Hot-carrier transport in diamond controlled by femtosecond laser pulses

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Abstract
A laser-induced transient grating technique with femtosecond temporal resolution was used for the study of hot-carrier diffusion and anisotropy of an ambipolar diffusion coefficient in monocrystalline diamond. A hot-carrier transport regime observed at temperatures below 200 K and excited carrier densities lower than $10^{16}$ cm$^{-3}$ persist in the sample 20–30 ps after photoexcitation. Measured drift velocity of hot carriers was approximately 4–8 times higher compared to thermalized carriers. At low sample temperatures and excited carrier densities, the ambipolar diffusion coefficient was found to be anisotropic between $\langle 100 \rangle$ and $\langle 110 \rangle$ crystallographic directions. We demonstrated experimentally that the carrier energy distribution can be controlled on a sub-picosecond timescale by an additional laser pulse with photon energy below the width of a diamond band gap absorbed by the excited carrier system. Our experimental data were reproduced well by Monte Carlo simulations that confirm the presence of a hot-carrier diffusion regime in diamond.

1. Introduction
New concepts of information processing and storage based on another electron property rather than its electrical charge are emerging. They include spintronics, valleytronics, or their combination with optics (e.g., opto-spintronics). Devices driven by ultrashort light pulses can exploit new principles and can operate with much faster switching times than electrical circuits. Current research activity is aimed not only to search for new operational principles, but also to create material platforms for relevant devices. Among the variety of advanced materials, intrinsic semiconductors still play an important role due to highly developed growth and treatment technology. Most of the basic physical properties of these materials are well known from numerous experimental and theoretical studies. However, simulations and design of devices based on new operation principles require knowledge and understanding of previously often-neglected or unknown properties. Diamond is one of the prospective materials due to its unique parameters, which include extremely high heat conductivity, breakdown voltage, and high charge carrier mobilities. It has already found application in power electronics [1] and high-energy particle detection [2]. Also, luminescent centers in diamond have been demonstrated to be excellent platforms for quantum optics and computing [3, 4] and the free-exciton electroluminescence is considered for ultraviolet optoelectronics [5, 6].

Despite the research interest in diamond, there is a lack of information about carrier relaxation dynamics in this material. A few picoseconds after optical excitation or in the presence of high electric fields, excited carriers are not in thermal equilibrium with crystal lattice and their energy distributions differ from the Fermi–Dirac function [7]. The carrier energy relaxation rate in bulk semiconductors is given mainly by interaction with lattice vibrations (optical and acoustic phonons) with typical timescales of 1–100 ps [8, 9]. When the temperature of crystal decreases, scattering on acoustic and optical phonons becomes less efficient and relaxation dynamics slows down. High-energy carriers can then transport apart from their charge the excess energy with much higher velocity than is achievable for thermalized carriers. In other traditional covalent semiconductors, such as germanium or silicon, the temperature range needed for this transport regime is far from practically useful values. However, in diamond, due to its extremely high phonon energies, the temperature necessary for...
observation of hot-carrier diffusion is below 200 K, as shown in this paper. Also, the diffusion length is long enough to use hot-carrier transport in real macroscopic devices, which can bring a significant increase of their speed.

In the regime of weak electron-phonon scattering, another feature of diamond electronic energy structure can serve for information processing. Diamond is an indirect semiconductor with six equivalent conduction band minima in (100) directions (T−K) at |k| ≈ 76% of the first Brillouin zone \([10]\). These minima are highly anisotropic, which leads to different transversal and longitudinal electron effective masses, namely \(m_t = 0.28 m_0\) and \(m_l = 1.56 m_0\) \([11]\). Anisotropy is reflected also in transport properties of electrons from a single valley, where the transversal components of the mobility tensor are approximately 5.5× higher than its longitudinal component \([12]\). Besides classical encoding of information in an electric current, there was recently proposed a different way of information storage in degenerated semiconductors \([13]\). In so-called ‘semiconductor valleytronics’, the specific conduction band minima (valleys) are used to store and transport information. There are several materials with which the concept of electron valley polarization has been demonstrated \([14−17]\).

Isberg et al generated and detected valley-polarized electrons in high purity diamond at liquid nitrogen temperature \([14]\). Different times that low density electrons (below \(10^{10} \text{ cm}^{-3}\)) from different conduction band minima need to pass through the sample were measured by the time-of-flight (TOF) technique \([18]\). Due to the macroscopic width of the sample (0.5 mm), the observed flight times were of the order of 10–100 ns, suggesting the long scattering time for intervalley transitions \(\tau_s = 300\) ns.

