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Tunable compact narrow band THz sources for frequency domain THz anisotropic spectroscopy

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Abstract

We demonstrate frequency domain THz anisotropy signature detection for protein crystal models using newly developed compact tunable narrow band THz sources based on Orientation Patterned Gallium Phosphide for turn-key spectroscopic systems.

Keywords

Terahertz; anisotropy; orientation patterned gallium phosphide; biomolecules; optical rectification; femtosecond; THz generation

1. INTRODUCTION AND BACKGROUND

Terahertz spectroscopy as a tool for material identification and characterization is well established^(1–4). Underlying principle of the technology is the fact that molecular vibrations of many substances of interest in security, drug development etc. are in the THz frequency range, making molecular ‘fingerprinting’ possible. These applications are typically based on intermolecular vibrations of small or medium size molecules. This is evident from the fact that the features appear only in crystalline samples while amorphous samples are usually featureless⁽⁵⁾. On the other hand, intra-molecular domain level vibrations of large biomolecules like proteins also fall in the same frequency range. But conventional THz spectroscopy which measures isotropic absorption cannot resolve features of these large molecules due to the inherent complexity and abundance of closely spaced vibrational modes present in such systems as well as due to the strong background absorption from the solvent. The result is a broad absorption spectrum devoid of any peaks⁽⁶⁾. Recently developed Anisotropic Terahertz Microscopy (ATM) overcome this problem by measuring polarization dependent absorption of aligned molecules^(7–9).

ATM is a polarization sensitive technique which measures orientation dependent changes in THz absorption. It generates a comprehensive map of the vibrational modes, featuring their frequencies as well as their directions introducing another dimension in characterization of large molecules. The changes in the detected anisotropy provides unique opportunities in

exploring the dynamics of biomolecules, which are typically hidden from simple absorption measurements which are sensitive only to vibrational energy distributions^(7–10).

However, the current techniques for doing these measurements are too complex and expensive for the broader biochemical and biomedical community. Therefore, research and development of low cost, small foot print and high dynamic range systems are critical.

Optical rectification of broadband pulses in a nonlinear crystal is a well-known and simpler method of generating pulses in the THz region of the spectrum. Single cycle, broadband THz pulses are generated using crystals where phase matching can be achieved for the entire bandwidth, or by using crystals with a length shorter than the coherence length of the interaction. But for applications like that in this paper, it may be desirable to have narrow band multi-cycle pulses of high intensity instead. This can be achieved by optical rectification in quasi-phase matched crystals. THz pulses are generated using quasi phase matched (QPM) crystals, where the sign of the non-linearity is reversed after each coherence length, as shown in Figure 1 below. For an optical pulse duration τ_p walk-off length is given by $L_w = c\tau_p (n_{THz} - n_{opt})$ where n_{THz} and n_{opt} are the refractive indices of the THz and optical pulses respectively. In QPM, polarization domains reverses sign at a length scale $L_d \approx L_w$. Polarization generated in crystal will radiate THz field consisting of $N/2$ cycles, where N is the number of domains. For perfectly periodic domains, narrow band THz will be generated with a period of $tf = 2L_d (n_{THz} - n_{opt}) / c$. THz frequency can be varied by changing domain length L_d . Bandwidth of the spectrum is given by $2/N$ when loss and domain fluctuations are neglected. The longer the crystals, narrower the bandwidth. When loss is included, bandwidth is limited by damping. For short-period crystals, bandwidth may be limited by domain length fluctuations⁽¹¹⁾. The first practical realization of such a structure was periodically-poled ferroelectric oxide crystals, like LiNbO₃ (PPLN)⁽¹¹⁾.

Quasi phase matching for THz generation are realized in semiconductors like GaAs using orientation patterning techniques⁽¹²⁾. In newer approaches a template of alternating domain orientation is created first with techniques like Molecular Beam Epitaxy (MBE) on which a thick layer of OP layer is grown with other techniques. Semiconductors offer advantages of being able to pump with more accessible wavelengths, like with commercially available fiber lasers. Moreover, orientation patterning technique based on techniques like MBE allows finer control of the domain widths allowing generation of higher wavelengths with narrower bandwidth.

Even though GaAs growth techniques are very mature allowing scalable manufacturing, it has some limitations like large 2-photon absorption, which necessitates the use of lasers operating at 2 μm or longer. Gallium phosphide (GaP) is an attractive alternative for THz generation with advantages over both LiNbO₃ and GaAs^(13, 14). Like GaAs, and unlike LiNbO₃, GaP is highly transparent to THz radiation. Comparing to GaAs, GaP has very low two photon absorption, so can be pumped with mature, commercially available fiber lasers operating near 1 μm . It also has higher thermal conductivity which helps to reduce the heat generated in the crystals due to pumping with high laser power.

