

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 06-01-2020		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1-Aug-2015 - 31-Aug-2019	
4. TITLE AND SUBTITLE Final Report: Modeling, Fabrication and Characterization of Self-Aligned 2D and 3D Nanowire Arrays for Terahertz Operation			5a. CONTRACT NUMBER W911NF-15-1-0297		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611102		
6. AUTHORS			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Texas at San Antonio One UTSA Circle San Antonio, TX 78249 -1644			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 66703-EL-H.21		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Arturo Ayon
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 210-458-6564

RPPR Final Report

as of 28-Jan-2020

Agency Code:

Proposal Number: 66703ELH

Agreement Number: W911NF-15-1-0297

INVESTIGATOR(S):

Name: Arturo A. Ayon aayon@utsa
Email: ARTURO.AYON@UTSA.EDU
Phone Number: 2104586564
Principal: Y

Organization: **University of Texas at San Antonio**

Address: One UTSA Circle, San Antonio, TX 782491644

Country: USA

DUNS Number: 800189185

EIN: 741717115

Report Date: 30-Nov-2019

Date Received: 06-Jan-2020

Final Report for Period Beginning 01-Aug-2015 and Ending 31-Aug-2019

Title: Modeling, Fabrication and Characterization of Self-Aligned 2D and 3D Nanowire Arrays for Terahertz Operation

Begin Performance Period: 01-Aug-2015

End Performance Period: 31-Aug-2019

Report Term: 0-Other

Submitted By: Arturo Ayon

Email: ARTURO.AYON@UTSA.EDU

Phone: (210) 458-6564

Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 1

STEM Participants: 3

Major Goals: Fabricate and characterize passive and active devices for Terahertz applications

Accomplishments: In terms of accomplishments the following activities were performed:

- (1.) Computational modeling efforts of passive structures based on (i.) metallic parallel nanowire arrays, and (ii.) Hexagonal as well as (iii.) X-shaped metamaterials were completed, presented at prestigious international conferences and published in both archival journals and a Ph.D. thesis.
- (2.) Dr. Dany Shreiber from the Army Research Laboratory actively participated in the program and nanostructures were characterized for their utilization in reconfigurable devices employing UV excitation,
- (3.) Dr. John Cetnar from the Air Force Research Laboratory also actively participated in the characterization of the temperature stability of nanostructures in the Terahertz regime. Additionally, Clarissa Vazquez-Colon who participated as a Ph.D. candidate in this program and graduated in August, 2019, will join the AFRL under the supervision of Dr. Cetnar on January 27, 2020.

Training Opportunities: During the period the following Hispanic graduate students participated in this project:

Clarissa Vazquez-Colon (Hispanic, female U.S. Citizen, graduated in August, 2019),

Adrian Zepeda (Hispanic, male Ph.D. student, scheduled to graduate in May, 2020).

Additionally, a third student joined the program in August 2017, namely, Janeth Garcia (Hispanic, female student, scheduled to graduate in May, 2021), however the third student is being supported with internal funds.

Results Dissemination: To date the dissemination effort includes 3 manuscripts,

11 contributions in 8 international conferences, as well as

4 seminars presented at universities in Mexico to explore collaboration and identify

prospective graduate students

RPPR Final Report

as of 28-Jan-2020

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: (1.) Dr. Dany Shreiber from the Army Research Laboratory actively participated in the program and nanostructures were characterized for their utilization in reconfigurable devices employing UV excitation,

(2.) Dr. John Cetnar from the Air Force Research Laboratory also actively participated in the characterization of the temperature stability of nanostructures in the Terahertz regime.

(3.) Additionally, Clarissa Vazquez-Colon who participated as a Ph.D. candidate in this program and graduated in August, 2019, will join the AFRL under the supervision of Dr. Cetnar on January 27, 2020.

PARTICIPANTS:

Participant Type: Graduate Student (research assistant)

Participant: Janeth Alexandra García-Monge

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Adrian Zepeda-Galvéz

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Clarissa D. Vazquez-Colon

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Other Professional

Participant: Daniel Shreiber

Person Months Worked: 1.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Other Professional

Participant: John Cetnar

Person Months Worked: 1.00

Funding Support:

RPPR Final Report
as of 28-Jan-2020

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: PD/PI

Participant: Arturo A Ayon

Person Months Worked: 1.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

ARTICLES:

Publication Type: Journal Article

Peer Reviewed: Y

Publication Status: 1-Published

Journal: J. of Inorganic Non-metallic Materials

Publication Identifier Type: DOI

Publication Identifier: <https://doi.org/10.4236/ojinm.2019.91001>

Volume: 1

Issue: 1

First Page #: 1

Date Submitted: 1/6/20 12:00AM

Date Published: 1/31/19 8:51PM

Publication Location:

Article Title: Terahertz Modulation of Hexagonal-shaped Metamaterials employing ZnO Quantum Dots

Authors: Clarissa D. Vázquez-Colón, Alvaro Flores-Pacheco, Janeth Alexandra García-Monge, Juan Adrián Zepeda

Keywords: Terahertz, Metamaterials, Quantum Dots, Terahertz Spectroscopy, Modulation

Abstract: The utilization of UV excitation to verify the terahertz (THz) wave modulation of hexagonal-shaped metamaterial (MM) arrays coated with synthesized photoluminescent, down-shifting ZnO quantum dots (QDs) of two different radius sizes, namely, 3.00 nm (pH 10) and 2.12 nm (pH 12), respectively is reported. In order to characterize the behavior of the MM before and after deployment of the ZnO QDs, THz time domain spectroscopy in transmission mode was employed. Upon exposure to UV excitation, the collected amplitude modulation values were 9.21% for the pH 12 and 4.55% for the pH 10 ZnO QDs, respectively. It is anticipated that the ability to actively tune the performance of otherwise passive structures will promote the proliferation of THz signal modulation devices in the near future.

Distribution Statement: 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support: Y

CONFERENCE PAPERS:

Publication Type: Conference Paper or Presentation

Publication Status: 0-Other

Conference Name: XXV International Materials Research Congress

Date Received: 04-Oct-2018

Conference Date: 15-Aug-2016

Date Published: 15-Aug-2016

Conference Location: Cancun, Mexico

Paper Title: COMPUTATIONAL MODELING OF 2D METAL ARRAY AT TERAHERTZ FREQUENCIES

Authors: Clarissa Vazquez, Arturo Ayon

Acknowledged Federal Support: Y

RPPR Final Report
as of 28-Jan-2020

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: Micro and Nanoengineering
Date Received: 15-Sep-2017 Conference Date: 19-Sep-2016 Date Published: 19-Sep-2016
Conference Location: Vienna, Austria
Paper Title: Computational modeling of a metamaterial made of 2D metal arrays in the terahertz regime
Authors: Clarissa D. Vázquez-Colón, Arturo A. Ayón
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 0-Other
Conference Name: Design, Test, intergration and Packaging of MEMS and NOEMS
Date Received: 15-Sep-2017 Conference Date: 30-May-2016 Date Published: 30-May-2016
Conference Location: Bordeaux, France
Paper Title: Reconfigurable Behavior of CdTe Quantum Dots at Terahertz Frequencies employing UV excitation
Authors: Clarissa D. Vázquez-Colón, Juan Adrián Zepeda-Galvez, Daniel Shreiber, Arturo A. Ayón
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 0-Other
Conference Name: Micro and Nanoengineering 2017
Date Received: 15-Sep-2017 Conference Date: 18-Sep-2017 Date Published: 18-Sep-2017
Conference Location: Braga, Portugal
Paper Title: Terahertz Characterization of CdTe Quantum Dots under UV Excitation
Authors: Clarissa D. Vázquez-Colón, Juan Adrián Zepeda-Galvez, Daniel Shreiber, Arturo A. Ayón
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 3-Accepted
Conference Name: 5th Nano Today Conference
Date Received: 15-Sep-2017 Conference Date: 06-Dec-2017 Date Published: 06-Dec-2017
Conference Location: Hawaii, USA
Paper Title: Characterization of CdTe quantum dots for terahertz applications
Authors: Clarissa D. Vázquez-Colón, Juan Adrián Zepeda-Galvez, Daniel Shreiber, Arturo Ayón
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: Micro and Nanoengineering 2016
Date Received: 15-Sep-2017 Conference Date: 19-Sep-2016 Date Published: 19-Sep-2016
Conference Location: Vienna, Austria
Paper Title: Characterization of CdTe quantum dots for THz applications
Authors: Juan Adrian Zepeda-Galvez, Clarissa D. Vazquez-Colon, Arturo A. Ayon
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 0-Other
Conference Name: 42nd International Conf. on Infrared, Millimeter and Terahertz Waves
Date Received: 15-Sep-2017 Conference Date: 27-Aug-2017 Date Published: 27-Aug-2017
Conference Location: Cancun, Mexico
Paper Title: EFFECT OF UV LIGHT ON SYSTEMATIC ERRORS IN THZ-TDS SPECTROSCOPY
Authors: Juan Adrián Zepeda-Galvez, Clarissa D. Vázquez-Colón, Daniel Shreiber, Arturo Ayón
Acknowledged Federal Support: **Y**

RPPR Final Report
as of 28-Jan-2020

Publication Type: Conference Paper or Presentation **Publication Status:** 2-Awaiting Publication
Conference Name: Micro and Nanoengineering 2017
Date Received: 15-Sep-2017 Conference Date: 18-Sep-2017 Date Published: 18-Sep-2017
Conference Location: Braga, Portugal
Paper Title: UV-TUNABLE TERAHERTZ CHARACTERIZATION OF CARBON QUANTUM DOTS
Authors: Juan Adrián Zepeda-Galvez, Clarissa D. Vázquez-Colón, Daniel Shreiber, Arturo Ayón
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 0-Other
Conference Name: 5th Nano Today Conference
Date Received: 04-Oct-2018 Conference Date: 06-Dec-2017 Date Published: 06-Dec-2017
Conference Location: Hawaii, USA
Paper Title: Determination of the Optical Properties under UV excitation of Carbon Quantum Dots in the Terahertz Regime
Authors: Juan Adrian Zepeda-Galvez, Clarissa D. Vazquez-Colon, Daniel Shreiber, Arturo A. Ayon
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 0-Other
Conference Name: Micro and Nanoengineering 2018
Date Received: 04-Oct-2018 Conference Date: 24-Sep-2018 Date Published: 27-Sep-2018
Conference Location: Copenhagen, Denmark
Paper Title: Stability of Carbon Quantum Dots in the THz regime under Temperature Variations
Authors: Juan Adrian Zepeda, Clarissa D. Vazquez-Colon, John Cetnar and Arturo Ayon,
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 0-Other
Conference Name: Micro and Nanoengineering 2018
Date Received: 04-Oct-2018 Conference Date: 24-Sep-2018 Date Published: 27-Sep-2018
Conference Location: Copenhagen, Denmark
Paper Title: Reconfigurable Metamaterials at THz Frequencies using Quantum Dots,
Authors: Clarissa D. Vazquez-Colon, Juan A. Zepeda-Galvez, Geoffrey Xiao, Daniel Shreiber and Arturo A. Ayon
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: Design, Test, Integration and Packaging of MEMS (DTIP) 2019
Date Received: 06-Jan-2020 Conference Date: 13-May-2019 Date Published: 16-May-2019
Conference Location: Paris, France
Paper Title: Computational Modeling of 3D Metamaterial Wire Arrays for Terahertz Operation
Authors: Juan Adrian Zepeda-Galvez, Clarissa D. Vazquez-Colon, Daniel Shreiber, Arturo A. Ayon
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: Design, Test, Integration and Packaging of MEMS (DTIP) 2019
Date Received: 06-Jan-2020 Conference Date: 13-May-2019 Date Published: 16-May-2019
Conference Location: Paris, France
Paper Title: Reconfigurable X-shaped THz Metamaterials employing Quantum Dots
Authors: Clarissa D. Vazquez-Colon, Juan A. Zepeda-Galvez, Roberto Guzman, Arturo A. Ayon
Acknowledged Federal Support: **Y**

DISSERTATIONS:

RPPR Final Report
as of 28-Jan-2020

Publication Type: Thesis or Dissertation

Institution: University of Texas at San Antonio

Date Received: 06-Jan-2020

Completion Date: 8/31/19 7:39PM

Title: TERAHERTZ MODULATION DEVICES EMPLOYING ZNO QUANTUM DOTS AND HEXAGONAL SHAPED METAMATERIALS

Authors: Clarissa Vazquez-Colon

Acknowledged Federal Support: Y

**TERAHERTZ MODULATION DEVICES EMPLOYING ZNO QUANTUM DOTS AND
HEXAGONAL SHAPED METAMATERIALS**

by

CLARISSA D. VAZQUEZ COLON, M.Sc.

DISSERTATION

Presented to the Graduate Faculty of
The University of Texas at San Antonio
In Partial Fulfillment
Of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY IN PHYSICS

COMMITTEE MEMBERS:

Arturo A. Ayon, Ph.D., Chair

Lorenzo Brancaleon, Ph.D.

Nicolas Large, Ph.D.

Carlos Monton, Ph.D.

Daniel Shreiber, Ph.D.

THE UNIVERSITY OF TEXAS AT SAN ANTONIO
College of Sciences
Department of Physics and Astronomy
August 2019

DEDICATION

This thesis is dedicated to my beloved great-grandmother Catalina. Thank you for your wisdom and comforting words. To my mother Mariel to always encouraging to follow my dreams and supporting me. To my family for their support through these years. Thank you for inspiring me.

ACKNOWLEDGEMENTS

I would like to thank professor Arturo Ayón for his trust, support and guidance. Thank you for sharing your professional and personal experience with me and for becoming something of a father figure to me. I would also like to thank my committee members for their help and support during these years. Thank you to my Army Research Lab collaborator and my Air Force Research Lab collaborators. Special thank you to my UTSA MEMS Lab research collaborators for sharing knowledge and ideas with me. In particular, Janeth García, Adrián Zepeda, Rosendo Lopez for their friendship and support during these years. I would also like to acknowledge my teachers and professors up to now for their guidance and support. The journey to reach this life milestone has not been easy. I am very grateful for the people that God has put on my path. I would like to thank God, family and friends. Especially, to Abuela Catalina for your trust, support and love. Thank you for helping me to become the woman I am, I will remember and love you for the rest of my life and I wish you were here with me. Also, thank you mom, for being there for me when I needed you the most, for being my guide and example and mostly for pushing me up to follow my dreams. Carla thank you teaching me the responsibility of being a sister, I hope I have been a good example for you. Thank you, Abuela Monín, Guingo and Tití Clary for taking care of me and support me and mom on these journeys, I would not be here if it wasn't for you all. Norma thank you for creating the most amazing man in this world, I couldn't find someone better than him. Thank you to the love of my life, Roberto for all the help and support. I need to give a special thanks to my professor for my education, support and trust. To my friends who more than friends are family for their support and help. Thank you to all the people that in a way or the other contributed to who I am to today.

Also, I would like to thank the U.S. Army Research Office (Grant W911NF-13-1-0110), Air Force Office of Sponsored Research (AFOSR) (Grant W911NF-15-1-0297) and the Physics and Astronomy Department at the University of Texas at San Antonio for the financial support.

This Masters Thesis/Recital Document or Doctoral Dissertation was produced in accordance with guidelines which permit the inclusion as part of the Masters Thesis/Recital Document or

Doctoral Dissertation the text of an original paper, or papers, submitted for publication. The Masters Thesis/Recital Document or Doctoral Dissertation must still conform to all other requirements explained in the Guide for the Preparation of a Masters Thesis/Recital Document or Doctoral Dissertation at The University of Texas at San Antonio. It must include a comprehensive abstract, a full introduction and literature review, and a final overall conclusion. Additional material (procedural and design data as well as descriptions of equipment) must be provided in sufficient detail to allow a clear and precise judgment to be made of the importance and originality of the research reported.

It is acceptable for this Masters Thesis/Recital Document or Doctoral Dissertation to include as chapters authentic copies of papers already published, provided these meet type size, margin, and legibility requirements. In such cases, connecting texts, which provide logical bridges between different manuscripts, are mandatory. Where the student is not the sole author of a manuscript, the student is required to make an explicit statement in the introductory material to that manuscript describing the students contribution to the work and acknowledging the contribution of the other author(s). The signatures of the Supervising Committee which precede all other material in the Masters Thesis/Recital Document or Doctoral Dissertation attest to the accuracy of this statement.

August 2019

TERAHERTZ MODULATION DEVICES EMPLOYING ZNO QUANTUM DOTS AND HEXAGONAL SHAPED METAMATERIALS

Clarissa D. Vazquez Colon, Ph.D.
The University of Texas at San Antonio, 2019

Supervising Professor: Arturo A. Ayon, Ph.D.

Materials characterization in the terahertz (THz) regime has been of interest for several years due to the relatively sparse availability of THz generation and detection devices. The development of devices in this region of the electromagnetic spectrum could lead to groundbreaking applications in security, communications, and healthcare, among others. Additionally, THz radiation is non-ionizing, thus human exposure to THz signals is not considered to be harmful. Nowadays technology is mainly developed in the microwave and infrared regions of the electromagnetic spectrum, leaving a gap in the THz region (~ 0.1 THz – 1 THz) in which the performance of typical materials is relatively poor. For this reason, the use of metamaterials (MM) in this region has become a recent topic of research interest. MMs are man-made metallic or polymeric periodic structures, typically in the micrometer scale, capable of exhibiting tailored electromagnetic properties. In general, MMs can be fabricated employing conventional fabrication schemes and, for the same reason, tend to be considered rather affordable. However, the final MM product usually comprises passive devices exhibiting fixed electromagnetic properties. The demonstration of reconfigurable devices that can be actively tuned would benefit the prospective utilization of THz technology in a variety of applications. This behavior could be achieved by the incorporation of semiconducting materials and the utilization of UV-tunable quantum dots. To this end, we propose the study the performance of MM arrays at THz frequencies. The effort will also include the characterization of the electromagnetic properties of ZnO colloidal quantum dots (QDs) of two different sizes pH12 (2.12 nm) and pH10 (3.00 nm) using THz Time Domain spectroscopy (THz-TDS) with and without UV excitation for the purposes of exploring possible pathways towards reconfigurable behavior.

TABLE OF CONTENTS

Acknowledgements	iii
Abstract	v
List of Tables	viii
List of Figures	ix
Chapter 1: Introduction	1
1.1 Literature review	2
1.1.1 Characterization of Nanoscale Systems at THz Frequencies	3
1.1.2 Electromagnetic Spectrum and THz Regime	4
1.1.3 THz Reconfigurable metamaterials	6
Chapter 2: Methodology	9
2.1 THz Time Domain Spectroscopy	9
2.1.1 THz Generation	11
2.1.2 Detection of THz Pulses	13
2.1.3 Data collection and analysis	14
2.2 Characterization of materials using THz-TDS	17
2.2.1 Solid samples	17
Chapter 3: ZnO Quantum dots terahertz characterization	19
3.1 ZnO QDs Synthesis	19
3.2 ZnO QD Absorption and Emission Characterization	21
3.3 ZnO QD THz Characterization	24
3.4 Conclusions	30

Chapter 4: THz Modulation of a Hexagonal Metamaterial using ZnO Quantum Dots .	31
4.1 Introduction	31
4.2 Methods	32
4.2.1 Metamaterial fabrication	32
4.2.2 Metamaterial THz Characterization	33
4.3 Conclusions	38
Chapter 5: Ohmic contact formation in III-V semiconductor materials	40
5.1 Introduction	40
5.1.1 Surface contacts	42
5.1.2 Indented contacts	43
5.1.3 Scribed contacts	44
5.1.4 Tunneling model	45
5.2 Conclusions	47
Chapter 6: Concluding Remarks	48
Bibliography	51
Vita	

LIST OF TABLES

Table 3.1	ZnO estimated bandgap and sizes values	24
Table 4.1	Hexagonal-shaped MMs results summary	38
Table 5.1	Contact resistance dependence on annealing temperature	44
Table 5.2	Contact resistance values on samples with diagonally-scribed lines without thermal treatment.	44

LIST OF FIGURES

Figure 1.1	All possible properties of isotropic materials in the $\varepsilon - \mu$ domain.	7
Figure 2.1	EM spectrum.	10
Figure 2.2	THz-TDS beam diagram.	10
Figure 2.3	Top and side view of the photoconductive antenna.	12
Figure 2.4	Time spectra of air measured with THz-TDS	12
Figure 2.5	GaAs coplanar transmission line detection antenna.	14
Figure 2.6	Sketch of the electric field transmitted through a slab of material with refractive index n_s	15
Figure 2.7	The typical THz-TDs setup for measuring solid samples.	18
Figure 2.8	THz-TDS beam diagram including the UV lamp to investigate the reconfigurability of certain samples studied in this work.	18
Figure 3.1	Synthesis procedure for ZnO QDs.	20
Figure 3.2	(a.) PDMS membrane under UV excitation, (b.) ZnO QDs embedded in PDMS under UV excitation.	21
Figure 3.3	Collected absorbance spectra of the ZnO QDs colloidal solutions synthesized with pH values of 10 and 12 (solid lines), respectively. The dotted lines show the photoluminescence spectra of the ZnO quantum dots colloidal solutions.	22
Figure 3.4	ZnO QDs pH10 (a.) and ZnO pH12 (b.) estimated bandgap sizes calculation.	23
Figure 3.5	ZnO QDs TEM images.	24
Figure 3.6	THz-TDS system in transmission mode	25
Figure 3.7	Extracted real part of the effective refractive index at THz frequencies of the media with the incorporated ZnO QDs without UV excitation.	27

Figure 3.8	Extracted refractive index of ZnO pH12 QDs embedded in PDMS in the THz regime with and without excitation of UV lamps with wavelengths of 302 nm and 365 nm.	27
Figure 3.9	Extracted refractive index of ZnO pH10 QDs embedded in PDMS in the THz regime with and without excitation of UV lamps with wavelengths of 302 nm and 365 nm.	28
Figure 3.10	Extracted refractive index of ZnO pH12 QDs embedded in PDMS in the THz regime with and without excitation of a UV laser with a wavelength of 400 nm.	28
Figure 3.11	Extracted refractive index of ZnO pH10 QDs embedded in PDMS in the THz regime with and without excitation of a UV laser with a wavelength of 400 nm.	29
Figure 4.1	Hexagonal metamaterials used in this study (MM1).	33
Figure 4.2	Hexagonal metamaterials with smaller metallic inclusions compare to Figure 4.1 used in this study(MM2).	33
Figure 4.3	Hexagonal metamaterials used in this study (MM1) before and after deploying the ZnO QDs.	34
Figure 4.4	Hexagonal metamaterials used in this study (MM1) with ZnO pH12 and pH10 before and after being exposed to UV lamps with wavelengths of 302 nm and 365 nm.	35
Figure 4.5	Hexagonal metamaterials used in this study (MM1) with ZnO pH12 and pH10 before and after being exposed to a UV laser with a wavelength of 400 nm.	35
Figure 4.6	Resonant frequency of hexagonal-shaped MM2 before and after deploying the ZnO pH12 and ZnO pH12 QDs.	36

Figure 4.7	Hexagonal metamaterials used in this study (MM2) with ZnO pH12 and pH10 before and after being exposed to UV lamps with wavelengths of 302 nm and 365 nm.	36
Figure 4.8	Hexagonal metamaterials used in this study (MM2) with ZnO pH12 and pH10 before and after being exposed to a UV laser with a wavelength of 400 nm.	37
Figure 5.1	HEMT structure grown by MOCVD.	41
Figure 5.2	Normal contact sketch. Filled circles denote indium contacts	42
Figure 5.3	Sample with indentations filled with indium as contacts. Filled circles denote indium contacts. Open circles denote indentations in the sample. . .	43
Figure 5.4	Sample with diagonally scribed lines filled with indium as contacts.	44
Figure 5.5	Depth of the scribed line employing a high-resolution laser microscope. . .	45
Figure 5.6	Depth of the scribed line employing a Zygo white light interferometer. . .	45
Figure 5.7	Temperature dependent measurement for the diagonally scribed sample. The smaller temperature dependence of the contact resistance compared to that of the sheet resistance indicates the presence of tunneling effects. . . .	46
Figure 5.8	Distribution of the electron density in the AlGaIn/GaN 2DEG.	46

CHAPTER 1: INTRODUCTION

Manipulation and control of the electromagnetic spectrum is the foundation of most of our society's technological advances. Studies focused on the electromagnetic spectrum started in 1800 with William Herschel by discovering what we now call the infrared region of the spectrum. He accomplished this by studying different colors of light with a thermometer. Inspired by Herschel's experiments, Johann Wilhelm Ritter discovered ultraviolet light in 1801. Subsequently, in 1865, James Clerk Maxwell made predictions regarding the existence of light beyond the infrared light or what we now refer to as electromagnetic waves and these predictions were experimentally confirmed in 1887 by the German scientist Heinrich Hertz. This was followed by the discovery of X-rays in 1895 by Wilhelm Conrad Rontgen and gamma-rays in 1900 by Paul Villard.