The next step in this field of research is to study and control the valley polarization of electrons in diamond with much higher temporal resolution using interaction with optical pulses. For this purpose, the knowledge of carrier relaxation times, intervalley scattering rates, and nonequilibrium transport coefficients in a short time after interaction with ultrashort laser pulse is needed. The aim of this paper is to investigate transport properties of low density carriers in diamond at picosecond timescales using the all-optical laser-induced transient grating (LITG) technique. In our experiments, we measured the ambipolar diffusion of optically excited electrons and holes in chemical vapor deposition (CVD) monocrystalline diamond without the presence of an electric field. We observed clearly two-componential diffusion at low temperatures (below 200 K) and low injected carrier densities (below \(\sim 10^{13} \text{ cm}^{-3}\)). The initial fast part of the LITG signal is shown to be caused by fast diffusion of hot carriers, while the slower signal component corresponds to diffusion of thermalized electrons and holes. Moreover, the ambipolar diffusion coefficient at these conditions was found to be anisotropic between (100) and (110) crystallographic directions, while at higher temperatures and higher excited carrier densities, diffusion behaves isotropically. We also show that the speed of carrier diffusion can be controlled by an additional laser pulse that heats up the excited carrier system by excited state absorption.

2. Experimental

This study was performed on a freestanding monocrystalline diamond plate with dimensions \(4.5 \times 4.5 \times 0.5\) mm prepared by CVD technique by Element Six. The manufacturer-specified amount of impurities is \(<1\) ppb of boron and \(<5\) ppb of nitrogen. Sample faces were cutted with \(\langle 100\rangle\) crystallographic orientation with edges in the \((110)\) direction.

Carrier diffusion was studied using the standard LITG technique in the setup shown in figure 1. As a source, a femtosecond amplifier (Spitfire XF, Newport/Spectra Physics) working at 1 kHz repetition rate was used. Duration of amplified pulses was 100 fs with average pulse energy 3.5 mJ at wavelength 800 nm. One-third of the amplifier output was used for second harmonic generation of the excitation beam (400 nm, 3.1 eV) and the basic wavelength was blocked by a dichroic mirror. The polarization was set to vertical by a Glen-laser polarizer. Afterward, the beam was divided into two arms by a dielectric beamsplitter. The time delay of the resulting pulses was adjusted to zero by optical delay line DL1 and both pulses were focused on the sample placed in closed-cycle helium cryostat (Janis) by a 10D lens. The angle \(\theta\) between both excitation beam arms was changed in the range 5–11° to create the transient carrier density grating with grating periods \(A = \lambda/(2\sin\theta) = 2.1−4.5 \mu\text{m}\) (here, \(\lambda\) is the wavelength of excitation light, for details see \([19]\)). Probe pulses at wavelength 1300 nm (0.95 eV) with length 70 fs were generated in the optical parametric amplifier (Topas, Newport/Spectra Physics). The probe pulse delay time was changed by the second optical delay line DL2. Incidence angle of the probe pulse was adjusted to match the Bragg condition at each grating period. Then, the diffraction in the direction given by the Bragg equation was detected by a cooled InAs photodiode using a phase-sensitive detection (lock-in amplifier) scheme, with every second pump pulse blocked by a digital optical chopper.

In the additional experiment in which the carriers were heated by the fourth pulse (similarly as in \([20]\)) to restore the conditions necessary for hot-carrier diffusion, the part of the original amplifier output (800 nm, 1.55 eV) and delay line DL3 were used (dashed line in figure 1).
The initial excited carrier density distribution in the two-photon excited femtosecond LITG experiment can be written as

\[ n(x, t = 0) = n_0 \left[ 1 + \cos \left( \frac{2\pi x}{\Lambda} \right) \right]^2 / 4, \]

where \( n_0 \) is the peak excited carrier density and \( x \) is the direction of the grating wavevector. In theoretical simulations (see the next section), we used the average carrier density \( n_{av} \), which was calculated from the measured spot size of excitation laser beam (typical \( w_{FWHM} \) spot size was 70–100 μm) and the total energy absorbed in the sample using relation:

