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科学研究費助成事業　　研究成果報告書

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研究課題名（和文）Development of time resolved STM-THz-TDS system for studying the ultrafast carrier dynamics of graphene

研究課題名（英文）Development of time resolved STM-THz-TDS system for studying the ultrafast carrier dynamics of graphene

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研究成果の概要（和文）：本研究では、テラヘルツ(THz)光と走査プローブ顕微鏡(SPM)を用いた3種類のナノ分光システムを開発した。SPM-THz時間領域分光、SPM光ポンプ・プローブ分光、SPMレーザー励起THz顕微分光が行え、1つのシステムとして格納されている。切り替えはフリップ式ミラーを動かすだけで可能であり、その他の部分はそのまま利用できることから、同一サンプルに対して全手法を適用できる。加えて、THz用の光学素子やSPMなど重要な部品は真空ボックス内に配置されており、ノイズや水吸収によるTHzの減衰の低減を実現している。この分光システムを用いて、低温成長GaAsやInAs、CVD成長グラフェンを研究した。

研究成果の学術的意義や社会的意義
To find the practical applications of newly discovered nanomaterials, understanding their properties is crucial. Our developed setup allows us to investigate these new nanomaterials. Full understanding of these sample properties would then lead to the discovery of their practical applications.

研究成果の概要（英文）：In this project, three types of nanospectroscopy system was developed which utilizes Terahertz (THz) radiation and scanning probe microscopy (SPM). Owing to this combination, our setup allows for the investigation of various materials with nanoscale dimensions. In one compact arrangement, our system is composed of SPM THz time domain spectroscopy (SPM-THz-TDS), SPM optical pump-probe spectroscopy (SPM-OPTP), and SPM laser terahertz emission microscopy (SPM-LTEM). Switching between all of these setups is achieved by movement of flip mirrors and fixing other parts such as the delay stage. Moreover, we placed all of the critical components such as the THz related optics, the SPM, and other electronics inside a vacuum sealable box. This configuration was done in order to reduce the noice as well as to avoid water vapor absorption of the THz radiation. Using these setups, we have investigated low temperature grown GaAs, InAs and CVD grown graphene samples.

研究分野：Optics

キーワード：Terahertz　SPM　Nanomaterials　Nanospectroscopy　tip enhancement

1．研究開始当初の背景 (background)

Graphene is a 2 dimensional material consisting of a single sheet of carbon atoms. It is one of the earlies discovered 2D materials and has gained popular attention due its interesting properties such as high mechanical strength, high conductivity, zero band gap, etc. A variety of applications for graphene has been demonstrated and many applications are still being discovered. For it's potential in optoelectronic applications such as sensing, it is important to understand it's temporal response characteristics. It is important to note that the temporal information is not only useful for graphene but for any new material that is desired to be used for practical applications.

A popular technique to study the temporal response of different materials is optical pump-THz probe spectroscopy. In this technique, a target sample is illuminated by an ultrafast laser in optical frequencies and THz radiation is introduced to the sample as well. The THz absorption response on the optical excitation is then measured. If a time delay is added between the THz "probe" and the optical "pump" temporal response can be measured by the change in the THz absorption of the material. Previously, such a technique has been used to study the carrier dynamics of semiconductors such as nanowires. Information such as carrier lifetime, hot carrier relaxation time, has been reported previously.

Although optical pump THz probe spectroscopy is a powerful platform for understanding the temporal characteristic of a sample, it lacks the necessary spatial resolution to study nanoscale materials in detail. This lack of nanoscale spatial resolution is an inherent problem to optical based spectroscopy system because of the diffraction limit. The diffraction limit defines that the absolute resolution limit of any imaging systems to be one half of the wavelength of light used. For optical pump THz probe spectroscopy, the light used is usually in the NIR range (800 nm) and THz range (300 μm), limiting the maximum achievable spatial resolution in the 100 μm range. Clearly, if the target material have nanoscale features, such a technique is not applicable. Specifically, using conventional optical pump THz probe experiment would only provide averaged information of a target sample.

To solve this problem, I developed in this project a time resolved broadband scanning probe microscope-based system for measuring the ultrafast carrier dynamics of nanoscale sample such as graphene. This system is composed of a scanning probe microscope and THz radiation. The SPM tip serves as a kind of antenna in order to push the spatial resolution to nanoscale levels. Such a technique was successfully implemented for THz spectroscopy, Raman spectroscopy, Photoluminescence spectroscopy to name a few. Moreover, I used a PCA based THz generation mechanism which requires far weaker pumping. The setup also retains spectroscopic information as the THz radiation provided by the PCA antenna is broadband.