In this paper we demonstrate the viability of this spectroscopic approach through anisotropic spectroscopic signature detection of molecular crystals using narrow band sources. We compare the signature of molecular crystals using narrow band frequency domain setup and a broadband time domain THz setup. Molecular crystals provide an excellent environmentally insensitive model system for developing Terahertz Microscopy methods for protein and RNA characterization.

2. EXPERIMENTAL SETUP AND PROCEDURE

2.1 Narrow band THz sources

OP-GaP crystals were produced at BAE systems following the methods described in the references^(13–15). The crystals were fabricated by Hydride Vapor Phase Epitaxy (HVPE) on quasi-phase matched templates grown by MBE. The period Λ of the domain for quasi-phase matched generation at a wavelength λ_{THz} is obtained from $\Lambda = \lambda_{\text{THz}} / n$, where $n = n_{\text{group(optical)}} - n_{\text{thz}}$ is the difference between the optical group index and the phase index at the THz wavelength. Using the GaP dispersion relation from Parsons and Coleman⁽¹⁶⁾, and the laser center wavelength of 1064 nm, the expected periods for generating THz frequencies of 1 – 4 THz at 0.5 THz increments were calculated and the corresponding samples produced. The periods ranged from 6.6 mm to 0.08 mm, and total lengths of the crystals were between 5.6 and 14 mm. The ends of the OP-GaP crystals were cut and polished and AR coated for 1064 nm.

Terahertz pulses were generated by placing the crystals at the focus of the output of a high-power fiber laser (Fianium, Femtopower, 8W, 180 fs, 80 MHz, 1064 nm). A 90° off-axis parabolic mirror (OAP) was used to collimate the THz output. A 3 mm diameter hole drilled through the center of the OAP allowed most of the pump light to pass through while minimizing THz losses.

A Michelson type interferometer was used to characterize the emitted spectrum for each sample. The intensity was recorded with a Golay cell as one arm of the interferometer was scanned. The Fourier transform of the resulting interferogram produced the pulse spectrum. Power measurements were made by focusing the THz beam onto a calibrated Golay cell. Long Pass filters were used to remove any residual pump light. Using the known transmission curves of the filters and the responsivity of the Golay cell, the average THz power emitted from each sample was measured.

2.2 Anisotropy measurements in the frequency domain

The experimental setup for sample characterization followed a similar setup as the one described above as is shown in Figure 2. Another parabolic mirror was used to create a THz beam focus for measurements. The detector was placed right after the focus. A THz wire grid polarizer was placed in the collimated path to clean up any ellipticity in polarization and to ensure that the direction of polarization of the incoming beam to the sample was well defined. An optical chopper along with a lock-in amplifier was used to detect the THz beam. Sucrose, Fructose and Oxalic acid crystals were used for measurements. Samples were affixed on a circular sample plate with 5 mm diameter central aperture and mounted on a

rotation stage (Thorlabs K10CR1) and placed at the focus of the THz beam. For each THz frequency band, the molecular crystals were rotated through 360 degrees at 5-degree increments, recording the transmitted intensity at each step. Steps were taken to identify the orientation of the crystal axes with respect to the facets of the samples. A particular orientation of the crystal axis with respect to the incoming THz polarization was chosen as the initial orientation for all measurements for that sample. As a first step, plots were generated for each band showing the percentage change in transmitted intensity for a sample to determine the strength of anisotropy. Anisotropic absorption plots were generated by taking the negative logarithm of the transmitted intensity at each angle normalized to that at the 0° orientation and combining the data for all bands for a given sample.

2.3 Anisotropy measurements using broadband time domain terahertz

Similar rotation measurements were performed on the samples using a far field Terahertz time domain spectroscopy (THz TDS) system. In this case the transmitted THz pulses were recorded in the time domain for each angular orientation at 15° increments. Fourier transform of the time domain pulses gave the broadband electric field magnitude in the frequency range 0.2 to 3 THz. In order to generate the anisotropic absorption maps, the data for different orientations were combined and normalized to the absorption at 0° orientation. Results were plotted as a function of frequency vs sample orientation. Bilinear interpolation was employed for the angular axis. Sucrose, fructose and oxalic acid crystals were grown and polished down to around 700 μm thickness parallel to a crystal face following the methods described in the reference⁽¹⁷⁾.

3. RESULTS AND DISCUSSION

3.1 OP-GaP THz characterization

The spectra obtained from the OP-GaP crystals are shown in figure 3. The individual spectra are normalized and offset for clarity. Each curve is labeled with the QPM period, the total length, and the average THz power obtained. Figure 3b and 3c show representative interferogram and the spectrum for $\Lambda = 4090 \mu\text{m}$ overlaid with the atmospheric transmission (in arbitrary units). It can be seen that the structure in the THz spectrum is due to the sharp water absorption lines.