The electromagnetic spectrum has been divided and categorized by the phenomena and technological applications associated with different frequencies of said spectrum. At frequencies extending to the Gigahertz regime and even at the threshold of Terahertz frequencies we find most electronic devices, whereas at higher frequencies we find electronic transitions of molecules and atoms. Between these two regions, we have what the scope of this study is, namely, the THz region. Thus, the THz regime is the region between the microwave and the infrared bands, extending from approximately 0.1 THz (100 GHz) up to 10 THz [1]. 1THz corresponds to $300\mu\text{m}$ in wavelength and a photon energy of 4.1 meV [2]. The energies covering the THz gap are less energetic than the electronic state transitions of most atoms and molecules. For this reason, electromagnetic wave emission at these frequencies is considered nonionizing and suitable for applications involving human exposure [3]. This technology has opened the possibility to many applications in the pharmaceutical [4], medical [5–7], astronomical [8], textile [9], communication [10, 11] and security industries [12–15].

Fabricating devices that operate at THz frequencies has traditionally been challenging. This difficulty originates in the limitation of the frequency response of semiconducting and photonic

materials. Difficulties for the generation, detection and manipulation of THz frequencies could be overcome with the combination of both electronic and photonic regime properties [16].

1.1 Literature review

Development of THz tunable devices has been demonstrated by electronic, optical, thermal, magnetic and photoelectric [17, 18]. Control of one or more physical parameter (amplitude, phase, among others) of the carrier signal had been achieved with the use and development of different materials such as: photonic crystals, metamaterial structures, high electron mobility transistors (HEMTs) and graphene [18]. In this work we present the utilization of THz metamaterial modulation.

Metamaterials are engineered materials that exhibit specific electromagnetic properties not found in natural materials [19]. In fact, MMs are fabricated to control their magnetic or electronic response or both, and their performance at THz frequencies is of interest because of the paucity of natural materials exhibiting suitable behavior at this regime. MMs are mostly 2D periodic structures on a flat surface with size and periodicity much smaller than the wavelengths used to determine their complex electric permittivity and magnetic permeability. At THz frequencies the most commonly employed MMs are those based on Split-Ring-Resonators (SRRs), with dimensions on the orders of microns, therefore making them compatible with standard microfabrication processes. Presently, the demonstration of 3D THz metamaterials faces major challenges in terms of fabrication because it is difficult to obtain out of plane resonators with commonly used microfabrication techniques. However, due to increases of metal losses and kinetic inductance, the requirements of metamaterials at THz frequencies are slightly different from MMs with applications in the microwave regime. In terms of substrates, high resistivity silicon is one of the most commonly employed materials for THz metamaterials, providing mechanical support and introducing electromagnetic functionalities.

The characterization in the THz regime can be performed by employing Fourier transform infrared spectroscopy (FTIR) and terahertz time-domain spectroscopy (THz-TDS). However, the

former only provides intensity information, while THz-TDS provides a time domain waveform which can be manipulated to obtain spectral amplitude and phase. Additionally, the THz-TDS technique provides more measurement versatility because it can be performed in transmission or reflection mode, for the same reason, it is the most commonly used technique for THz metamaterials characterization. With this technique the THz amplitude and phase obtained are used to calculate the effective permittivity and permeability of the metamaterials.

Nonetheless, in spite of the progress made to date, one of the major challenges in the development and demonstration of THz circuitry is the ability to fabricate reconfigurable devices. One of the proposed methods to address this shortcoming is by the utilization of materials whose electromagnetic properties could be dynamically modified by an external variable, for instance semiconducting quantum dots in the presence of UV excitation [20].

1.1.1 Characterization of Nanoscale Systems at THz Frequencies

The electronic properties of semiconductor have been a topic of interest since the invention of the transistor in the 1950s [21]. These studies have led many electronics advances up to now. On the other hand, compared to the electronic properties, the optical properties were not studied with the same intensity due perhaps to the lack of possible applications [21]. The optical and electrical properties of semiconducting nanoparticles can be controlled by varying their shape or composition [22]. Furthermore, decreasing the dimensions of the semiconducting structures under consideration enables the conspicuous observation of quantum effects in the nanometer regime and, therefore their physical properties are also size dependent in said regime [23]. Some of the properties that are size dependent when a semiconducting particle falls in the nanometer regime comprise: (i.) increases in the bandgap, (ii.) shifts in the absorption and luminescence characteristics, and (iii.) phase transitions. The study of electronic transitions on these materials can be further be studied using THz-TDS without deleterious effects on the sample. Specifically, their exciton transitions, binding energies, mobile carriers and polarons response, which all exhibit specific responses in the meV energies. The study of charge carriers in this frequency

regime allows a deep investigation of the spectral signatures at these frequencies [24]. Also, the use of THz spectroscopy is a convenient and contact way to obtain key material information such as conductivity, carrier densities and mobility as a function of frequency [24]. Also, there is a special need for materials for emission and detection to improve the performance of THz spectrometers [20]. One of the most common physical properties that can be measured by this technique is the photoconductivity as a function of size [23]. In spite of the fact that the bulk photoconductive properties scale directly with size and therefore decrease as the particles become smaller due to the limited mobility of the charge carriers, nonetheless a THz detection can still be obtained due to electron-hole pair polarization [25]. These materials are also characterized by exhibiting very interesting optical, thermal and electronic properties due to the formation of electron-hole pairs bound almost entirely by Coulomb attraction and the excitation from the ground state to higher energy bands. These excitation will promote an ultrafast creation of electron-phonon and electron-electron interactions [22,26].

1.1.2 Electromagnetic Spectrum and THz Regime

The interest in the study of THz frequencies started to emerge in the 1920s, however, it was not until the 1980s that meaningful developments started to happen. The reason for this rapid technological growth was due to improvements of lasers systems and advances in photoconductive antenna fabrication [8,27]. Then, further developments were done in the 1990s by the realization of better THz emitters and detectors. This advancement opened the possibility of THz spectroscopy and imaging. At the present time, THz technology market has grown substantially in terms of availability and size. In spite of the relatively broad scope of applications of this technology, it has been difficult to apply them to a wider commercial market.

For example, one of the most used devices of generation and detecting THz waves is the photoconductive antennas (PCA). Fabrication of PCAs is challenging due to the lack of availability of materials exhibiting specific characteristics to obtain an effective antenna performance. Heterostructures of combinations of GaAs, InGaAs and InAlAs and other

combinations of group III-V materials have been the most implemented materials for the fabrication of these THz antennas. In this work, the optimization of an AlGaIn/GaN heterostructure is described. Even though the generation and detection of THz waves is challenging, the study of this region of the electromagnetic spectrum has continued and is developing in a fast way [28]. This relatively quick development has led to many applications in the pharmaceutical, medical, astronomical, textile, communication and security industries. Examples of these applications are the following:

1. Pharmaceutical: THz technology has been proposed for the study of tablet coatings. Coating quality and uniformity are very important for effective drug release in the body, and their visual appearance for marketing purposes. Different methods have been used for the characterization of coating on tablets and to detect tablet ingredient degradation. However, most of those methods are destructive and unsuitable for high-throughput characterization, whereas THz spectroscopy and imaging can be successfully employed to obtain coatings thicknesses, detect surface defects and a complete 3D chemical and physical study of the tablets [29].
2. Medical: In the medicine industry THz signals have demonstrated to be useful in the study of dental cavities. For instance, damages to tooth enamel may or may not be visible to the naked eye. In fact, early detection of such damages without visible appearance can be challenging. The current method used for the early detection of cavities is the utilization of X-rays which solely provides information when the damage is on a late stage without mentioning that continuous human exposure to X-rays is harmful. In contrast, images produced employing THz technology enable discerning different tooth tissues and the detection of cavities at an early stage without being harmful to human patients [30].
3. Security: Considering that THz electromagnetic waves can penetrate plastics and fabrics, THz spectroscopy and imaging can be used for security screening to remotely detect concealed weapons. Also, since many materials have specific spectral features at THz

frequencies, dangerous materials and explosives can be detected [31].

1.1.3 THz Reconfigurable metamaterials

Metamaterials are artificial materials made of arrays of elements from materials such as metals or plastics, engineered to exhibit certain properties not existing in nature, including negative refractive index, superlensing, cloaking and other EM behaviors [2]. The interest in the study of these artificially structured electromagnetic (EM) materials resides in the prospective exploitation of the aforementioned properties. It is known that the properties of these materials depend on the properties of the subunits and their spatial distribution. In fact, their electromagnetic properties can be determined by the ratio of the lattice constant a and λ , the wavelength of the incident photons. The ratio between wavelength and lattice constant differentiates metamaterials from other engineered structures such as photonic crystals, metallic hole arrays or frequency-selective surfaces [3].

On the other hand, the electromagnetic properties of all materials can be explained in terms of their complex electric permittivity ($\epsilon = \epsilon_1 + i\epsilon_2$ where ϵ_1 and ϵ_2 are the real and imaginary part of the permittivity respectively) and their complex magnetic permeability ($\mu = \mu_1 + i\mu_2$ where μ_1 and μ_2 are the real and imaginary part of the permeability respectively), quantities that are frequency dependent. In terms of their electric permittivity and magnetic permeability, all materials can be classified as:

- (i.) right-handed materials for which $\epsilon > 0, \mu > 0$,
- (ii.) electric plasmas for which $\epsilon < 0, \mu > 0$,
- (iii.) magnetic plasmas for which $\epsilon > 0, \mu < 0$,
- (iv.) left-handed materials for which $\epsilon < 0$ and $\mu < 0$, see Figure 1.1 [3].

Metamaterials were first theoretically studied by Veselago in 1968 [32]. He proposed the possibility of obtaining interesting new electromagnetic behavior by considering both the negative

values of permittivity and the permeability. Veselago's negative permittivity prediction was confirmed by Pendry in 1996, who used an array of thin metallic wires to create an artificial plasma [32, 33]. Subsequently, the experimental verification of negative permeability was confirmed by Smith in 1999 using split-ring resonators (SRRs) [34].

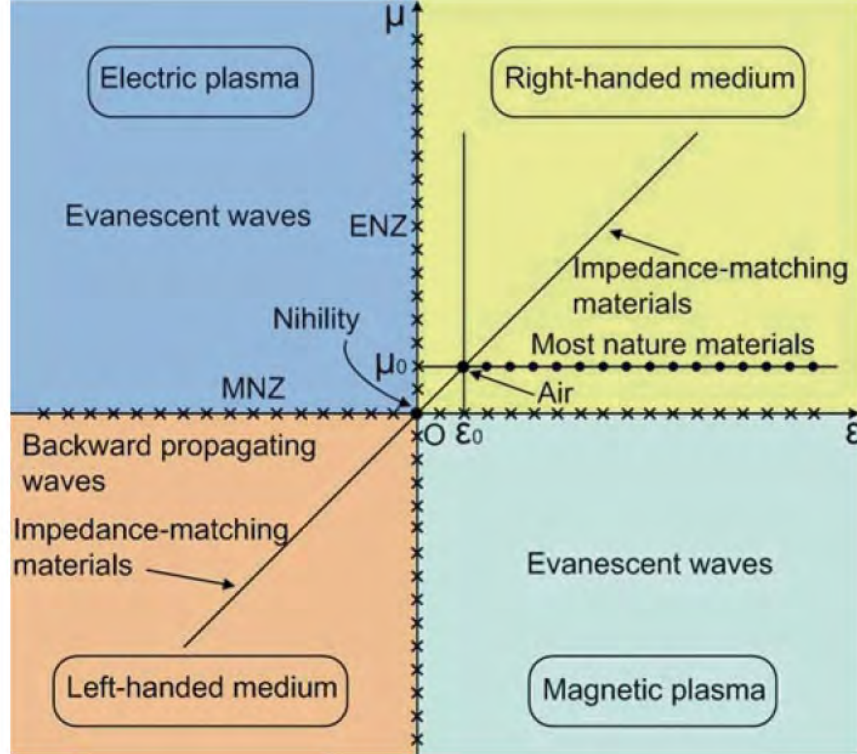


Figure 1.1: All possible properties of isotropic materials in the $\varepsilon - \mu$ domain [35].

As mentioned before, metamaterials are engineered materials that exhibit specific electromagnetic properties not found in natural materials [19]. MMs also have numerous applications in other ranges of the electromagnetic spectrum for instance, microwaves and optical frequencies. In addition to the anticipated passive behavior of any MM array, important applications would benefit from having structures exhibiting a reconfigurable behavior, such that it could be possible to actively modulate electromagnetic properties including but not limited to intensity, phase, polarization and/or propagation direction [36]. Reconfigurability of MMs could be performed by external electrical, optical, thermal and mechanical excitation [36]. Thus, in this work we focus on the prospective reconfigurable behavior of THz MMs by the application of an

external optical modulation. The underlying idea is to modulate the EM properties of the MM in the THz regime by incorporating a UV sensitive semiconductor. For our purposes we are going to employ semiconducting quantum dots (QDs) deployed on top of a hexagonal metallic array MM.

CHAPTER 2: METHODOLOGY

2.1 THz Time Domain Spectroscopy

Important physical and chemical information of materials can be obtained with the use of THz characterization [37]. THz electromagnetic waves can penetrate most non-metallic materials and therefore are non-invasive. In addition, considering their relatively low energy content, they also are non-ionizing. This region of the EM spectrum is very useful to detect material's vibrational, translational, rotational and torsional resonances which are usually out of the range of infrared and microwave spectrometers [38].

One of the most powerful and used techniques for materials characterization in the THz regime is THz time domain spectroscopy (THz-TDs) [37]. This technique covers a range from 0.1 THz to 10 THz (3.3 cm^{-1} to 333.6 cm^{-1}) (see Fig 2.1). Compared to the previous spectroscopic techniques employed in the far infrared, in THz-TDs the signal to noise ratio (SNR) is improved by employing coherent sources [19, 39]. Unlike other characterization techniques such as Fourier transform infrared spectroscopy (FTIR) that solely provides signal intensity information, THz-TDs provides spectral amplitude and phase. With this information, material parameters such as the absorption coefficient, the refractive index and the effective permittivity of the medium can be obtained without recurring to Kramers-Kronig analysis [25], as described below. Additionally, the THz-TDS technique provides more measurement versatility because it can be performed in transmission or reflection mode. For this reason, it is one of the most commonly used technique for THz materials and devices characterization. THz generation, detection and data processing will be explained in detail in this chapter.

Although the THz-TDS technique is very useful, its development has been slow due to challenges in terms of availability of emitters and detectors at the frequencies of interest. At the boundary between microwaves and THz frequencies, typical semiconductor-based electronic devices reach their limit in terms of performance vs power handling capabilities or, otherwise, what the electronic circuitry can tolerate without performance degradation. In contrast, at the

boundary between THz frequencies and the infrared the power requirements exceed what photonic devices can provide [20].

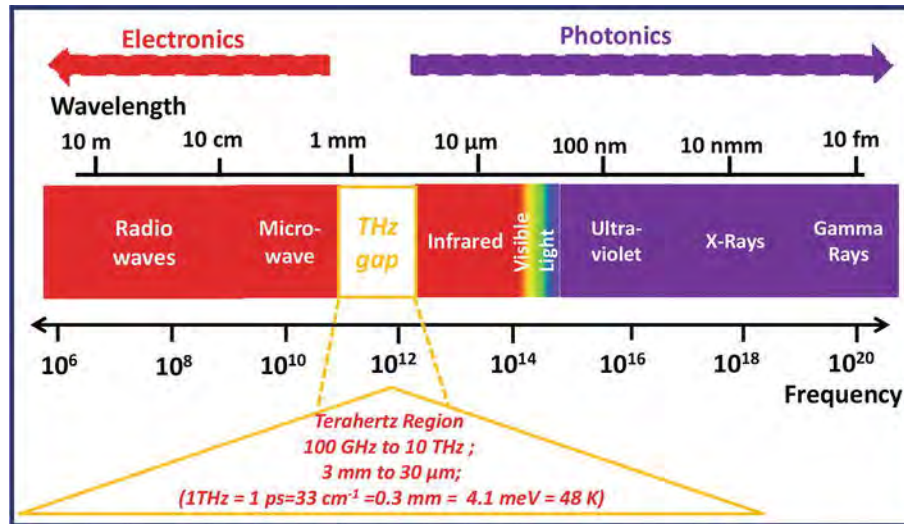


Figure 2.1: EM spectrum. Adapted from [40].

A common THz spectroscopy setup consists of a photoconductive antenna usually made with a low carrier lifetime semiconductor material on which a femtosecond laser is focused to hit the photoconductive antenna (see Fig 2.2).

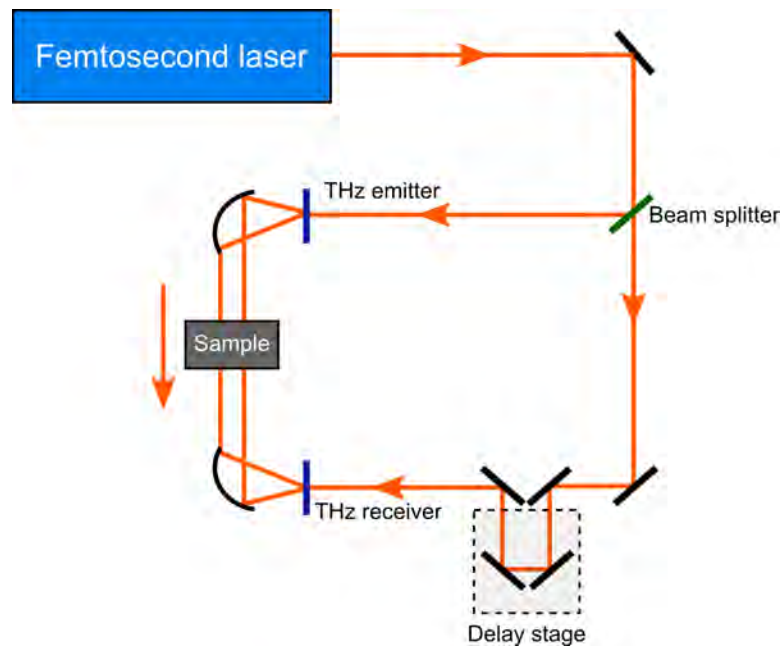


Figure 2.2: THz-TDS beam diagram. Adapted from Ref. [41]

2.1.1 THz Generation

A common method of generating and detecting THz wave is by using a photoconductive antennas (PCA). The photoconductive antenna is composed of metallic parallel plates on top of a photoconductive material, usually GaAs (as shown in Figure 2.3). The PCA is usually activated by a femtosecond laser. A THz beam is emitted and focused on the sample; then it is reemitted and focused on the detector by using different lenses and mirrors. The time delay between the generated and detected THz wave is adjusted with an optical delay line. The final sample waveform should be delayed compared to the reference depending on the optical properties of the material [20]. Materials optical information can be obtained after post processing and by Fourier transformation (FFT) of the time domain data.

The PCA used for the characterization of the samples presented in this work is made of low temperature Gallium Arsenide (LT-GaAs). The process starts when the PCA is excited with a femtosecond laser [26,28]. The PCA antenna is connected to a DC power supply, which accelerates the generated electron-hole pair. The carriers time evolution can be described with the following equation [26]:

$$N(t) = \int_0^t G(\tau) d\tau - N_0 e^{-\frac{t}{\tau_c}} \quad (2.1)$$

where $N(t)$ is the time scale of the laser pulse, τ_c is the carrier lifetime, $G(t)$ is the optical carrier generation rate and N_0 is the total number of carriers generated. An electric field in the opposite direction of the original one will be promoted by polarization of charges in the material. Then a photocurrent is created which generates a THz pulse. Upon pulse generation, the electron-hole pair recombines, and the cycle –that lasts approximately one picosecond– can be repeated. The THz pulse generated by this method is described with the following equation:

$$\vec{E}_{\text{THz}} \propto \frac{dI_{\text{PC}}(t)}{dt} \quad (2.2)$$

where $\vec{E}_{\text{THz}}$ is the THz electric field generated by the emitter antenna and I_{PC} is the photocurrent generated. Figure 2.4 shows a typical THz pulse of air obtained with this method.

One of the main challenges that arises with the generation and detection of THz waves using PCAs is the availability of identifying photo conducting materials with the specific optoelectronic properties. The appropriate material must have low carrier lifetime, high carrier mobility, appropriate bandgap, high breakdown voltage, suppression of zero bias photocurrent and must maximize material dark resistivity [28]. A possible solution to these limitations in generation and detection of THz radiation could be the utilization of wide bandgap semiconductor materials [16].

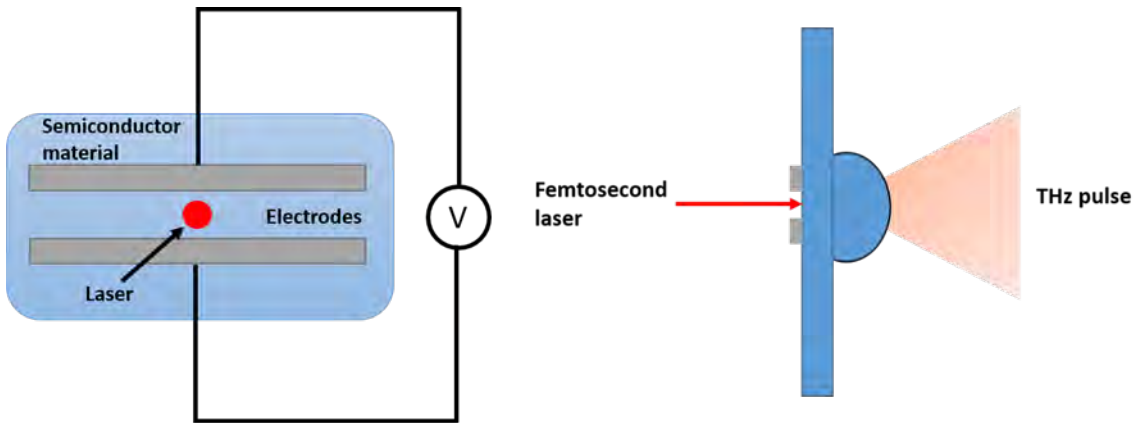


Figure 2.3: Top and side view of the photoconductive antenna [42].

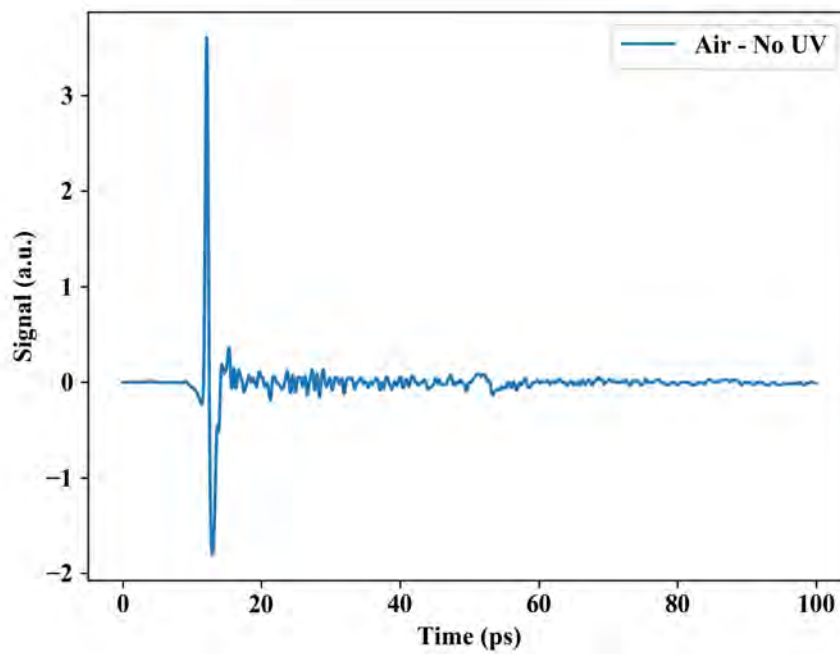


Figure 2.4: Time spectra of air measured with THz-TDS

2.1.2 Detection of THz Pulses

There are two common method of detecting THz pulses, namely, (i.) electro-optic (EO) and (ii.) photoconductive (PC) detection. We will only describe the PC method in this chapter [43]. The detection process, like the generation process, requires a photoconductive antenna. In this case the PC antenna is an excited centered dipole in between coplanar strip lines on top of a semiconductor film (as shown in Figure 2.3).

The process starts with the generation of electrons and holes in the semiconductor caused by illuminating the material with an ultrafast laser pulse, which decreases the conductivity in the antenna. The conductivity of the antenna can be described by the following equation [26]:

$$\sigma(t) = N(t)e\mu \quad (2.3)$$

where $N(t)$ is the time evolution of the carrier density and μ is the semiconductor mobility. The reduction of the conductivity is similar to closing a switch, the gap will be closed, and the antenna will start to conduct. It is important to emphasize that if the semiconductor is not excited, the gap remains open, the antenna behaves as an insulator and no detection occurs. Thus, the THz pulse is obtained when the detection antenna is conducting and when the THz pulse passing through the sample coincides with the detector antenna [26].

Our experiments were done employing a TeraSmart system from the company MenloSystems. The photoconductive antenna of this system is made of low temperature Gallium Arsenide (LT-GaAs). The femtosecond pulse is generated from femtosecond Erbium laser of 1560 nm. The equipment provides a dynamic range >90dB with a repetition rate of 100 MHz [44].

2.1.3 Data collection and analysis

Consider a light wave propagating through a homogeneous dielectric slab of thickness d and complex refractive index n . Due to reflection and refraction at the interface of the slab there will be multiple light paths. A sketch of the setup is shown in Figure 2.6.

