Narrow Spectral Features of Cellulose Nanocomposites Characterized by a Frequency Domain Terahertz Spectroscopy

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***Abstract*—A frequency domain terahertz (THz) spectroscopy system has been developed to operate at room temperature from 570 – 630 GHz for cellulose nanocomposites characterization. The system has been demonstrated to have measurement accuracy of better than 2%. Cellulose nanocomposites have been measured using this system, and the results show narrow THz spectral features that can be used for characterization and identification of these samples. Cellulose sample with magnetic nanoparticles shows enhanced THz transmission that may find applications in THz chemical and biological sensing.**

I. INTRODUCTION AND BACKGROUND

In recent years, terahertz (THz) spectroscopy has attracted much interest due to its applications in material characterization, chemical sensing and DNA identification [1, 2]. Cellulose nanofiber and nanocomposite materials have also emerged to suggest enormous potential for many applications due to their renewability, ubiquitousness, cost-effectiveness, and unique properties. Their promising applications include a range of areas from reinforced nanomaterials, adhesives, optical paper, flexible displays, tissue regeneration, and biosensors [3]. THz techniques provide an alternative means to characterize cellulose materials. However, due to the lack of continuous wave THz sources and broadband detectors, most of the medical/chemical/biology research using THz techniques have been focused on time domain with pulsed system (e.g. TeraView: TPS spectra 3000) [4], [5]. Continuous wave (CW) THz systems have much better spectra resolution (better than 1 MHz) as compared to a pulsed system, thus providing unique opportunity to detect a specific “fingerprints” (e.g. resonant peaks or absorption spikes) for a sample. In addition, CW systems have higher average beam power, faster data acquisition and room-temperature operation, leading to system simplicity and low cost [6].

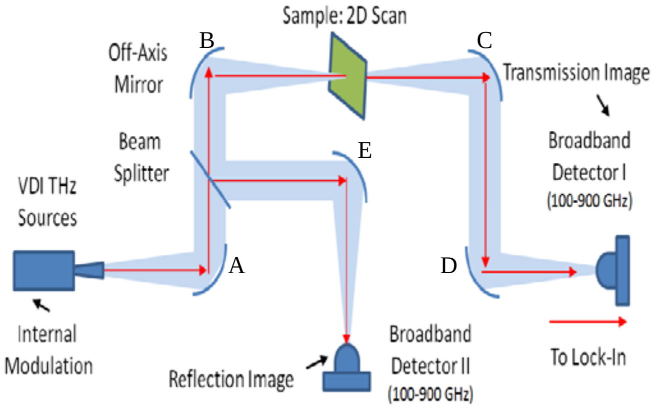
II. FREQUENCY DOMAIN THZ SPECTROSCOPY

The frequency domain THz spectroscopy system is shown in Fig. 1 (a). The THz radiation is provided by A VDI (Virginia Diodes, Inc.) frequency extension module (FEM, or multiplier chain) which converts microwave (10-20 GHz) emission from a synthesizer to THz range covers the bands of 570-630 GHz. The THz energy is coupled to a detector (detector I) through four off-axis parabolic mirrors A-D (see Fig. 1). In between the mirror B and C, the sample under test is placed at the focal point of the THz beam, and the sample itself is mounted on a XY scanning stage controlled by a computer. The system is designed to have a Gaussian beam waist of sub-mm (spatial resolution) at the sample. A beam splitter is inserted in the beam path between the mirrors A and B. The reflected beam retraces its incident path and is split by the beam splitter and focused by the mirror E into another detector (detector II) for reflection measurement. In this study, we focused our work on transmission measurement.

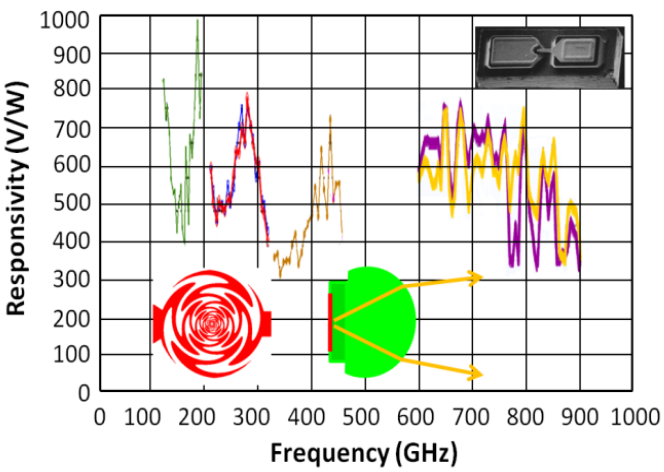
The THz detector was designed on the basis of Schottky diodes and sinuous antenna for ultra-broadband operation in the frequency range of 0.1 – 1 THz [7]. The detector was designed using quasi-optical configuration, and the responsivity of the detector was measured to range from 300-1000 V/W over the frequency range of 100-900 GHz, as shown in Fig. 1 (b). The estimated noise equivalent power (NEP) level is 5-10 $pW/Hz^{1/2}$. During the testing, the THz source is internally modulated at a frequency of 1 kHz, and the chopped DC signals from both detectors are sent to lock-in amplifiers for processing. Data acquisition and processing software along with controlling program will be written using National Instruments LabVIEW.