The average THz power only takes into account the filters used to remove the pump light and the responsivity of the Golay cell; the attenuation due to atmospheric propagation was ignored. Thus, we can expect higher total power (and less structured spectra) with a nitrogen purged set-up.

We note that the measured center frequencies are consistently lower than the expected frequencies calculated from the Sellmeier equations. This is illustrated in figure 4, where the expected and measured THz frequencies are plotted vs the QPM period. Using this data, adjustments to the Sellmeier equations could be made to obtain a more accurate prediction of the QPM period required for a desired THz frequency. Alternatively, a simple exponential fit would give an *ad hoc* method for obtaining QPM periods.

3.2 Molecular crystal anisotropy

Figure 5 shows a representative plot for the change in transmission percentage as a function of sample orientation for sucrose crystal for the different THz frequencies. The peak position of the intensity plots as a function of angle is an indication of directionality of the different vibrational modes with respect to the crystal orientation. On the other hand, the height of the peaks is a measure of the anisotropy. A mode with a strong anisotropy is expected to exhibit rapid change with orientation.

3.3 Comparison of features using broadband and narrow band setups

In order to verify the results of our narrow band setup, here we compare the anisotropic data obtained using a traditional time domain THz setup with that obtained using the OP-GaP sources. Figure 6a shows the THz TDS data while 6b shows the plot generated from the narrow band sources. The plots show the change in absorption as a function of crystal orientation with respect to the THz polarization direction. As indicated by the color bar, a change towards red color indicates an increase in absorption while a change towards violet indicates a decrease in absorption. Each vertical bin in figure 5 b represents the signal generated by a single band. The name of each band indicates the upper limit of the THz frequency generated by that source. For example, the third source generates THz from 1.5 THz to 2THz and is denoted as 2 THz. The plots are vertically aligned to match the actual frequencies on the vertical axis. Red horizontal lines are added to figure 5 to highlight the corresponding region on the two plots which represents the same frequencies.

Comparing Figure 6a and 6b, we can see clear similarities in both plots. For example, from the broadband data we would expect an increase in strength of the mode between 1.5 THz and 2.0 THz as the crystal is rotated by 90°. The narrow band source in this frequency region (denoted by the name 2 THz) shows the expected behavior. Similar comparisons can be made for other frequency bands as well strongly indicating that the broadband spectra can be effectively reproduced using individual narrow band sources.

3.4 Identification of molecular crystals using narrow band technique

Next, we investigate the feasibility of identifying two different molecular crystals using narrow band technique. Here we choose sucrose and fructose as the model systems. Figure 7 shows comparison absorption spectra of the two crystals obtained using THz TDS. The red dotted lines show regions of the spectra that could be used to differentiate between the two. Between 1.0 THz and 1.5 THz, the two spectra show opposite polarity while the region between 3 and 3.5 THz shows same polarity. Figure 8 shows the comparison spectra generated by the narrow band setup for fructose and sucrose. Other regions of the spectra show a more complex behavior possibly due to overlap of modes happening in the same band.

3.5 Discussion and conclusion

This preliminary study demonstrates the feasibility of extending the ATM techniques to even narrow band sources. In the case of sucrose, similar features can be identified in both broadband and narrow band sources. On the other hand, it is clear that many sharp features are washed out in the narrow band plot due to the finite bandwidth (~0.5 THz) of individual

sources which is evident in comparing fructose and sucrose. In the future narrower sources may be produced by increasing the number of domains in the QPM crystals. Using Fabry-Perot filters may be another option.

Room temperature detection is another significant area to be developed. At present the sources have enough dynamic range to be detected using room temperature detector like a Golay cell. But in order to characterize high absorptive samples like proteins and molecular crystals the dynamic range needs to be increased by another 10–20 dB.

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Figure 1.

Illustrates the concept of quasi phase-matching for THz generation. The orientation of the crystal is flipped each $\frac{1}{2}$ period as indicated by the + and - signs. Frequencies within the pump pulse whose difference are phase matched by the crystal grow in intensity with crystal length.

Figure 2.
Experimental setup for anisotropic measurements using narrow band sources

Figure 3.

a) Normalized THz output spectra, offset for clarity. b) Representative interferogram recorded with Michelson interferometer c) Spectrum for $\Lambda = 4090 \mu\text{m}$ sample. Dashed line is the atmospheric absorption.

Figure 4.
Measured and calculated THz output frequency plotted vs. QPM period.

Figure 5.
 'Strength of Anisotropy' of a *c* cut sucrose crystal for different bands

Figure 6.
Anisotropic response of an *a* cut sucrose crystal. 6a shows THz TDS while 6b was

Figure 7.
Anisotropic response of fructose (left) and sucrose (right) using THz TDS

Figure 8.

Anisotropic response of fructose (left) and sucrose (right) using narrow band sources