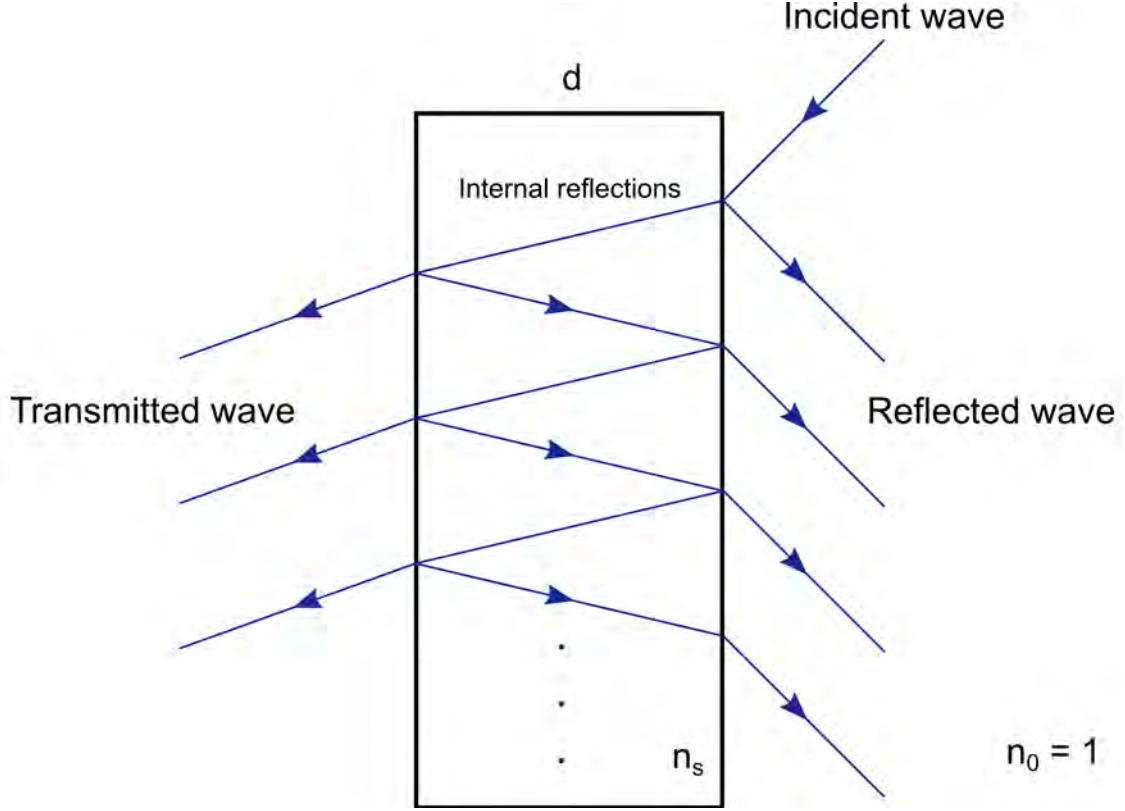


Figure 2.5: Sketch of the electric field transmitted through a slab of material with refractive index n_s . Adapted from Ref. [45].

This light path can be described by the multiplication of the incident electric field and its corresponding Fresnel coefficient. If we assume normal incidence for which $\theta_i = 0$, the total transmission is the summation of waves at the interface. The transmitted wave $E_t(\omega)$ is described by the following equation:

$$E_t(\omega) = \tau \tau' \cdot \exp \left[-j \tilde{n}_s(\omega) \frac{\omega d}{c} \right] \cdot \text{FP}(\omega) \cdot E_0(\omega) \quad (2.4)$$

In Eq. 2.4, τ is the complex transmission coefficient, $\tilde{n}_s(\omega)$ is the refractive index as a function of angular frequency ω , $\text{FP}(\omega)$ are the Fabry-Perot effects due to reflections inside the sample, and $E_0(\omega)$ is the incident wave. The Fabry-Perot reflections are given in Eq. 2.5.

$$\text{FP}(\omega) = \left\{ 1 - \rho'^2 \cdot \exp \left[-2j \tilde{n}_s(\omega) \frac{\omega d}{c} \right] \right\}^{-1} \quad (2.5)$$

in Eq. 2.5, ρ is the complex reflection coefficient.

In the case of pure transmission and normal angle of incidence, the electric field traveling through the sample is given by Eq. 2.6

$$E_{\text{sam}}(\omega) = \frac{4\tilde{n}_s(\omega)}{[\tilde{n}_s(\omega) + n_0]^2} \cdot \exp\left[-j\tilde{n}_s(\omega)\frac{\omega d}{c}\right] \cdot E_0(\omega), \quad (2.6)$$

in which n_0 is the index of refraction of the surrounding medium. In all experiments shown here, this medium is air and therefore $n_0 = 1$. We typically also measure the spectrum of a reference signal, that is, a signal in the absence of the sample. This is given by Eq. 2.7

$$E_{\text{ref}}(\omega) = \exp\left[-j\frac{\omega d}{c}\right] \cdot E_0(\omega) \quad (2.7)$$

We now define the complex transfer function $\tilde{T}(\omega)$ defined as the ratio between $E_{\text{sam}}(\omega)$ and $E_{\text{ref}}(\omega)$ and shown in Eq. 2.8

$$\tilde{T}(\omega) = \frac{4\tilde{n}_s(\omega)}{[\tilde{n}_s(\omega) + n_0]^2} \cdot \exp\left(-\frac{\kappa_s(\omega)\omega d}{c}\right) \cdot \exp\left(-\frac{(n_s(\omega) - n_0)\omega d}{c}\right), \quad (2.8)$$

where $n_s(\omega)$ and $\kappa_s(\omega)$ are the refractive index and extinction coefficient of the sample defined by Eq. 2.9.

$$\tilde{n}_s(\omega) = n_s(\omega) - j\kappa_s(\omega) \quad (2.9)$$

Filtering time domain data

Typical time domain data is presented in Figure 2.4. In order to remove the Fabry-Perot reflections previously described, we apply a windowing function to filter our data [43]. This method must be applied carefully because it could distort the data in undesirable ways that could lead to loss of important spectral information [43]. Some of the typical windowing functions used are the following: boxcar function, Gaussian, Hamming, Norton-Beer, Blackman-Harris. Another method of minimizing noise and to clean the time domain signal is by zero-padding. This consists of adding

zeros to the end of the time domain data in order to enhance the temporal resolution.

Fast Fourier Transform (FFT)

The data obtained from the spectrometer is the time domain shape of the electric field of the THz pulse. In order to convert the time data to the frequency domain, a Fast Fourier Transform (FFT) must be performed. The FFT is defined as follows:

$$F_n = \sum_{i=0}^{N-1} x_i \exp\left(-\frac{2\pi j}{N} ni\right) \quad (2.10)$$

where x_i and N are the sequence of values and the sequence length, respectively. The FFT provides phase and amplitude information as a function of frequency. The phase and amplitude are defined as follows: $\phi = \arctan\left(\frac{\text{Im}(F_n)}{\text{Re}(F_n)}\right)$ and $\text{amp} = \frac{\sqrt{\text{Re}(F_n)^2 + \text{Im}(F_n)^2}}{n}$, respectively. Using the information obtained from the FFT it is possible to calculate important physical parameters such as the refractive index, permittivity, and conductivity. Specifically, after the FFT has been applied to the data, from the phase angle the transfer function of the material can be obtained. The transfer function is shown in Eq. 2.8. From the transfer function, we may extract the refractive index n_s , extinction coefficient κ_s and absorption coefficient α_s of the sample as follows [46, 47]

$$n_s(\omega) = n_0 - \frac{c}{\omega d} \phi(\omega) \quad (2.11)$$

$$\kappa_s(\omega) = \frac{c}{\omega d} \left\{ \ln \left[\frac{4n_s(\omega) n_0}{(n_s(\omega) + n_0)^2} \right] - \ln |\tilde{T}(\omega)| \right\} \quad (2.12)$$

$$\alpha_s(\omega) = \frac{2\omega \kappa_s(\omega)}{c} \quad (2.13)$$

2.2 Characterization of materials using THz-TDS

2.2.1 Solid samples

In the case of solid samples, the procedure to characterize using THz is as follows. These experiments typically involve a substrate on which we deposit our samples. This reduces the

number of interfaces we need to consider from 5 to 3 – 4, depending on the application. A representative schematic of the setup for solid samples is shown in Figure 2.7.

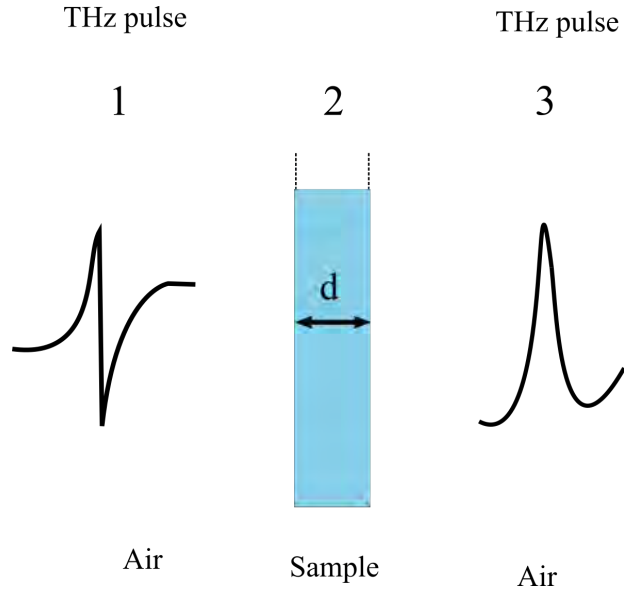


Figure 2.6: The typical THz-TDs setup for measuring solid samples.

For some of the experiments presented in this work, we investigated the effect of UV excitation on the optical properties of the materials studied at THz frequencies. These measurements involve adding a UV lamp to the setup shown in Figure 2.2 for the purposes of illuminating the samples. This is shown in Figure 2.8.

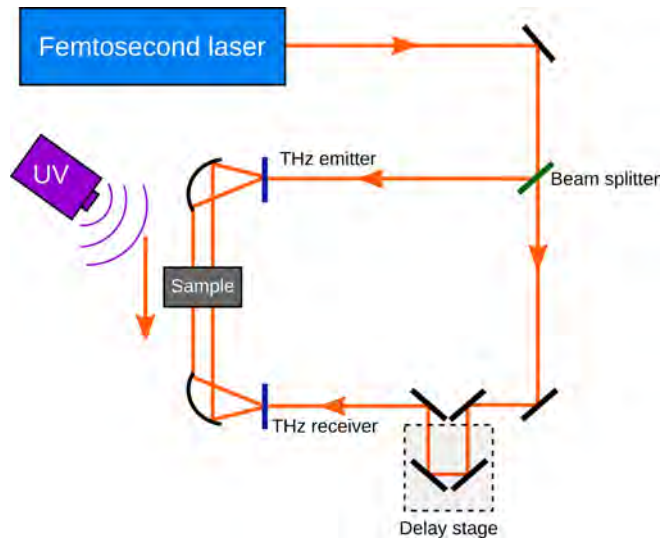


Figure 2.7: THz-TDS beam diagram including the UV lamp to investigate the reconfigurability of certain samples studied in this work.

CHAPTER 3: ZNO QUANTUM DOTS TERAHERTZ CHARACTERIZATION

Parts of this chapter are based on the manuscript *Terahertz Modulation of Hexagonal-shaped Metamaterials employing ZnO Quantum Dots* by Clarissa Vazquez Colon, Alvaro Flores-Pacheco, Janeth Alexandra García-Monge, Juan Adrián Zepeda-Galv  z, Daniel Shreiber and Arturo A. Ay  n (2019), accepted for publication at the Open Journal of Inorganic Non-metallic Materials.

Despite the fast evolution on devices in these frequency regime, active manipulation of THz waves is still under development. A possible solution to this problem could be the utilization of functional materials that can respond to an external stimulus. In this work we present the utilization of UV tunable ZnO Quantum Dots (QDs). The ZnO QDs THz UV response was characterized using Terahertz Time Domain Spectroscopy (THz-TDS) in transmission mode. THz-TDS is a useful technique to obtain photoconductivity, charge transport and optical properties of semiconductor nanostructures at THz frequencies [23]. These technique is convenient because the characterization can be carry without requiring external wiring or damaging to the sample [48]. This chapter describes the synthesis process, UV-Vis, photoluminescence and THz characterization of ZnO QDs.

3.1 ZnO QDs Synthesis

Colloidal ZnO QDs were synthesized at room temperature by a sonochemical method [49, 50] in which acoustic cavitation precludes the formation of intermediate products, including Zn(OH)₂, converts the reactants into ZnO QDs and calcination steps are not required. This method has proven useful for accelerating chemical reactions in liquid-solid systems [49]. Specifically, ZnO QD synthesis was accomplished by preparing an initial solution of 0.02 M zinc acetate (ZnAc) (99.99%, Sigma-Aldrich) in pure ethanol. A second and independent solution of 0.01 M of lithium hydroxide (LiOH) ($\geq 98\%$ Sigma-Aldrich) was prepared also in pure ethanol. Subsequently, the

LiOH solution was incorporated dropwise to the ZnAc solution until a pH value of 10 or 12 was obtained. Once the targeted pH value was reached, the mixture was placed in a sonication bath for 3 hours [51,52]. The chosen pH values were found to yield stable nanoparticles and relatively minimal agglomeration. Furthermore, the ultimate size of the obtained QDs was determined by the pH value of the final solution employed during synthesis and observed to be in agreement with the dependence of ZnO nanoparticle size on pH reported elsewhere [53]. A summary of the synthesis and an image of the final solutions under UV light is shown in Figure 3.1.

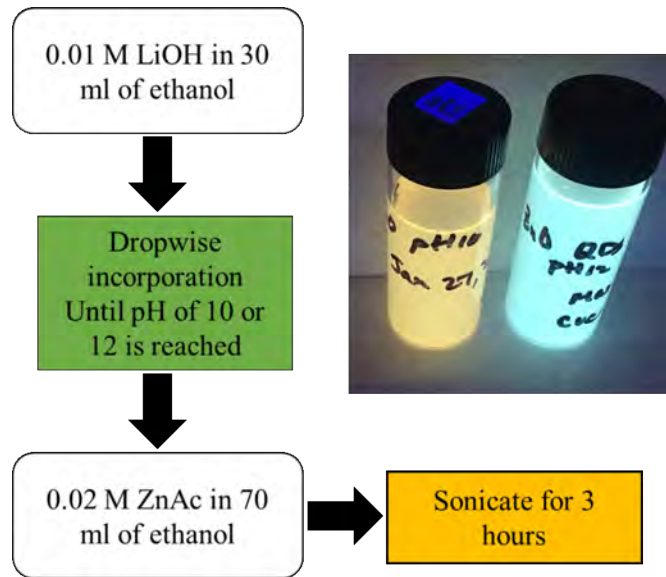


Figure 3.1: Synthesis procedure for ZnO QDs.

In order to characterize the synthesized ZnO QDs in the terahertz regime, the nanoparticles were dispersed in a polydimethylsiloxane (PDMS) matrix. To this end, the ZnO QDs were harvested by drying up the final solution on a hotplate maintained at 70°C , and prior to dispersing them in the aforementioned matrix, the QD samples were thoroughly pulverized using a mortar. Once the solvent had completely evaporated, the ZnO QD powder was mixed with a PDMS solution that had been previously prepared by mixing 5 wt.% of a curing agent in a silicone elastomer [54,55]. The mixture of PDMS and ZnO QDs was then cured at 90°C for 3 hours (see Figure 3.2).

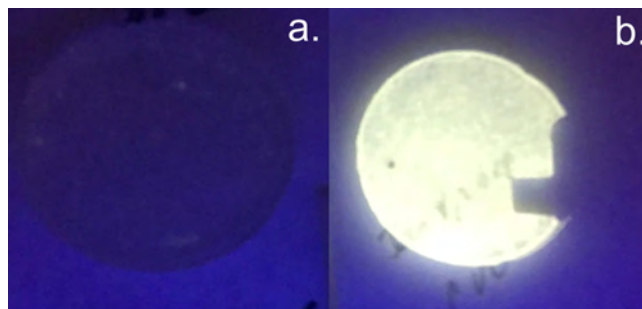


Figure 3.2: (a.) PDMS membrane under UV excitation, (b.) ZnO QDs embedded in PDMS under UV excitation.

3.2 ZnO QD Absorption and Emission Characterization

The UV-vis absorption characterization of the ZnO QDs was performed using an Ocean Optics Flame-S-UV-VIS spectrometer and the collected absorption spectra corresponding to nanocrystals synthesized with the previously mentioned colloidal solution pH values of 10 and 12, are shown in Figure 3.3, along with their corresponding photoluminescent response. The emission wavelength is directly related to quantum dot size, therefore, the larger the nanoparticles the longer the wavelength of their characteristic photoluminescent peak [56, 57]. Thus, QDs synthesized with a pH value of 12 have an emission peak located at 510 nm, while QDs synthesized with a pH value of 10 have the peak located at 540 nm, indicating that lower pH values produce larger nanoparticles.

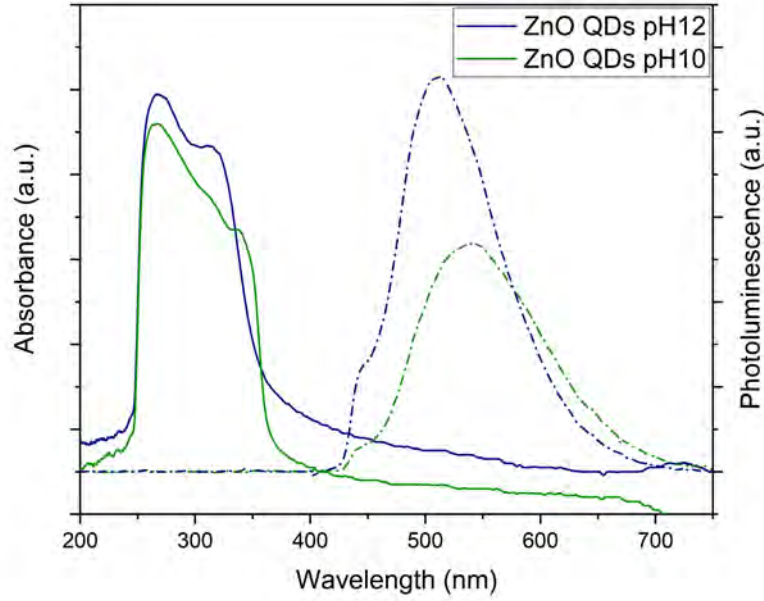


Figure 3.3: Collected absorbance spectra of the ZnO QDs colloidal solutions synthesized with pH values of 10 and 12 (solid lines), respectively. The dotted lines show the photoluminescence spectra of the ZnO quantum dots colloidal solutions.

The observed QD absorbance measurements are related to QD bandgap by the following expression

$$\alpha = \frac{A}{h\nu} (h\nu - E_g)^m, \quad (3.1)$$

where α is the absorption coefficient, A is an optical constant, m represents the type of optical transition in the semiconducting material; specifically, m can only take the values of 1/2, 2, 3/2 or 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect, respectively [58], and E_g is the band gap of the semiconducting quantum dots. Multiplying Eq. 3.1 by $h\nu$, obtaining the natural logarithm and finally taking the derivative with respect to $h\nu$, it can be expressed as follows the resultant equation is

$$\frac{d(\ln[\alpha h\nu])}{d(h\nu)} = \frac{m}{h\nu - E_g}. \quad (3.2)$$

The bandgap can then be estimated by plotting Eq. 3.2 with respect to energy [58], and this approach permits the identification of the inflection point (i.e., the bandgap value) where the slope changes sign (see Figure 3.4). In other words, the bandgap value will be determined as a discontinuity at $h\nu - E_g = 0$ [58]. The extracted bandgap values were 3.43 eV and 3.62 eV for the ZnO QDs synthesized with the colloidal solutions with a pH of 10 and 12, respectively. The observed emission peaks were located at 510 nm (pH 12) and 540 nm (pH 10). Since the wavelength emission is directly related to QD size, i.e., the larger the particle, the longer the wavelength of emission, the emission peak wavelength observations corroborate that higher pH values during synthesis indeed lead to smaller ZnO quantum dots.

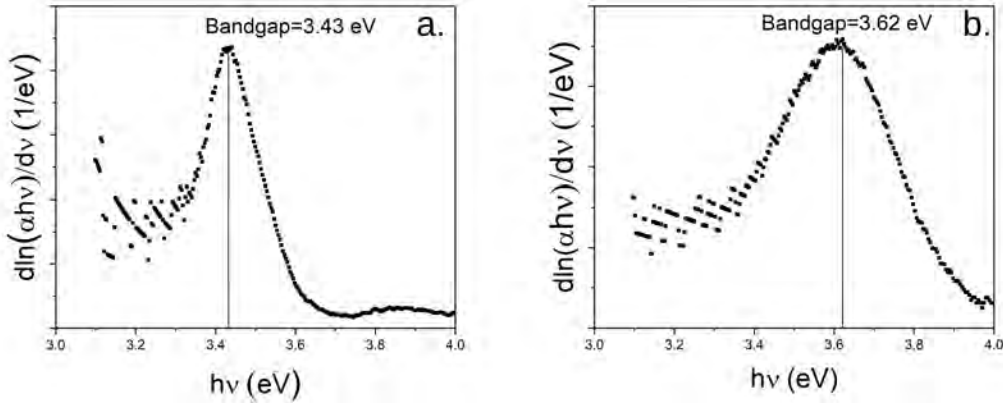


Figure 3.4: ZnO QDs pH10 (a.) and ZnO pH12 (b.) estimated bandgap sizes calculation.

Once the bandgap value had been calculated, the size of the QDs was estimated employing Brus' quantum mechanical approximation [59]

$$E_{\text{bulk}} \cong E_g + \frac{\hbar\pi^2}{8r^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{r\epsilon}, \quad (3.3)$$

where E_g is the band gap energy of the semiconductor quantum dots, E_{Bulk} is the band gap energy of the bulk semiconductor material, $\hbar$ is the reduced Planck constant, m_e^* and m_h^* represent the effective mass of electron and hole of the material under consideration, ϵ is the bulk relative permittivity, and r is the QD radius. For the pH 10 ZnO QDs we estimated a diameter radius size value of 3.00 nm and for the pH 12 ZnO QDs we obtained a diameter radius value of

2.12 nm. To corroborate the estimated sizes, transmission electron microscope (TEM) images for both samples were obtained and are shown in Figure 3.5. The measured values were approximately 3.2 nm and 1.85 nm radius for the ZnO pH 10 and ZnO pH 12 samples, respectively, in reasonable agreement with the sizes obtained via Eq. 3.3

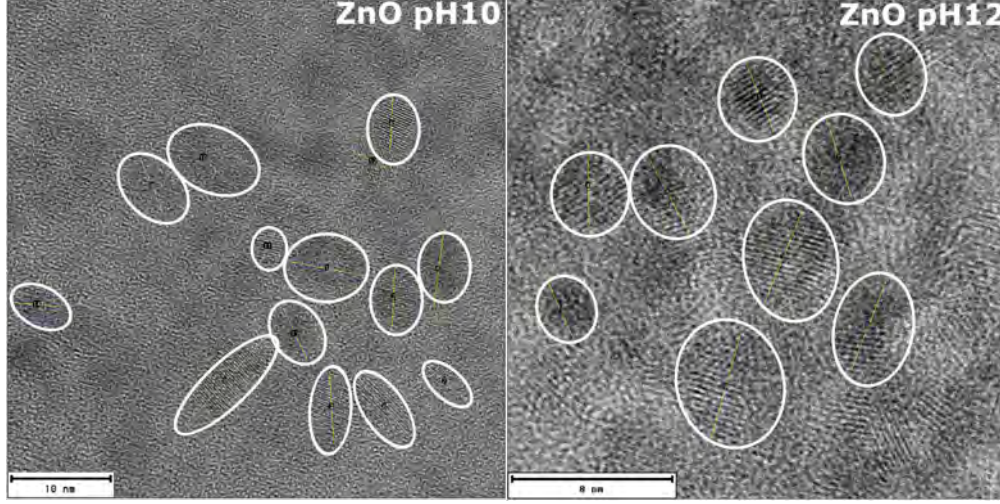


Figure 3.5: ZnO QDs TEM images.

A summary of ZnO QDs bandgap and sizes estimations are shown in Table 3.1.

Table 3.1: ZnO estimated bandgap and sizes values

ZnO QDs	Bandgap (eV)	Radius (Brus) (nm)	Radius (TEM) (nm)
pH 10	3.43	3.00	3.20
pH 12	3.62	2.12	1.85

3.3 ZnO QD THz Characterization

The THz time domain spectroscopy (THz-TDS) characterization was performed by employing a Menlo Systems TeraSmart equipment [44], operated in transmission mode (see Figure 3.6). This system employs a photoconductive antenna based on an InGaAs/InAlAs multilayered mesa as the emitter and detector, which are activated by a femtosecond laser with a wavelength of 800 nm. The system was aligned until the THz amplitude was at its maximum. Subsequently, the equipment was thermalized for 1 hour, and the sample was positioned at the focal point of the THz beam path.

Five measurements at room temperature were collected for each reference and samples, each of which corresponded to a thousand-point averaging.

Stand-alone PDMS membranes with and without QDs were tested and exposed to UV lamps with wavelengths of 302 nm and 365 nm, as well with a UV laser with a wavelength of 400 nm to determine the prospective modulation behavior of the QDs for further utilization on a metamaterial arrangement.

