4 Time-Domain Spectroscopic System

4-1 Broadband Terahertz Time-Domain Spectroscopic System

SAITO Shingo and SAKAI Kiyomi

It is now accepted that the terahertz time-domain spectroscopy (THz-TDS) has many advantages over the traditional spectroscopy. But one weak point is that the frequency range which the THz-TDS covers has been limited to less than several THz. In order to extend this limitation to higher frequencies, we have developed a broadband THz-TDS system based on our series of researches.

The system consists of a ML Ti:Sapphire ultra short pulse laser as an excitation light source and photoconductive antennas as terahertz radiation emitter and detector. The system is designed so as to cover 0.1〜15 THz and the spectrometer is enclosed in a vacuum-tight box, which is purged with nitrogen gas. It has a revolving sample stage and it can be controlled automatically.

Keywords
THz wave, Ultra short pulse laser, Photo-conductive antenna, Ultrabroad band, Electromagnetic waveform

1 Introduction

The range of electromagnetic waves in the frequency band from approximately 0.1 THz to 10 THz ($T = 10^{12}$) lying between visible light and radio waves has long been recognized as an unexplored field. For years this range has been studied by only a small number of researchers in the fields of physics, chemistry, and astronomy. Recent developments in lasers, semiconductor crystals, and device fabrication technologies has widened the applicable fields, with active research and development now underway focusing on the electromagnetic waves now referred to as THz waves[1][2].

The energy range of the THz band includes elemental excitations such as molecular vibrations of gases and liquids and phonons, magnons, and plasmons of solids, and thus shows a characteristic absorption structure. For this reason, this band is also referred to as the “fingerprint region”, and expectations are high for the use of this region as a band for spectroscopic analyses. Specific applications are now being proposed in diverse fields including electronic materials, analyses of novel materials, applications to biotechnology and medical treatment, product inspection for drugs, food quality control, ambient air monitoring, and security applications[3]-[8].

However, the frequency range near the THz band also contains absorption bands unique to certain substances. From the standpoint of spectroscopic analysis, we cannot ignore this rich field.

This article briefly describes the history of

THz spectroscopy. It then proceeds to describe technological development related to the generation and detection of ultrabroadband THz waves using photoconductive antennas, the focus of one of the research and development activities centering on THz waves conducted since the establishment of the Kansai Advanced Research Center (the predecessor of the present Kobe Advanced ICT Research Center) in 1989. The article also describes a broadband THz spectroscopic system built as the result of this research.

2 History of THz spectroscopy

In its early stages, spectroscopic analysis in the THz band made use of spectroscopy based on prisms and diffraction gratings. Later, as computers advanced, Fourier transform far-infrared spectrometers (FT-FIR) were also used in the THz band. However, detectors employing liquid-helium coolant such as bolometers continued to be used for detecting THz waves in the low frequency range or for high-sensitivity detection. These detectors were difficult to handle. Demand grew for the development of powerful, room-temperature methods of THz-waves spectroscopy.

It was recently reported that the Ti:Sapphire laser (Ti:S laser), which uses a sapphire crystal doped with titanium ions as the laser gain medium, can operate as an ultra-short-pulse laser. This report widened the range of use of ultra-short-pulse lasers and promoted the development of pulse lasers that are relatively small but that produce large output power. Technologies also advanced in fabrication of semiconductors used as the substrate material of photoconductive antennas. In addition, researchers and engineers developed new growth techniques for nonlinear optical crystals and also explored new types of such crystals. As a result, research and development into THz wave generation and detection rapidly progressed, based on a number of innovative methods[2].

In particular, the method of sampling detection of the magnitude and direction of the electric field of THz waves coherently generated by an ultra-short-pulse laser created a new movement in THz-band technology. This development had such an impact that the frequency band referred to simply as the far-infrared region at that time was given the more specific designation we use today: the THz band. The measurement method through which the spectrum is acquired by measuring the electromagnetic waveform of THz waves and performing the corresponding Fourier transform is referred to as THz-TDS (Terahertz Time-Domain Spectroscopy) measurement. THz-TDS can be applied to a wide range of fields. For example, this method has been applied to the fields of superconducting materials[3], elementary excitation in solids[4], imaging[5], DNA[6], thin films[7], and THz tomography[8].

