Nanosecond cyclotron resonance in ultrapure diamond

Nobuko Naka [a,*], Katsuyuki Fukai [b], Yushi Handa [b], Ikuko Akimoto [b]

[a] Department of Physics, Graduate School of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto 606-8502, Japan
[b] Department of Materials Science and Chemistry, Wakayama University, Wakayama 640-8510, Japan

ARTICLE INFO

ABSTRACT

We have investigated temporal properties of photo-excited carriers in ultrapure diamond by the nanosecond cyclotron resonance (CR) method. The ramp time and the amplitude of the CR signals are found to be dependent on the incident laser pulse energy as well as on the photon energy for excitation. The dependences are discussed based on the photoabsorption process due to the indirect excitons in diamond, which is assisted by absorption of the transverse-acoustic phonons. Similarities to the free-carrier generation via two-body excitonic collisions in a dipole-forbidden direct gap semiconductor, Cu_2O, are pointed out.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The cyclotron resonance (CR) method has been utilized to determine effective masses of electrons and holes in many materials [1]. However, time-resolved CR in a nanosecond time scale had long been a challenging task. We have developed such a technique by using an electron-spin-resonance cavity, and demonstrated its applicability to optically excited carriers in a direct-gap semiconductor, Cu_2O [2–4]. Recently, we have also succeeded in detecting CR in an indirect-gap semiconductor, diamond, and reported the angular dependence of the effective masses [5].

Diamond has six-fold conduction band minima at the delta points in the Brillouin zone. Therefore, the energy surface of the electrons in the conduction band is expected to form six ellipsoids. There was no direct experimental proof on this, because of the difficulty in preparing n-type diamond crystals. Even when the doped samples are available, the deep donor states require a high temperature for thermal activation of the carriers [6,7], and this hinders measurements at low temperatures. On the other hand, there are some limited number of reports on the hole effective masses in p-doped diamonds [8–10]. The effective mass values, however, widely scatter depending on the literature [11].

Among various solid materials, diamond possesses extraordinary properties such as the high mechanical hardness, high thermal conductivity, and the long spin coherence of a localized electron [12]. Diamond is considered to be a potential alternative to the conventional semiconductors, because of the high carrier mobilities and the high breakdown voltage [13]. Furthermore, photo-excited carriers in diamond form a rich quasi-particle system composed of excitons, polyexcitons [14], and electron–hole liquid [15,16]. The effective mass determines both the carrier mobilities and the phase boundary for the gas–liquid phase transitions. Therefore, the direct determination of the effective masses in diamond is a key issue for both application and basic sciences.

In this paper, we present transients of the CR signals due to the optically excited electrons and holes in ultrapure diamond at 10 K. Detailed analysis on the nanosecond transients and excitation-wavelength dependences will be given in the following sections.

2. Experiments

We used a chemical-vapor-deposition (CVD) diamond supplied by Element Six as the sample. The surfaces were oriented to (001), (110), and $(1-10)$ crystal planes. The sample in a dimension of $2 \times 2 \times 0.5$ mm^3 was mounted into a dielectric cavity (Bruker, MD5W1) at 10 K in a flow-type cryostat [3]. As shown in the inset of Fig. 1(a), a quartz prism was attached to the sample in the cavity. The laser beam was loosely focused on a spot with an area of 3×1.5 mm^2 on the sapphire cylinder surrounding the sample and the prism. Only several % of the pulse energy of the laser beam reaches the sample due to attenuation by the cryostat windows, cavity mesh, and the tube surrounding the sample. Some portions of the incident laser light are scattered by the cylinder wall, and incident on the side of the prism with various incident angles. Although we do not know the exact path of the main beam in the prism, this configuration improves the coupling between the sample and the excitation light as well as the coupling of the microwave with the photoexcited carriers. An external magnetic field up to 1 T was applied while the microwave of 0.1 mW at a frequency of $f = 9.64$ GHz irradiated the sample. The temporal

* Corresponding author.
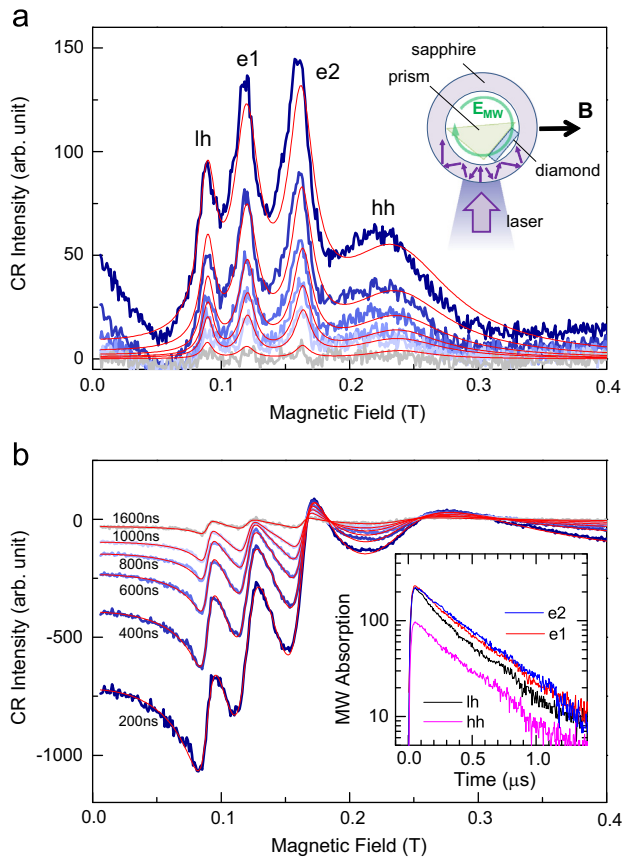E-mail address: naka@scphys.kyoto-u.ac.jp (N. Naka).