2．研究の目的 (purpose)

The purpose of this research is to develop an experimental setup capable of attaining nanoscale spatial resolution as well as temporal sensitivity. Such a setup could provide both temporal resolution and nanoscale spatial resolution. This would allow for investigating the temporal response of nanoscale materials which is an important property for determining the applications of new materials.

３．研究の方法 (method)

In this project, we built a trimodal system consisting of THz-time domain spectroscopy (THz-TDS), laser THz emission microscopy (LTEM) and optical pump THz probe spectroscopy (OPTP). All of these three unique experimental setups allow for coupling of the pump radiation onto the tip of a scanning probe microscope (SPM). The desired experiment can be chosen just by small adjustments of mirrors and other optics in the setup. For the SPM, we chose an atomic force microscope (AFM) based on the qPlus sensor. The choice of an AFM is to allow the modulation of the signal via the tip vibration. This methodology was found to be effective in reducing the background noise of our setup. The critical parts of the system which includes the SPM head and its electronics, the THz optics are all placed in a vacuum sealable chamber. By pumping the chamber, further reduction of the background noise can be achieved. Absorption of the THz radiation by water vapour in the atmosphere is also significantly reduced because of the pumping which then results in a cleaner spectroscopy data. Apart from vacuum pumping, the chamber can also be purged with nitrogen gas to reduce the humidity when vacuum pumping is not suitable for the sample. Purging with other gases can also be performed in order to investigate the gas sensing capabilities of a sample.

In any SPM based experiment, the tip is one of the most critical components. Fortunately, our group has developed a repeatable, and reliable methodology for producing high quality gold tips. This custom made gold tips can then be attached to the qPlus sensors manually. As the qPlus sensor are quite expensive, a technique to recycle used qPlus sensors was also developed. With this methodology, we only need to remove the old tips and part of the qPlus sensor and attach a new one so that the sensor can be used again.

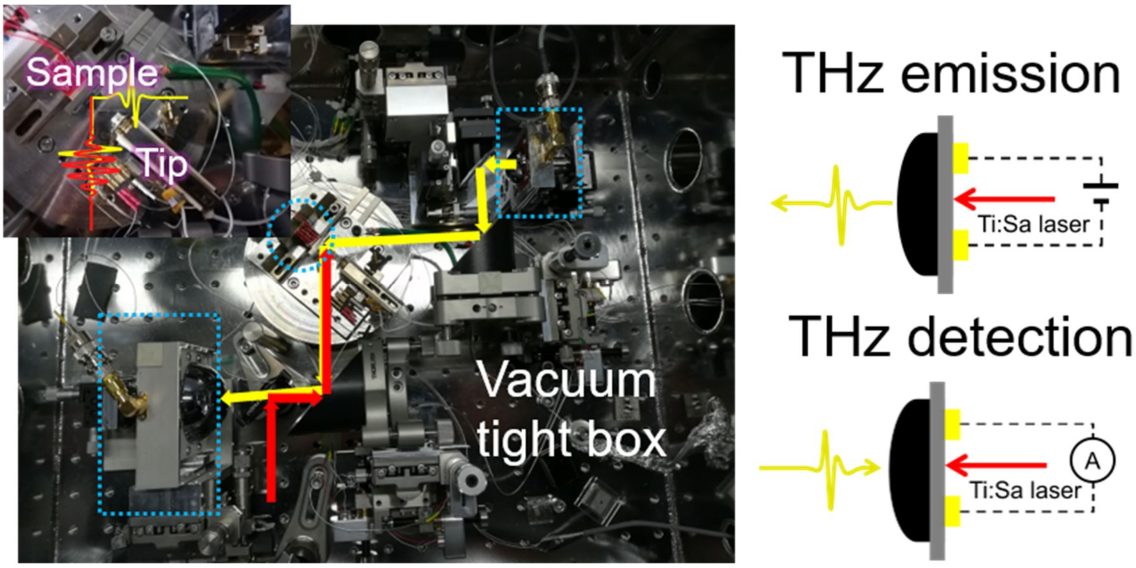

Figure 1. Photo of the inside of the environment-controlled chamber for the developed experimental setup which houses the SPM as well as THz and other optics. Also shown in the figure is a schematic of the THz emission and detection scheme used in this project.

