GaP Raman Terahertz high accuracy spectrometer and its application to detect organic and inorganic crystalline defects

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Abstract: One of the most important uses of THz spectrometry is to detect defects in molecular structure or in crystals efficiently. We applied GaP Raman THz (GRT) spectrometer to detect and evaluate defects in organic and inorganic materials. High THz-wave absorption due to high defect density of GaSe crystal lowered the efficiency of THz wave generation, when the crystal is used as nonlinear material for DFG (Difference Frequency Generation). Defects in organic molecules could be observed as changes in frequency, intensities of the absorption, and broadenings of the spectra.

Key words: Terahertz; GaP Raman THz (GRT) spectrometer; defects; GaSe; glucose; asparagine.

Introduction. Following the proposal of THz-wave generation via the resonance of lattice or molecular vibrations by Nishizawa,1,2 Nishizawa and Suto realized a semiconductor GaP Raman laser3 and generated a coherent 12-THz wave with a peak power as high as 3W using a GaP Raman oscillator containing a GaAs mixing crystal.4 On the same way, using LiNbO3 crystals Kawase et al. realized frequency-tunable THz-wave generator (TPG, THz Parametric Generator).5 We developed widely frequency-tunable high-power THz-wave generator (GaP-Raman THz, GRT generator) based on difference-frequency generation (DFG) via excitation of phonon-polaritons in GaP crystals using a YAG laser and an optical parametric oscillator (OPO)6–8 as a practical THz-wave source, and constructed a THz spectrometer.9 We constructed another type of GaP Raman THz (GRT) spectrometer using Cr:forsterite lasers (Cr: F-source system). The advantages of this spectrometer are its compact, simple structure, high resolution and low cost. We also recently improved its spectral resolution to below 500 MHz.10 High-resolution THz spectra can now be applied not only to measure the sharp absorption lines of gases but also to reveal fine-structures in the spectra of solids.11 These fine structures are thought to be caused by defects in either the molecular structure or the crystals.

It has been suggested that in addition to carrier absorption, absorption by defects in a crystal is the principal cause for the reduction of efficiency in THz-wave generation from a semiconductor.12 This implies that THz spectrometry is sensitive to defects in semiconductors. Vibrational spectra of weak intermolecular interactions, such as hydrogen bonding and van der Waals’ force, can be detected in the THz region. Skeletal vibrations of the molecule and phonon modes of organic crystals also lie in this frequency band. THz spectrometry should also be sensitive to defects in organic molecules.

Many kinds of disease are caused by abnormal genes or the invasion of pathogenic viruses. Genetic alterations could be classified as defects in biomolecules. If these defects can be detected sensitively, and analyzed precisely, new diagnoses and advanced treatments could be realized. For example, the accumulation of genetic alterations is thought to drive normal cells into becoming invasive cancer.13 Nishizawa proposed diagnosing cancer by detecting defects in biomolecules using THz spectrometry, and then suggested treatment using THz-wave radiation to generate selective oscillation of a particular target bond in the cancer tissue.14
In this paper, we describe our use of a GRT spectrometer to detect and evaluate defects in organic and inorganic materials, and show the relationship between these defects and the THz spectra.

**THz spectrometer.** Details of THz generation and the equipment for THz-transmittance measurements have been described in our previous papers. Briefly, THz waves were generated by difference frequency generation (DFG) via the Raman effect in a GaP crystal. Both the pump and signal beams for the DFG fed from two Cr: forsterite lasers were combined at a very small angle to fulfill the phase-matching condition. The THz waves generated were collected using a pair of off-axis parabolic reflectors. Pyroelectric deuterium triglycine sulfate (DTGS) detectors, operating at room temperature, were used as THz-wave detectors. The insufficiently high sensitivity of these detectors, compared with a 4 K Si bolometer, limits the measurable frequency range to 0.5 – 6.3 THz. Using the double beam method to reduce the noise due to the power fluctuation of the generated THz wave, we achieved a high S/N ratio for the measurement. The linewidth of the THz wave generated using the usual system is 30 GHz, but the high-resolution width was recently confirmed to be below 500 MHz. The THz spectrometer was purged with dry air to eliminate water vapor absorption.

**Results and discussions.**

**A. Defects in semiconductor crystals and their effects on THz wave generation.** We have generated THz waves using DFG in GaSe, as well as in GaP. The GaSe crystal, with its large second-order nonlinear optical (NLO) coefficient ($d_{22} = 54$ pm/V), is another superior semiconductor for efficient THz wave generation. Furthermore, THz waves were generated in a wide frequency range, from THz to the mid-infrared region (0.3 – 100 THz, 1000 – 3 µm). Since a GaSe crystal is birefringent, the collinear phase-matching condition for THz wave generation is fulfilled by rotating only the crystal. The optical system becomes much simpler than that of non-collinear, phase-matched THz wave generation from GaP. In previous studies, the THz-wave output power was shown to be greatly dependent on the crystallinity of the semiconductor crystals. Due to its layer structure, it is easy to contain crystal defects and dislocations in a GaSe crystal.

