Characterization of deep defects in boron-doped CVD diamond films using transient photocapacitance method

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ABSTRACT

We have developed a highly-sensitive transient photocapacitance measurement (TPM) system for deep defects in wide bandgap materials, and applied it to characterize the boron-doped diamond films grown on a high-pressure/high-temperature-synthesized Ib diamond substrate using high-power-density microwave-plasma chemical vapor deposition method. The developed TPM system has both a low detection limit of less than 0.5 fF for changes in the photocapacitance and a low measurement temperature drift of less than 0.03 K in 12 h. By using the TPM system, we have successfully found an acceptor-type defect around 1.2 eV above the valence-band maximum for the B-doped diamond film with a considerably high crystalline quality that had some strong exciton emission peaks in the cathodoluminescence spectra taken at $\approx$80 K. The photoionization cross section and the defect density estimated for the observed defect were 3.1×10^{-15} cm^2 and 2.8×10^{16} cm^{-3}, respectively.

1. Introduction

With the increase in demand for higher frequency and higher power device operation, expectations for the wide-bandgap semiconductor (WBS) materials are increasing since silicon devices have almost reached their theoretical limits. In recent years, development in several WBS devices having a bandgap of about 3 eV, such as gallium nitride and silicon carbide, has been achieved. Furthermore, diamond is expected as a potential material for high-performance devices in the next generation, because of its various interesting physical properties such as large bandgap [1], high thermal conductivity [2,3] and high breakdown field strength [4]. However, a practical diamond semiconductor device has not been realized yet because diamond crystal to be employed has some imperfections in the crystal structure, for example, dislocations and impurities. Thus, for the realization of diamond semiconductor devices, it is essential to reduce such crystal defects as much as possible. In order to do that, it should be required to identify the origin of such crystal defects.

In the case of narrow-bandgap semiconductor materials such as silicon, deep level transient spectroscopy (DLTS) is one of the most versatile techniques to characterize the electrically active defects located at any energy in the almost full range of the bandgap [5–7]. DLTS method is based on the investigation of thermal emission of the carrier from defect levels located within the bandgap. In the Shockley-Read-Hall model, the thermal emission rate of electrons (holes) $e_{n(p)}$ can be expressed at the temperature T with the Boltzmann constant k_B as [8]

$$e_{n(p)}=\sigma_{n(p)}v_{n(p)}N_{C(V)}\exp\left(-\frac{\Delta E_{n(p)}}{k_B T}\right),\tag{1.1}$$

where $\sigma_{n(p)}$ is the capture cross section for electrons (holes), $v_{n(p)}$ is the thermal velocity of electrons (holes), $N_{C(V)}$ is the effective density of states in the conduction (valence) band, and $\Delta E_{n(p)}$ is the energy separation between the trap level from the conduction band minimum (valence band maximum). It is obvious that the charge emission rates for very deep traps become very small at reasonable temperatures. In the case of a hole emission from a hypothetical defect of diamond crystal, assuming that σ_p, v_p and ΔE_p are 10^{-15} cm^2, 10^5 cm s^{-1} and 1.5 eV, respectively, e_p is calculated to be about 10^{-23} s^{-1} for $T = 300$K. One of the solutions to this problem is an optical excitation of the carrier from defect levels within the bandgap by means of monoenergetic light illumination. Optical emission processes give rise to a capacitance transient. This transient photocapacitance measurement (TPM) method can provide the spectrum of the photoionization cross-sections of the deep defects, which cannot be probed by means of DLTS method. In this method, the measurement temperature has to be low enough so that thermal emission can be neglected. However, the junction capacitance of the diamond device decreases in the high-frequency region, which is used in the conventional TPM, because the energy level of the dopant for the diamond crystal is substantially deep (i. e. B: 0.36 eV, P: 0.60 eV) [9,10].

In this study, we have developed a highly-sensitive TPM system that

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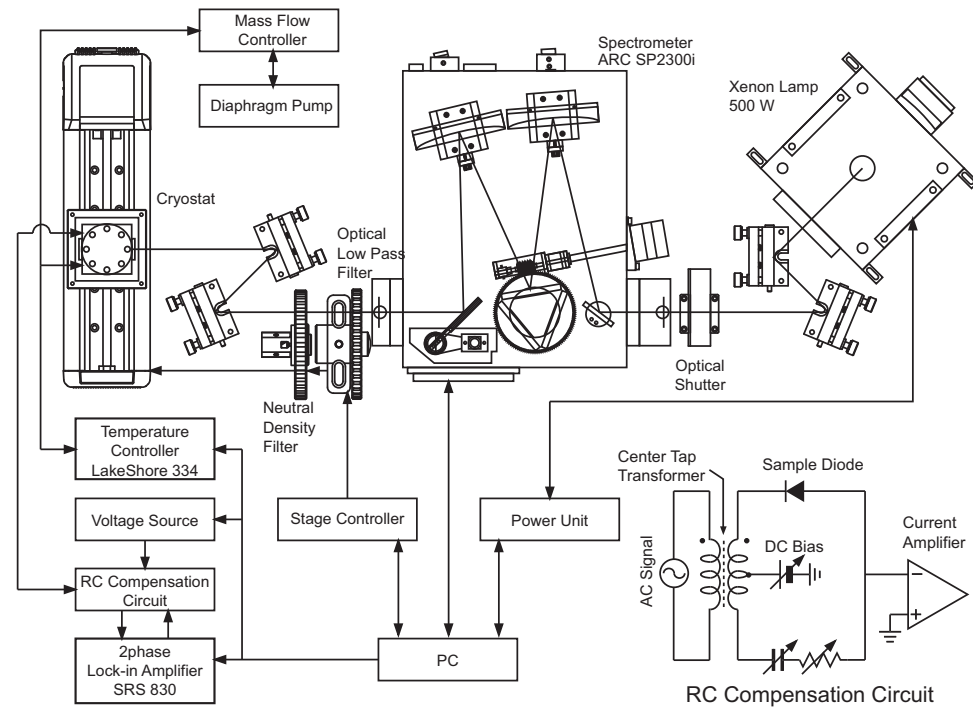*E-mail address:* maida@eei.eng.osaka-u.ac.jp (O. Maida).