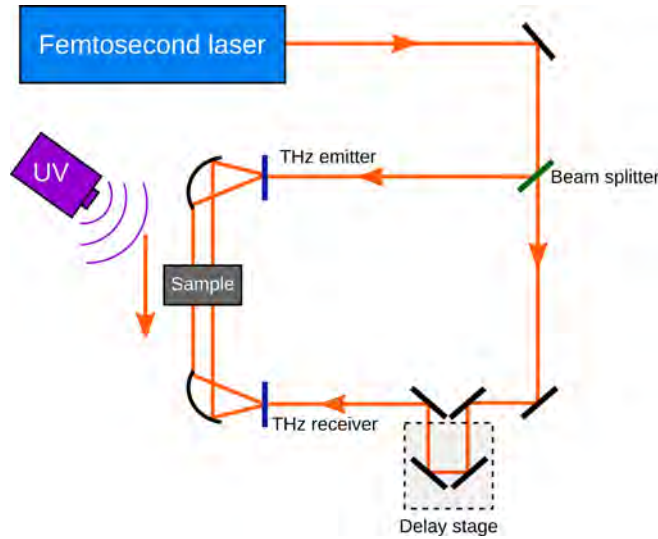


Figure 3.6: THz-TDS system in transmission mode

The obtained THz time domain waveform signal was processed by applying a Gaussian window to remove reflections after the main THz pulse [45] and, subsequently, a Fast Fourier transformed (FFT) was employed to obtain the amplitude and phase information of both the reference as well as of the sample under study. In both cases, i.e., a stand-alone PDMS membrane, samples without QDs were employed as a reference. The transmittance as a function of frequency of the samples was calculated using the following equation [45]

$$\tilde{T}(\omega) = \frac{\tilde{E}_{\text{sam}}(\omega)}{\tilde{E}_{\text{ref}}(\omega)} = \frac{A_{\text{sam}}(\omega)}{A_{\text{ref}}(\omega)} e^{i(\phi_{\text{sam}}(\omega) - \phi_{\text{ref}}(\omega))} \quad (3.4)$$

where $\tilde{E}_{\text{sam}}$ and $\tilde{E}_{\text{ref}}$ are the complex electric fields, A_{sam} and A_{ref} are the THz amplitudes and ϕ_{sam} and ϕ_{ref} are the phase angles of the sample and reference, respectively. Depending on the

sample transmittance results could show specific features as a function of frequency.

From the collected THz-TDS data, optical properties of interest such as refractive index, permittivity and conductivity can be extracted. The real part $n(\omega)$ and imaginary part $\kappa(\omega)$ of the refractive index can be calculated by using the following equations [45]

$$n(\omega) = 1 + \frac{c(\phi_{\text{sam}}(\omega) - \phi_{\text{ref}}(\omega))}{\omega d} \quad (3.5)$$

$$\kappa(\omega) = -\frac{c}{\omega d} \ln \left| \frac{A_{\text{sam}}(\omega)}{A_{\text{ref}}(\omega)} \right| \quad (3.6)$$

respectively. Similarly, the permittivity and the index of refraction are related by

$$\tilde{\epsilon}(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) = n^2(\omega) - \kappa^2(\omega) + i(2n(\omega)\kappa(\omega)) \quad (3.7)$$

where $\tilde{\epsilon}(\omega)$ is the complex permittivity, $\epsilon'(\omega)$ is the real part of the permittivity, $\epsilon''(\omega)$ is the imaginary part of the permittivity,

The extracted real effective refractive index of the PDMS+QDs membrane at 1 THz (see Figure 3.7), was of 1.50 for the smaller QDs synthesized with a pH value of 12 (orange trace), and to 1.85 (blue trace) for the larger QDs synthesized with a pH value of 10. Subsequently, the samples were exposed to UV excitations with wavelengths of 302 and 365 nm, respectively (see Figures 3.8 and 3.9). The intensities of the UV sources were measured using ILT2400 Light Meter and were found to be $3.52 \times 10^{-5} \frac{W}{cm^2}$ and $2.88 \times 10^{-5} \frac{W}{cm^2}$ for the 302 nm and 365 nm of wavelength, respectively. Since result were inconsistent between measurements we changed the UV lamps for a UV laser source with a wavelength of 400 nm with a measured intensity value of $2.510^{-4} \frac{W}{cm^2}$. The refractive index of the PDMS with ZnO QDs illuminated with the UV laser with a wavelength of 400 nm are shown in Figures 3.10 and 3.11. The observations indicates that the larger quantum dots exhibit a relatively more pronounced response to UV excitation.

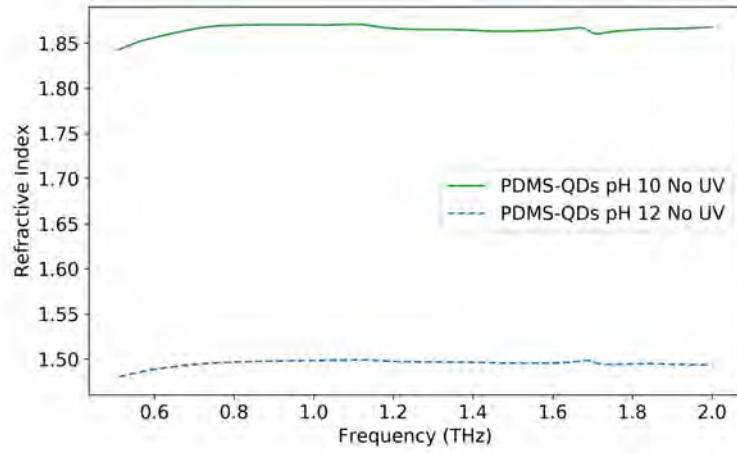


Figure 3.7: Extracted real part of the effective refractive index at THz frequencies of the media with the incorporated ZnO QDs without UV excitation.

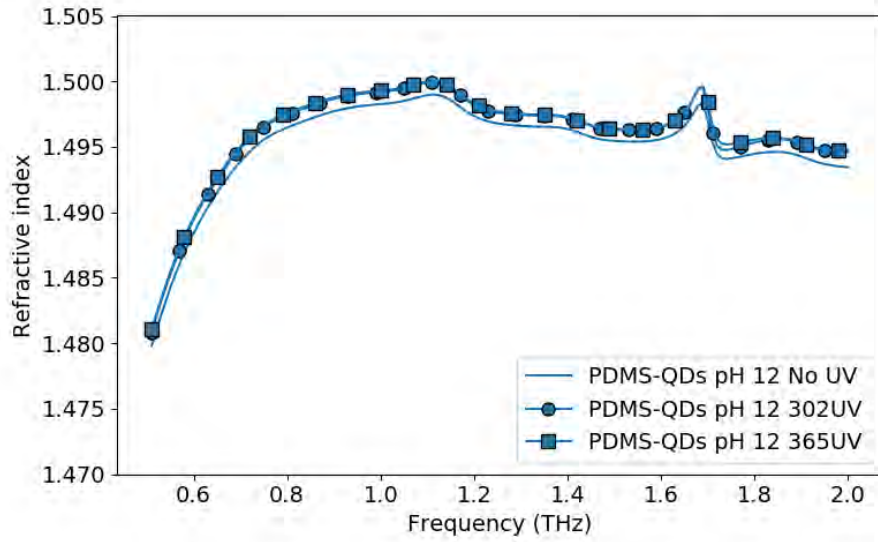


Figure 3.8: Extracted refractive index of ZnO pH12 QDs embedded in PDMS in the THz regime with and without excitation of UV lamps with wavelengths of 302 nm and 365 nm.

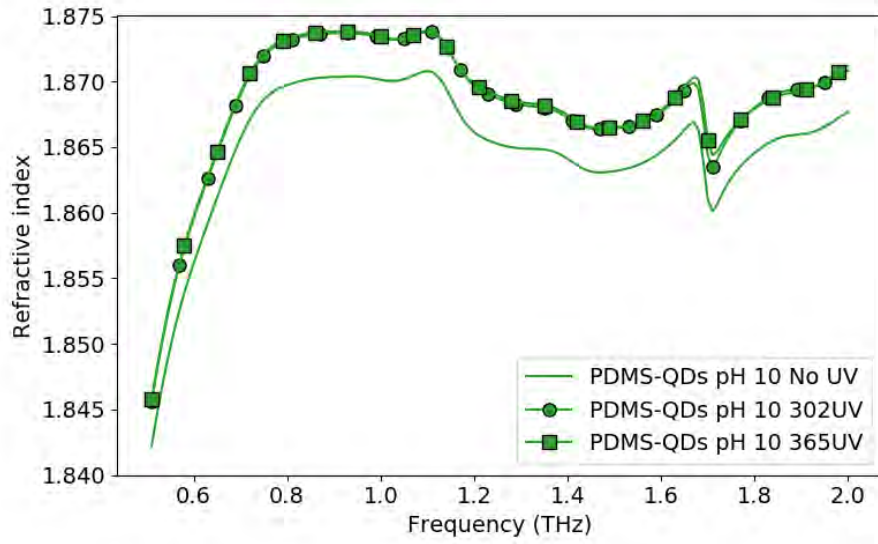


Figure 3.9: Extracted refractive index of ZnO pH10 QDs embedded in PDMS in the THz regime with and without excitation of UV lamps with wavelengths of 302 nm and 365 nm.

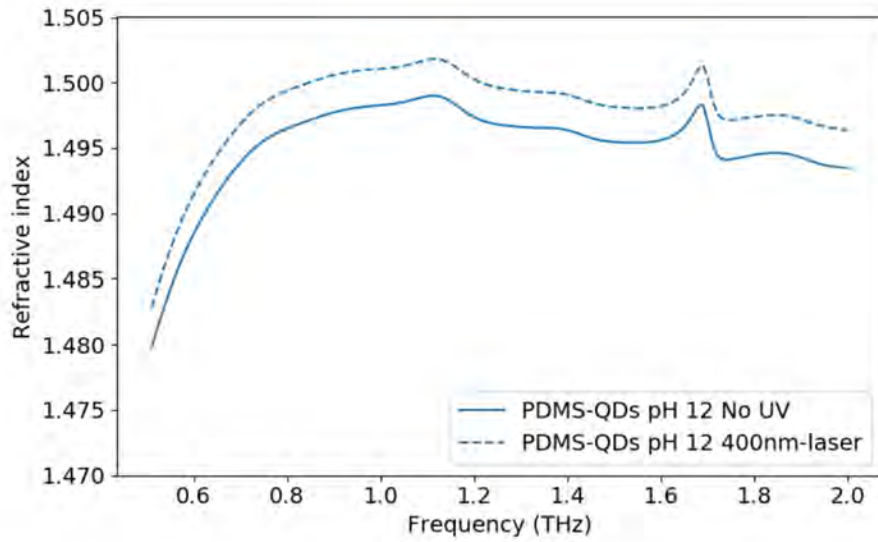


Figure 3.10: Extracted refractive index of ZnO pH12 QDs embedded in PDMS in the THz regime with and without excitation of a UV laser with a wavelength of 400 nm.

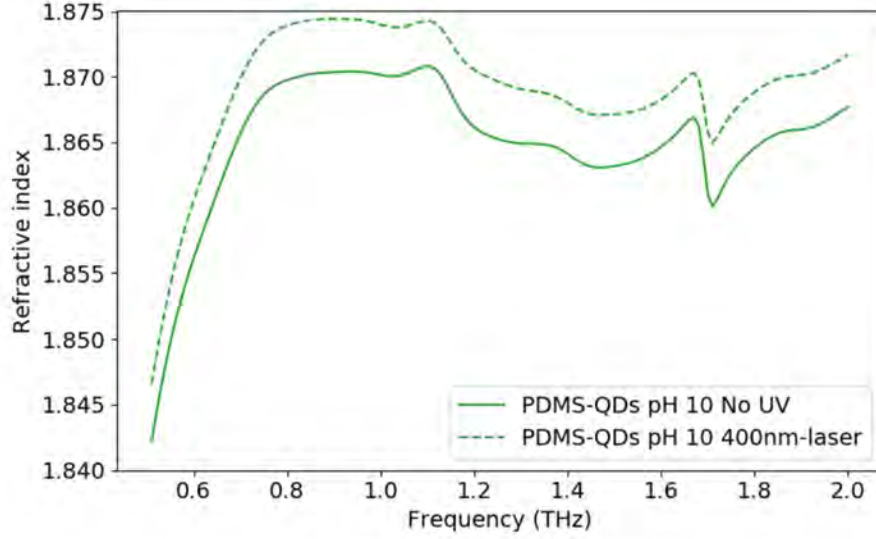


Figure 3.11: Extracted refractive index of ZnO pH10 QDs embedded in PDMS in the THz regime with and without excitation of a UV laser with a wavelength of 400 nm.

The observations presented herein indicate that larger quantum dots exhibit a relatively more pronounced response to UV excitation. This can be explained on the grounds that the synthesized semiconducting nanoparticles exhibit quantum confinement effects where exciton polarizability, reported to be proportional to the fourth power of the radius ($\alpha \sim R^4$), can be defined as [60]

$$\alpha = \frac{\Delta\chi_s (\epsilon_{\text{QD}} + 2\epsilon)^2}{9n_s\epsilon^2} \quad (3.8)$$

where $\Delta\chi_s$ is the susceptibility of the material (related to the permittivity by $\chi_s = 1 - \epsilon$), ϵ_{QD} is the permittivity of the quantum dots, ϵ is the permittivity of the medium and n_s is the sheet excitation density. Ostensibly, studies of polarizability as a function of frequency and quantum dot dimensions can be performed employing THz-TDS. Also, the detection of a response after using UV light using THz-TDS anticipate the possible utilization of QDs to actively modulate THz waves. Experiment using ZnO QDs to modulate THz signal will be presented on the following chapter.

3.4 Conclusions

ZnO quantum dots were sonochemically synthesized for two different pH values, pH10 and pH12. UV-Vis absorbance measurements were performed and the data was used to estimate the material bandgap values. For the pH12 the bandgap value was 3.62 eV and 3.43 eV for the pH10 ZnO QDs. These bandgap values were then used to estimate the QDs sizes values using Brus' quantum mechanical approximation, we found 2.12 nm and 3.00 nm radius values for the ZnO pH12 and ZnO pH10, respectively. Sizes values were corroborated by TEM images of the QDs (TEM radius values were obtained to be 1.85 nm and 3.20 nm for the ZnO pH12 and ZnO pH10, respectively). For THz characterization purposes ZnO QDs powder were prepared and embedded on a PDMS membrane. THz-TDS in transmission mode measurements were performed and real refractive indexes were calculated for the different samples on its own and under UV excitation. Without UV excitation we observed an increase on the THz refractive index after incorporating the ZnO QDs of different sizes, for the smaller QDs (ZnO pH12 QDs) the refractive index at 1 THz was approximately 1.50 and 1.85 for the larger (ZnO pH10 QDs). These results suggest an increase on the permittivity of the material. Then the samples were exposed to UV lamps with wavelengths of 302 nm and 365 nm, respectively and a UV laser source with a wavelength of 400 nm. After illuminating the samples with UV light we observed an increase on the refractive index of the membrane with the QDs, which implies a THz modulation of the QDs after being illuminated with UV light. These results suggest the possibility of incorporating UV sensitive QDs to THz devices and presumably the active modulation of the system under study.

CHAPTER 4: THZ MODULATION OF A HEXAGONAL METAMATERIAL USING ZNO QUANTUM DOTS

Parts of this chapter are based on the manuscript *Terahertz Modulation of Hexagonal-shaped Metamaterials employing ZnO Quantum Dots* by Clarissa Vazquez Colon, Alvaro Flores-Pacheco, Janeth Alexandra García-Monge, Juan Adrián Zepeda-Galv  z, Daniel Shreiber and Arturo A. Ay  n (2019), accepted for publication at the Open Journal of Inorganic Non-metallic Materials.

4.1 Introduction

Controlling electromagnetic waves especially in the THz gap is of fundamental importance for many applications including THz wireless communications, ultrafast THz interconnections, security and imaging among others. Additionally, properties that are not naturally available in conventional materials could be obtained using metamaterials (MM). As described in Ch. 1, metamaterials are laboratory-made materials with geometric features smaller than the typical source wavelength. These structures are usually made of metal or plastic. Their properties can be engineered to exhibit specific desired responses. Notwithstanding their many advantages, there is still a recognized need of on-demand modulation [61, 62]. In this chapter we propose the use of the previously discussed QDs deployed on top of a MM composed of an array of metallic hexagons. Then the tunability property was tested by exciting the samples with UV excitation sources while the collecting the THz spectroscopy measurements.

In this chapter we describe the characterization of hexagonally-shaped metallic metamaterial in the THz ranges from 0.5–1.5 THz. The structures are adapted from those presented by Bingham and coworkers [63]. The frequency response of these structure can be defined with the following equations [63]:

$$\tilde{\epsilon}(\omega) = \epsilon_{\infty} + \sum_m \frac{F_m \omega^2}{\omega_{0m}^2 - \omega^2 - i\Gamma_m \omega} \quad (4.1)$$

$$\tilde{\mu}(\omega) = \mu_{\infty} + \sum_m \frac{F_m \omega^2}{\omega_{0m}^2 - \omega^2 - i\Gamma_m \omega} \quad (4.2)$$

where ω_0 is the frequency of the oscillator, μ_{∞} and ϵ_{∞} are the real parts of real part of the permeability and permittivity respectively at $\omega = \infty$, Γ represents the losses and F_m is the filling fraction. The filling fraction is defined with the following equation [63]:

$$F_m = \frac{a_m}{nA} \quad (4.3)$$

where a_m is the area of the metamaterial element, n is the number of primitive cells and A is the area of the primitive cell.

These equations are important to explain the reconfigurability of the metamaterial. These structures can also be described as circuit components, with capacitances and inductors.

$$\omega_0 = \sqrt{\frac{1}{LC}} \quad (4.4)$$

where the capacitance is directly related to the effective permittivity and the inductance is directly related to the effective permeability of the medium before and after the deployment of the aforementioned quantum dots [64, 65]. Also, we describe how changes in the properties of the aggregated material can be obtained due to UV light exposure. This opens up the possibility of achieving tunability of the MM due to controllable changes to its external environment.

4.2 Methods

4.2.1 Metamaterial fabrication

The metamaterials were fabricated using standard lift-off photolithography process using SU-8 as the photosensitive material. The MM was patterned on top of high resistivity, single crystal, silicon wafers and metalized by evaporating 20 nm of chromium as an adhesion layer, followed by the deposition of 200 nm of silver. A diagram of sizes and distances, followed by an optical

microscope image of the final MMs structures are shown in Figure 4.1 and Figure 4.2. For the purposes of discussion these structures will be called "MM1" and "MM2", respectively. MM1 represents larger metallic regions of the unit cell, while MM2 represents a smaller metallic region on the unit cell. These changes to the unit cells presumably will have an influence on the resonance frequency of the structure due to changes on the permittivity of the material.

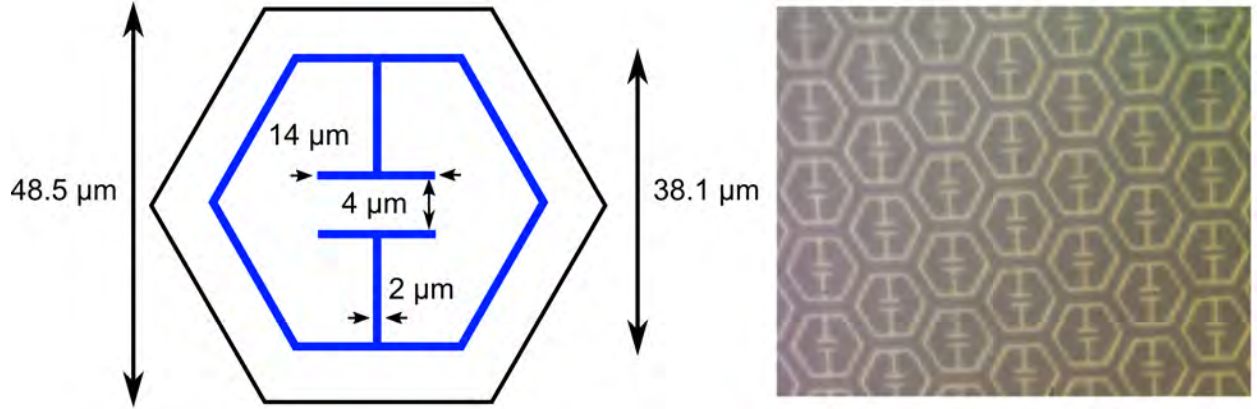


Figure 4.1: Hexagonal metamaterials used in this study (MM1).

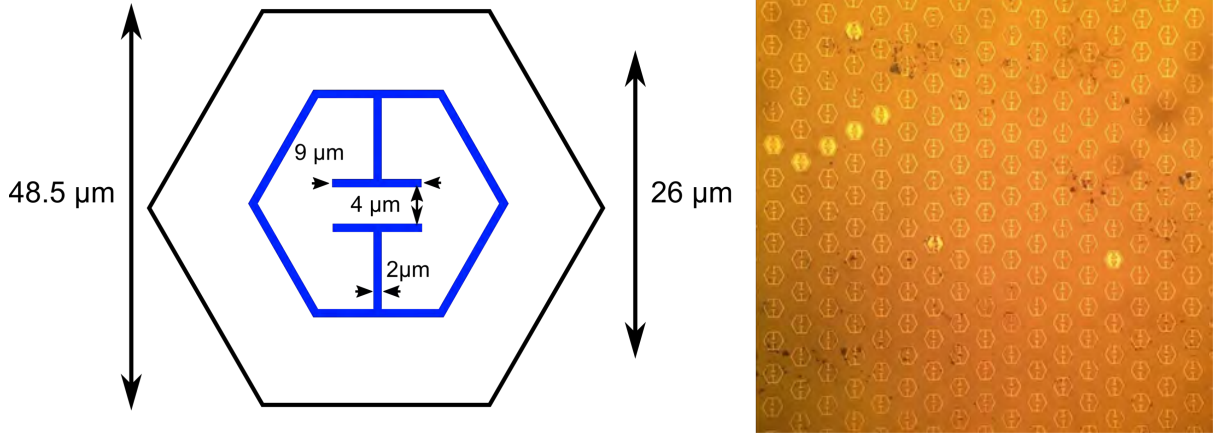


Figure 4.2: Hexagonal metamaterials with smaller metallic inclusions compare to Figure 4.1 used in this study (MM2).

4.2.2 Metamaterial THz Characterization

The structures were characterized using the THz-TDS in transmission mode. As mentioned before the system was aligned until the THz amplitude was at its maximum. The equipment was thermalized for 1 hour, and the sample was positioned at the focal point of the THz beam path.

Several measurements were performed: air reference, silicon wafer reference and the hexagonal-shaped metamaterial before and after deploying the ZnO QDs. The QDs were spin cast directly on the surface of the sample and the solvent was allowed to evaporate. For the MM1, Transmission vs frequency results are shown in Figure 4.3 for ZnO pH10 and ZnO pH12, respectively. These results show a resonance frequency of 1 THz for the metamaterial MM1 without the ZnO QDs (represented by the brown dotted line in Figure 4.3). After the ZnO pH12 and pH10 were deployed the resonance frequency was shifted to 0.96 THz and 0.95 THz, respectively.

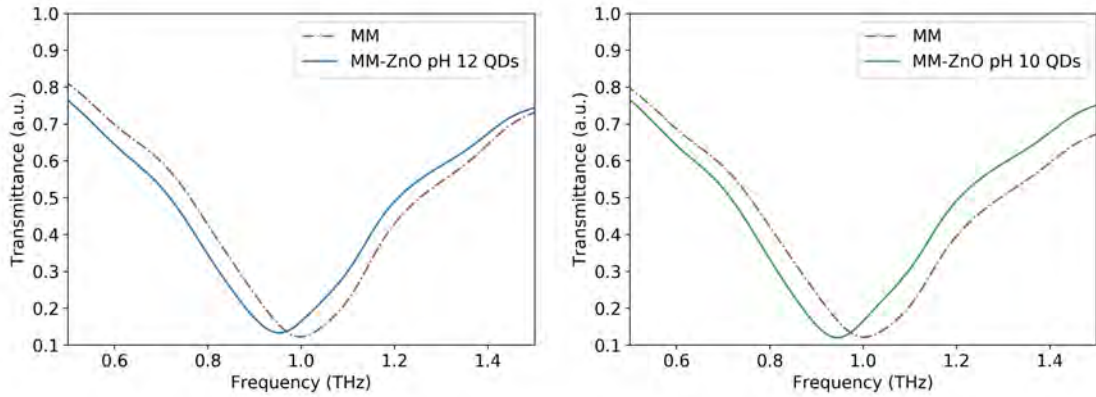


Figure 4.3: Hexagonal metamaterials used in this study (MM1) before and after deploying the ZnO QDs.