THz waves in THz-TDS measurement are usually generated using either photoconductive antennas or nonlinear optical crystals. It has also been reported that semiconductor surfaces and superconductors can be unique sources of THz waves. In the case of photoconductive antennas and semiconductor surfaces, the time derivative of the photoexcited charges determines the form of the electric field of the THz waves. On the other hand, in the case of nonlinear optical crystals, the mechanism of THz generation is optical rectification. Photoconductive antennas and nonlinear optical crystals are also used for detecting the waveform of coherently generated THz waves. A method based on photoconductive antennas employs a device in which electrical transmission lines and micro-gaps that operate as optical switches are fabricated by metal evaporation on a semiconductor substrate, such as low-temperature-grown GaAs (LT-GaAs or LTG-GaAs). Pulse light from an ultra-short pulse laser with an energy greater than the band gap energy of the semiconductor substrate material is irradiated to the micro-gap as the gate pulse and generates carriers in the micro-gap, through which the device operates as an antenna. When THz waves are irradiated to this gap, the waves accelerate the carriers and induce a current. By detecting this current, we can find the waveform of the relevant THz waves. In photoconductive antenna detection, the integrated average of the current, I (τ), corresponds to the time integration of the product of the magnitude, E (t), of the THz and the charge density, n (t), expressed as in the following expression.

$$I(\tau) \propto \int E(t)\, n(\tau - t)\, dt \quad (1)$$

Here, τ is the injection time difference between the THz waves and the gate light pulse that generates the photoexcited carriers. Another method is based on a nonlinear optical crystal and employs the EO effect in crystals such as ZnTe. This method involves detection of a change in the complex refractive index induced by the electric field of the THz waves, as a change in the polarization direction of the pulse light passing through the crystal. Both methods require light at a pulse width shorter than the period of the THz waves.

THz-TDS measurement as such offers the advantages listed below, relative to the conventional FT-FIR method.

(1) It is important to know the complex dielectric constants of materials in spectroscopic analyses. Conventional FT-FIR and similar methods can only provide information on the power spectrum. In order to acquire complex dielectric constants from this power spectrum we have to perform complicated calculations of the Kramers-Kronig conversion under certain assumptions. THz-TDS measurement, on the other hand, allows for the direct acquisition of phase information, as well as the power spectrum, from the electromagnetic waveform.

(2) The peak intensity of the electric field of THz waves generated by ultra-short pulse light is sufficiently greater than the noise generated by thermal excitation, such that a high signal-to-noise ratio (SNR) can be obtained even in room-temperature operation.

(3) The detector does not require coolants such as liquid helium, which enables simple handling.

(4) THz-TDS measurement offers a wider dynamic range than bolometer-based detection methods and enables more accurate measurement of optical responses.

(5) THz waves generated as short pulses permit analysis of the multi-reflective structure of substances having a multilayer structure and enable non-destructive measurement of the characteristics of each film.

Figure 1 shows an example of a THz-TDS system that uses photoconductive antennas for THz wave generation and detection elements. High-resistance silicon lenses processed into hemispheres are attached to the generation and detection antennas and reduce reflection on the interface between air or vacuum and the antenna substrate to increase the THz wave signal intensity. However, lattice vibration is present in the antenna substrate that is unique to the material, and the refractive index changes significantly near the energy of this vibration. This effect increases the reflection of THz waves, rendering the detection of THz waves in this band difficult. This band is referred to as the Restrahlen band and is situated in the range from approximately 5 THz to 10 THz.

For the reasons described above, many THz-TDS measurements performed in the past were limited to a range below 3 THz, leading to demand for extension of the available measurement band.