Fig. 1. Schematic diagram of the transient photocapacitance evaluation system for deep defects in diamond.
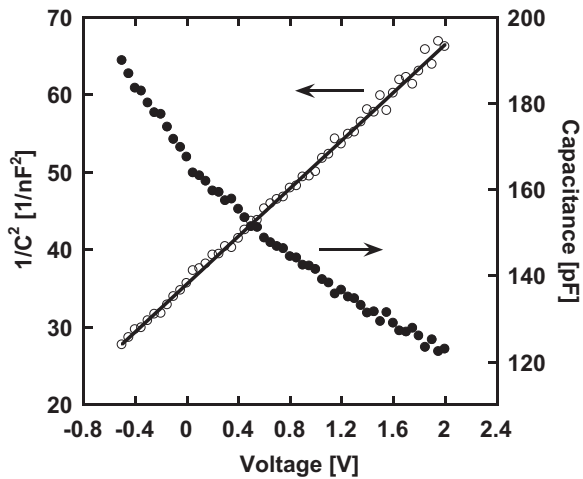

Fig. 2. Capacitance-voltage characteristics of the diamond Schottky diode with the modulation frequency of 1 kHz at room temperature. The net acceptor density and the diffusion voltage estimated from the slope of the $1/C^2$ plot were $4.15 \pm 0.03 \times 10^{17}$ cm^{-3} and 2.30 ± 0.03 V, respectively.

Fig. 3. CL spectra taken at ≈80 K for B-doped diamond film synthesized at 1020 °C. The inset shows an enlarged spectrum in the near-band-edge region. The emission peaks observed at 235 and 238 nm were attributed to the FE$_{TO}$ and BE$_{TO}$(B), respectively.

was optimized for detection of deep defects in diamond, and characterized the boron-doped diamond films homoepitaxially grown by using a high-power-density microwave-plasma chemical vapor deposition (MWPCVD) method.

2. Experiments

2.1. Fabrication of a boron-doped diamond Schottky diode

Commercially available high-pressure/high-temperature-synthesized (HPHT) Ib (001) diamond substrates with a size of $3.0 \times 3.0 \times 0.5$ mm^3 were cleaned in wet chemical processes and then annealed at approximately 1000 °C under a hydrogen atmosphere to remove possible impurities on the specimen surfaces [11]. Using a high-power-density MWPCVD apparatus (ASTeX: AX-5400) [12], undoped buffer and B-doped diamond films were homoepitaxially
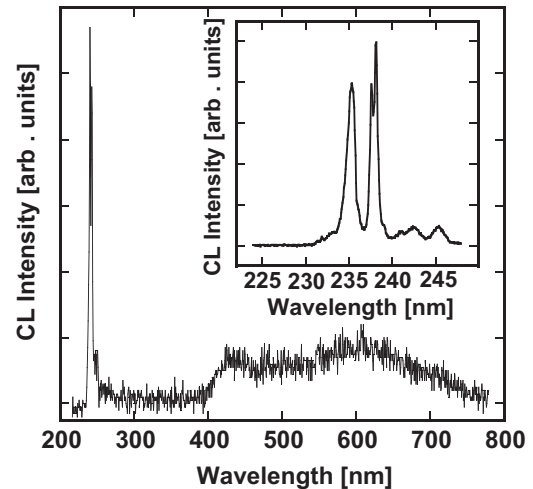
grown on HPHT substrates. The source gases used for depositions of undoped buffer and B-doped films were composed of 6N-purity CH$_4$ and a 100-ppm trimethylboron (B(CH$_3$)$_3$) diluted with H$_2$. The B(CH$_3$)$_3$/CH$_4$ ratio of 5 ppm was employed for the B-doped diamond growth. The total gas pressure, microwave power, CH$_4$/H$_2$ ratio and substrate temperature employed were 120–130 Torr, 3.8–4.2 kW, 4% and 1020 °C, respectively. The thicknesses of the undoped buffer and B-doped films evaluated by a laser displacement sensor were ≈20 and ≈8 μm, respectively. The resultant growth rates of the undoped buffer and B-doped films were approximately 4.0 and 3.5 μm/h, respectively. The diamond films were characterized using a scanning electron microscope equipped with a cathodoluminescence (CL) measurement system.

As a Schottky electrode, some semi-transparent Au electrodes (15 nm in thickness and 500 μm in diameter) were fabricated by using an electron beam evaporator. Spectral transmittance of the Au films in