These results suggested an influence on the resonance frequency of the MM1 after ZnO QDs of two different sizes were deposited on the surface. We also wanted to test the possibility of actively modulate this behavior. We started by illuminating the MM1 with ZnO QDs on top with UV lamps with wavelength of 302 nm and 365 nm. The intensities of the lamps were $3.52 \times 10^{-5} \frac{W}{cm^2}$ for the 302 nm and $2.88 \times 10^{-5} \frac{W}{cm^2}$ for the 365 nm lamp. These results for the MM1 with ZnO pH12 and ZnO pH10 on top are shown in Figure 4.4, respectively. Although there was a variation on the amplitude with the two different UV lamps, we observed that the result were not consistent through the measurements. We attribute these inconsistencies to differences in power of the lamps and incoherence characteristics of the UV sources. To obtain more consistent results we decided to illuminate the samples with a coherent laser with wavelength of 400 nm, which an intensity that

was measured to be $2.5 \times 10^{-4} \frac{W}{cm^2}$. The results for the MM1 with ZnO pH12 and ZnO pH10 on top before and after being illuminated with the laser are shown in Figure 4.5. For these measurements the modulation was 9.21% and 4.55% for the ZnO pH12 and ZnO pH10, respectively.

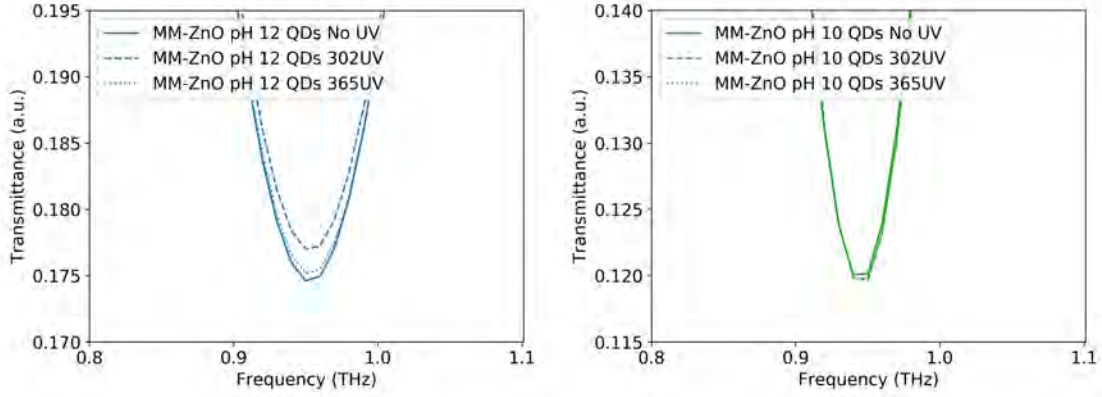


Figure 4.4: Hexagonal metamaterials used in this study (MM1) with ZnO pH12 and pH10 before and after being exposed to UV lamps with wavelengths of 302 nm and 365 nm.

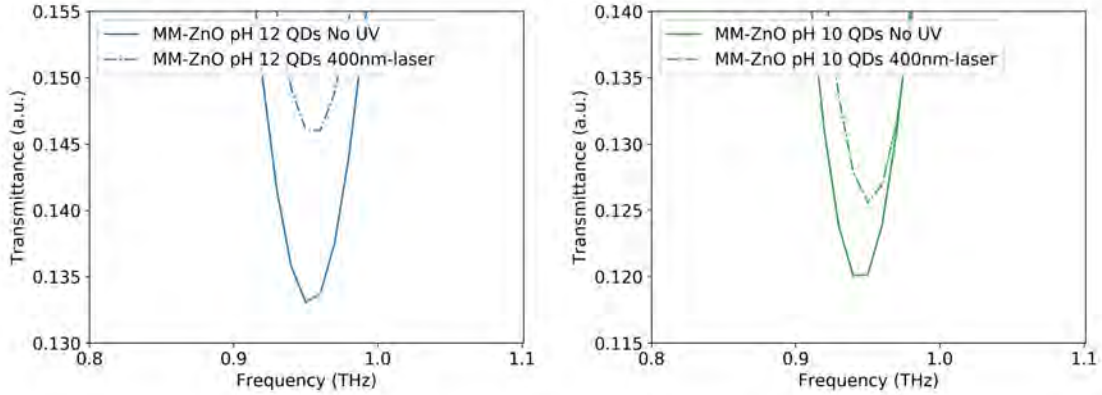


Figure 4.5: Hexagonal metamaterials used in this study (MM1) with ZnO pH12 and pH10 before and after being exposed to a UV laser with a wavelength of 400 nm.

To verify our results we performed the same set of measurements but on the second hexagonal MM shape (MM2). The THz-TDS results before and after deploying the ZnO pH12 and ZnO pH10 on the MM surface are shown in Figure 4.6. The MM2 by itself shows a resonance frequency at 1.09 THz (represented by the brown dotted line), after the addition of the ZnO QDs of different sizes the frequency was shifted to 1.07 THz and 1.06 THz for pH12 and pH10, respectively. Similarly, the samples were illuminated with UV sources with wavelengths of

302 nm and 365 nm. The results for the MM1 with ZnO QDs illuminated with UV lamps 302 nm and 365 nm of wavelength are shown in Figure 4.7. We observed a relatively small effect on the samples, with a modulation change percent of approximately 0.2% and 0.8% for pH12 and pH10, respectively. Similar to the results presented for MM1, the UV lamps result were not consistent thought the samples so we decided to performed the experiments using a coherent laser source with a wavelength of 400 nm. The result are shown in Figure 4.8. The modulation percent for these measurements were obtained to be 1.79% and 2.56% for the MM2 sample with ZnO pH12 and pH10, respectively.

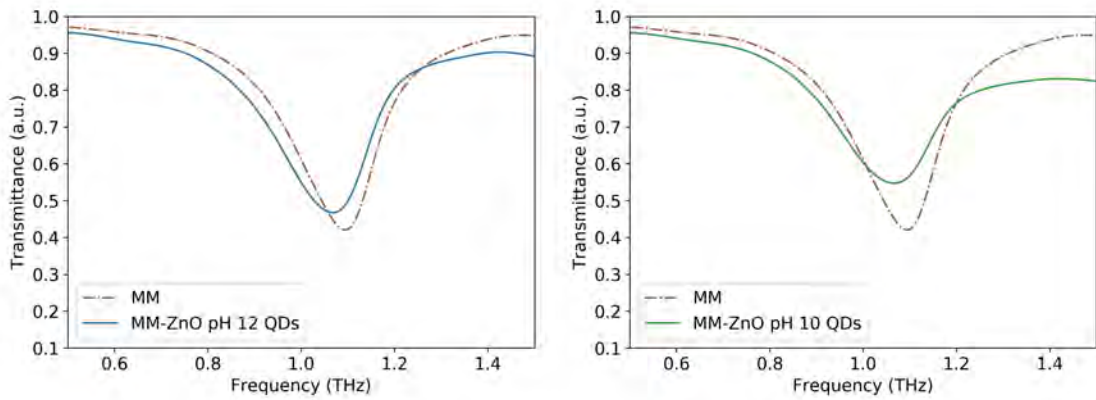


Figure 4.6: Resonant frequency of hexagonal-shaped MM2 before and after deploying the ZnO pH12 and ZnO pH10 QDs.

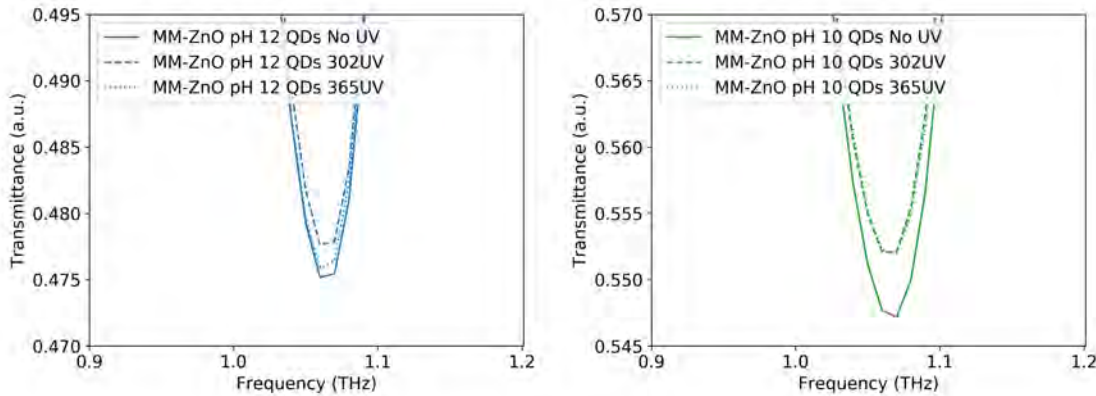


Figure 4.7: Hexagonal metamaterials used in this study (MM2) with ZnO pH12 and pH10 before and after being exposed to UV lamps with wavelengths of 302 nm and 365 nm.

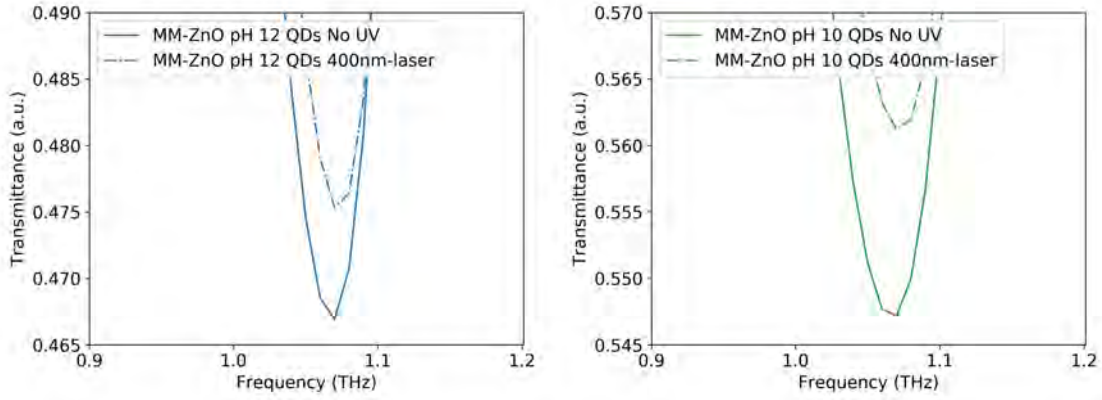


Figure 4.8: Hexagonal metamaterials used in this study (MM2) with ZnO pH12 and pH10 before and after being exposed to a UV laser with a wavelength of 400 nm.

The measurements using the laser showed significant improvement on the modulation for both configurations in comparison with UV lamps. For the MM1 with ZnO pH10 a modulation of 4.55% was obtained and for the MM1 with ZnO pH 12 QDs a modulation of 2.76% was observed. We attribute the observed results to a higher degree of confinement effect in smaller quantum dots. For the MM2 samples, we obtained modulation percentages of 2.56% and 1.79% for the ZnO QDs pH10 and ZnO pH12, respectively. These results are puzzling since we expected the pH 12 QDs (which are smaller, as shown above) to yield higher modulation depths for MM2 as well. We suspect that, since the spacing between cells in MM2 is larger (see Fig. 4.2), the overall density of ZnO on MM2 is smaller in the pH 12 case, which will affect the modulation depth. In the case of MM1, the cell spacing is smaller and we expect that the density of ZnO is similar between pH 10 and pH 12, leading to enhanced interactions between the QDs and providing the observed dependence of the modulation depth with QD size. Direct determination of the ZnO concentrations on the MMs, would help settle this issue.

The results are summarized in 4.1. Also, these changes in modulation depth demonstrate the capability of hexagonal MM via the deployment of ZnO QDs to actively tune THz electromagnetic signals.

Table 4.1: Hexagonal-shaped MMs results summary

MM1	ZnO pH10	ZnO pH12
modulation (400 nm laser) (%)	4.55	9.21
modulation (302 nm UV lamp) (%)	0.37	1.36
modulation (365 nm UV lamp) (%)	0.46	0.33
MM minimum (THz)	1	1
MM + QDs minimum (THz)	0.94	0.95
MM2		
modulation (400 nm laser) (%)	2.56	1.79
modulation (302 nm UV lamp) (%)	0.8	0.2
modulation (365 nm UV lamp) (%)	0.87	0.73
MM minimum (THz)	1.09	1.09
MM + QDs minimum (THz)	1.06	1.07

4.3 Conclusions

Two different hexagonally shaped MMs, MM1 and MM2 namely were fabricated using conventional lift-off lithography process on a single crystal Silicon wafer. The MMs were tested in the THz regime using THz-TDS in transmission mode. Transmission results for the MMs without ZnO QDs showed resonance frequencies at 1 THz and 1.09 THz for MM1 and MM2, respectively. Then ZnO QDs of two different sizes pH12 (2.12 nm) and pH10 (3.00 nm) were deployed on the MMs surfaces. The resonance frequencies were shifted to 0.95 THz and 0.94 THz for the MM1 with the two different sizes QDs, and to 1.07 THz and 1.06 THz for the MM2. Then the samples were illuminated with incoherent UV sources with wavelengths of 302 nm and 365 nm, and with intensities of $3.52 \times 10^{-5} \frac{W}{cm^2}$ and $2.88 \times 10^{-5} \frac{W}{cm^2}$, respectively. With the UV lamps we observed relatively small changes on our results maybe due to the coherent nature of the lamps and the low intensities. To minimize these systematic errors and have more consistent measurements we performed the measurements using a coherent laser source with a wavelength of 400 nm. The results shows a relatively larger effect on the THz modulation after illuminating the samples with the laser. We attribute our results to the higher degree of confinement effect in smaller quantum dots. Additionally, we anticipate the reported effects could also be more conspicuous by employing a higher amount of QDs and/or by deploying the QDs on

specific region of the MMs, specifically in the capacitive region to change the permittivity of the resonator and as consequence improving the reconfigurability of the devices in the THz regime.

CHAPTER 5: OHMIC CONTACT FORMATION IN III-V SEMICONDUCTOR MATERIALS

This chapter is based on the manuscript *Low temperature ohmic contacts for AlGaIn/GaN HEMTs* by Clarissa Vazquez Colon, David Look, Eric Heller, John Cetnar, and Arturo Ayon (2019), currently under review at the Optical Engineering Journal.

As mentioned throughout this work THz is a very useful and powerful technique for materials and devices characterization. However, this technique still have limitations such as: low resolution and low intensity [66]. A possible solution to overcome these limitations is the study and utilization of Gallium Nitride (GaN) devices. Due to their higher bandgap, higher saturation velocities, good thermal conductivity and their high 2D electron gas (2DEG) density, these materials are expected to exhibit higher output power and higher operation frequencies than other III-V devices [66]. A collaborative project related to the study of a GaN-based, specifically AlGaIn/GaN is presented in the following chapter.

5.1 Introduction

Semiconductor materials for electronic devices are selected on the basis of their energy bandgap value and electrical characteristics [67]. Recently, III-V semiconductor materials have captured the attention of the research community because, compared to silicon (Si), they exhibit several attractive properties including larger band gaps, higher electron mobilities, and higher saturation velocities [68–70]. These are the reasons why they have been considered as a feasible option for optoelectronics and bandgap engineering-based microelectronics [71]. This work is focused on the study of AlGaIn/GaN-based high electron mobility transistors (HEMT). These heterostructures contain a two-dimensional electron gas (2DEG), with high electron mobilities of about $1500 - 2000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature [72–75], and saturation velocities larger than $3 \times 10^7 \text{ cm s}^{-1}$ [71]. However, such structures also exhibit critical limitations such as electron trapping, gradual degradation over time, and thermal instability when metal contacts are applied [76, 77]. Thus,

there is still room for improvement in terms of material and device fabrication stability [78, 79], especially for ohmic contact formation which currently requires high thermal treatments and low work function metal species [80]. Good ohmic contacts lower the on-resistance of the device, thus reducing switching losses and enabling higher operating voltages.

A common method of achieving ohmic contacts is to place a highly doped semiconductor layer in between the contact metal and the device in order to reduce the thickness of the depletion region [81]. For AlGaN/GaN, this method requires high temperature annealing, which can sometimes adversely affect the material properties [82]. In this work we study ohmic contact formation on AlGaN/GaN heterostructures and the effect of thermal treatment on the quality of the contacts. Also, we present a relatively simple procedure for making ohmic contact without employing thermal treatments, by inscribing shallow trenches on the surface and filling them with indium (In) metal. The process proposed here is to be taken as proof-of-concept only and is not intended as an immediate replacement for existing industrial/commercial manufacturing techniques. Temperature-dependent electrical measurements imply the presence of tunneling currents that are also predicted by Schrödinger-Poisson modeling.

The structure was grown by metal organic chemical vapor deposition (MOCVD) on 4" 6H-SiC substrates. It consists of the following material stack: AlN nucleation layer / 1.8 μm Fe-doped GaN buffer layer / GaN channel / 1nm AlN / 16-nm- $\text{Al}_{0.27}\text{Ga}_{0.73}\text{N}$ / 3nm GaN cap (see Fig. 5.1) [83].



Figure 5.1: HEMT structure grown by MOCVD.

Hall-effect measurements were performed on 10-mm-square samples (planar view in Fig. 5.2) in a Van der Pauw configuration, which requires flatness, uniformity, and point contacts on the

surface periphery [84–86]. Our contacts were placed close to the sample corners and the contact resistance value was estimated from Eq. 5.1 [84]

$$R_T \approx 2R_c + \frac{r_s l}{w} \quad (5.1)$$

where R_T is the total resistance (measured), R_c is the resistance of single contact (calculated from Eq. 5.1), r_s is the material sheet resistance (measured), and w and l are the sample width and length, respectively (measured). For our samples, $l/w = 1$.

5.1.1 Surface contacts

Ohmic contacts were first prepared by our usual process, i.e., soldering indium (In) dots on the sample corners, as shown in Fig. 5.2. The values of sheet resistance r_s and sheet concentration n_s were determined from standard 4-point Van der Pauw measurements using an Accent 5500 Hall effect measurement system at room temperature. Also, the total resistances of each of the contact pairs were averaged to get R_T . Then, from Eq. 5.1, the contact resistance R_c was calculated to be 33.6 k Ω . The measured contact resistance is higher than that of many surface contacts reported elsewhere [71, 77, 87, 88], but this is likely because no anneal was carried out on our samples.

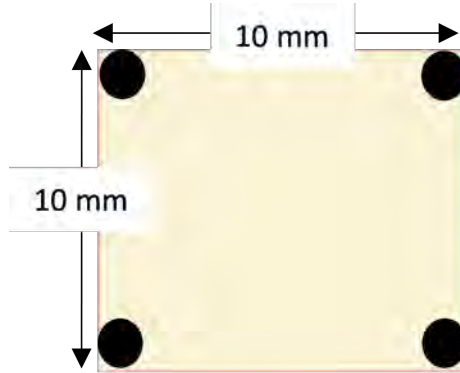


Figure 5.2: Normal contact sketch. Filled circles denote indium contacts

5.1.2 Indented contacts

The contacts were improved by indenting the surface at each corner of the sample using a diamond-tip scribe and subsequently filling the indentation with indium as shown in Fig. 5.3. Indeed, the contact resistance R_c decreased to 3.32 k Ω , 10-times lower than the previously measured value of 33.6 k Ω .

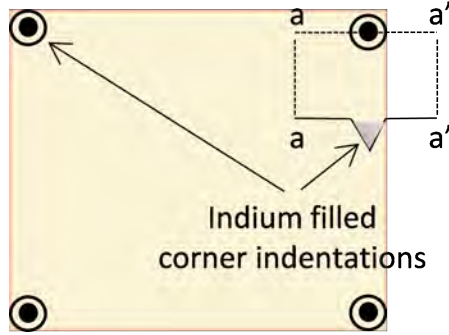


Figure 5.3: Sample with indentations filled with indium as contacts. Filled circles denote indium contacts. Open circles denote indentations in the sample.

In order to clarify the dependence of the contact resistance on annealing temperature, the samples were subsequently annealed in a N_2 ambient at 300°C and 400°C, respectively. In all cases, regardless of the applied current employed, the annealed samples exhibited a higher contact resistance than that of the unannealed samples. The largest variations were observed to occur with an applied current of 1 μA (see Table 5.1) where R_c increased from ~3.22 k Ω for the sample without an annealing treatment to ~24.3 k Ω when annealed at 300°C and to a higher value of ~323 k Ω when annealed at 400°C. Clearly, annealing in N_2 does not improve the contact resistance and this behavior is thought to be associated to the introduction of contact defects such as rough surfaces, material diffusion and oxidation [89]. Also, the difference in contact resistance values between the annealed and non-annealed samples is lower at higher applied currents in what is referred to as an inverted current dependence associated with relatively low quality contacts [90].

Table 5.1: Contact resistance dependence on annealing temperature

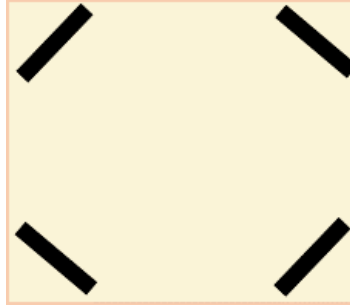
Applied Current (μA)	Contact Resistance ($\text{k}\Omega$) no anneal	R_c ($\text{k}\Omega$) 300 °C anneal	R_c ($\text{k}\Omega$) 400 °C anneal
1	3.22	24.3	323
50	3.32	11.9	26.2
100	3.41	7.85	-

Table 5.2: Contact resistance values on samples with diagonally-scribed lines without thermal treatment.

Applied Current (μA)	Contact Resistance ($\text{k}\Omega$)
1	1.35
50	2.52
100	2.69

5.1.3 Scribed contacts

Per the discussion above, contact resistance values deteriorated upon performing annealing treatments. An additional test was performed to determine the dependence of R_c on topological variations of the indium-filled indentations. To this end, diagonally-scribed lines were introduced at the corners of the sample, and subsequently filled with indium, as shown in Fig. 5.4. The contact resistance with an applied current of 1 μA was $\sim 1.35 \text{ k}\Omega$ (see Table 5.2), which shows an improvement of roughly a factor two over that of the unannealed point-indentation sample.

**Figure 5.4:** Sample with diagonally scribed lines filled with indium as contacts.

The depths of the scribed lines were measured using a high-resolution laser microscope, a profilometer, and a Zygo white light interferometer. All methods consistently indicated a depth of ~ 1.7 to $2 \mu\text{m}$ (see Figs. 5.5 and 5.6).

Subsequently, temperature-dependent Hall-effect measurements from 10 to 300 K were performed using a LakeShore 7507 system. The results are shown in Fig. 5.7 and indicate that the

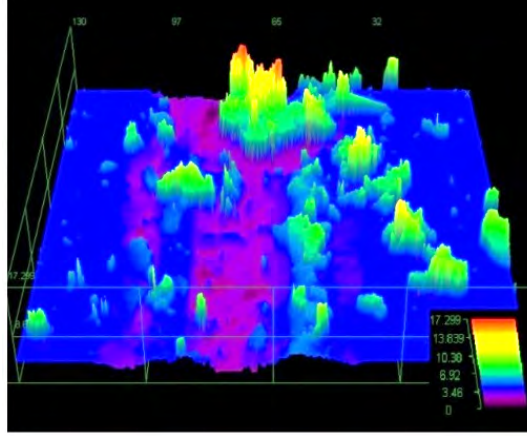


Figure 5.5: Depth of the scribed line employing a high-resolution laser microscope.

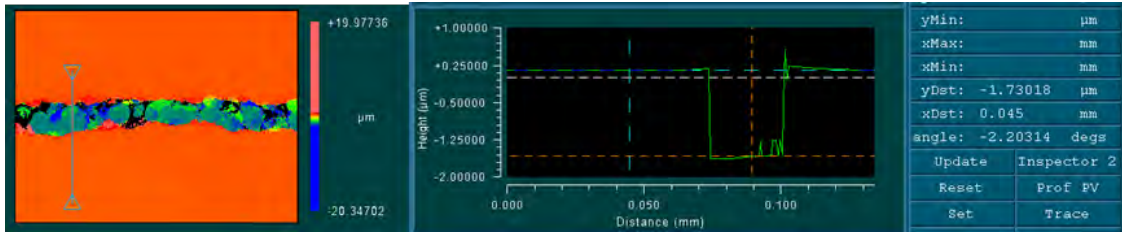


Figure 5.6: Depth of the scribed line employing a Zygo white light interferometer.

contact resistance exhibits a smaller temperature dependence than the sheet resistance. This weak dependence on temperature suggests that thermionic emission is not the dominant transport mechanism, but instead that current flows due to a tunneling effect [91]. This is also validated by the computational model shown above, where we determine that the characteristic tunneling energy $\epsilon_{00} > kT$, implying the dominance of tunneling currents. Similar observations were made when this procedure was repeated on an AlScN/GaN HEMT device, showing the universal nature of this effect (data not shown).

