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Dynamics of photoexcited carriers in CVD diamond studied by mid-infrared femtosecond spectroscopy

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ABSTRACT

We report on the dynamics of high-density photoexcited charge carriers in CVD diamond at low (13 K) and moderate (250 K) temperatures studied by femtosecond pump and probe spectroscopy. We measured the transient transmission at wavelengths in the mid-infrared spectral region (3–8 μm) to study the electron-hole liquid system around its plasma frequency. Drude theory of free carrier absorption is used to determine the parameters of the electron-hole drops. For probe wavelength of 8 μm and lattice temperature of 250 K, a fast component of the transient transmission signal with the decay time ~38 ps is resolved in addition to a slow ~1.8 ns component common to all probe wavelengths. The initial picosecond decay is ascribed to the dependence of the excited carrier absorption coefficient on the effective carrier temperature. This allows us to monitor the charge carrier relaxation after optical excitation. A quantum model of free carrier absorption including the optical and acoustic phonon scattering processes is used to support our interpretation.

1. Introduction

Quantum correlated systems in condensed matter are interesting due to their potential applications in laser technology, nonlinear optics and quantum computation. One example of such a system is so-called electron-hole plasma (EHP) which has been studied in various semiconductors [1–4]. Parameters of contemporary lasers make it possible to study plasma at high carrier densities and measure its time evolution on very short time scales with a femtosecond time resolution. Extending the laser tunability into the deep-ultraviolet spectral region opened the way for investigation of wide-bandgap semiconductors including diamond with its many exceptional material parameters like hardness, biocompatibility, high breakdown field, high electron and hole mobilities [5,6], and specific properties of single defect centers [7]. These features predetermine diamond for a variety of applications including high power electronics, optics, quantum computing, optoelectronics, and medicine [8,9]. Furthermore, the availability of advanced fabrication techniques producing extremely pure single-crystal diamond [10,11] made it possible to use this material for investigation of effects occurring in the presence of dense carrier plasmas and electron–hole liquid (EHL).

The condensation of EHL was first investigated in silicon and germanium in the late sixties of the 20th century (for details see a review in Ref. [12]). If an indirect semiconductor is cooled down below the critical temperature T_c, the gas of excitons and excited carriers can condense into EHL and form droplets, i.e. spatial regions with high and constant carrier density. EHL condensation in diamond was theoretically predicted by Vouk in 1979 [13] and experimentally observed for the first time in 2000 [14]. The reason for such a time gap between the theoretical prediction and the experimental observation was the difficulty of achieving sufficiently high density of excited charge carriers on very short time-scales along with maintaining a sub-critical temperature. Diamond differs significantly from other semiconductors where EHL was studied in its wide band gap (5.5 eV) and low dielectric constant ($\varepsilon = 5.7$) leading to only weak screening of Coulomb interaction. This results in high critical temperature for EHL condensation ($T_c \approx 160$ K).

Most of the published experimental studies of EHP and EHL in diamond have been performed using optical techniques in which electron-hole pairs are excited by strong light pulses. The resulting EHP that can be investigated by analyzing the emitted light (luminescence methods [15–18]) or by monitoring changes of the material complex dielectric constant (usually using the pump and probe techniques [19–21]). The properties of EHL in diamond were experimentally studied and reported in [20,22–26]. Despite its quantum origin, many features of EHL can be described well by a simple Drude model of electron-hole plasma. In this paper we report on the measurements of femtosecond transient dynamics at mid-infrared (MIR) wavelengths. EHP and EHL are studied in monocrystalline diamond grown by chemical vapor deposition (CVD). The key advantage of MIR probing wavelength is a higher value of excited carrier absorption coefficient due its expected dependence on square of the probe wavelength. Moreover, two effects connected with resonances in MIR spectral region are expected: 1) the resonance of a probe photon with wavelength $\lambda = 7.5$ μm with an

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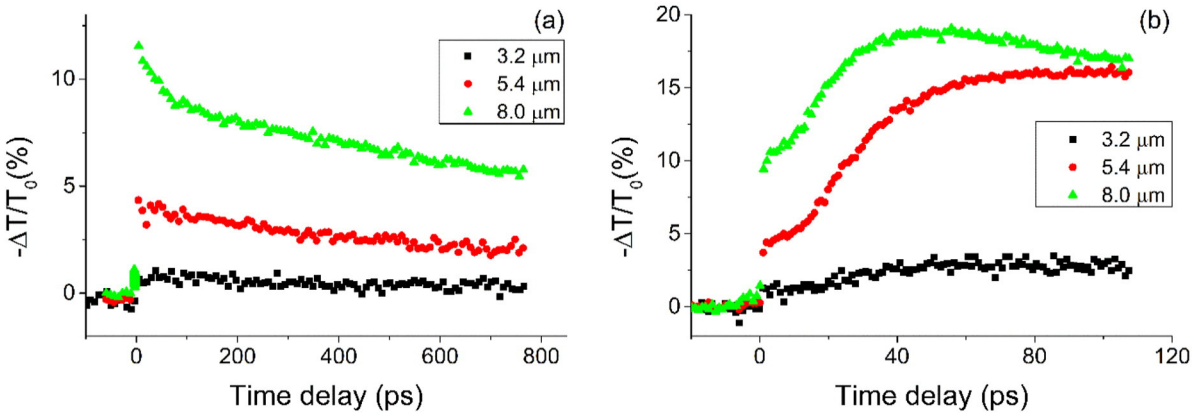

Fig. 1. Transient transmission of CVD diamond at 250 K (a) and 13 K (b) for various probe wavelengths excited by the pump pulse at wavelength of 200 nm with fluence of 0.5 mJ/cm^2.

optical phonon (165 meV [27]), 2) at low temperatures, the change of absorption and reflectivity of excited carriers around plasma frequency of EHL (λ_p ~ 4.7 μm).