Several research groups have developed a number of broadband THz-TDS measurement

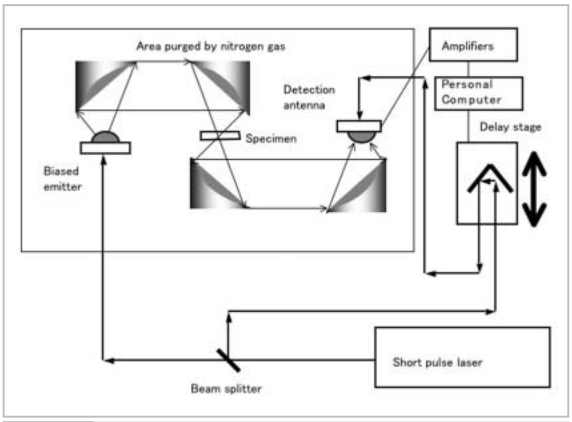

Fig. 1 Schematic drawing of typical THz-TDS system

techniques[9][10]. However, as it was believed that the detection band of photoconductive antennas was not wide, these development activities were mainly based on nonlinear optical crystals. To measure the real-time waveform of THz waves using the EO effect of nonlinear optical crystals, we must first satisfy the so-called phase-matching condition, in order to increase the sensitivity of detection. This characteristic requires that the probe light and the THz waves feature the same velocity within the crystal. In particular, for broadband spectroscopy extended to the high-frequency side — as required in the current research and development — we must satisfy the phase-matching condition by reducing the thickness of the nonlinear optical crystal. The ZnTe crystal generally used as the EO crystal is approximately 1 mm thick. When broadband detection is targeted in particular, we must use an ultra-short pulse laser in order to implement broadband generation by the optical rectification effect (for generation) and to shorten the gate width (for detection). In addition, an extremely thin crystal is needed to satisfy the phase-matching condition. Sometimes, the thickness of the crystal used was approximately several tens of μm, and required careful handling. Nonetheless, a wide insensitive band due to the Restrahlen band remained present within the spectrum. In addition, as a thin crystal is used, the reflection structure is superposed on the waveform of the electric field, leading to concerns regarding the effect of this superposition on spectrum resolution. Nevertheless, a series of research projects was initiated based on photoconductive antennas, at the Kansai Advanced Research Center of the Communications Research Laboratory[11]. Here again, it was necessary to use an ultra-short-pulse laser. However, we reconsidered the spatial arrangement of the generation and detection antennas and modified this arrangement to reduce the effects of THz waves attributable to the photoconductive antenna substrate. With these techniques, we demonstrated experimentally the possibility of practical broadband detection of THz waves. Later, it was demonstrated that ultrabroadband detection reaching 100 THz is possible with optimized ultra-short-pulse lasers and optical systems. Research and development continues with respect to super-ultrabroadband detection. Figure 2 shows an example of a broadband THz-TDS system.

3 Development of broadband terahertz time-domain spectroscopic system

Figure 3 shows the outward appearance of the broadband terahertz time-domain spectroscopic system that we developed based on the above research, under the Competitive Research Fund for applied development of NICT technologies. The details are as follows. A mode-locking Ti:S laser that generates pulsed light with a pulse width of 10 fs (f

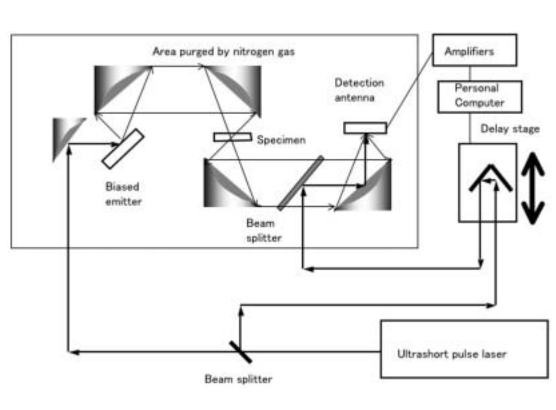

Fig.2 Schematic drawing of broadband THz-TDS system

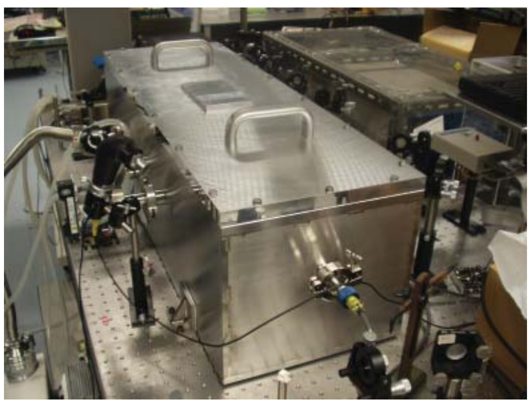

Fig.3 Outward appearance of broadband THz-TDS system

stands for femto; f = 10^{-15}; light propagates only 3 μm during this period) is used as the excitation light source for generating and detecting the THz waves. [The repetition rate of the pulse laser was approximately 78 MHz, the center wavelength of the laser light was 800 nm (which corresponds to 375 THz), and the average output power was approximately 450 mW.] The pulsed light output from this laser is divided into halves. One of the halves is irradiated to a photoconductive antenna applied with a bias to generate THz waves. The other half is irradiated to another photoconductive antenna for detecting THz waves. This half is used as the gate light for the sampling measurement. The microcurrent generated by simultaneously irradiating the THz waves and the gate light to the antenna is amplified by a preamplifier and detected by a lock-in amplifier. We know that the pulse width of ultra-short pulse light inevitably increases when the light passes through dispersing media such as beam splitters and lenses. This effect renders the pulse unsuitable as a gate pulse for broadband detection. For this reason, the optical arrangement is devised to reduce the transmitting media to the full extent possible, and dispersion compensating optics are also introduced in order to reduce elongation of the pulse width of the gate light. In addition, to reduce the effects of gases such as water vapor, the optical system is enclosed in a vacuum-tight box that can be purged with nitrogen gas. We built the broadband spectroscopic system in light of these conditions required for broadband detection. Our best results so far show detection of 100 THz at maximum. However, we decided to cover the band in which we can perform measurement continuously and without modifying the alignment of the system. As a result, we decided on a detection band of 0.1 THz to 15 THz. The SNR of the developed system is approximately 1000:1.