5.1.4 Tunneling model

Our contact can be essentially modeled as an In/GaN structure, since the indium in the scribed hole directly contacts the 2DEG in the GaN, circumventing the AlGaN. Current can tunnel through the In/GaN barrier if its width can be sufficiently reduced by a high enough volume electron concentration n in the 2DEG. A Schrödinger-Poisson analysis of n in the 2DEG is

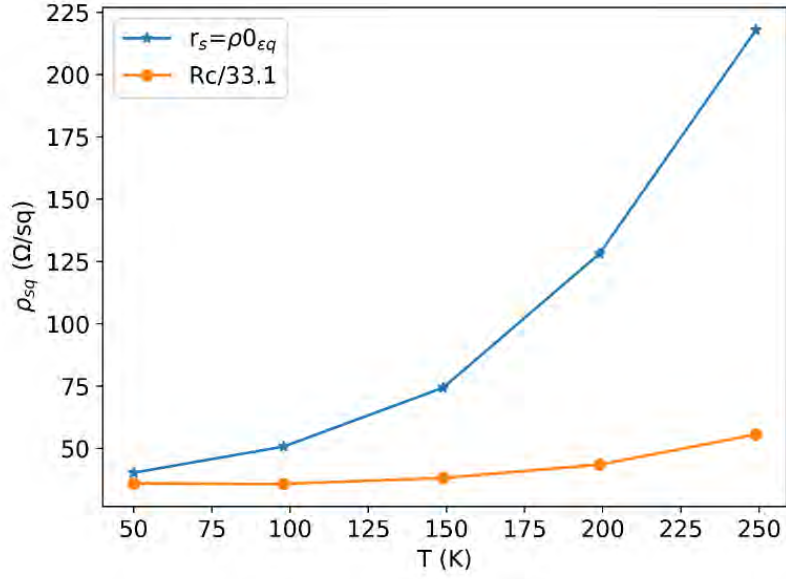


Figure 5.7: Temperature dependent measurement for the diagonally scribed sample. The smaller temperature dependence of the contact resistance compared to that of the sheet resistance indicates the presence of tunneling effects.

displayed in Fig. 5.8, showing that $n \sim 3 - 4 \times 10^{19} \text{ cm}^{-3}$ a few nm below the interface.

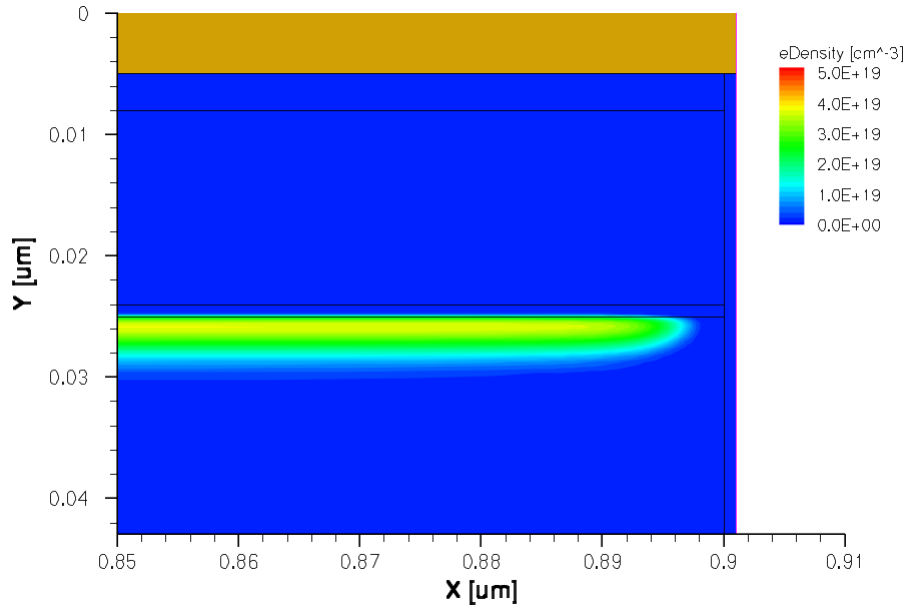


Figure 5.8: Distribution of the electron density in the AlGaIn/GaN 2DEG.

The tunneling probability is defined as [84]:

$$P = \exp \left[\frac{e(V - V_{bi})}{\varepsilon_{00}} \right] \quad (5.2)$$

where e is the electron charge, V and V_{bi} are the barrier potential and the built-in potential, respectively, and ε_{00} is the characteristic energy, defined as follows [84]:

$$\varepsilon_{00} = \frac{e\hbar}{2} \sqrt{\frac{n}{\varepsilon m^*}} \quad (5.3)$$

where e is the electron charge, $\hbar$ is the reduced Planck constant, n is the volume carrier concentration, ε is the permittivity, and m^* is the electron effective mass of the GaN. In our case, $\varepsilon = 9.9\varepsilon_{vac}$, $m^* = 0.22m_0$, and $n = 3.7 \times 10^{19} \text{ cm}^{-3}$, giving a result $\varepsilon_{00} = 0.077 \text{ eV} = 894 \text{ K}$ [81]. Thus $\varepsilon_{00} > kT$, suggesting the dominance of tunneling currents. Another process that may have relevance is defect-assisted tunneling, perhaps enhanced by the scribing action [92]. This possibility will be further investigated by the use of photolithography to create the trench and also to generate different trench shapes.

5.2 Conclusions

We have developed a simple, fast method of creating ohmic contacts on AlGaIn/GaN heterostructures. Straight trenches about 2-mm long, 1-mm wide, and 2- μm deep, are scribed into the sample near the corners and filled with indium from a soldering iron. The indium directly contacts the 2DEG in the GaN, forming an ohmic contact without annealing. At room temperature, the sheet resistance $r_s \approx 0.3\text{k}\Omega$ and the contact resistance $R_c \approx 1\text{k}\Omega$. The latter can be compared with $R_c \approx 30\text{k}\Omega$ for normal indium contacts placed directly on the AlGaIn surface. The temperature dependence of r_s was much less than that of R_c , suggesting tunneling conduction. Confirmation comes from a Schrödinger-Poisson analysis of carrier concentration n in the 2DEG along with a calculation of the tunneling probability based on the peak value of n . This methodology was also successfully applied to AlScN/GaN heterostructures, and indeed will likely be useful for all HEMT structures that present problems with ohmic contact formation.

CHAPTER 6: CONCLUDING REMARKS

We have investigated materials and devices properties at terahertz frequencies. The THz characterization was performed using THz-TDS, from this technique we extracted transmission and optical properties of the materials under study. These properties were obtained after further signal processing, that involved Gaussian window filtering, followed by Fast Fourier transformation (FFT) explained in detail on reference2. The characterization measurements were taken with and without the exposure of three different sources, UV lamps with wavelengths of 302 nm and 365 nm and a UV laser with a wavelength of 400 nm.

In this work we presented the synthesis of ZnO pH12 and pH10 using sonochemical method. The bandgaps and sizes were estimated using the absorbance measurements and Brus quantum mechanical approximation. The bandgap values were estimated to be 3.43 eV for the pH10 and 3.62 eV for the pH12 and sizes values were estimated to be 3.00 nm and 2.12 nm, respectively. These values were corroborated by TEM images showing sizes values of 3.20 nm and 1.85 nm for the ZnO QDs pH 10 and pH12, respectively. For the THz characterization the samples were pulverized and embedded in a PDMS membrane. These THz measurements were performed taking several measurements of the reference (PDMS membrane) and then the sample (PDMS + ZnO QDs) with and without UV excitation. We observed an increase on the index of refraction of the PDMS after the addition of the ZnO QDs to the membrane. Our results show that the larger ZnO QDs (pH10) exhibit a higher index of refraction than the smaller ZnO QDs (pH12). Then the samples were exposed to UV excitation, in all three cases an increase in the index of refraction was observed in comparison with the non exposed samples. More consistent and pronounced effects were observed after illuminating the samples with a coherent laser with wavelength of 400 nm. The results presented reflect that larger ZnO QDs (pH10) exhibit a bigger change in the index of refraction at THz frequencies maybe due to their characteristic of exhibiting quantum confinement effects.

The observed apparent THz modulation of the ZnO QDs of different sizes and under UV

excitation of the QDs was tested on THz circuitry. We fabricated two (MM1 and MM2) hexagonal shaped THz metamaterial (the metamaterials has been on reference [63]), using conventional lift-off process on high resistivity silicon wafers. Transmission as function of frequency results for the MM1 and MM2 samples were obtained by THz-TDS measurements, the samples exhibited a resonance frequency at 1 THz for the MM1 and 1.09 THz for the MM2. Then, ZnO QDs of pH10 and pH12 were deployed on the MMs surface and characterized at THz frequencies. The results for the MM1 showed a shift on the resonance frequency to 0.94 THz and 0.95 THz after deploying the ZnO QDs pH10 and pH12, respectively. Similarly, for the MM2 we observed a shift in the resonant frequency to 1.06 THz and 1.06 THz for the ZnO QDs of pHs 10 and 12, respectively. These samples were then exposed to UV lamps with wavelengths of 302 nm and 365 nm, for the MM1 we observed THz modulations of 0.37 % and 0.36 % (302 nm wavelength) and 0.46 % and 0.33 % (365 nm wavelength), respectively. Similar results were obtained for the MM2 and are summarized in table 4.1 in chapter 4. The samples were then exposed to coherent UV laser with wavelength of 400 nm. The modulation was 4.55 % and 9.21 % for the MM1 with ZnO pH10 and pH12, respectively. For the MM2, the modulation was 2.56 % (MM2 with ZnO pH10) and 1.79 % (MM2 with ZnOpH12). These quantum dot-enhanced structures showed marked differences in their response to terahertz frequencies versus the ones without quantum dots. We presumably, observed THz active modulation after illuminating the samples with UV light. The reported results exhibited a higher effect when larger size QDs were deposited on the surface. These results can be explained on the grounds that the synthesized semiconducting nanoparticles exhibit quantum confinement effects where exciton polarizability, reported to be proportional to the fourth power of the radius ($\alpha \sim R^4$) [93]. Further refinement in preparation, synthesis, and deposition techniques will likely enhance the effects shown here. Furthermore, since the photolithographic process for the MM fabrication is mass-production compatible [94], while the ZnO QDs are stable, biologically compatible, and low-cost [95], the MM-ZnO QD setup described herein is considered to be attractive for industrial applications.

Finally, we described an effort to create stable ohmic contacts in AlGaIn/GaN

heterostructures. This involved introducing indium-filled indentation in the sample, which had the effect of decreasing the contact resistance R_c by a factor of 10. We then explored the dependence of the contact resistance on the topological variations of the indium filled indentations. To this end, we inscribed diagonal trenches at the corners of the sample. This improved the contact resistance by a factor of roughly two. This result is promising in light of GaN-based device's higher bandgap, saturation velocities, and better thermal conductivity, which could help overcome some of the resolution and intensity limitations of terahertz-based devices.

BIBLIOGRAPHY

- [1] J. Z. Xu, C. L. Zhang, and X. C. Zhang, “Recent progress in terahertz science and technology,” 2002.
- [2] H. Tao, W. J. Padilla, X. Zhang, and R. D. Averitt, “Recent progress in electromagnetic metamaterial devices for Terahertz applications,” *IEEE Journal on Selected Topics in Quantum Electronics*, vol. 17, no. 1, pp. 92–101, 2011.
- [3] W. Withayachumnankul and D. Abbott, “Metamaterials in the Terahertz Regime,” 2009.
- [4] I. S. Russe, D. Brock, K. Knop, P. Kleinebudde, and J. A. Zeitler, “Validation of terahertz coating thickness measurements using X-ray microtomography,” *Molecular Pharmaceutics*, vol. 9, pp. 3551–3559, dec 2012.
- [5] S. J. Park and Y. H. Ahn, “Terahertz metamaterials application in sensing bacteria and fungi,” in *2015 40th International Conference on Infrared, Millimeter, and Terahertz waves (IRMMW-THz)*, p. 1, IEEE, aug 2015.
- [6] R. M. Woodward, B. E. Cole, V. P. Wallace, R. J. Pye, D. D. Arnone, E. H. Linfield, and M. Pepper, “Terahertz pulse imaging in reflection geometry of human skin cancer and skin tissue,” *Physics in Medicine and Biology*, vol. 47, pp. 3853–3863, nov 2002.
- [7] D. A. Crawley, C. Longbottom, V. P. Wallace, B. E. Cole, D. D. Arnone, and M. Pepper, “Three-dimensional terahertz pulse imaging of dental tissue,” vol. 4633, p. 84, International Society for Optics and Photonics, apr 2002.
- [8] P. H. Siegel, *THz Technology: An Overview*. World Scientific Publishing Co. Pte. Ltd., 2003.
- [9] A. I. Hernandez-Serrano, S. C. Corzo-Garcia, E. Garcia-Sanchez, M. Alfaro, and E. Castro-Camus, “Quality control of leather by terahertz time-domain spectroscopy,” *Applied Optics*, vol. 53, p. 7872, nov 2014.

- [10] J. Liu, J. Dai, S. L. Chin, and X.-C. Zhang, “Broadband terahertz wave remote sensing using coherent manipulation of fluorescence from asymmetrically ionized gases,” *Nature Photonics*, vol. 4, pp. 627–631, sep 2010.
- [11] T. Kleine-Ostmann, K. Pierz, G. Hein, P. Dawson, and M. Koch, “Audio signal over THz communication channel using semiconductor modulator,” *Journal of the Pakistan Medical Association*, vol. 62, no. 5, pp. 487–489, 2012.
- [12] A. G. Davies, A. D. Burnett, W. Fan, E. H. Linfield, and J. E. Cunningham, “Terahertz spectroscopy of explosives and drugs,” *Materials Today*, vol. 11, pp. 18–26, mar 2008.
- [13] D. Banerjee, W. von Spiegel, M. D. Thomson, S. Schabel, and H. G. Roskos, “Diagnosing water content in paper by terahertz radiation,” *Optics Express*, vol. 16, p. 9060, jun 2008.
- [14] K. Baaske, M. Salhi, F. Rutz, T. Hasek, R. Wilk, H. Richter, and M. Koch, “Mail inspection using THz imaging: a comparison of three different systems,” *Terahertz for Military and Security Applications IV*, vol. 6212, no. May 2006, p. 62120U, 2006.
- [15] Y. C. Shen, T. Lo, P. F. Taday, B. E. Cole, W. R. Tribe, and M. C. Kemp, “Detection and identification of explosives using terahertz pulsed spectroscopic imaging,” *Applied Physics Letters*, vol. 86, p. 241116, jun 2005.
- [16] D. Dragoman and M. Dragoman, “Terahertz fields and applications,” *Progress in Quantum Electronics*, vol. 28, no. 1, pp. 1–66, 2004.
- [17] J. T. Hong, J.-Y. Park, S. Lee, and Y. H. Ahn, “UV-induced terahertz wave modulation in free-standing ZnO nanowire films,” vol. 6, no. 12, pp. 3751–3758, 2016.
- [18] Z. T. Ma, Z. X. Geng, Z. Y. Fan, J. Liu, and H. D. Chen, “Modulators for Terahertz Communication: The Current State of the Art,” *Research*, vol. 2019, no. 3, pp. 1–22, 2019.

- [19] A. I. McIntosh, B. Yang, S. M. Goldup, M. Watkinson, and R. S. Donnan, “Terahertz spectroscopy: a powerful new tool for the chemical sciences?,” *Chem. Soc. Rev.*, vol. 41, pp. 2072–2082, feb 2012.
- [20] J. B. Baxter and G. W. Guglietta, “Terahertz spectroscopy,” *Analytical Chemistry*, vol. 83, no. 12, pp. 4342–4368, 2011.
- [21] N. Peygambarian, S. W. Koch, and A. Mysyrowicz, *Introduction to Semiconductor Optics*. Prentice Hall Series in Solid State Physical Electronics, Prentice Hall, 1993.
- [22] J. Tilchin, F. T. Rabouw, M. Isarov, R. Vaxenburg, R. J. A. Van Dijk-Moes, E. Lifshitz, and D. Vanmaekelbergh, “Quantum Confinement Regimes in CdTe Nanocrystals Probed by Single Dot Spectroscopy: From Strong Confinement to the Bulk Limit,” *ACS Nano*, vol. 9, pp. 7840–7845, aug 2015.
- [23] M. C. Beard, G. M. Turner, and C. A. Schmittenmaer, “Size-Dependent Photoconductivity in CdSe Nanoparticles as Measured by Time-Resolved Terahertz Spectroscopy,” *Nano Letters*, vol. 2, pp. 983–987, sep 2002.
- [24] R. Ulbricht, E. Hendry, J. Shan, T. F. Heinz, and M. Bonn, “Carrier dynamics in semiconductors studied with time-resolved terahertz spectroscopy,” *Reviews of Modern Physics*, vol. 83, no. 2, pp. 543–586, 2011.
- [25] M. C. Beard, G. M. Turner, and C. A. Schmittenmaer, “Terahertz Spectroscopy,” *The Journal of Physical Chemistry B*, vol. 106, pp. 7146–7159, jul 2002.
- [26] S. L. Dexheimer, “Terahertz spectroscopy: principles and applications ,” 2008.
- [27] A. Redo-Sanchez and X. C. Zhang, “Terahertz Science and Technology Trends,” 2008.
- [28] N. M. Burford and M. O. El-Shenawee, “Review of terahertz photoconductive antenna technology,” *Optical Engineering*, vol. 56, no. 1, p. 10901, 2017.

- [29] A. Y. Pawar, D. D. Sonawane, K. B. Erande, and D. V. Derle, "Terahertz technology and its applications," *Drug Invention Today*, vol. 5, pp. 157–163, jun 2013.
- [30] M. Schirmer, M. Fujio, M. Minami, J. Miura, T. Araki, and T. Yasui, "Biomedical applications of a real-time terahertz color scanner," *Biomedical Optics Express*, vol. 1, no. 2, p. 354, 2010.
- [31] J. F. Federici, B. Schulkin, F. Huang, D. Gary, R. Barat, F. Oliveira, and D. Zimdars, "THz imaging and sensing for security application explosives, weapons and drugs," *Semiconductor Science and Technology*, vol. 20, 2005.
- [32] V. G. Veselago, "The electrodynamics of substances with simultaneously negative values of ϵ and μ ," *Soviet Physics Uspekhi*, vol. 10, no. 4, pp. 509–514, 1968.
- [33] J. B. Pendry, "Calculating photonic band structure," *J. Phys.: Condes. Matter*, vol. 8, pp. 1085–1108, 1996.
- [34] D. R. Smith, D. C. Vier, W. Padilla, S. C. Nemat-Nasser, and S. Schultz, "Loop-wire medium for investigating plasmons at microwave frequencies," 1999.
- [35] T. J. Cui, D. R. Smith, and R. Liu, "Metamaterials: theory, design, and applications," 2010.
- [36] M. R. Hashemi, S. Cakmakyapan, and M. Jarrahi, "Reconfigurable metamaterials for terahertz wave manipulation," *Reports on Progress in Physics*, vol. 80, no. 9, 2017.
- [37] S. Nishizawa, K. Sakai, M. Hanyo, T. Nagashima, M. W. Takeda, K. Tominaga, A. Oka, T. Koichiro, and O. Morikawa, "Terahertz Time-Domain Spectroscopy," vol. 271, no. July, pp. 203–271, 2012.
- [38] W. Ghann and J. Uddin, "Terahertz (THz) Spectroscopy: A Cutting-Edge Technology," p. 13, IntechOpen, 2017.
- [39] Y. UENO and K. AJITO, "Analytical Terahertz Spectroscopy," *Analytical Sciences*, vol. 24, no. 2, pp. 185–192, 2008.

- [40] W. Ghann and J. Uddin, *Terahertz Spectroscopy - A Cutting Edge Technology*. InTech, mar 2017.
- [41] J. R. Freeman, H. E. Beere, and D. A. Ritchie, *Generation and Detection of Terahertz Radiation*, pp. 1–28. Berlin, Heidelberg: Springer Berlin Heidelberg, 2013.
- [42] X. C. Zhang and J. Xu, “Introduction to THz wave photonics .”
- [43] R. M. Smith and M. A. Arnold, “Terahertz time-domain spectroscopy of solid samples: Principles, applications, and challenges,” *Applied Spectroscopy Reviews*, vol. 46, no. 8, pp. 636–679, 2011.
- [44] MenloSystems, “TeraSmart.”
- [45] W. Withayachumnankul and M. Naftaly, “Fundamentals of measurement in terahertz time-domain spectroscopy,” *Journal of Infrared, Millimeter, and Terahertz Waves*, vol. 35, no. 8, pp. 610–637, 2014.
- [46] W. Withayachumnankul, H. Lin, S. P. Micken, B. M. Fischer, and D. Abbott, “Analysis of Measurement Uncertainty in THz-TDS,” *Proc of SPIE*, vol. 6593, pp. 659318–659326, 2007.
- [47] I. Pupeza, R. Wilk, and M. Koch, “Highly accurate optical material parameter determination with THz time-domain spectroscopy,” *Optics Express*, vol. 15, no. 7, p. 4335, 2007.
- [48] J. B. Baxter and C. A. Schmuttenmaer, “Conductivity of ZnO nanowires, nanoparticles, and thin films using time-resolved terahertz spectroscopy,” *Journal of Physical Chemistry B*, vol. 110, no. 50, pp. 25229–25239, 2006.
- [49] K. S. Suslick and G. J. Price, “Applications of Ultrasound to Materials Chemistry,” *Annual review of material science*, pp. 295–326, 1999.
- [50] A. B. Pandit and A. U. Badnore, “Effect of pH on sonication assisted synthesis of ZnO nanostructures: Process details,” *Chemical Engineering and Processing: Process Intensification*, vol. 122, no. August, pp. 235–244, 2017.

- [51] A. Zazueta-Raynaud, J. E. Pelayo-Ceja, R. Lopez-Delgado, and A. Ayon, “ZnO photoluminescent quantum dots with down-shifting effect applied in solar cells,” *Journal of Physics: Conference Series*, vol. 773, no. 1, 2016.
- [52] A. C. Caballero, M. Villegas, C. Moure, and J. F. Ferna, “Controlled precipitation methods : formation mechanism of ZnO nanoparticles,” vol. 21, pp. 925–930, 2001.
- [53] S. S. Alias, A. B. Ismail, and A. A. Mohamad, “Effect of pH on ZnO nanoparticle properties synthesized by sol-gel centrifugation,” *Journal of Alloys and Compounds*, vol. 499, no. 2, pp. 231–237, 2010.
- [54] A. Podzorov and G. Gallot, “Density of states and vibrational modes of PDMS studied by terahertz time-domain spectroscopy,” *Chemical Physics Letters*, vol. 495, no. 1-3, pp. 46–49, 2010.
- [55] S. Alfihed, M. H. Bergen, J. F. Holzman, and I. G. Foulds, “A detailed investigation on the terahertz absorption characteristics of polydimethylsiloxane (PDMS),” *Polymer*, vol. 153, no. August, pp. 325–330, 2018.
- [56] A. A. Guzelian, J. E. B. Katari, A. V. Kadavanich, U. Banin, K. Hamad, E. Juban, A. P. Alivisatos, R. H. Wolters, C. C. Arnold, and J. R. Heath, “Synthesis of Size-Selected, Surface-Passivated InP Nanocrystals,” 1996.
- [57] K. F. Lin, H. M. Cheng, H. C. Hsu, and W. F. Hsieh, “Bandgap engineering and spatial confinement of optical phonon in ZnO quantum dots,” *Applied Physics Letters*, vol. 88, no. 263117, 2006.
- [58] S. Kar and S. Chaudhuri, “Synthesis and optical properties of single and bicrystalline ZnS nanoribbons,” *Chemical Physics Letters*, vol. 414, no. 1, pp. 40–46, 2005.
- [59] L. Brus, “Electronic wave functions in semiconductor clusters: experiment and theory,” *The Journal of Physical Chemistry*, vol. 90, pp. 2555–2560, jun 1986.

- [60] F. Wang, J. Shan, M. A. Islam, I. P. Herman, M. Bonn, and T. F. Heinz, “Exciton polarizability in semiconductor nanocrystals,” *Nat Mater*, vol. 5, pp. 861–864, nov 2006.
- [61] H.-T. Chen, H.-T. Chen, W. J. Padilla, W. J. Padilla, J. M. O. Zide, J. M. O. Zide, A. C. Gossard, A. C. Gossard, A. J. Taylor, A. J. Taylor, R. D. Averitt, and R. D. Averitt, “Active terahertz metamaterial devices,” *Nature*, vol. 444, pp. 597–600, nov 2006.
- [62] H. Tao, A. C. Strikwerda, K. Fan, W. J. Padilla, X. Zhang, and R. D. Averitt, “Reconfigurable terahertz metamaterials,” *Physical Review Letters*, vol. 103, no. 14, pp. 1–4, 2009.
- [63] C. M. Bingham, H. Tao, X. Liu, R. D. Averitt, X. Zhang, and W. J. Padilla, “Planar wallpaper group metamaterials for novel terahertz applications,” *Optics Express*, vol. 16, no. 23, pp. 18565–18575, 2008.
- [64] J. D. Baena, J. Bonache, F. Martin, R. M. Sillero, F. Falcone, T. Lopetegi, M. A. G. Laso, J. Garcia-Garcia, I. Gil, M. F. Portillo, and M. Sorolla, “Equivalent-circuit models for split-ring resonators and complementary split-ring resonators coupled to planar transmission lines,” *IEEE Transactions on Microwave Theory and Techniques*, vol. 53, pp. 1451–1461, apr 2005.
- [65] D. Schurig, J. J. Mock, and D. R. Smith, “Electric-field-coupled resonators for negative permittivity metamaterials,” *Applied Physics Letters*, vol. 88, p. 41109, jan 2006.
- [66] K. Ahi, “Review of GaN-based devices for terahertz operation,” *Optical Engineering*, vol. 56, no. 09, p. 1, 2017.
- [67] B. J. Sealy, “Review of III-V semiconductor materials and,” *Journal of the Institution of Electronic and Radio Engineers*, vol. 57, no. 1, pp. S2–S12, 1987.
- [68] R. J. Trew, G. L. Bilbro, W. Kuang, Y. Liu, and H. Yin, “Microwave AlGaIn/InGaAs HFETs,” *IEEE microwave magazine*, pp. 56–66, 2005.

