(\tau) - w^2(0) \), where \( w(\tau) \) is the width of the profile at probe delay \( \tau_0=0.08 \) ps, as shown in Fig. 2(D). We choose this time range because the \( \Delta T/T_0 \) signal in this range is large enough for reliable measurements of \( w \). From a linear fit (solid line), we deduce a diffusion coefficient of \( D=1.2 \times 10^4 \) cm\(^2\) s\(^{-1}\). Since in the time range of the measurement, \( T_c \) changes from 4300 to 2900 K, we have measured the \( D \) of hot carriers with a temperature in that range.

It is worth noting that the measurement of \( D \) is not influenced by the finite lifetime of carriers since the recombination of carriers only changes the height of the density profile not the width.\(^{46} \) Furthermore, the finite size of the probe spot does not influence the measurement either. Since the probe spot size is comparable to the pump spot size, the profile measured by scanning the probe spot across the pump spot is actually a convolution of the probe spot and the actual carrier-density profiles. However, since both the probe spot and the carrier-density profiles are Gaussian, \( w^2 = w_p^2 + w_x^2 \), where \( w_p \) and \( w_x \) are the widths of the probe spot and the carrier-density profile, respectively. Since \( w_x^2 \) exists in both sides of Eq. (3), the convolution does not influence the measurement of \( D \).

We use this procedure to systematically investigate the carrier diffusion in both types of graphene samples. First, at sample temperatures of 300 and 10 K, no change in the diffusion coefficient was observed when the carrier density is lowered by a factor of five. This indicates that the carrier-carrier scattering does not influence the diffusion process under our experimental conditions. The diffusion coefficient is also measured as a function of the sample temperature in the range of 10–300 K. The results are shown in Fig. 3 as the solid squares for the epitaxial sample and the solid circles for the reduced graphene-oxide sample. These measurements were taken at different locations of the samples. The uncertainties on the deduced diffusion coefficient are caused by both the stability of the experimental setup and the inhomogeneity and reproducibility of the samples.
diffusion occurs during the energy-relaxation process. During the time range of the measurement, $T_e$ changes from 4300 to 2900 K [Fig. 2(B), right axis]. To estimate the mobility corresponding to the measured diffusion coefficients, we use an average temperature in this range of 3600 K. The deduced mobilities are shown in Fig. 3 with the same symbols as the diffusion coefficients but with the right axis. For the epitaxial graphene sample, we obtain a mobility of $7.0 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Previous mobility measurements on epitaxial graphene have obtained rather different results. However, the highest reported values are typically in the range of $1.5 \times 10^4 - 2.7 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Fig. 3). Almost independent of sample temperature. We note that the mobility we deduced are for a carrier temperature on the order of 3600 K, diffusion coefficients of $1.1 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $5.5 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are determined in epitaxial graphene and reduced graphene oxide samples, respectively. It is quite encouraging that the hot carrier transport properties of the reduced graphene oxide sample is only a factor of two worse than the epitaxial graphene, since the fabrication of this type of graphene is low cost. Furthermore, the optical technique is noncontacting and noninvasive. It can be used for in situ detection of transport properties at different locations of a sample or for direct comparison of multiple samples. Since no electrode is needed, its potential influence on the transport measurement is excluded.

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**IV. SUMMARY**

In summary, we have shown that an optical technique with high temporal and spatial resolution can be used to study transport of hot carriers in graphene and to directly measure the diffusion coefficients. With a carrier temperature on the order of 3600 K, diffusion coefficients of $1.1 \times 10^4 \text{ cm}^2 \text{ s}^{-1}$ and $5.5 \times 10^3 \text{ cm}^2 \text{ s}^{-1}$ are determined in epitaxial graphene and reduced graphene oxide samples, respectively. It is quite encouraging that the hot carrier transport properties of the reduced graphene oxide sample is only a factor of two worse than the epitaxial graphene, since the fabrication of this type of graphene is low cost. Furthermore, the optical technique is noncontacting and noninvasive. It can be used for in situ detection of transport properties at different locations of a sample or for direct comparison of multiple samples. Since no electrode is needed, its potential influence on the transport measurement is excluded.