III. SYSTEM CALIBRATION

The frequency domain THz spectroscopy was first calibrated prior to cellulose sample characterization. To further improve the measurement repeatability and



(a)

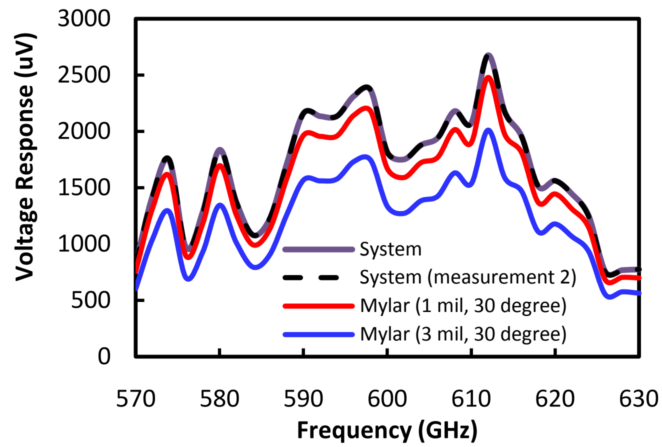


(b)

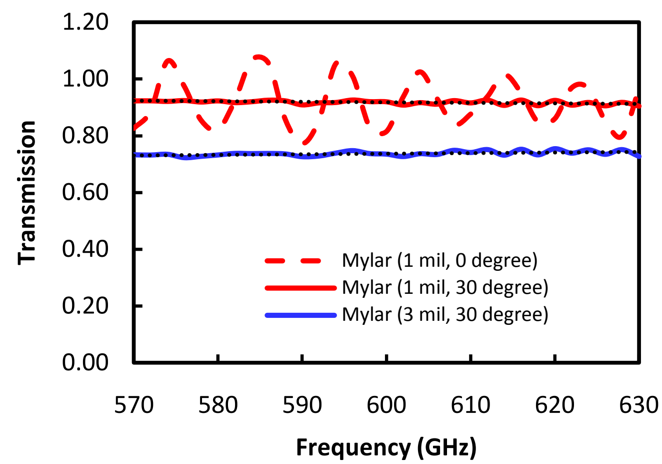
Fig. 1. Solid state frequency domain THz spectroscopy based on quasi-optical ultra-broadband Schottky diode detector: (a) system diagram, and (b) responsivity measurement of the detector over the frequency range of 0.1-1 THz.

accuracy, the frequency scan will be controlled by a computer, and the voltage response from the detector will be taken by averaging each frequency point for 5 seconds. The sample holder was slightly tilted to reduce the standing wave effects in the system. Shown in Fig. 2 (a) is the raw data for the system without sample, and two Mylar thin films with 1-mil, and 2-mil thickness. Fig. 2 (b) shows the transmission of the Mylar films compared to the simulation results, demonstrating a system measurement accuracy of ~ 2% at this time.

Fig. 2 (c) shows the measurement results of two THz mesh filters. The first mesh filter has a center frequency of 599 GHz and 3-dB band width of 10%, and the second achieves maximum transmission at 612 GHz with 11% bandwidth. These measurements demonstrated the system has good repeatability and accuracy, which is ready for cellulose sample characterization.



(a)



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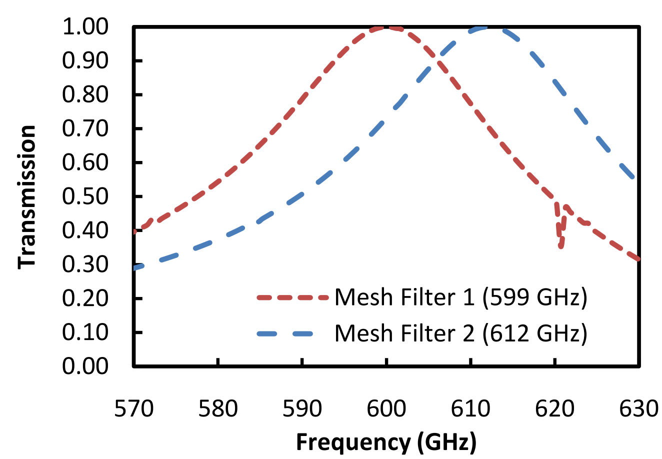

(c)

Fig. 2. System calibration: (a) voltage response for system without sample, 1-mil and 3-mil Mylar thin films, (b) transmission of Mylar thin films (solid lines) compared to simulation results (black dotted lines). Strong standing waves are observed for a measurement of 1-mil Mylar film perpendicular to the THz beam, and (c) measurement results for two THz mesh filters based on cross-slot arrays. The first filter has center frequency of 599 GHz and a 3-dB bandwidth of 10%, and the second achieves transmission maximum at 612 GHz, with bandwidth of 11%.

