Temperature-dependent carrier injection routes under optical excitation in high-purity diamond crystals

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Abstract. We have investigated carrier injection routes in high-purity diamond crystals in a wide temperature range using the time-resolved cyclotron resonance method. By analysing the excitation spectra, we find that carriers are injected under optical excitation above the energy threshold for exciton generation with emission of a transverse acoustic phonon at 10 K and 80 K, whereas with absorption of a transverse optical phonon at 300 K. The excitation power dependence clearly shows that the carriers are generated by thermal dissociation of excitons at 300 K.

1. Introduction
Diamond is the last frontier among the group IV semiconductors, with the large indirect energy gap of 5.47 eV at 300 K. Because of the outstanding properties, such as the high dielectric breakdown voltage, long spin relaxation time, and multivalley structure of the conduction band, diamond is an attractive material for next generation devices in the fields of power electronics, spintronics, and valleytronics [1, 2]. As in the case of pure silicon, which had been applied to a light-triggered thyristor as a successful power device, clarifying the optical routes for carrier injection in pure diamond is an urgent issue. In particular, detailed understanding of the coexistent state of carriers and excitons is necessary for the development of diamond devices working at room temperature, as the excitons in diamond are highly stabilized by the large exciton binding energy [3, 4]. This situation is characteristic of diamond, in contrast to the currently relevant materials, e.g., silicon or gallium arsenide, in which excitons are unstable at room temperature due to their small exciton binding energies [5].

For diamond, it is known that neutral excitons are primarily generated under optical excitation [3, 4] and they subsequently equilibrate with charge carriers [6, 7]. In this study, we investigate the ultraviolet spectral aspect of carrier injection in a high-purity diamond crystal using the time-resolved cyclotron resonance (TRCR) method. This measurement principle was already demonstrated for pure silicon [8] and pure diamond [9] at 10 K, in which two carrier injection routes (the band-to-band transition and dissociation of excitons) were unveiled and the exciton binding energy of diamond was renewed [9]. Here, we extend the measurements up to device-operation temperatures.

2. Experiment
We used a high-purity diamond crystal grown by the chemical-vaper-deposition (CVD) method in dimensions of 1.2 × 4.5 × 0.07 mm³, where the largest plane was oriented to the (001) crystal plane.
The sample was carefully mounted on a $2 \times 8$ mm$^2$ face of a right-angle prism using a small amount of vacuum grease. The prism was attached to a truncated quartz rod of $\phi$ 3.0 in diameter, and the rod was inserted into a quartz tube of $\phi$ 3.2/ $\phi$ 5.0 in inner/outer diameter (see the inset in Fig. 1). This tube was inserted in a dielectric cavity containing a sapphire tube (Bruker, MD5W1) in a cryostat, with an adjustable quality factor for microwave at 9.6 GHz. The [001] crystal axis was tilted by 40 degrees in the (110) plane with respect to the direction of the external magnetic field.

We measured temporal power responses of microwave resonating with the cyclotron motion of carriers using time-resolved paramagnetic resonance equipment (Bruker, ELEXSYS E580). The cavity quality factor was set at 400, corresponding to a time resolution of 7 ns. The sample was irradiated by laser pulses through the optical window of the cryostat, the sapphire tube of the dielectric cavity, and the prism. The wavelength ranged from 219.4 nm to 226.4 nm, where the light source was an optical parametric oscillator (Spectra-Physics, MOPO, 10 Hz, 5 ns) pumped by the third harmonics of infrared light from a Nd:YAG laser. We obtained excitation spectra by measuring the signal intensity divided by the simultaneously measured laser power as a function of the excitation wavelength. The incident laser power was reduced to the range of a few $\mu$J by an optical attenuator, and further reduced by neutral density filters for measurements of the excitation power dependence.

3. Results and discussion

Figure 1 shows CR spectra at temperatures of 10 K and 80 K. Four peaks are separated at 10 K as previously reported [10], that are resonant to the light hole (lh), heavy hole (hh), and two electrons (e1, e2) belonging to distinct valleys under the magnetic field. The spectrum obtained at 80 K was broader than that at 10 K, probably owing to the enhanced rate of acoustic phonon scattering obeying the $T^{3/2}$ rule, where $T$ is the temperature [11]. The spectrum at 300 K was much broader (not shown in Fig. 1), and the microwave response was still measurable. Hereafter, we focus on the CR intensity at 0.16 T which is resonant to the electron (e2).