\[
\int \pi \Lambda \left( \frac{n E}{E_{abs}} \right) E_{abs} w_{FWHM} L n(x, 0) d\Lambda / 0.375, \quad (1)
\]

where \( E_{abs} \) is the energy per excitation pulse absorbed in the sample and \( E_{ph} \) is the excitation photon energy. For evaluation of the diffusion coefficient in a standard LITG experiment, diffraction efficiency dynamics is measured as a function of the grating period. Obtained exponential decay rates are associated with the diffusion coefficient and the square of the inverse grating period via relation \( 1/(2\tau_d) = 1/(\tau_r + 4\pi^2D/\Lambda^2) \). Here, \( \tau_d \) is diffusion efficiency decay time and \( \tau_r \) is carrier recombination decay time. From fitting the experimental data by this function, values of both diffusion coefficient and recombination decay time can be obtained. In our experiments, we used this simple data processing only for estimation of diffusion velocity of hot carriers and thermally equilibrated carriers. However, the steady-state diffusion equation cannot describe the hot-carrier diffusion correctly. Therefore, we applied the Monte Carlo (MC) technique for this purpose.

There are several publications dealing with optical measurements of ambipolar diffusion in diamond using the LITG technique [21–24]. Due to the low diffraction efficiency by the thin grating produced by above-band gap excitation, diffusion at high carrier densities was investigated (10^{16}–10^{19} cm\(^{-3}\)). Typical observed grating decay times with the grating period \( \Lambda = 2–5 \mu m \) are 5–500 ps and they depend on carrier density, sample temperature, and amount of impurities [21–24]. Dynamics of electrons from different conduction band valleys can possibly be observed by this experimental technique only when the intervalley scattering time is longer than the measured LITG dynamics. To fulfill this condition, carrier densities as low as possible (10^{14}–10^{15} cm\(^{-3}\)) were used in this study.

3. Theory and simulations

The photoexcited carrier diffusion in diamond as measured by LITG is a result of a variety of microscopic processes that include carrier transport as well as carrier–carrier scattering, carrier cooling by carrier–phonon interaction, and carrier recombination. Therefore, it seems to be difficult to analyze the results of measurements in a traditional way using the single diffusion constant as described in the previous section. However, our experimental data suggest that we can approximate the description in terms of two diffusion constants corresponding to the fast (hot carriers) and slow (equilibrium carriers) diffusion processes. Nevertheless, the subsequent theoretical modeling goes beyond this simple approach.

After optical excitation, every electron-hole pair has excess energy above the band edge. There are no experimental data on carrier cooling dynamics in diamond. Generally, the cooling rate in covalent semiconductors is dependent on the probability of optical and acoustic phonon scattering [25]. Shortly after excitation when the energy of carriers is high enough, the fast relaxation via optical phonon emission occurs. When energy of carriers decreases below the energy of optical phonon, relaxation continues only by the emission of acoustic phonons, which usually proceeds on much longer timescales. During the relaxation, carrier diffusion cannot be described by the diffusion equation and Einstein relation \( D_a = \mu_a k_b T/e \), where \( D_a \) is the ambipolar...
diffusion coefficient of charge carriers and $\mu_a$ is ambipolar carrier mobility. These are valid only for carriers in thermal equilibrium with crystal lattice. For simultaneous description of spatiotemporal evolution of hot-carrier diffusion and relaxation, stochastical methods have to be applied.

We simulate our experimental LITG data using a combination of the MC approach (carrier relaxation and diffusion) with scalar light diffraction theory (calculations of the resulting LITG signal). The hot-carrier relaxation and transport was simulated by MC technique described in detail in [25]. Because of the extreme complexity of the problem (anisotropic electron and hole effective masses, presence of excitons, ambipolar transport), we calculated only the diffusion of electrons in approximation of spherical parabolic bands. As will be shown further, this approximation is sufficient for qualitative description of the transient transport behavior of hot carriers in diamond. In MC simulations, individual scattering mechanisms are treated quantum mechanically, while carrier trajectories between scattering events are calculated classically. We started from the carrier position randomly chosen with a probability given by carrier density excited by LITG using a two-photon absorption process:

$$p(x) = \left(1 + \cos(2\pi x/A)\right)^2$$  \hspace{1cm} (2)