THz detection in all of the experimental setups was attained using a photoconductive antenna (PCA). The PCA device was fabricated by our collaborators from the Research Center for Development of Far-Infrared Region, University of Fukui (FIR-UF) led by Prof. Masahiko Tani. They specifically designed our PCA in order to allow for collimated THz light from the sample to be detected. In the usual designs, the THz radiation needs to be focused unto the PCA detector. However, this would increase the necessary size of the setup so being able perform the experiment with fewer optics is preferred. For the SPM-THz TDS experiments, the THz generation is also via a PCA antenna prepared by our collaborators from FIR-UF. Both the detection and illumination PCA antenna was pumped by a Tsunami femtosecond laser. The detection PCA was connected to a current preamplifier and a lockin amplifier in order to reduce the background noise. The illumination PCA was biased using an AC voltage generator which also serves as the reference signal for the lockin amplifier. For the OPTP experiment, in addition to the THz beam, a near infrared beam from the femtosecond laser was used to excite the sample in order, the change in the THz absorption was then measured by the PCA. A mechanical delay stage is used to introduce a temporal delay between the arrival of the NIR pump pulse and the THz probe pulse. This then allows us to measure the temporal response of the sample. The SPM system was controlled by a nanonis controller. Both the THz optics and the SPM system are computer controlled and are controllable by LabVIEW designed by myself. A photo of the experimental setup and a schematic of the PCA antenna-based detection and excitation is shown in figure 1.

For samples, we investigated low temperature grown Gallium arsenide (LT-GaAs), cover slip coated with gold and graphene grown on Au (111) via CVD. The LT-GaAs samples were grown by our collaborators from the National Institute of Physics in the University of the Philippines-Diliman. The graphene sample was prepared by our collaborators from Japan Atomic Energy Agency (JAEA) led by Dr. Satoshi Yasuda. The Graphene samples was specially prepared to be compatible with our experimental setup. Apart from SPM-THz experiments, we also investigate the Graphene samples using scanning tunneling Wmicroscope-based tip enhanced Raman spectroscopy (STM-TERS). This experiment involves the measurement of the signature Raman signals from the sample with nanoscale spatial resolution. Results of STM-TERS experiments are complementary to the data that can be obtained from the SPM-THz experiments and would then give us a more complete picture of the properties of our samples.

４．研究成果（results）

As the main goal of this project is to build an experimental setup based on THz spectroscopy, the project was started by building a conventional laser terahertz emission spectroscopy setup. Here, the setup uses the laser from the femtosecond laser as a pump source and as mentioned above, a specially designed PCA is used as a detector. As the system is custom built, I wrote a software to control all the important components such as the delay stage and lockin amplifiers using LabVIEW. In order to ascertain if the experimental setup is working as intended, I initially investigated indium arsenide wafers which is a common standard sample for THz experiments. The results obtained from our home-built THz TDS setup was found to be in line with the available literature. Next the setup was converted to a THz absorption setup by using a PCA as an emitter and replacing the InAs sample.

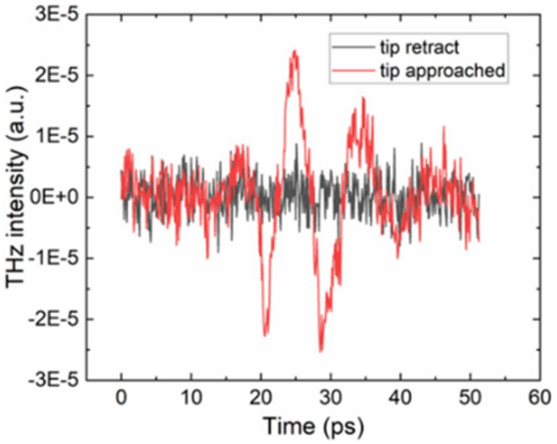

Figure 2. THz-TDS spectra of a Graphene on Au(111) sample in the presence or absence of a gold tip.

After the far field THz-TDS system was built, the next steps were to couple the THz radiation to the SPM tip. Based on my experience with tip-enhanced Raman spectroscopy, I know that this step is the most difficult and has the most drastic effect to the enhancement of the signals. An additional challenge in our experimental setup is that the THz radiation is not visible to the naked eye so it cannot be aligned using conventional means. In order to facilitate the alignment of the optical system, I used a small gold sample (1 x 1 µm). This sample was prepared by depositing gold on a cover slip and then removing the gold around the edges and keeping only a small area covered with gold. I found this to be effective in fine tuning the alignment of the THz-TDS setup. After the optical alignment was done, I then placed the SPM head near the sample. Afterwards, the gold coated sample was replaced by Graphene. The gold tip was then approached to the graphene surface and SPM-THz TDS was performed. Figure 2 show the THz-TDS spectrum both when the tip is in contact or far away from the sample. I found that in the absence of the gold tip, no THz signals were observed. In contrast when the gold tip is in contact with the Graphene sample, THz-TDS signals are obtained. This is a clear evidence that THz modulation is attained by the use of a gold tip. I also THz signals moving the tip towards and away from the sample. I found that the tip-sample distance dependence agrees well with literature.