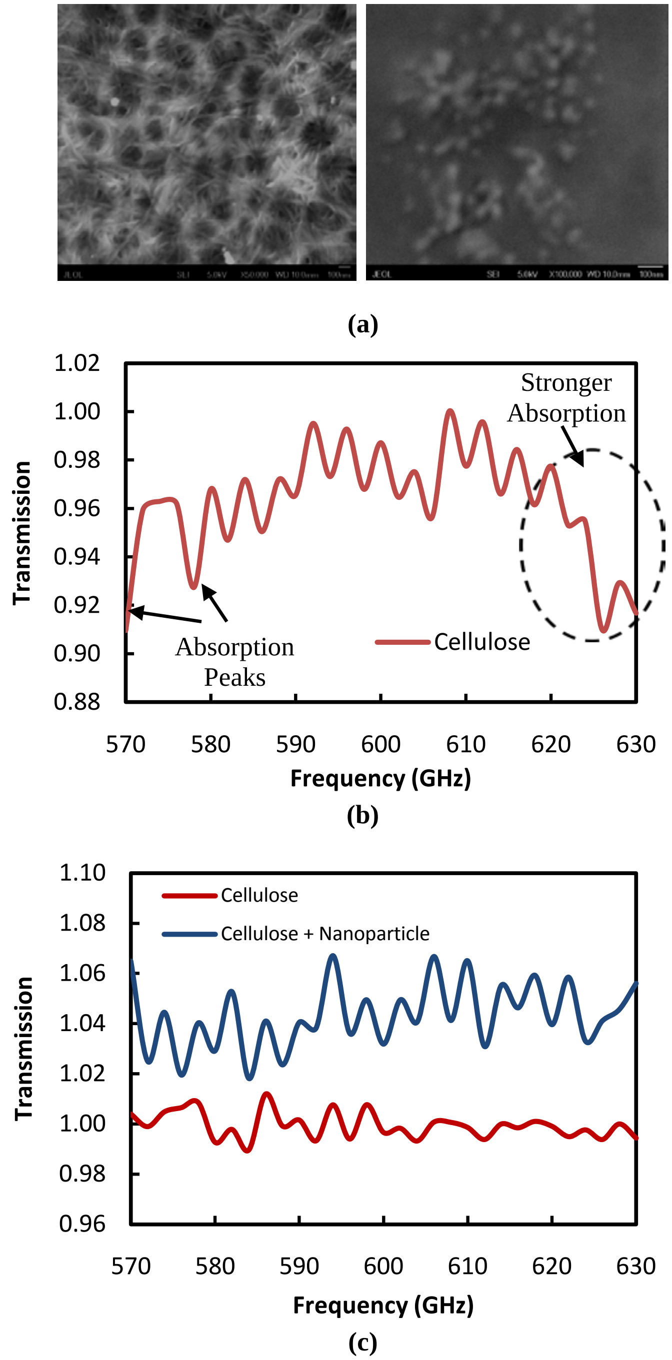

Fig. 3. Measurement results: (a) SEM pictures of cellulose sample (Left) and cellulose with nanoparticles (Right), (b) THz transmission spectrum of cellulose sample, narrow absorption features have been observed, and (c) THz transmission comparison of cellulose sample and cellulose with magnetic nanoparticles. Enhanced THz transmission is observed for cellulose with nanoparticles sample.

IV. Measurement Results

The developed system has been applied to characterize cellulose samples shown in Fig. 3 (a). The samples under test are prepared by dropping and drying liquids on 3-mil Mylar thin films, and the measured data is normalized to the voltage response of the blank Mylar thin film measured using this system for THz transmission. Shown in Fig. 3 (b) is the THz spectrum of one cellulose sample in the frequency range of 570-630 GHz. Stronger absorption is observed at 620-630 GHz, 570 GHz and 580 GHz. The absorption peaks show narrow frequency bandwidths less than 10 GHz. These spectral features are difficult to be discovered using conventional time-domain THz techniques, and could be used for characterization and identification of cellulose samples.

The THz spectrum of cellulose sample with nanoparticles was also measured and compared to cellulose sample under same preparation conditions, as shown in Fig. 3 (b). The sample with nanoparticles shows higher transmission than sample without. In addition, the transmission of magnetic nanoparticles sample is larger than one over the entire frequency range of 570 – 630 GHz, indicating a field enhancement. This property may find applications in THz chemical and biological sensing.

V. Conclusion

In this paper, a frequency domain solid state THz spectroscopy system operating from 570-630 GHz was developed, and the system repeatability and accuracy have been demonstrated by measuring Mylar thin films and THz mesh filters. The system has been successfully applied to cellulose samples. Initial measurement shows that cellulose sample has narrow spectral features in the THz region, which could be used for sample characterization and identification. Cellulose sample with magnetic nanoparticles shows enhanced THz transmission that may find applications in THz chemical and biological sensing.

VI. Acknowledgement

This work is supported by the Advanced Diagnostics and Therapeutics Initiative and the Center for Nanoscience and Technology (NDnano) at the University of Notre Dame. We thank Dr. H.-C. Chang, Dr. P. Bohn and Dr. D. Jena at the University of Notre Dame for valuable discussion.

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