The initial position in the x direction (parallel to the grating wavevector) was selected using the rejection technique [25]. We neglected the spatial profile of the excitation beam because its width was much larger than the grating period used in our experiments. Then we simulated the motion of each particle separately (total number of simulated electrons in every round was 30 000). In every time step, total scattering probability was calculated only the diffusion of electrons in approximation of spherical parabolic bands. As will be shown further, this approximation is sufficient for qualitative description of the transient transport behavior of hot carriers in diamond. In MC simulations, individual scattering mechanisms are treated quantum mechanically, while carrier trajectories between scattering events are calculated classically. We started from the carrier position randomly chosen with a probability given by carrier density excited by LITG using a two-photon absorption process:

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**Acoustic phonons:**

$$P_{ac}\left(\mathbf{k}, \mathbf{k}'\right) = \frac{\pi q D_{ac}^2}{V \rho v_{vl}} \left\{ \frac{N_q}{N_q + 1} \right\} \delta\left( E\left(\mathbf{k}'\right) - E\left(\mathbf{k}\right) \mp \hbar \nu_{vl} \right)$$  \hspace{1cm} (3)

**Optical phonons:**

$$P_{op}\left(\mathbf{k}, \mathbf{k}'\right) = \frac{4\pi D_{op}^2}{V \rho \omega_{op}} \left\{ \frac{N_{op}}{N_{op} + 1} \right\} \delta\left( E\left(\mathbf{k}'\right) - E\left(\mathbf{k}\right) \mp \hbar \omega_{op} \right)$$  \hspace{1cm} (4)

**Carrier–carrier:**

$$P_{cc}(E) = \frac{\sqrt{2} n_a e^4}{32 \pi^2 m_e^{1/2} E^{3/2}} \ln \left(1 + \frac{16 \pi^2 e^2 E^2}{e^4 n_a^{2/3}}\right)$$  \hspace{1cm} (5)

where $\mathbf{k}$ and $\mathbf{k}'$ are initial and final electron states, $E$ is electron energy, $q$ is the length of the acoustic phonon wavevector, $\rho = 3.51$ g cm$^{-3}$ is diamond density, $v_{vl}$ is longitudinal acoustic velocity, $\omega_{op}$ is optical phonon frequency, $V = 4.54 \times 10^{-23}$ cm$^3$ is unit cell volume of diamond crystal lattice, and $\varepsilon = 5.7 \varepsilon_0$ is diamond dielectric constant. $N_q$ and $N_{op}$ are acoustic and optical phonon equilibrium populations given by:

$$N_{q, op} = \left( \frac{E_{q, op}}{e^{\varepsilon_0 E_{q, op}} - 1} \right)^{-1}$$  \hspace{1cm} (6)

where $E_q = \hbar \nu_{vl}$ and $E_{op} = \hbar \omega_{op}$ are the appropriate acoustic and optical phonon energy, respectively. Due to low density of excited carriers, the nonequilibrium phonon population can be neglected. In equations (3) and (4), upper and lower signs refer to phonon absorption and emission processes, respectively. Parameters used in our calculations are summarized in table 1. The values of deformation potentials $D_{ac}$ and $D_{op}$ used in this work are close to the values obtained from MC simulations of TOF measurements [28]. In every time step, we calculated carrier density distribution, which served for calculation of diffraction efficiency using scalar diffraction theory as described in [21]. The results of MC simulations will be shown in the following section in comparison with experimental data.
4. Results and Discussion

Measured LITG dynamics at peak initial carrier density \( n_0 = 1.2 \times 10^{15} \text{ cm}^{-2} \) with the grating period \( \Lambda = 3.7 \mu \text{m} \) at different sample temperatures are shown in figure 2 in semilogarithmic scale. The diffusion was studied in the (100) crystallographic direction. When diffusion proceeds with a constant diffusion coefficient and negligible carrier recombination, LITG dynamics is expected to be single-exponential \([19]\). This is the case for measurement at room temperature, but the LITG signal decay is more complex for low temperature (below 150 K) where the diffraction efficiency dynamics can be fitted well by a two-exponential decay

\[
\eta_{\text{diff}} = A_1 \exp\left(-t/\tau_{\text{fast}}\right) + A_2 \exp\left(-t/\tau_{\text{slow}}\right),
\]

as shown in figure 2. To reveal the effect of carrier diffusion and recombination on the LITG signal, we repeated the measurements with different sizes of the grating period. We have found that dynamics of both the slow and the fast signal depend on the grating period in a typical way for diffusion processes (\( \tau_{\text{fast}} \approx \Lambda^2 \)). This excludes possible origin of the fast signal in any recombination phenomenon. From the linear fit of the theoretical dependence \(1/(2\tau_{\text{fast(slow)}})=1/\tau_r + 4\pi^2 D_{\text{fast(slow)}}/\Lambda^2\) we obtained two values of diffusion coefficient corresponding to fast and slow carriers. This description is only approximate and should serve as an illustration of the difference between diffusion velocities immediately (time delay <30 ps) and long after (>30 ps) excitation.