After successfully coupling the THz radiation to the SPM tip, I next proceeded to construct the far field optical pump terahertz probe spectroscopy setup. Here a second NIR pump pulse from the femtosecond laser is introduced apart from the THz probe pulse from the PCA. In such an experiment, a much higher pump pulse is necessary to attain better signals. Hence, instead of using a 50:50 beamsplitter, a 90:10 beamsplitter was used. Moreover, a second mechanical delay stage is added in order to introduce a temporal delay between the probe pulse and the pump pulse. Overall, the experimental setup is designed in such a way that it can be switched to three different experiments by only moving a few optics. This allows for the investigation of the same sample area. Using this setup, I investigated the carrier dynamics of a low temperature grown GaAs and Graphene on Gold samples.

５．主な発表論文等

〔雑誌論文〕　計10件（うち査読付論文　10件／うち国際共著　9件／うちオープンアクセス　0件）

１．著者名 Escano Mary Clare、Balgos Maria Herminia、Nguyen Tien Quang、Prieto Elizabeth Ann、Estacio Elmer、Salvador Arnel、Somintac Armando、Jaculbia Rafael、Hayazawa Norihiko、Kim Yousoo、Tani Masahiko	４．巻 511
２．論文標題 True bulk As-antisite defect in GaAs(110) identified by DFT calculations and probed by STM/STS measurements	５．発行年 2020年
３．雑誌名 Applied Surface Science	６．最初と最後の頁 145590～145590
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.apsusc.2020.145590	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Jaculbia Rafael、Hayazawa Norihiko、Imada Hiroshi、Kim Yousoo	４．巻 11
２．論文標題 EXPRESS: Controlling the Resonance Raman Effect in Tip-Enhanced Raman Spectroscopy Using a Thin Insulating Film	５．発行年 2020年
３．雑誌名 Applied Spectroscopy	６．最初と最後の頁 1391～1397
掲載論文のDOI（デジタルオブジェクト識別子） 10.1177/0003702820938366	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Jaculbia Rafael B.、Imada Hiroshi、Miwa Kuniyuki、Iwasa Takeshi、Takenaka Masato、Yang Bo、Kazuma Emiko、Hayazawa Norihiko、Taketsugu Tetsuya、Kim Yousoo	４．巻 15
２．論文標題 Single-molecule resonance Raman effect in a plasmonic nanocavity	５．発行年 2020年
３．雑誌名 Nature Nanotechnology	６．最初と最後の頁 105～110
掲載論文のDOI（デジタルオブジェクト識別子） 10.1038/s41565-019-0614-8	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Balgos M. H.、Jaculbia R.、Prieto E. A.、Tani M.、Estacio E.、Salvador A.、Somintac A.、Hayazawa N.、Kim Y.	４．巻 126
２．論文標題 Atomically-resolved interface imaging and terahertz emission measurements of gallium arsenide epilayers	５．発行年 2019年
３．雑誌名 Journal of Applied Physics	６．最初と最後の頁 235706～235706
掲載論文のDOI（デジタルオブジェクト識別子） 10.1063/1.5118815	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Escano Mary Clare、Balgos Maria Herminia、Nguyen Tien Quang、Prieto Elizabeth Ann、Estacio Elmer、Salvador Arnel、Somintac Armando、Jaculbia Rafael、Hayazawa Norihiko、Kim Yousoo、Tani Masahiko	４．巻 511
２．論文標題 True bulk As-antisite defect in GaAs(1?1?0) identified by DFT calculations and probed by STM/STS measurements	５．発行年 2020年
３．雑誌名 Applied Surface Science	６．最初と最後の頁 145590～145590
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.apsusc.2020.145590	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Balgos Maria Herminia M.、Esca?o Mary Clare S.、Jaculbia Rafael B.、Quang Nguyen Tien、Prieto Elizabeth Ann P.、Estacio Elmer S.、Salvador Arnel A.、Somintac Armando S.、Tani Masahiko、Hayazawa Norihiko、Kim Yousoo	４．巻 1
２．論文標題 Atomically Precise Delineation of As Antisite Defect States from Undoped Gallium Arsenide Host Lattice by Scanning Tunneling Microscopy and Spectroscopy Measurements and Density Functional Theory Calculations	５．発行年 2022年
３．雑誌名 physica status solidi (b)	６．最初と最後の頁 2100652～2100652
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/pssb.202100652	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Imai-Imada Miyabi、Imada Hiroshi、Miwa Kuniyuki、Tanaka Yusuke、Kimura Kensuke、Zoh Inhae、Jaculbia Rafael B.、Yoshino Hiroko、Muranaka Atsuya、Uchiyama Masanobu、Kim Yousoo	４．巻 603
２．論文標題 Orbital-resolved visualization of single-molecule photocurrent channels	５．発行年 2022年
３．雑誌名 Nature	６．最初と最後の頁 829～834
掲載論文のDOI（デジタルオブジェクト識別子） 10.1038/s41586-022-04401-0	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Dasallas Lean、Jaculbia Rafael、Balois-Oguchi Maria Vanessa、Garcia Wilson、Hayazawa Norihiko	４．巻 39
２．論文標題 Effect of detection angle and substrate in the polarization analysis of 1D dipole emission	５．発行年 2021年
３．雑誌名 Journal of the Optical Society of America B	６．最初と最後の頁 307～307
掲載論文のDOI（デジタルオブジェクト識別子） 10.1364/JOSAB.442109	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Zhang Chi、Jaculbia Rafael B.、Tanaka Yusuke、Kazuma Emiko、Imada Hiroshi、Hayazawa Norihiko、Muranaka Atsuya、Uchiyama Masanobu、Kim Yousoo	４．巻 143
２．論文標題 Chemical Identification and Bond Control of π-Skeletons in a Coupling Reaction	５．発行年 2021年
３．雑誌名 Journal of the American Chemical Society	６．最初と最後の頁 9461～9467
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/jacs.1c02624	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 JACULBIA Rafael B.、IMADA Hiroshi、HAYAZAWA Norihiko、KIM Yousoo	４．巻 64
２．論文標題 Single-Molecule Resonance Raman Spectroscopy	５．発行年 2021年
３．雑誌名 Vacuum and Surface Science	６．最初と最後の頁 34～39
掲載論文のDOI（デジタルオブジェクト識別子） 10.1380/vss.64.34	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