2. Experimental

We have used a commercially available sample of IIa diamond single crystal from Element Six prepared by CVD and cut in ⟨100⟩ direction with dimensions 4.5 × 4.5 × 0.5 mm. The sample possessed very high purity; according to manufacturer's specifications, the concentrations of boron and nitrogen were <1 ppb and <5 ppb, respectively. The sample was mounted in a closed-cycle helium cryostat (Janis) for measurements at temperatures down to 13 K. We have used the femtosecond laser system with a regenerative amplifier (Spitfire, Newport/Spectra Physics) providing pulses at photon energy 1.55 eV (λ = 800 nm), with pulse duration of 100 fs and pulse energy of 3.5 mJ at repetition rate 1 kHz. One third of the amplifier output was sent to a 4th harmonic generator where the photon energy was converted to 6.2 eV (200 nm) for single-photon excitation of diamond reaching fluences in the range of 0.04–0.5 mJ/cm^2. The rest of the output was used to pump the optical parametric amplifier TOPAS (Light Conversion). The signal and idler pulses from the amplifier were sent to an $AgGaS_2$ crystal. Here the MIR pulses tunable in the range of 155–400 meV (8–3 μm) were obtained via difference frequency generation. We used pump and probe spectroscopy to monitor the time evolution of transmission of the excited sample. The transmission of the MIR probe pulse was measured at a certain time delay after the sample excitation by the 200 nm pump pulse. We detected every probe pulse by a thermoelectrically cooled HgCdTe photodetector connected to AD convertor PC card. Every other excitation pulse was blocked by an optical chopper. Subsequently, the transmissions of the excited and unexcited sample were digitally subtracted. The resulting transient transmission signal can be written as $\Delta T(t) = (T_{exc}(t) - T_0) / T_0$, where T_{exc} (T_0) is the transmission of the excited (unexcited) sample. The time window of measurement was limited by the length of a computer controlled delay line to 900 ps. The spot sizes of pump and probe beams were adjusted by a focusing lens to the 1/e^2 Gaussian radius of w_{pump} = 150 μm and w_{probe} = 45 μm, respectively. This ensured a good homogeneity of excited carrier population (<10% difference in carrier density across the probed region). The beams intersected under an angle of 15 degrees on the sample. The probe pulse spectra were characterized using a grating monochromator (Jobin Yvon). The spectral widths of the probe pulse ranged from 90 nm (3 μm central wavelength) to 1200 nm (8 μm central wavelength).

3. Results and discussion

3.1. Measurement of EHL condensation dynamics

The results of the pump and probe measurement at 250 K and 13 K for three selected probe wavelengths (8 μm, 5.4 μm and 3.2 μm) are shown in Fig. 1a and b, respectively. Maximum excited carrier density at the sample surface corresponding to the pump fluence of 0.5 mJ/cm^2 was $n_c = 4.4 \times 10^{18}$ cm^{-3}. The transient transmission change is negative indicating induced absorption of the infrared probe beam. The initial signal appearing immediately after excitation is due

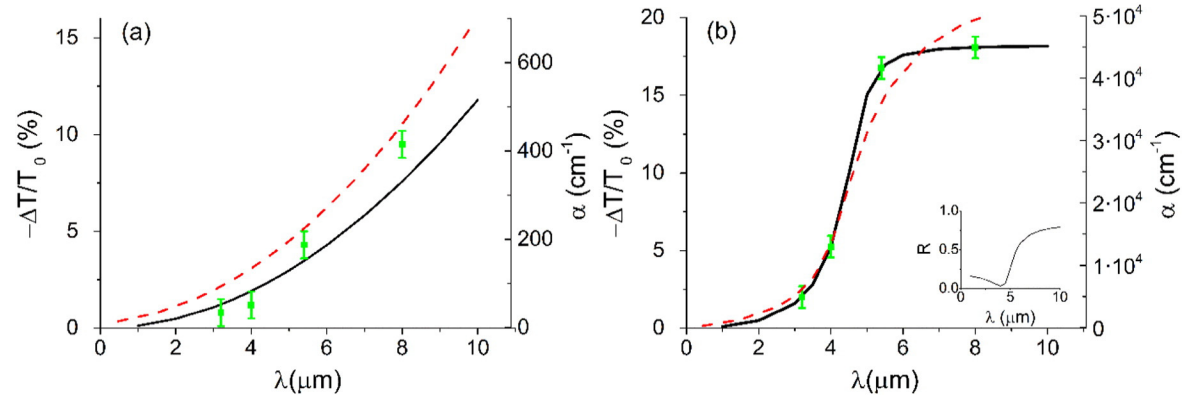

Fig. 2. The peak values of the pump and probe signal in diamond versus the probe wavelength (symbols) for sample temperature 250 K (a) and 13 K (b). Solid curves are the fits by the model described in the text. Dashed curves represent the calculated absorption coefficient α (5a). Inset: Dependence of reflectivity (5b) of e-h drops on wavelength.