Figure 4 shows the preliminary data of the transmission spectrum of THz waves in air measured using this spectroscopic system. The thickness of the air is approximately 80 cm. Although the data show many absorption lines, regions with few absorption lines are also noted. As is clear from the figure, it is not true that THz waves do not propagate.

Further, we evaporated ethanol in the vacuum-tight box to measure the transmission characteristics of ethanol gas. Figure 5 shows the results. Here we see a wide absorption band near 6 THz. As we do not accurately know the concentration of the ethanol gas, we cannot directly compare the results with other measurements. However, the results here qualitatively agree with the results of Fourier interferometer measurement performed in the past[12].

Accordingly, we were able to demonstrate that a broadband THz spectroscopic system — built based on technological development related to ultrabroadband THz wave generation and detection using photoconductive antennas — can prove effective for broadband spectroscopic measurements, as intended. We are also conducting measurements of various

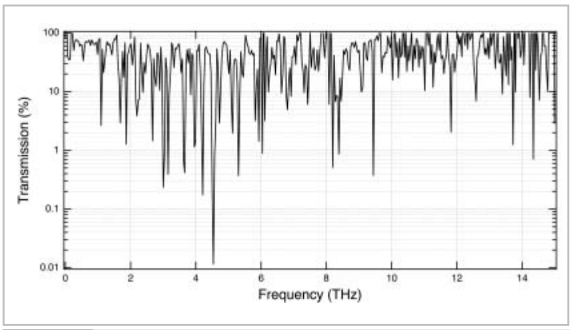

Fig.4 *Transmission spectrum of air with light path of approximately 80 cm*

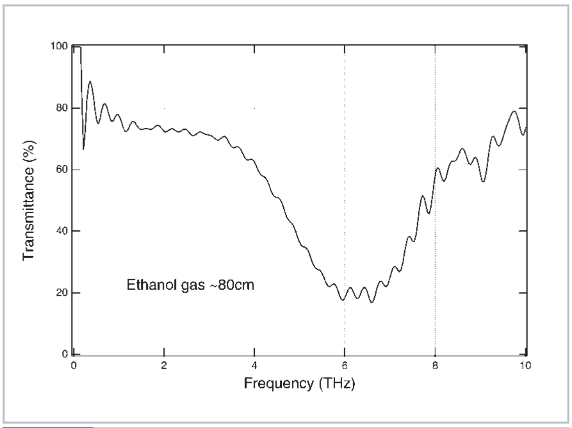

Fig.5 *Transmission spectrum of ethanol gas with light path of approximately 80 cm*

substances, taking advantage of the large dynamic range now available, which cannot be described in the current article. As a point of note, we would also like to add that the application of THz waves is now advancing as a new tool for spectroscopic analysis.

4 Conclusions

This article describes the history of spectroscopic measurement by THz waves and the demands of broadband measurement. It also describes the development of a broadband terahertz time-domain spectroscopic system built based on research results obtained at the Kansai Advanced Research Center and reports on part of the transmission characteristic data measured by this system.

This research was carried out with the collaboration of Dr. Atsushi Syouji; Dr. Shunsuke Kono; Professor Koji Mizoguchi of the Graduate School of Science, Osaka Prefecture University; Associate Professor Masaaki Ashida of the Graduate School of Engineering Science, Osaka University; Mr. Atsushi Doi, Mr. Hiroshi Shimosato, and many others. We are deeply grateful to all those who assisted in this collaboration.