〔学会発表〕　計6件（うち招待講演　3件／うち国際学会　4件）

１．発表者名 Rafael B. Jaculbia
２．発表標題 Tip-enhanced Resonance Raman spectroscopy and imaging of a single molecule
３．学会等名 SPP Physics Conference, Online（招待講演）（国際学会）
４．発表年 2020年

１．発表者名 Rafael B. Jaculbia
２．発表標題 Tip-enhanced Raman spectroscopy and imaging of a single molecule in ultrahigh vacuum and low temperature environments
３．学会等名 The Philippine-American Academy of Science and Engineering, Online（招待講演）（国際学会）
４．発表年 2020年

１．発表者名
Jaculbia, Rafael; Imada, Hiroshi; Miwa, Kuniyuki; Yang, Bo; Kazuma, Emiko; Hayazawa, Norihiko; Kim, Yousoo

２．発表標題
Vibrationally resolved imaging of a single molecule using tip-enhanced Resonance Raman spectroscopy

３．学会等名
10th International Conference on Advanced Vibrational Spectroscopy（国際学会）

４．発表年
2019年

１．発表者名
Rafael B. Jaculbia, Hiroshi Imada, Kuniyuki Miwa, Takeshi Iwasa, Masato Takenaka, Bo Yang, Emiko Kazuma, Norihiko Hayazawa, Tetsuya Taketsugu, Yousoo Kim

２．発表標題
Vibrational symmetry of a single molecule revealed by tip-enhanced Raman spectroscopy

３．学会等名
80th JSAP autumn meeting（国際学会）

４．発表年
2019年

１．発表者名
Rafael B. Jaculbia, Hiroshi Imada, Kuniyuki Miwa, Takeshi Iwasa, Masato Takenaka, Bo Yang, Emiko Kazuma, Norihiko Hayazawa, Tetsuya Taketsugu, Yousoo Kim

２．発表標題
Single molecule tip-enhanced Resonance Raman spectroscopy in low temperature environments

３．学会等名
Philippine-Japan Conference on Photonics and Optical Materials（招待講演）

４．発表年
2019年

１．発表者名
Rafael Jaculbia

２．発表標題
Investigation of the adsorption structure of CuPc on NaCl/Ag(111) using STM

３．学会等名
14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-14)＆26th International Colloquium on Scanning Probe Microscopy (ICSPM26), Sendai, Japan

４．発表年
2018年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関