- [69] M. Snure, G. Siegel, D. C. Look, and Q. Paduano, “GaN and AlGaN/GaN heterostructures grown on two dimensional BN templates,” *Journal of Crystal Growth*, vol. 464, pp. 168–174, 2017.
- [70] S. S. Li, *Semiconductor Physics Electronics*. No. 1, Springer, 2014.
- [71] J. Würfl, V. Abrosimova, J. Hilsenbeck, E. Nebauer, W. Rieger, and G. Tränkle, “Reliability considerations of III-nitride microelectronic devices,” *Microelectronics Reliability*, vol. 39, no. 12, pp. 1737–1757, 1999.
- [72] Y. Wu, B. P. Keller, S. Keller, D. Kapolnek, P. Kozodoy, S. P. Denbaars, and U. K. Mishra, “Very high breakdown voltage and large transconductance realized on GaN heterojunction field effect transistors,” *Applied Physics Letters*, vol. 69, p. 1438, aug 1998.
- [73] M. E. Levinshtein, S. L. Rumyantsev, R. Gaska, J. W. Yang, and M. S. Shur, “AlGaN/GaN high electron mobility field effect transistors with low 1/f noise,” *Applied Physics Letters*, vol. 73, p. 1089, aug 1998.
- [74] R. Gaska, A. Osinsky, J. W. Yang, and M. S. Shur, “Self-heating in high-power AlGaN-GaN HFETs,” *IEEE Electron Device Letters*, vol. 19, pp. 89–91, mar 1998.
- [75] R. Oberhuber, G. Zandler, and P. Vogl, “Mobility of two-dimensional electrons in AlGaN/GaN modulation-doped field-effect transistors,” *Applied Physics Letters*, vol. 73, p. 818, aug 1998.
- [76] Y. C. Chou, D. Leung, I. Smorchkova, M. Wojtowicz, R. Grundbacher, L. Callejo, Q. Kan, R. Lai, P. H. Liu, D. Eng, and A. Oki, “Degradation of AlGaN/GaN HEMTs under elevated temperature lifetesting,” *Microelectronics Reliability*, vol. 44, no. 7, pp. 1033–1038, 2004.
- [77] H. Kim, V. Tilak, B. Green, J. Smart, W. Schaff, J. Shealy, and L. Eastman, “Reliability Evaluation of High Power AlGaN/GaN HEMTs on SiC Substrate,” *physica status solidi (a)*, vol. 188, pp. 203–206, nov 2001.

- [78] D. Maier, M. Alomari, N. Grandjean, J. F. Carlin, M. A. Diforte-Poisson, C. Dua, A. Chuvilin, D. Troadec, C. Gaquière, U. Kaiser, S. L. Delage, and E. Kohn, “Testing the temperature limits of GaN-based HEMT devices,” *IEEE Transactions on Device and Materials Reliability*, vol. 10, no. 4, pp. 427–436, 2010.
- [79] G. Meneghesso, G. Verzellesi, F. Danesin, F. Rampazzo, F. Zanon, A. Tazzoli, M. Meneghini, and E. Zanoni, “Reliability of GaN high-electron-mobility transistors: State of the art and perspectives,” *IEEE Transactions on Device and Materials Reliability*, vol. 8, no. 2, pp. 332–343, 2008.
- [80] L. Wang, F. M. Mohammed, and I. Adesida, “Formation mechanism of Ohmic contacts on AlGaNGaN heterostructure: Electrical and microstructural characterizations,” *Journal of Applied Physics*, vol. 103, no. 9, 2008.
- [81] A. Piotrowska, A. Guivarc’h, and G. Pelous, “Ohmic contacts to IIIV compound semiconductors: A review of fabrication techniques,” *Solid-State Electronics*, vol. 26, no. 3, pp. 179–197, 1983.
- [82] H. Yu and T. Duan, *Gallium Nitride Power Devices*. Pan Stanford Publishing Pte. Ltd., 2017.
- [83] R. C. Fitch, D. E. Walker, A. J. Green, S. E. Tetlak, J. K. Gillespie, M. Ieee, R. D. Gilbert, K. A. Sutherlin, W. D. Gouty, J. P. Theimer, G. D. Via, K. D. Chabak, G. H. Jessen, and S. Member, “Implementation of High-Power-Density X -Band AlGaN / GaN High Electron Mobility Transistors in a Millimeter-Wave Monolithic Microwave Integrated Circuit Process,” vol. 36, no. 10, pp. 1004–1007, 2015.
- [84] D. C. Look, *Electrical Characterization of GaAs Materials and Devices*. Design And Measurement in Electronic Engineering, Wiley, 1992.
- [85] L. J. van der Pauw, “A Method of Measuring Specific Resistivity and Hall Effect on Discs or Arbitrary Shape,” *Philips Research Reports*, vol. 13, no. 1, pp. 1–9, 1958.

- [86] H. Castro, J. Galvis, and S. Castro, “Automated setup for Van der Pauw Hall measurements,” *IEEE Transactions on Instrumentation and Measurement*, vol. 60, no. 1, pp. 198–205, 2011.
- [87] M. Neuburger, I. Daumiller, M. Kunze, M. Seyboth, T. Jenkins, J. Van Nostrand, and E. Kohn, “Influence of polarization on the properties of GaN based FET structures,” *Physica Status Solidi C*, vol. 0, pp. 1919–1939, 2003.
- [88] Z. Q. Fang, B. Claflin, and D. C. Look, “Deep traps in AlGaIn/GaN heterostructure field-effect transistors studied by current-mode deep-level transient spectroscopy: Influence of device location,” *Journal of Electronic Materials*, vol. 40, no. 12, pp. 2337–2343, 2011.
- [89] L. Kolaklieva and R. Kakanakov, “Ohmic Contacts for High Power and High Temperature Microelectronics,” *Micro Electronic and Mechanical Systems*, vol. 2, p. 572, 2009.
- [90] K. C. Lee, “Ohmic Contacts to Quantized Hall Resistors,” vol. 48, no. 2, pp. 319–324, 1999.
- [91] A. Y. C. Yu, “Electron tunneling and contact resistance of metal-silicon contact barriers,” *Solid State Electronics*, vol. 13, no. 2, pp. 239–247, 1970.
- [92] L. Rideout and Y. Heights, “A review of the theory and technology for ohmic contacts to group III-V compound semiconductors,” *Solid-State Electronics*, vol. 18, pp. 541–550, 1975.
- [93] F. Wang, J. Shan, M. A. Islam, I. P. Herman, M. Bonn, and T. F. Heinz, “Exciton polarizability in semiconductor nanocrystals,” *Nature Materials*, vol. 5, pp. 861–864, nov 2006.
- [94] X. Zhao, G. Duan, A. Li, C. Chen, and X. Zhang, “Integrating microsystems with metamaterials towards metadevices,” *Microsystems and Nanoengineering*, vol. 5, no. 1, pp. 1–17, 2019.
- [95] M. K. Patra, M. Manoth, V. K. Singh, G. Siddaramana Gowd, V. S. Choudhry, S. R. Vadera, and N. Kumar, “Synthesis of stable dispersion of ZnO quantum dots in aqueous medium showing visible emission from bluish green to yellow,” *Journal of Luminescence*, vol. 129, no. 3, pp. 320–324, 2009.

VITA

Clarissa D. Vazquez Colon was born on June 16, 1992 in Humacao, Puerto Rico. She finished her undergraduate studies in Applied Physics at The University of Puerto Rico at Humacao in 2014. She continued her education as a Ph.D. student in the Physics and Astronomy Department at The University of Texas at San Antonio. Her graduate research was under the supervision of Dr. Arturo Ayon in the MEMS Research Laboratory.

Terahertz Modulation of Hexagonal-Shaped Metamaterials Employing ZnO Quantum Dots

Clarissa D. Vázquez-Colón¹, Alvaro Flores-Pacheco², Janeth Alexandra García-Monge¹, Juan Adrián Zepeda-Galvéz¹, Daniel Shreiber³, Arturo Ayón^{1*}

¹The University of Texas at San Antonio, San Antonio, Texas, USA

²Departamento de Física, Universidad de Sonora, Hermosillo, Sonora, México

³US Army Research Laboratory, Aberdeen Proving Ground, MD, USA

Email: *aayon@utsa.edu

How to cite this paper: Vázquez-Colón, C.D., Flores-Pacheco, A., García-Monge, J.A., Zepeda-Galvéz, J.A., Shreiber, D. and Ayón, A. (2019) Terahertz Modulation of Hexagonal-Shaped Metamaterials Employing ZnO Quantum Dots. *Open Journal of Inorganic Non-metallic Materials*, 9, 1-13. <https://doi.org/10.4236/ojinm.2019.91001>

Received: January 2, 2019

Accepted: January 28, 2019

Published: January 31, 2019

Copyright © 2019 by author(s) and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0). <http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

The utilization of UV excitation to verify the terahertz (THz) wave modulation of hexagonal-shaped metamaterial (MM) arrays coated with synthesized photoluminescent, down-shifting ZnO quantum dots (QDs) of two different radius sizes, namely, 3.00 nm (pH 10) and 2.12 nm (pH 12), respectively is reported. In order to characterize the behavior of the MM before and after deployment of the ZnO QDs, THz time domain spectroscopy in transmission mode was employed. Upon exposure to UV excitation, the collected amplitude modulation values were 9.21% for the pH 12 and 4.55% for the pH 10 ZnO QDs, respectively. It is anticipated that the ability to actively tune the performance of otherwise passive structures will promote the proliferation of THz signal modulation devices in the near future.

Keywords

Terahertz, Metamaterials, Quantum Dots, Terahertz Spectroscopy, Modulation

1. Introduction

The terahertz (THz) portion of the electromagnetic spectrum is located between the microwave and infrared segments and has remained relatively underdeveloped because the power output of conventional electronic circuitry (*i.e.*, IMPATT, MMIC, Gunn, TUNNET, multiplexers, photomixers, RTD, etc.) drops significantly as the transition is made from the microwaves to the THz region. Similarly, photonic structures (*i.e.*, III-V lasers, QCL, etc.) also exhibit a similar and noticeable deterioration in the power output as the transition is made from

infrared to THz frequencies. In view of the unrelenting saturation of the electromagnetic spectrum, there is an increased interest in developing passive and active devices with suitable performance in the THz portion of the spectrum, including tunable structures that could alleviate said saturation. Additionally, THz electromagnetic waves are nonionizing and, for the same reason, attractive for applications where microwave interactions with organic materials could be a source of concern [1]-[10]. One option to overcome the performance limitations of conventional electronic circuitry and/or photonic devices at THz frequencies is the utilization of metamaterials (MMs), which are subwavelength, unit-cell laboratory-made structures that are fabricated to exhibit specific electromagnetic properties not encountered in naturally available materials. The topology encountered in MMs customarily consists of a metallic or polymeric array, in which the passive electromagnetic properties are determined by the dimensions of the unit cell, the fill factor of said cells and the materials employed in their fabrication [11]. Incorporating functional materials to MM designs capable of responding in real time to an external stimulus would improve tunability and, more generally, enable the demonstration of THz modulation devices [12] by modifying signal intensity, phase, propagation direction, beam shape or resonant frequency. To this end, the utilization of UV excitation with a wavelength of 400 nm, to verify the modulation of THz waves of a metamaterial array coated with previously synthesized photoluminescent, down-shifting ZnO QDs synthesized in colloidal solutions with pH values of 10 and 12, respectively, is discussed in this work.

2. Experimental Details

The employed MM array (see **Figure 1**) which has been described elsewhere [13], was fabricated using a conventional lift-off process on high resistivity, <100> silicon wafers and had dimensions such that the array exhibited a resonance frequency of 1 THz. The metallization of the tested MM structures was performed by evaporating 200 nm of silver on a 20 nm layer of chromium that served as an adhesion layer.

2.1. ZnO QD Synthesis

Colloidal ZnO QDs were synthesized at room temperature by a sonochemical

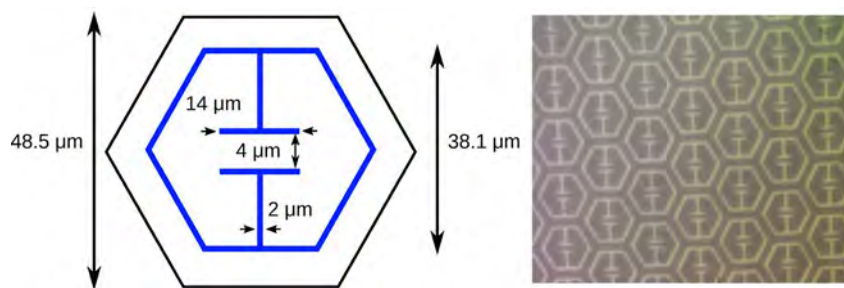


Figure 1. (a) Dimensions of the MM unit cell employed in this exercise. The black and blue lines represent the unit cell and metallic features, respectively. (b) Optical microscope image of the microfabricated array.

method [14] [15] in which acoustic cavitation precludes the formation of intermediate products, including $\text{Zn}(\text{OH})_2$, converts the reactants into ZnO QDs and calcination steps are not required. This method has proven useful for accelerating chemical reactions in liquid-solid systems [14]. Specifically, ZnO QD synthesis was accomplished by preparing an initial solution of 0.02 M zinc acetate (ZnAc) (99.99%, Sigma-Aldrich) in pure ethanol. A second and independent solution of 0.01 M of lithium hydroxide (LiOH) ($\geq 98\%$ Sigma-Aldrich) was prepared also in pure ethanol. Subsequently, the LiOH solution was incorporated dropwise to the ZnAc solution until a pH value of 10 or 12 was obtained. Once the targeted pH value was reached, the mixture was placed in a sonication bath for 3 hours [16] [17]. The chosen pH values were found to yield stable nanoparticles and relatively minimal agglomeration. Furthermore, the ultimate size of the obtained QDs was determined by the pH value of the final solution employed during synthesis and observed to be in agreement with the dependence of ZnO nanoparticle size on pH reported elsewhere [18]. A summary of the synthesis is shown in **Figure 2**. The ZnO QDs were then deposited onto the surface of the MM shown in **Figure 1**.

In order to characterize the synthesized ZnO QDs in the terahertz regime, the nanoparticles were dispersed in a polydimethylsiloxane (PDMS) matrix. To this end, the ZnO QDs were harvested by drying the final solution on a hotplate maintained at 70°C , and prior to dispersing them in the aforementioned matrix, the QD samples were thoroughly pulverized using a mortar. Once the solvent had completely evaporated, the ZnO QD powder was mixed with a PDMS solution that had been previously prepared by mixing 5 wt% of a curing agent in a silicone elastomer [19] [20]. The mixture of PDMS and ZnO QDs was then cured at 90°C for 3 hours (see **Figure 3**).

2.2. ZnO QD Absorption and Emission Characterization

The UV-vis absorption characterization of the ZnO QDs was performed using

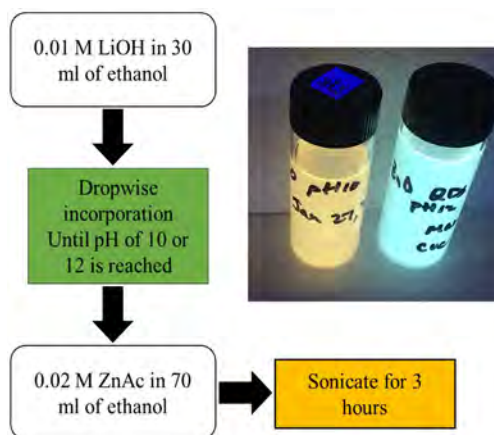


Figure 2. ZnO QD synthesis approach and their visual appearance under UV excitation. The synthesis pH values employed were 10 (yellowish solution on the left) and 12 (blue solution on the right).

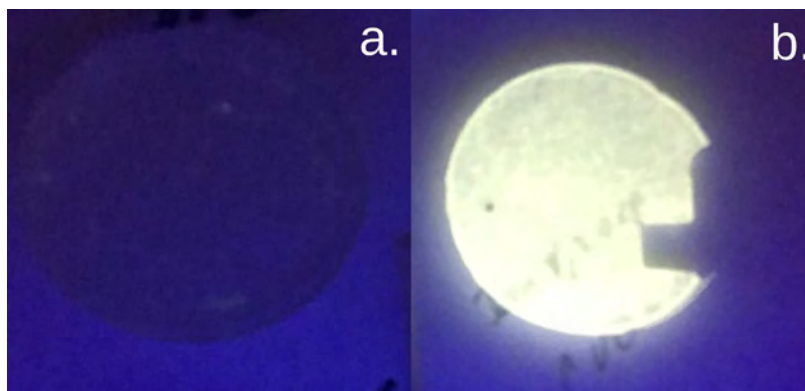


Figure 3. (a) Cured PDMS membranes exhibit no photoluminescent properties under UV excitation. (b) Observed photoluminescence of ZnO QDs synthesized with a pH value of 12 and dispersed in a PDMS matrix.

an Ocean Optics Flame-S-UV-VIS spectrometer and the collected absorption spectra corresponding to nanocrystals synthesized with the previously mentioned colloidal solution pH values of 10 and 12, are shown in **Figure 4**, along with their corresponding photoluminescent response. The emission wavelength is directly related to quantum dot size, therefore, the larger the nanoparticles the longer the wavelength of their characteristic photoluminescent peak [21] [22]. Thus, QDs synthesized with a pH value of 12 have an emission peak located at 510 nm, while QDs synthesized with a pH value of 10 have the peak located at 540 nm, indicating that lower pH values produce larger nanoparticles.

The observed QD absorbance measurements are related to QD bandgap by the following expression

$$\alpha = \left(\frac{A}{h\nu} \right) (h\nu - E_g)^m \quad (1)$$

where α is the absorption coefficient, A is an optical constant, m represents the type of optical transition in the semiconducting material; specifically, m can only take the values of 1/2, 2, 3/2 or 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect, respectively [23], and E_g is the band gap of the semiconducting quantum dots. Multiplying Equation (1) by $h\nu$, obtaining the natural logarithm and finally taking the derivative with respect to $h\nu$, the resultant equation is

$$\frac{d(\ln(\alpha h\nu))}{d(h\nu)} = \frac{m}{h\nu - E_g} \quad (2)$$

The bandgap can then be estimated by plotting Equation (2) with respect to energy [23], and this approach permits the identification of the inflection point (*i.e.*, the bandgap value) where the slope changes sign (see **Figure 5**). In other words, the bandgap value will be determined as a discontinuity at $h\nu - E_g = 0$ [23]. The extracted bandgap values were 3.43 eV and 3.62 eV for the ZnO QDs synthesized with the colloidal solutions with a pH of 10 and 12, respectively. The observed emission peaks were located at 510 nm (pH 12) and 540 nm (pH 10).

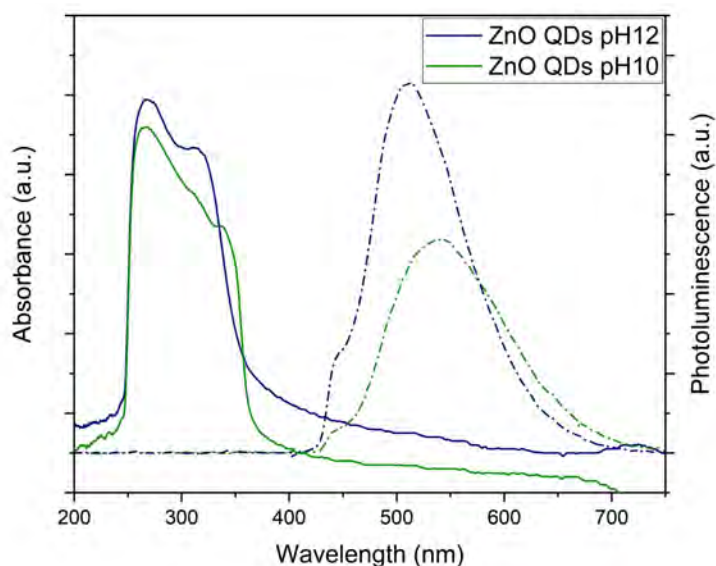


Figure 4. Collected absorbance spectra of the ZnO QDs colloidal solutions synthesized with pH values of 10 and 12 (solid lines), respectively. The dotted lines show the photoluminescence spectra of the corresponding ZnO quantum dot colloidal solutions.

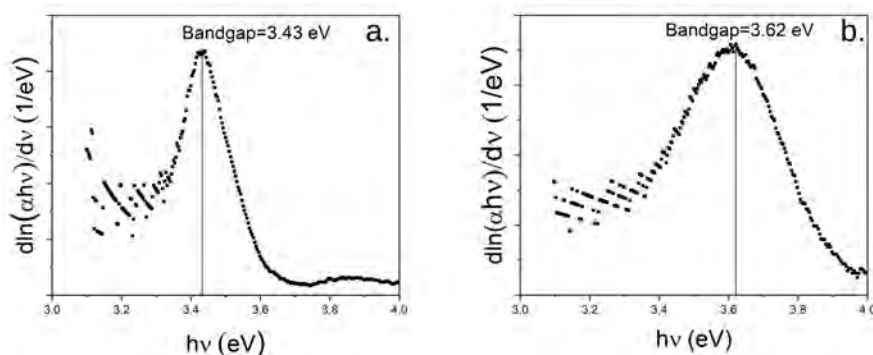


Figure 5. Estimated bandgap values of the ZnO QDs synthesized with pH values of 10 and 12, respectively.

Since the wavelength emission is directly related to QD size, *i.e.*, the larger the particle, the longer the wavelength of emission, the emission peak wavelength observations corroborate that higher pH values during synthesis indeed lead to smaller ZnO quantum dots.

Once the bandgap value had been calculated, the size of the QDs was estimated employing Brus' quantum mechanical approximation [24]

$$E_g = E_{Bulk} + \frac{\hbar^2 \pi^2}{2r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{r\epsilon} \quad (3)$$

where E_g is the band gap energy of the semiconductor quantum dots, E_{Bulk} is the band gap energy of the bulk semiconductor material, $\hbar$ is the reduced Planck constant, m_e^* and m_h^* represent the effective mass of electron and hole of the material under consideration, ϵ is the bulk relative permittivity, and r is the QD radius. For the pH 10 ZnO QDs we estimated a radius of 3.00 nm and

for the pH 12 ZnO QDs we obtained a radius of 2.12 nm. To corroborate the estimated sizes, transmission electron microscope (TEM) images for both samples were obtained and are shown in **Figure 6**. The measured values were approximately 3.2 nm and 1.85 nm radius for the ZnO pH 10 and ZnO pH 12 samples, respectively, in reasonable agreement with the sizes estimated via Equation (3).

3. Experimental Results and Discussion

The THz time domain spectroscopy (THz-TDS) characterization was performed by employing a Menlo Systems TeraSmart equipment [25], operated in transmission mode (see **Figure 7**). This system employs a photoconductive antenna based on an InGaAs/InAlAs multilayered mesa as the emitter and detector, which are activated by a femtosecond laser of wavelength 800 nm. The system

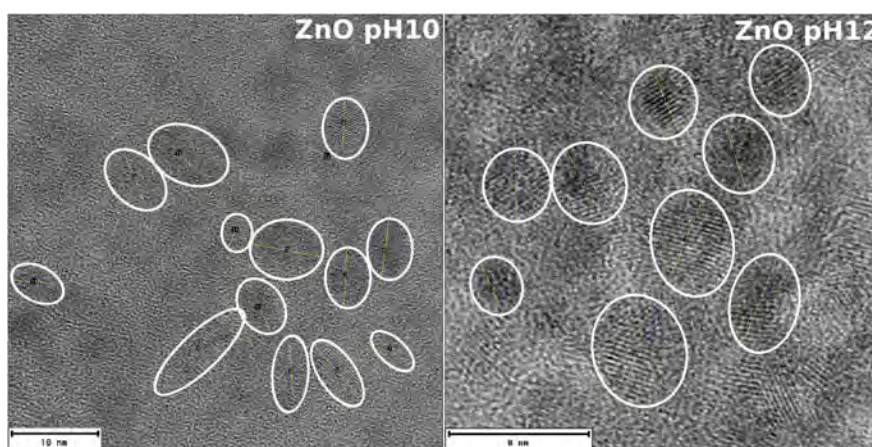


Figure 6. ZnO pH10 and ZnO pH12 TEM images used to corroborate sizes estimated values.

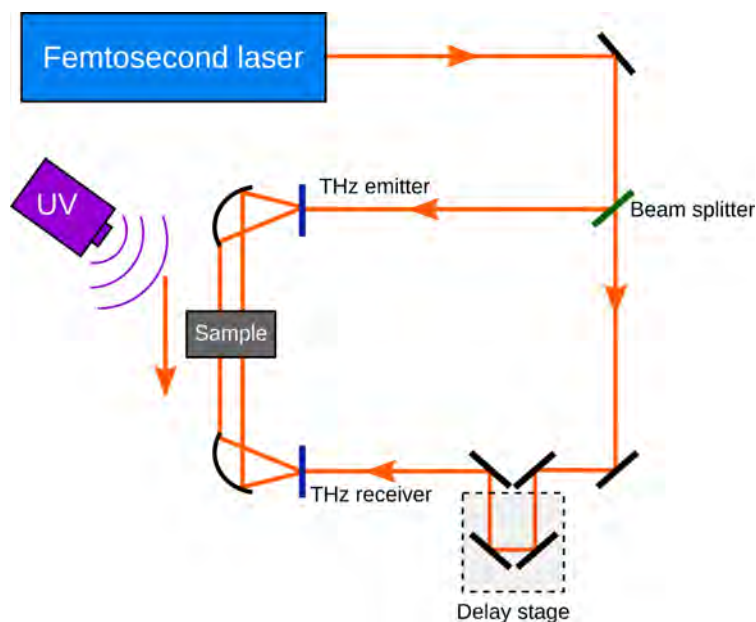


Figure 7. THz Time Domain Spectroscopy test setup.

was aligned until the THz amplitude was at its maximum. Subsequently, the equipment was thermalized for ~1 hour, and the sample was positioned at the focal point of the THz beam path. Five measurements at room temperature were collected for each reference and samples, each of which corresponded to a thousand-point averaging.