We used two z-cut GaSe crystals, with carrier densities of (a) $10^{10}$ cm$^{-3}$ and (b) $10^{14}$ cm$^{-3}$, respectively. The crystals were grown using a Bridgman method; they were both 2 mm long along the c-axis, and were not (intentionally) doped with impurities.

The crystallinity of the GaSe crystals was investigated using (0001) X-ray symmetric diffraction on a (0001) reciprocal space map. The lattice constants to the c-axis direction of the GaSe crystals (a) and (b) were 15.9633 Å and 15.9636 Å, respectively. Both GaSe crystals structures were confirmed to be epsilon, and their full width at half-maximum (FWHM) was almost the same, suggesting that the lattice strains of the two crystals were similar. Figure 1 shows the (0001) reciprocal space maps. ω and 2θ are incident angle and detector angle, respectively. The lattice strain was almost identical in the two maps, but the crystal with the carrier density of $10^{10}$ cm$^{-3}$ had a greater dislocation than the other crystal with that of $10^{14}$ cm$^{-3}$; it also contained twins, and defects that scattered the THz waves. Figure 2 shows the THz-wave output power

![Fig. 1. (0001) reciprocal space maps of GaSe crystals. (a) for lower carrier density and (b) for higher carrier density.](image-url)
spectrum from the two crystals. At frequencies below 1.3 THz, the output power from crystal (a) was enhanced. This was because the free carrier absorption is dominant in this region.\textsuperscript{17} The THz wave was also absorbed due to defects in the crystal. Therefore, higher-power THz waves were generated from crystal (b), which had a lower density of defects (the higher-carrier-density crystal) in the frequency range over 1.3 THz.

To achieve a higher output power, the defects and free carriers in the GaSe should be minimized simultaneously. An effective means to achieve this is to grow and heat-treat the GaSe crystals with Se vapor under stoichiometric control, as seen in various compound semiconductors.\textsuperscript{21–24} Using the temperature-difference method under controlled vapor pressure liquid phase epitaxy (TDM-CVP LPE) approach of GaSe crystals, bulk crystals were grown with controlled stoichiometry. The GaSe crystals grown with TDM-CVP LPE were bright red, while the crystals grown without TDM-CVP were dark red.\textsuperscript{25} Figure 3 shows the THz absorption spectra of GaSe crystals grown without (c) and with (d) TDM-CVP. A small THz wave absorption coefficient was achieved with the TDM-CVP process. The periodic modulations in the spectra are caused by the multiple reflections of the THz waves between the both surfaces of GaSe crystal. The appearance of these modulations also shows the low transmission loss mainly due to good quality of the crystal. If THz wave absorption below 1.3 THz was mainly attributable to a free carrier, in comparison with spectra of GaSe crystals in which the absorption coefficient are known, the carrier density of the GaSe crystal (c) is estimated about $10^{14}$ cm\(^{-3}\), while that of the GaSe crystal (d) over $10^{14}$ cm\(^{-3}\). Details of the results and discussions will be described in the following report.\textsuperscript{25}

**B. Defects in organic molecules.** The previous section presented the relationship between defects in semiconductor crystals and THz waves in an application example for inorganic materials. Examples of defects induced in organic materials are now presented.

**B-I. Defects in a biomolecular crystal induced by gamma irradiation.** Defects were intentionally induced in organic molecules at a Co-60 gamma-ray irradiation facility (Takasaki Advanced Radiation Research Institute, Japan Atomic Energy Agency [JAEA]). $\alpha$-d-Glucose powder was placed in a polyethylene bag and irradiated at room temperature with a radiological dose in the range of 0.4 $\sim$ 40 kGy, controlled by the irradiation time and the distance from the $^{60}$Co radiation source. After irradiation, 15 mg of the $\alpha$-d-glucose powder were milled and mixed with 285 mg of polyethylene powder and pressed into 1-mm-thick, 20-mm-diameter pellets under a pressure of $3.12 \times 10^7$ Pa. The pellets were made into wedges to prevent possible THz-wave resonance via the etalon effect on both surfaces. The samples were measured at 5 K in a cryostat, with the stage...
temperature controlled by spraying helium gas and a heater. It was ensured that none of the surfaces in the THz beam path, including both window surfaces of the cryostat, were parallel.

The THz-transmittance spectra were measured using a high-resolution GRT spectrometer. The reproducibility of the frequency value at ±2 GHz, at worst, was confirmed by measuring the water vapor absorption lines in the 2.1 – 2.3 and 3.5 – 3.7 THz ranges, both before and after every measurement. It is thought that the major cause of frequency value errors is mechanical fluctuation in the tuning mirror rotation in the Cr: forsterite laser.