Two different values of diffusion coefficient (labeled further as \( D_{\text{fast}} \) and \( D_{\text{slow}} \)) that were observed can be a consequence of two effects: (1) electrons from different valleys have different effective masses (i.e., also different projection of the mobility tensor) in direction of the grating wavevector and (2) hot electrons and holes present shortly after excitation diffuse with higher velocity than thermalized carriers in times longer than 30 ps. We will show that our experimental results and MC simulations suggest the latter possibility.

If the former process was the source of two different diffusion velocities, the ratio between amplitudes of the fast and the slow LITG signal \( A_1/A_2 \) would not depend on the grating period because the instantaneous LITG signal depends only on the depth of spatial modulation of the carrier density. Immediately after excitation, electrons are equally distributed across all the conduction band valleys. If we assume negligible intervalley scattering and a temporally constant diffusion coefficient, the ratio between densities of electrons occupying fast and slow valleys will not change during diffusion. With sample (100) symmetry axis oriented parallel to the laser-induced grating wavevector, there are four valleys with a smaller effective mass component in the \( x \) direction (fast electrons) and two valleys with a higher effective mass component (slow electrons) \([14]\). Because different effective masses lead to different values of diffusion coefficient in the specified direction, the spatial density distribution of electrons from fast valleys will be smeared much faster than that of slow electrons. After a short time, only electrons in slow valleys will still form the grating (will be visible by LITG technique), while the density of fast ones will be constant in the \( x \) direction. This process would create small spatial regions with the size of half of the grating period with preferential electron valley polarization. The ratio of amplitudes \( A_1/A_2 \) is in this case expected to reflect the distribution of electron populations in individual conduction band valleys (for (100) direction 2:1) and not to depend on the grating period. However, in our experiments we observed increase

Table 1. Parameters used in MC simulations.

| \( m_e (m_0) \) | \( v_l (\text{km s}^{-1}) \) | \( E_{\text{op}} \) (meV) | \( D_a \) (eV) | \( D_{\text{op}} \) (eV) |
|---|---|---|---|---|
| 0.4 | 17.52 | 165 | 15 | 5 |

Figure 2. LITG dynamics in diamond at different sample temperatures (symbols) with double-exponential (\( T = 13–200 \) K) and single-exponential (\( T = 295 \) K) fits (curves), grating period \( \Lambda = 3.7 \mu \text{m} \), grating wavevector along (100) crystallographic direction. Data were vertically shifted for clarity.
of amplitudes ratio with decreasing grating period. This fact suggests that we did not observe electronic valley polarization.

The next point, which can clarify the origin of the fast signal component and which is of great ‘valleytronics’ importance, is the comparison of diffusion coefficient values obtained with grating wavevector parallel to (100) (sample position shown in figure 1) and (110) (sample rotated by 45° around the axis perpendicular to the front sample surface) crystallographic directions. Due to the ambipolar nature of observed diffusion, the anisotropy was expected not to reflect only the anisotropy of conduction band minima, as in [14], but it also contains the anisotropic features of the valence band of diamond. This is formed by light and heavy hole bands with approximately 6 meV [29]. Anisotropy of effective masses of heavy holes and electrons differs significantly (see [11]). Moreover, ambipolar transport in diamond is further complicated by the presence of excitons, whose binding energy is extremely high (80 meV) [30]. There was also observed a splitting ~10 meV of 1 s excitonic state due to spin–orbit and exchange interactions and mass-anisotropy effect [29], which can influence transport properties at low temperatures.