References

1 B. Ferguson and X. C. Zhang, "Materials for terahertz science and technology", Nature Materials, Vol.1, pp.26-33, Sep. 2002.
K. Sakai (Ed.), Terahertz Optoelectronics, Heidelberg: Springer Berlin, 2005.
2 D. H. Auston, K. P. Cheung, and P. R. Smith, "Picosecond photoconducting Hertzian dipoles", Appl. Phys. Lett. Vol.45, pp.284-286, Aug. 1984.
3 R. A. Kaindl, M. A. Carnahan, J. Orenstein, and D. S. Chemla, "Far-Infrared Optical Conductivity Gap in Superconducting MgB_2 Films", Phys. Rev. Lett., Vol.88, pp.027003-1-3, Jan. 2002.
4 R. Huber, B. A. Schmid, Y. R. Shen, D. S. Chemla, and RobertA. Kaindl, "Stimulated Terahertz Emission from Intraexcitonic Transitions in Cu_2O", Phys. Rev. Lett., Vol.96, pp.017402-1-4, Jan. 2006.
5 B. B. Hu and M. C. Nuss, "Imaging with terahertz waves", Optics Letters, Vol.20, No.16, pp.1716-1718, Aug. 1995.
Z. Jiang, X. G. Xu, X.-C. Zhang, "Improvement of terahertz imaging with a dynamic subtraction technique", Applied Optics, Vol.39, pp.2982-2987, Jun. 2000.
6 M. Brucherseifer, M. Nagel, P. H. Bolivar, H. Kurz, A. Bosserhoff, and R.Büttner, "Label-free probing of the binding state of DNA by time-domain terahertz sensing", Appl. Phys. Let. Vol.77, pp.4049-4052, Dec. 2000.
7 Z. Jiang, MingLi, and X.-C. Zhang, "Dielectric constant measurement of thin films by differential time-domain spectroscopy", Appl. Phys. Let. Vol.76, pp.3221-3223, May 2000.
8 B. Ferguson, S. Wang, D. Gray, D. Abbott, and X.-C. Zhang, "T-ray computed tomography", Optics Letters, Vol.27, pp.1312-1314, Aug. 2002.
9 C. Kübler, R. Huber, S. Tübel, and A. Leitenstorfer, "Ultrabroadband detection of multi-terahertz field transients with GaSe electro-optic sensors: Approaching the near infrared", Appl. Phys. Lett. Vol.85, pp.3360-3362, Oct. 2004.
R. Huber, F. Tauser, A. Brodschelm, M. Bichler, G. Abstreiter, and A. Leitenstorfer, "How many-particle ineractions develop after ultrafast exciaion of an electron-hole plasma", Nature Vol.414, pp.286-289, 2001.

10 Y. C. Shen, P. C. Upadhya, E. H. Linfield, H. E. Beere, and A. G. Davies, “Ultrabroadband terahertz radiation from low-temperature-grown GaAs photoconductive emitters”, Appl. Phys. Lett. Vol.83, pp.3117-3119, Oct. 2003.

Y. C. Shen, P. C. Upadhya, H. E. Beere, E. H. Linfield, A. G. Davies, I. S. Gregory, C. Baker, W. R. Tribe, and M. J. Evans, “Generation and detection of ultrabroadband terahertz radiation using photoconductive emitters and receivers”, Appl. Phys. Lett. Vol.85, pp.164-166, Jul. 2004.

11 S. Kono, M. Tani, P. Gu, and K. Sakai, “Detection of up to 20 THz with a low-temperature-grown GaAs photoconductive antenna gated with 15 fs light pulses”, Appl. Phys. Lett. Vol.77, pp.4104-4106, Dec. 2000.

S. Kono, M. Tani, and K. Sakai, “Ultrabroadband photoconductive detection: Comparison with free-space electro-optic sampling”, Appl. Phys. Lett. Vol.79, pp.898-900, Oct. 2001.

S. Kono, M. Tani, and K. Sakai, “Coherent detection of mid-infrared radiation up to 60 THz with an LT-GaAs photoconductive antenna”, IEEE Proceedings-Optoelectronics, Vol.149, pp.105-109, 2002.

H. Shimosato, S. Saito, M. Ashida, T. Itoh, and K. Sakai, Ultrafast Optics, Springer series in Optical Sciences 132, pp.317-323, 2007.

12 J. R. Durig and R. A. Larsen, “Torsional vibrations and barriers to internal rotation for ethanol and 2,2,2-trifluoroethanol”, J. Molecular Structure, Vol.238, pp.195-222, 1989.

***SAITO Shingo**, Ph.D.*

Senior Researcher, Advanced Communication Technology Group, New Generation Network Research Center

THz Spectroscopy

***SAKAI Kiyomi**, Dr. Eng.*

Senior Research Official, Advanced Communication Technology Group, New Generation Network Research Center

THz Spectroscopy