The THz-transmittance spectrum at 5 K for α-d-glucose irradiated by 40 kGy γ-rays is shown in Fig. 4. For comparison, the spectrum of non-irradiated α-d-glucose is also shown. The line width of the THz beam was less 500 MHz and the THz frequency was scanned by 1 GHz step. The frequency deviations enough larger than the spectral resolution due to γ-ray irradiation are clearly observed. Remarkable absorption peaks are labeled with the numbers 1 – 8, and each deviation in these peaks is shown in Table I. All of the deviations are toward lower frequencies, ranging from nearly 0 to −20 GHz.

Simple defect like vacancy is expected to induce split in the spectrum especially at lower density. Widely coupled defect, that is high density defect, is expected to induce deviation of the spectrum and widening of the peaks by resonance and absorption especially at higher density. In these experimental results shown in this figure, these characteristics are showing the tendency and will be reported precisely in the following paper.\textsuperscript{26}

Yamamoto et al. have reported the increasing of THz absorption in ultrahigh molecular weight polyethylene (UHMWPE) irradiated by γ-rays.\textsuperscript{27} However the spectral change was monotonous with the frequency and absorption frequency deviation was not observed. We firstly demonstrated defect detection in an organic material as a slight absorption frequency deviation in the THz region. Of course, we had the advantage of our high-resolution spectrometer, which can detect such slight spectral changes.

\textbf{B-II. Terahertz absorption properties of L-asparagine-L-aspartic acid solid solution.} L-Asparagine (L-Asn), crystallized from aqueous solution, forms monohydrate (Asn·H₂O). L-Aspartic acid (L-Asp) can dissolve in an Asn·H₂O crystal, while keeping its space group \textit{P2₁2₁2₁} at concentrations < 15 mol%. L-Asp substitutes for L-Asn, and the hydrogen bonding between the amine and carboxyl groups changes into a repulsive force (Fig. 5).\textsuperscript{28, 29}

L-Asn and L-Asp were dissolved in water with mol fractions of 0, 5, and 15 mol% L-Asp, and cooled slowly from 80°C to room temperature. The actual mole fractions of the solid solution were determined using an amino-acid analyzer after crystallization, and were estimated to be 4.6% and 12.3%, respectively. The crystals were ground into a powder with a mortar and pestle. Powder samples (7.1 or 18.8 mg) were mixed with polyethylene (300 mg) and pressed into disks. The pellets were again 20 mm in diameter and approximately 1 mm thick, resulting in concentrations of 0.15 and 0.40 M. A pure polyethylene pellet was also prepared as a reference for estimating transmittance.

The THz absorption spectra are shown in Fig. 6. The intensity of the peak at 1.645 THz decreases linearly with increasing Asp concentration. The linearity indicates that this peak corresponds to the molecular skeletal vibration or intramolecular vibration, where the guest concentration is low. Conversely, the peak at 2.3 THz decreases rapidly when the concentration of Asp exceeds 5%. Therefore, the origin of the 2.3-THz peak is possibly a lattice vibration, like a phonon, rather than a skeletal or local vibration in each molecule.

Hangyo investigated the 1.645-THz absorption peak (1.6 THz in the report) of Asn·H₂O using THz time-domain spectroscopy, and found that this peak decreases gradually with dehydration at 70°C.\textsuperscript{30} After 3 hours, the substance became an anhydrous crys-
Fig. 4. THz transmittance spectra of α-d-glucoses irradiated and not irradiated with γ-ray.

Their finding that the intensity of the 1.645-THz peak decreased by degrees with the dehydration progress supports our hypothesis that this absorption band corresponds not to a phonon, but to local vibrations, such as an intermolecular hydrogen bond or a skeletal vibration of the Asn molecule bonding to a water molecule.

Absorption lines at higher than 2.5 THz become unclear as the concentration of Asp increases. It is likely that because lattice defects affect the intramolecular vibration of each Asn molecule, the absorption peaks of the Asn molecule are lowered and broadened.

While details of the results and discussions will be described in the following paper, the results here indicate that terahertz spectroscopy is a promising tool for detecting point defects in organic materials, which play an important role in functional materials and biological systems, like proteins and genes.

**Conclusion.** We have shown that one of the most important uses of THz spectrometry is to detect defects. We applied GaP Raman THz spectrometer to evaluate defects in ε-GaSe crystals, as examples of inorganic material. THz-wave output power generated from ε-GaSe crystals were investi-
gated with a parameter of defect densities. Higher efficiency of THz generation at above 1.3 THz was corresponding to lower absorption by the crystal due to low density of defects. As other examples of organic material, defects in $\alpha$-d-glucose irradiated by $\gamma$-ray and l-asparagine-l-aspartic acid solid solution were also investigated. Defects were observed as fine structure in spectra, such as frequency deviations, change in intensities or broadenings of absorption lines, scarcely, splitting, in the case of weak binding with waves.

Acknowledgement. We would like to thank Dr. Hiroo Inokuchi, M.I.A., for helpful information. This work is partly supported by Grant-in-Aid for Scientific Research (Creative Scientific Research, 17GS0209) by Ministry of Education, Culture, Sports, Science and Technology (MEXT) and Japan Society for the Promotion of Science (JSPS).

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(Received Oct. 25, 2006; accepted Nov. 13, 2006)