LITG decay times obtained at grating periods \( A = 2.1, 3.7, \) and 4.5 \( \mu \)m were used for calculation of diffusion coefficient values \( D_{\text{fast}} \) and \( D_{\text{slow}} \), for both sample orientations ((100) and (110)). Their dependence on temperature and sample orientation is shown in figure 3. We found that at room temperature, the ambipolar diffusion is isotropic and single-componential (single-exponential decay of LITG dynamics). At temperatures below 200 K, diffusion in the (100) direction was approximately about 20% slower than in the (110) direction (both the slow and the fast component). The ratio \( D_{\text{fast}}/D_{\text{slow}} \) is independent of diffusion direction (see the inset of figure 3). The ambipolar diffusion coefficient can be understood as a combination of electron and hole diffusion coefficients \( (D_a = 2D_eD_h/(D_e + D_h)) \) in thermal equilibrium. The latter are indirectly proportional to the relevant effective masses. Our observation of anisotropic diffusion at low temperatures and carrier densities suggests that under these conditions indeed the effective mass anisotropy is important. However, for sample temperatures above 200 K, the scattering processes eliminate this effect and only the angle-averaged effective mass of electrons and holes is significant for carrier transport.

The observed ratio of ambipolar diffusion coefficients \( D_{\text{fast}}/D_{\text{slow}} \) (see the inset of figure 3) is temperature-dependent. If the signal corresponded to thermalized electrons from different valleys and thermalized holes, the ratio would depend only on carrier effective masses, which are almost temperature independent in this region [31]. The dynamics of fast diffusion was observed not to be dependent on lattice temperature (see calculated diffusion coefficient, empty symbols in figure 3). In contrast, the slow diffusion dynamics depends on sample temperature, suggesting a diffusion process in thermal equilibrium with diamond lattice at longer time scales. This supports our claim that the origin of the fast LITG signal can be attributed to transport of thermally nonequilibrated carriers.

Results of MC calculations of LITG dynamics for sample temperatures 100, 200, and 300 K are shown in figure 4(b) compared with measured data (figure 4(a)). To introduce hot carriers into simulations, all the carriers have initial excess energy randomly distributed around 0.5 eV (Gaussian distribution with FWHM 25 meV, same as the spectrum of excitation pulses). Very good agreement can be seen between temperature behavior of measured and calculated LITG dynamics. At 100 and 200 K, there are clearly two-exponential decays that switch to single-exponential decay at 300 K. Difference in absolute values of measured and calculated decay times is caused by approximations used in MC simulations. In the inset of figure 4(b), the calculated carrier average energy is plotted as a function of delay time. In our calculations, we observed that in the first few
hundreds femtoseconds, carriers rapidly relax via emission of optical phonons. Afterward, only acoustic phonons can be emitted and relaxation slows down. Relaxation time decreases with increasing sample temperature as a consequence of temperature-dependent phonon population. From the simulations, we can estimate that the time needed to achieve thermal equilibrium between carriers and the lattice changes from 100 ps at 100 K to 30 ps at 300 K (see the inset of figure 4(b)).

Another physical process that could possibly cause the temporal dependence of the diffusion coefficient after optical excitation is formation of excitons from free electrons and holes. In the first few picoseconds, nonthermalized electrons and holes can move faster than free excitons, which can be formed when the energy per carrier pair falls below the exciton binding energy. However, the value of the exciton diffusion coefficient is expected to be very similar to the ambipolar diffusion coefficient because the effective mass of the exciton can be well approximated with the sum of electron and hole effective masses [32]. In contrast, the observed ratio between fast and slow diffusion coefficients was 4–10 (see figure 3). Therefore, we assume that exciton formation influences the observed signal only marginally.

In order to support our interpretation of the fast diffusion in terms of hot carriers, we proposed an experiment in which the relaxed carriers are again heated up by another laser pulse (similar experiment as in [20]). An additional femtosecond pulse at photon energy 1.55 eV (below diamond band gap width) was used to heat the excited carrier system via excited carrier absorption (red dashed line in figure 1). The pulse interacts only with carriers that were previously excited by LITG. The sample temperature was 100 K and the heating pulse energy was 20 μJ (fluence 30 mJ cm⁻²). The pulse was delayed in respect to two excitation pulses about 85 ps, with the aim to hit the sample in the temporal region with slow diffusion where the thermal equilibrium between carriers and lattice had been established. After this additional heating of the excited carrier system, carriers diffused with the same drift velocity as immediately after excitation and measured LITG decay sped up. Several tens of picoseconds later, carriers relaxed again, causing a slowdown of LITG dynamics. In figure 5(a), the measured LITG signal (black squares) is compared to that without using the heating pulse (red circles). The experimental data are reproduced very well by MC simulations, which are shown in figure 5(b).