![Figure 1. CR spectrum at 10 K at a delay time of 88 ns and that at 80 K averaged for 50-200 ns. The excitation photon energy was 5.550 eV. The inset shows schematic of the mounted sample.](image)

Figure 2 shows the normalized CR time profiles at 10, 80, and 300 K. Under excitation at the photon energy of 5.520 eV (a) above the exciton absorption edge, signals peaked at delay times of 24, 48, and 16 ns at 10, 80, and 300 K, respectively. The signals decayed with lifetimes of 60, 425, and 125 ns at 10, 80, and 300 K, respectively. The lifetime was defined as the time for the 1/e of the peak intensity. We consider that the delayed peaks appeared owing to incubation of exciton dissociation, depending on the exciton lifetime and density [12]. The longest delay time at 80 K is considered to be caused by the exciton lifetime longest at approximately100 K [13], whereas the shorter delay time at 300 K is caused by the increase in the exciton density due to the higher absorption coefficient at higher temperatures [3]. On the other hand, under excitation at the photon energy of 5.620 eV (b), where carriers are directly generated by band-to-band transitions in addition to exciton dissociation [9], faster responses appeared within 40 ns. The signals peaked at 12, 16, and 8 ns at 10, 80, and 300 K, respectively, and decayed with lifetimes of 60, 300, and 104 ns at 10, 80, and 300 K, respectively.
Figure 2. Normalized time profiles of the CR signal resonant to c2 at 0.161 T at 10, 80, and 300 K. The excitation photon energy was (a) 5.520 eV and (b) 5.620 eV.

Figure 3 shows the TRCR excitation spectra obtained at 10, 80, and 300 K. The time windows were chosen as (a) 80–280 ns at 10 K, (b) 352–552 ns at 80 K, and (c) 156–356 ns at 300 K, after the signal decayed to the 1/e of the peak intensity. For such late times, we observed that carriers were dominantly generated by dissociation of excitons [9]. The excitation spectrum at 80 K was similar to that at 10 K in terms of the onset energies. The onset energy at 5.493 eV coincides with the exciton generation edge assisted by emission of a transverse acoustic (TA) phonon \( E_{ex} + \hbar \omega_{TA} \), where \( E_{ex} = 5.406 \) eV is the exciton energy and \( \hbar \omega_{TA} = 87 \) meV is the TA phonon energy [14] (See the inset). The second onset at 5.547 eV is assigned to exciton generation assisted by emission of a transverse optical (TO) phonon \( E_{ex} + \hbar \omega_{TO} \), where \( \hbar \omega_{TO} = 141 \) meV is the TO phonon energy [14]. Because of the large phonon energies in diamond, the excitation spectra exhibited onsets at the same positions and no trace of phonon absorption up to 80 K.

Figure 3. CR excitation spectra at (a) 10 K, (b) 80 K, and (c) 300 K. Vertical broken lines indicate the energy positions of \( E_{ex} \pm \hbar \omega_{TA}, E_{ex} \pm \hbar \omega_{TO} \) and \( E_{ex} \). The downward arrows indicate the excitation energies for the power dependence measurements shown in Fig. 4. The inset shows schematic of phonon-assisted transitions to the exciton band.

On the other hand, the signal at 300 K arose at the lower energy side with the onset at 5.265 eV. The onset energy coincides with the threshold for exciton generation assisted by absorption of a TO phonon \( E_{ex} - \hbar \omega_{TO} \) (See the inset). The onset energy for TA phonon absorption \( E_{ex} - \hbar \omega_{TA} \) is higher as indicated by the vertical broken line (the second one from the left) in Fig. 3(c). The above results make apparent that carriers are generated via excitons at 300 K with phonon absorption in addition to phonon emission. The measured excitation power dependence in Fig. 4 indicates that the CR signal intensity at 300 K proportionally varies with the excitation intensity, both under excitation
at 5.29 eV for phonon absorption and at 5.65 eV for phonon emission. Therefore, the carriers are generated dominantly via a one-body process, such as thermal ionization of excitons, instead of a two-body process due to collision of excitons at 10 K [7]. Finally, we would like to note that the excitation spectra in Fig. 3(a–c) deviated from a function $\frac{E - E_{ex}}{\hbar \omega_0}$, which is characteristic of phonon-assisted exciton transition, above 5.58 eV. This is caused by the reduction of the CR signal under a high carrier density condition owing to a high absorption coefficient [4].

**Figure 4.** Excitation power dependence of the CR signal at 300 K, measured under excitation photon energies at 5.29 and 5.65 eV. The signals were integrated over time after excitation.

4. Conclusion
We investigated the excitation spectra of cyclotron resonance signals due to electrons in a high-purity diamond crystal up to 300 K. Based on the spectroscopic analysis, we found that carriers are generated by dissociation of excitons generated only by phonon emission at 10 and 80 K, and by phonon emission and absorption at 300 K. This indicates that it is possible to inject carriers via thermal ionization of excitons, even under excitation at low photon-energy region (5.265–5.493 eV, i.e., 235.5–225.7 nm in wavelength) with an absorption coefficient smaller than 1 cm$^{-1}$ [3]. We believe that this knowledge is useful for device application, as bipolar carriers are uniformly injected over the entire crystal in such a condition.

Acknowledgements
We thank J. H. Kaneko (Hokkaido University) for providing the diamond sample grown by the CVD method. This work was supported by JSPS KAKENHI (Grant Nos. 15K05129 and 17H02910) and the Murata Science Foundation.

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