Fig. 1. Microwave absorption at 9.64 GHz due to cyclotron resonance in diamond at 10 K. The external magnetic field was applied along the direction by 40° tilted from the [001] crystal axis. The incident laser pulse energy was 3.2 µJ. (a) Real part and (b) imaginary part as a function of the magnitude of the external magnetic field. The delay time was set at 200, 400, 600, 800, 1000, and 1600 ns. Inset in (a) represents the configuration of the diamond crystal in the cavity. Inset in (b) shows temporal profiles of the heavy hole (hh), light hole (lh), and electron (e1, e2) resonances from the bottom to the top traces. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)
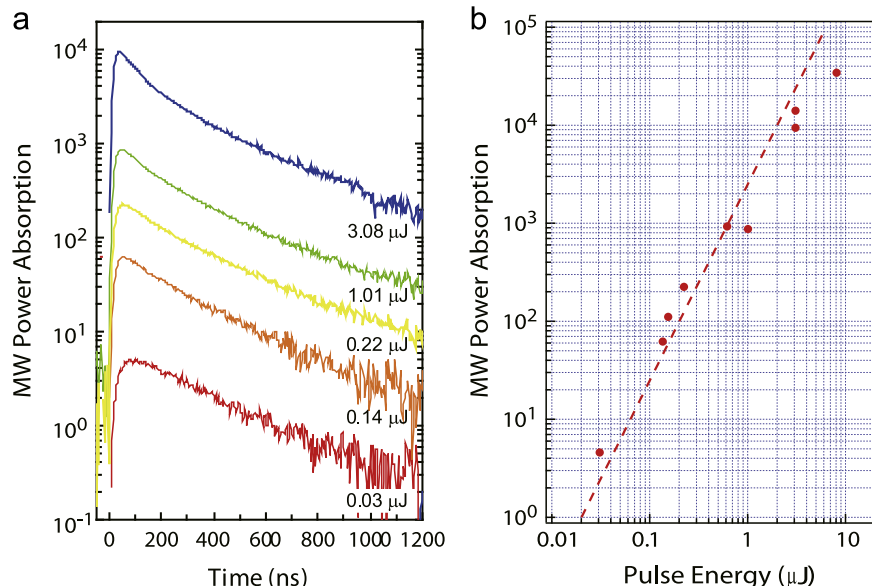
change of the microwave electric field was measured at a quadrature detector by separating the real and imaginary parts.

The sample was irradiated through the prism by the 5-ns pulses from an optical parametric oscillator (Spectra Physics, MOPO) pumped by a Nd:YAG laser. Since the sample contains nitrogen (boron) atoms only less than 5(1) ppb, we observed no CR signal without optical excitation of carriers. We paid careful attention to minimize plasma shifts of the resonance peaks [3] due to the high-density effect. Namely, the single pulse energy less than 10 µJ was incident on the sample surface at the repetition rate of 10 Hz for all the measurements. We investigated the excitation-wavelength dependence of the CR transients in the range of 226 nm (5.48 eV) to 225 nm (5.52 eV), in order to cover the Stokes component of the phonon-assisted absorption edges of the indirect excitons in diamond [17].

3. Results and discussion

Fig. 1 shows CR spectra obtained with the diamond crystal at 10 K, with the magnetic field applied along 40° to the [001] axis in the $(1\bar{1}0)$ plane. The real (a) and imaginary (b) parts at various delay times after the optical excitation are shown. The free carriers were excited at the wavelength of 225.6 nm (i.e., photon energy of 5.494 eV). The photon energy was slightly above the indirect gap of diamond (5.49 eV). In the CR spectra, four peaks are clearly resolved. Based on the detailed analysis of the angular dependence of the peak positions [5], two peaks, e1 and e2 in the range of 0.1–0.2 T are assigned as electrons in the conduction valleys in two inequivalent configurations with respect to the magnetic field. The other two peaks, around 0.088 T and around 0.23 T, are due to the light hole (lh) and the heavy hole (hh), respectively. The thin red lines show fitting results with the formula for complex conductivity, as the details are given in Ref. [3]. Up to the delay time of 600 ns, the experimental spectra, in particular the low-field region of the real parts, deviated from the calculated ones. This is due to the overlap of the magnetoplasma resonance of the high-density carriers. We find that the temporal range for the appearance of this magnetoplasma effect is common in Cu_2O [3] and in diamond.

Fig. 2. (a) Temporal profiles of the microwave absorption due to the light-hole resonance in diamond for different excitation pulse energies. The excitation photon energy was 5.499 eV. (b) Maximum signal amplitude at the light-hole resonance as a function of incident laser pulse energy.