This experiment also excludes diffraction on thermal grating and subsequent heat diffusion from possible sources of the fast LITG signal. Generally, the refractive index is a function of temperature. The LITG dynamics can consist of two parts: (1) diffraction on a carrier density grating and (2) diffraction on a thermal grating that is formed after the fast carrier relaxation. After heating of the carrier system by the fourth pulse and subsequent carrier relaxation, the thermal grating would have to be formed in a similar way as after the first excitation. When we assume that the amplitude of the signal corresponding to excited carrier density grating remains the same, we should be able to see a sudden increase in diffraction efficiency at time 85 ps in the case of the significant role of thermal grating. We did not observe experimentally any increase of LITG signal after impact of the fourth pulse, as can be seen in figure 5(a).

This experiment not only serves as evidence of observation of hot-carrier diffusion at low temperatures, but it also shows the possibility to use light to control transport properties of excited carriers in diamond. For example, the TOF of electrons and holes can be controlled using short laser pulses in the infrared spectral region. With decreasing photon energy of the fourth ‘heating’ pulse, the excited carrier absorption cross-section increases. Hence, much weaker infrared pulses will be sufficient to reach the hot-carrier transport regime. The next possibility of carrier heating is acceleration in high static electric fields [14]. This technique can be useful in electronic devices based on hot-carrier transport in diamond.
We also measured the dependence of LITG dynamics on initial excited carrier density at different sample temperatures. From previous studies [21, 24], the role of carrier–carrier scattering in carrier diffusion in diamond is well known. Our aim was to study how hot-carrier diffusion dynamics is influenced by this scattering mechanism. Figure 6(a) shows LITG measurements at \( T = 100 \) K. Here we observed the transition from two-exponential decay to single-exponential decay with increasing carrier density. Measured dependence on carrier density shows again very good qualitative agreement with MC simulations (see figure 6(b)), where the transition between double-exponential decay at low carrier density and single-exponential decay at higher carrier density was well reproduced. At carrier densities above \( \sim 10^{15} \) cm\(^{-3}\), the corresponding carrier–carrier scattering rate given by equation (5) is high and decreases drift velocity of both hot and thermalized carriers. For this reason, no fast diffusion in the initial phase of LITG dynamics is observed at the high-density regime.

There are two reasons why the hot-carrier diffusion was not observed in former measurements of LITG in diamond [21–24]. First, in most published papers, the picosecond laser pulses were used for LITG excitation and detection of diffraction efficiency. As we showed, the hot-carrier diffusion is present in diamond only in the first \( \sim 20–30 \) ps after excitation, which means that sub-picosecond pulses are necessary to observe these effects. Secondly, when femtosecond pulses were used [21], the dependence of LITG dynamics on excited carrier density was studied only at room temperature, where the hot-carrier diffusion is not observed even at low carrier densities.

5. Conclusions

In conclusion, we present the first direct observation of ambipolar hot-carrier diffusion in high purity CVD diamond. At low carrier densities and sample temperatures below 200 K, the hot-carrier transport regime was present during the initial 20–30 ps after optical excitation with the corresponding value of ambipolar diffusion...
coefficient $D_n = 90–160 \text{ cm}^2\text{ s}^{-1}$. Drift velocity of hot carriers was observed to be 4–8 times higher than that of thermalized carriers under the same conditions. Using MC simulations, we achieved very good qualitative agreement with the experiment and we confirmed the role of hot-carrier diffusion in femtosecond LITG measurements.

The next important observation was the anisotropy of diffusion coefficient values between $\langle 100 \rangle$ and $\langle 110 \rangle$ crystallographic directions, which differ by $\sim 20\%$. We showed that the diffusion coefficient is anisotropic only at low temperatures and low excited carrier densities, while at room temperature and carrier density above $10^{16} \text{ cm}^{-3}$, diffusion is isotropic. We also demonstrated experimentally that the fast hot-carrier diffusion can be restored by heating of the excited carrier system using a laser pulse with photon energy below the diamond band gap. This experiment brings new prospects of controlling carrier transport properties of semiconductors on sub-picosecond time scales.

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