Stand-alone PDMS membranes with and without QDs were tested, as well as MM arrays with QDs on the surface and exposed to UV laser excitation of 400 nm in wavelength to determine the prospective modulation behavior of the arrangement.

The obtained THz time domain waveform signal was processed by applying a Gaussian window to remove reflections after the main THz pulse [26] and, subsequently, a Fast Fourier transform (FFT) was employed to obtain the amplitude and phase information of both the reference as well as the sample under consideration. In both cases, *i.e.*, a stand-alone PDMS membrane and MM array, samples without QDs were employed as a reference. The transmittance as a function of frequency of the samples was calculated using the following equation [26]

$$\tilde{T}(\omega) = \frac{\tilde{E}_{sam}(\omega)}{\tilde{E}_{ref}(\omega)} = \frac{A_{sam}(\omega)}{A_{ref}(\omega)} \cdot e^{i(\phi_{sam}(\omega) - \phi_{ref}(\omega))} \quad (4)$$

where $\tilde{E}_{sam}$ and $\tilde{E}_{ref}$ are the complex electric fields, A_{sam} and A_{ref} are the THz amplitudes and ϕ_{sam} and ϕ_{ref} are the phase angles of the sample and reference, respectively. Depending on the sample transmittance results could show specific features as a function of frequency.

3.1. THz Quantum Dot Characterization

From the collected THz-TDS data, optical properties of interest such as refractive index, permittivity and conductivity can be extracted. The real part $n(\omega)$ and imaginary part $\kappa(\omega)$ of the refractive index can be calculated by using the following equations [26]

$$n(\omega) = 1 + \frac{c(\phi_{sam}(\omega) - \phi_{ref}(\omega))}{\omega d} \quad (5)$$

$$\kappa(\omega) = -\left(\frac{c}{\omega d}\right) \ln \left(\left| \frac{A_{sam}(\omega)}{A_{ref}(\omega)} \right| \right) \quad (6)$$

respectively. Similarly, the permittivity and the index of refraction are related by

$$\tilde{\epsilon}(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) = \left(n(\omega)^2 - \kappa(\omega)^2 \right) + i(2n(\omega)\kappa(\omega)) \quad (7)$$

where $\tilde{\epsilon}$ is the complex permittivity, ϵ' is the real part of the permittivity, ϵ'' is the imaginary part of the permittivity. The extracted real effective refractive index of the PDMS + QDs membrane at 1 THz (see **Figure 8**), was of ~1.50 for the smaller QDs synthesized with a pH value of 12 (blue dotted line), and to ~1.85 (green solid line) for the larger QDs synthesized with a pH value of 10. Subsequently, the samples were exposed to UV excitation of 400 nm wavelength (see **Figure 9** and **Figure 10**). The intensity of the UV source was measured using

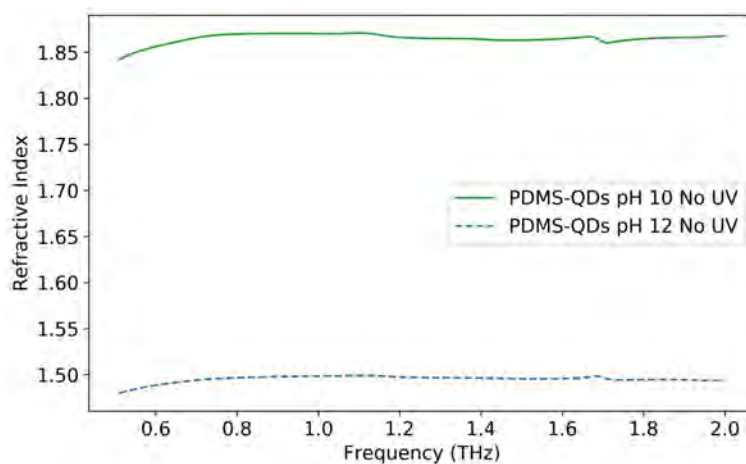


Figure 8. Extracted real part of the effective refractive index of the media with the incorporated ZnO QDs described herein.

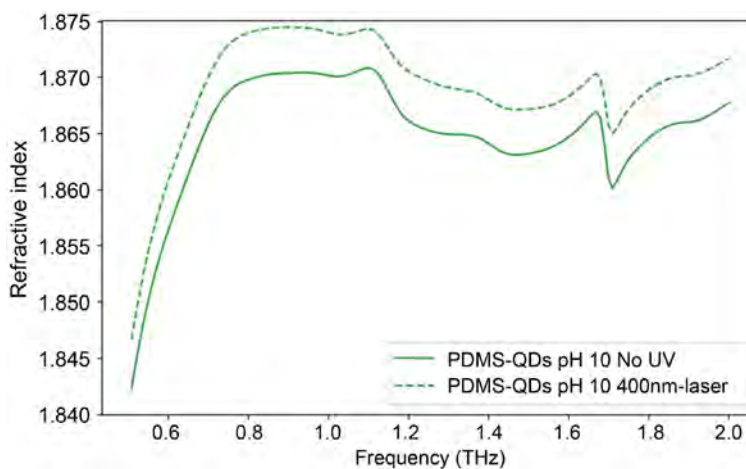


Figure 9. Extracted real part of the refractive index of the medium with the relatively larger ZnO QDs (pH 10) with (dotted line) and without UV excitation of 400 nm (solid line).

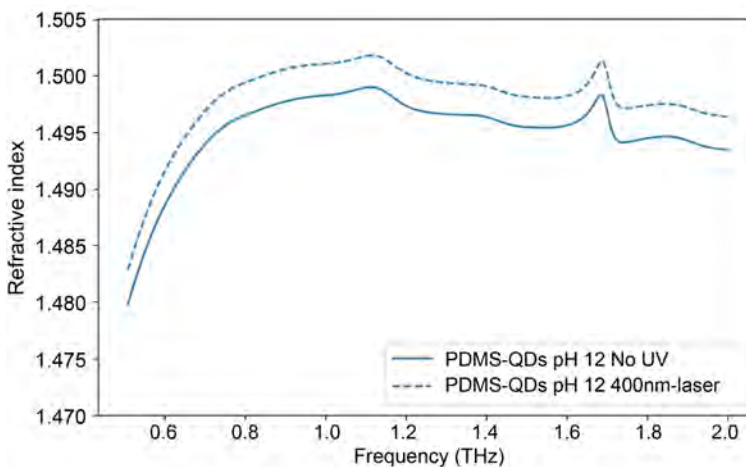


Figure 10. Extracted real part of the refractive index of the medium with the relatively smaller ZnO QDs (pH 12) with (dotted line) and without UV excitation of 400 nm (solid line).

an ILT2400 Light Meter and observed to be $2.5 \times 10^{-4} \text{ W/cm}^2$. The observations indicate that larger quantum dots exhibit a relatively more pronounced response to UV excitation. This can be explained on the grounds that the synthesized semiconducting nanoparticles exhibit quantum confinement effects where exciton polarizability, reported to be proportional to the fourth power of the radius ($\alpha \sim R^4$), can be defined as [27]

$$\alpha = \frac{\Delta\chi_s (\epsilon_{QD} + 2\epsilon)^2}{9n_s \epsilon^2} \quad (8)$$

where $\Delta\chi_s$ is the susceptibility of the material (related to the permittivity by $\chi_s = 1 - \epsilon$), ϵ_{QD} is the permittivity of the quantum dots, ϵ is the permittivity of the medium and n_s is the sheet excitation density. This result is in agreement with the extracted real part of the effective refractive index of the media with the incorporated ZnO QDs shown in **Figure 8**. Ostensibly, studies of polarizability as a function of frequency and quantum dot dimensions can be performed employing THz-TDS.

3.2. THz Metamaterial Characterization

The experimental characterization of the metamaterial array previously described and shown in **Figure 1**, corroborated the anticipated resonant frequency at 1 THz (dotted lines **Figure 11** and **Figure 12**). Subsequently, the synthesized ZnO QDs were deployed directly on the MM surface, and the resonance frequency was observed to shift to 0.95 THz and to 0.96 THz for the ZnO QDs synthesized with pH values of 10 and 12, respectively. The observed variation in the resonance frequency reflects the permittivity value trends presented in **Figure 8**, thus, larger permittivity values are associated with lower resonant frequencies.

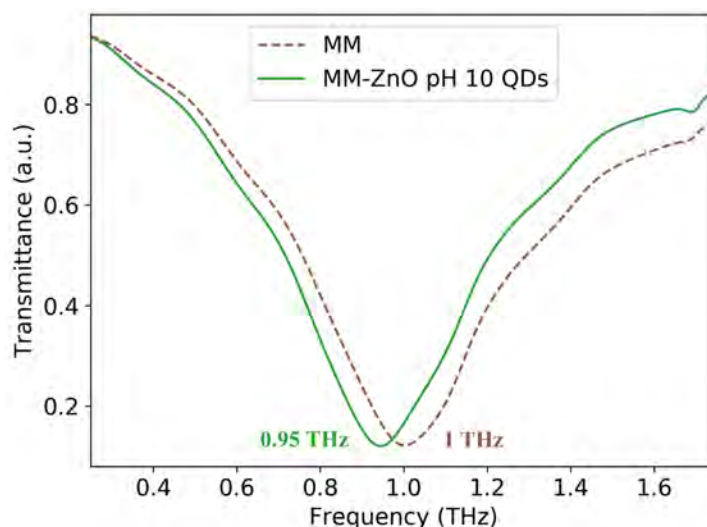


Figure 11. The modification of the effective permittivity of the medium by the deployment of the ZnO QDs synthesized with a pH value of 10, triggered the resonant frequency to decrease from 1 THz to 0.95 THz.

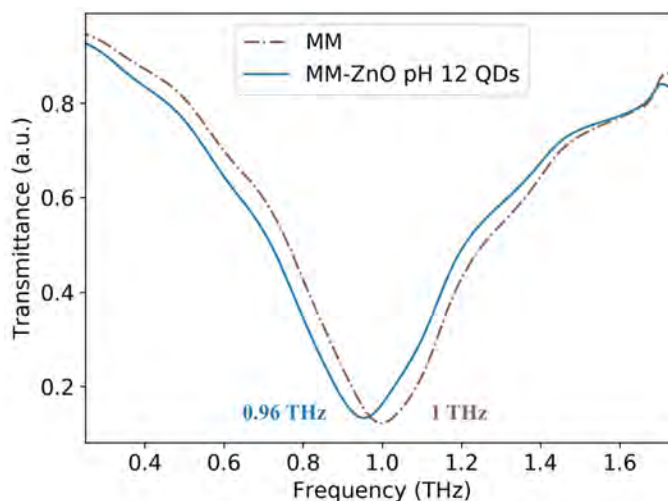


Figure 12. Variation of the resonant frequency of the MM array before (1 THz) and after (0.96 THz) deployment of the ZnO QDs synthesized with a pH value of 12.

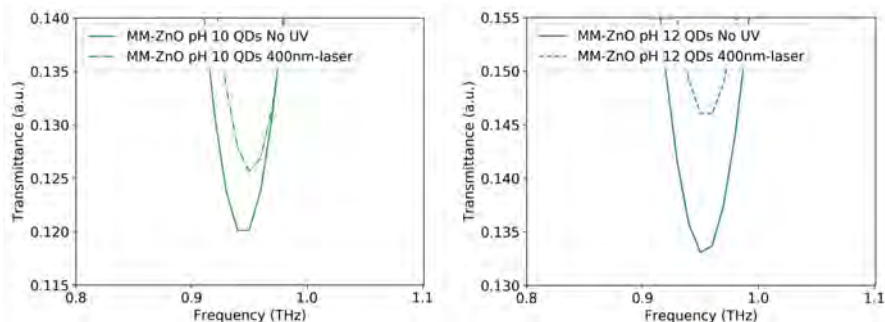


Figure 13. Transmittance calculation of the metamaterial with ZnO pH 10 QDs with and without UV excitation of 400 nm.

In order to measure the modulation of the metamaterial arrays with the deployed quantum dots, the samples were excited with a UV source of 400 nm while being tested with the THz-TDS (results are shown in **Figure 13**). The experimental observations yielded a modulation of 4.55% for the ZnO QDs synthesized with colloidal solutions with a pH value of 10, while the nanoparticles synthesized with a pH value of 12 exhibited a relatively large modulation of 9.21%. The observed results are thought to be due to a higher degree of confinement effects in smaller quantum dots [27]. These changes in modulation depth demonstrate the capability of hexagonal MM via the deployment of ZnO QDs to tune THz electromagnetic signals.

4. Conclusion

ZnO quantum dots were chemically synthesized employing colloidal solutions with pH values of 10 and 12, and the estimated bandgap and radii were calculated to be 3.37 eV (3.00 nm) and 3.50 eV (2.12 nm), respectively. Upon deploying the produced QDs on previously fabricated hexagonal metamaterial arrays and exposing the samples to UV excitation with a wavelength of 400 nm while

performing THz spectroscopy in transmission mode, signal modulation values of 4.55% and 9.21% were observed. The results reported herein could promote the proliferation of THz regime modulation devices. Furthermore, since the photolithographic process for the MM fabrication is mass-production compatible [28], while the ZnO QDs are stable, biologically compatible, and low-cost [29], the MM-ZnO QD setup described herein is considered to be attractive for industrial applications.

Acknowledgements

The authors would like to acknowledge the U.S. Army Research Office (Grant W911NF-13-1-0110), NSF (Grant 1650571) and the Department of Physics and Astronomy at the University of Texas at San Antonio, for the financial support provided for this research project.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Hashemi, M.R., Cakmakyapan, S. and Jarrahi, M. (2017) Reconfigurable Metamaterials for Terahertz Wave Manipulation. *Reports on Progress in Physics*, **80**, Article ID: 094501. <https://doi.org/10.1088/1361-6633/aa77cb>
- [2] Davies, A.G., Burnett, A.D., Fan, W., Linfield, E.H. and Cunningham, J.E. (2008) Terahertz spectroscopy of Explosives and Drugs. *Materials Today*, **11**, 18-26. [https://doi.org/10.1016/S1369-7021\(08\)70016-6](https://doi.org/10.1016/S1369-7021(08)70016-6)
- [3] Baaske, K., Salhi, M., Rutz, F., Hasek, T., Wilk, R., Richter, H., *et al.* (2006) Mail Inspection Using THz Imaging: A Comparison of Three Different Systems. *Terahertz for Military and Security Applications IV*, **6212**, 62120U. <https://doi.org/10.1117/12.665238>
- [4] Hernandez-Serrano, A.I., Corzo-Garcia, S.C., Garcia-Sanchez, E., Alfaro, M. and Castro-Camus, E. (2014) Quality Control of Leather by Terahertz Time-Domain Spectroscopy. *Applied Optics*, **53**, 7872-7876. <https://doi.org/10.1364/AO.53.007872>
- [5] Gowen, A.A., O'Sullivan, C. and O'Donnell, C.P. (2012) Terahertz Time Domain Spectroscopy and Imaging: Emerging Techniques for Food Process Monitoring and Quality Control. *Trends in Food Science & Technology*, **25**, 40-46. <https://doi.org/10.1016/j.tifs.2011.12.006>
- [6] Russe, I.S., Brock, D., Knop, K., Kleinebudde, P. and Zeitler, J.A. (2012) Validation of Terahertz Coating Thickness Measurements Using X-Ray Microtomography. *Molecular Pharmaceutics*, **9**, 3551-3559. <https://doi.org/10.1021/mp300383y>
- [7] Ho, L., Müller, R., Römer, M., Gordon, K.C., Heinämäki, J., Kleinebudde, P., *et al.* (2007) Analysis of Sustained-Release Tablet Film Coats Using Terahertz Pulsed Imaging. *Journal of Controlled Release*, **119**, 253-261. <https://doi.org/10.1016/j.jconrel.2007.03.011>
- [8] Woodward, R.M., Cole, B.E., Wallace, V.P., Pye, R.J., Arnone, D.D., Linfield, E.H., *et al.* (2002) Terahertz Pulse Imaging in Reflection Geometry of Human Skin Can-

- cer and Skin Tissue. *Physics in Medicine and Biology*, **47**, 3853-3863. <https://doi.org/10.1088/0031-9155/47/21/325>
- [9] Park, S.J. and Ahn, Y.H. (2015) Terahertz Metamaterials Application in Sensing Bacteria and Fungi. 2015 40th International Conference on Infrared, Millimeter, and Terahertz Waves (IRMMW-THz), Hong Kong, 23-28 August 2015, 1. <https://doi.org/10.1109/IRMMW-THz.2015.7327619>
- [10] Sim, Y.C., Park, J.Y., Ahn, K.-M., Park, C. and Son, J.-H. (2013) Terahertz Imaging of Excised Oral Cancer at Frozen Temperature. *Biomedical Optics Express*, **4**, 1413-1421. <https://doi.org/10.1364/BOE.4.001413>
- [11] Tao, H., Padilla, W.J., Zhang, X. and Averitt, R.D. (2011) Recent Progress in Electromagnetic Metamaterial Devices for Terahertz Applications. *IEEE Journal on Selected Topics in Quantum Electronics*, **17**, 92-101. <https://doi.org/10.1109/JSTOE.2010.2047847>
- [12] Chen, H.T. (2014) Semiconductor Activated Terahertz Metamaterials. *Frontiers of Optoelectronics*, **8**, 27-43. <https://doi.org/10.1007/s12200-014-0436-0>
- [13] Bingham, C.M., Tao, H., Liu, X., Averitt, R.D., Zhang, X. and Padilla, W.J. (2008) Planar Wallpaper Group Metamaterials for Novel Terahertz Applications. *Optics Express*, **16**, 18565-18575. <https://doi.org/10.1364/OE.16.018565>
- [14] Suslick, K.S. and Price, G.J. (1999) Applications of Ultrasound to Materials Chemistry. *Annual Review of Material Science*, **29**, 295-326. <https://doi.org/10.1146/annurev.matsci.29.1.295>
- [15] Pandit, A.B. and Badnore, A.U. (2017) Effect of pH on Sonication Assisted Synthesis of ZnO Nanostructures: Process Details. *Chemical Engineering and Processing: Process Intensification*, **122**, 235-244. <https://doi.org/10.1016/j.cep.2017.09.013>
- [16] Zazueta-Raynaud, A., Pelayo-Ceja, J.E., Lopez-Delgado, R. and Ayon, A. (2016) ZnO Photoluminescent Quantum Dots with Down-Shifting Effect Applied in Solar Cells. *Journal of Physics: Conference Series*, **773**, Article ID: 012036. <https://doi.org/10.1088/1742-6596/773/1/012036>
- [17] Caballero, A.C., Villegas, M., Moure, C. and Ferna, J.F. (2001) Controlled Precipitation Methods: Formation Mechanism of ZnO Nanoparticles. *Journal of the European Ceramic Society*, **21**, 925-930. [https://doi.org/10.1016/S0955-2219\(00\)00283-1](https://doi.org/10.1016/S0955-2219(00)00283-1)
- [18] Alias, S.S., Ismail, A.B. and Mohamad, A.A. (2010) Effect of pH on ZnO Nanoparticle Properties Synthesized by Sol-Gel Centrifugation. *Journal of Alloys and Compounds*, **499**, 231-237. <https://doi.org/10.1016/j.jallcom.2010.03.174>
- [19] Podzorov, A. and Gallot, G. (2010) Density of States and Vibrational Modes of PDMS Studied by Terahertz Time-Domain Spectroscopy. *Chemical Physics Letters*, **495**, 46-49. <https://doi.org/10.1016/j.cplett.2010.06.050>
- [20] Alfihed, S., Bergen, M.H., Holzman, J.F. and Foulds, I.G. (2018) A Detailed Investigation on the Terahertz Absorption Characteristics of Polydimethylsiloxane (PDMS). *Polymer*, **153**, 325-330. <https://doi.org/10.1016/j.polymer.2018.08.025>
- [21] Guzelian, A.A., Katari, J.E.B., Kadavanich, A. V., Banin, U., Hamad, K., Juban, E., *et al.* (1996) Synthesis of Size-Selected, Surface-Passivated InP Nanocrystals. *The Journal of Physical Chemistry*, **100**, 7212-7219. <https://doi.org/10.1021/jp953719f>
- [22] Lin, K.F., Cheng, H.M., Hsu, H.C. and Hsieh, W.F. (2006) Bandgap Engineering and Spatial Confinement of Optical Phonon in ZnO Quantum Dots. 19th Annual Meeting of the IEEE Lasers and Electro-Optics Society, Montreal, 29 October-2 November 2006, 939-940. <https://doi.org/10.1109/LEOS.2006.279156>
- [23] Kar, S. and Chaudhuri, S. (2005) Synthesis and Optical Properties of Single and Bi-

- crystalline ZnS Nanoribbons. *Chemical Physics Letters*, **414**, 40-46. <https://doi.org/10.1016/j.cplett.2005.08.021>
- [24] Brus, L. (1986) Electronic Wave Functions in Semiconductor Clusters: Experiment and Theory. *The Journal of Physical Chemistry*, **90**, 2555-2560. <https://doi.org/10.1021/j100403a003>
- [25] MenloSystems (2001) TeraSmart.
- [26] Withayachumnankul, W. and Naftaly, M. (2014) Fundamentals of Measurement in Terahertz Time-Domain Spectroscopy. *Journal of Infrared, Millimeter, and Terahertz Waves*, **35**, 610-637. <https://doi.org/10.1007/s10762-013-0042-z>
- [27] Wang, F., Shan, J., Islam, M.A., Herman, I.P., Bonn, M. and Heinz, T.F. (2006) Exciton Polarizability in Semiconductor Nanocrystals. *Nature Materials*, **5**, 861-864. <https://doi.org/10.1038/nmat1739>
- [28] Zhao, X., Duan, G., Li, A., Chen, C. and Zhang, X. (2019) Integrating Microsystems with Metamaterials towards Metadevices. *Microsystems and Nanoengineering*, **5**, 1-17. <https://doi.org/10.1038/s41378-018-0042-1>
- [29] Patra, M.K., Manoth, M., Singh, V.K., Siddaramana Gowd, G., Choudhry, V.S., Vadera, S.R., *et al.* (2009) Synthesis of Stable Dispersion of ZnO Quantum Dots in Aqueous Medium Showing Visible Emission from Bluish Green to Yellow. *Journal of Luminescence*, **129**, 320-324. <https://doi.org/10.1016/j.jlumin.2008.10.014>

Reconfigurable X-shaped THz Metamaterials employing Quantum Dots

Clarissa D. Vázquez-Colón
Physics and Astronomy Department
The University of Texas at San Antonio
San Antonio, USA
ORCID: 0000-0002-4428-4012

Juan Adrián Zepeda-Galvéz
Physics and Astronomy Department
The University of Texas at San Antonio
San Antonio, USA
juanadrian.zepeda-galvez@utsa.edu

Arturo A. Ayón
Physics and Astronomy Department
The University of Texas at San Antonio
San Antonio, USA
arturo.ayon@utsa.edu

Abstract— We report the utilization of an X-shaped metamaterial (MM) designed to have resonant frequencies in the THz regime. The reconfigurable behavior was observed when exciting photoluminescent down-shifting quantum dots deployed on the aforementioned MM with a UV source. The expected outcome will be the modification of the resonant frequency amplitude upon exposure of the metallic array with an UV source. The demonstration described herein is anticipated to enable the fabrication of additional circuitry elements operating in the THz regime.

Keywords— Terahertz, Metamaterials, Quantum Dots

I. INTRODUCTION

The terahertz region is located between the microwave and infrared segments of the electromagnetic spectrum (EM) ¹. This region is presently a topic of interest due to the paucity of readily available materials and circuits exhibiting a suitable performance including reconfigurable behavior ² at those frequencies, which has provided the impetus for considering metamaterials (MMs). Generally speaking, MMs are metallic or polymeric arrays characterized by having unit cells smaller than the excitation wavelength that have enabled scientists and technologists to demonstrate electromagnetic properties not found in the natural world and that can be designed to respond to THz frequencies. Furthermore, if the electromagnetic performance of the final MM product can be changed with an external controllable stimulus, reconfigurable behavior becomes feasible ³¹. This capability could be achieved by incorporating other materials sensitive to external excitations. To this end, we report the incorporation of UV sensitive semiconductor quantum dots (QDs) to actively reconfigure the EM characteristics of MM array. Specifically, we present the utilization of an X-shaped metallic array designed to have resonant frequencies in the THz regime, in which the reconfigurable behavior was observed when exciting the down-shifting QDs previously deployed on the MM array with UV light, such that amplitude of the transmitted signal could be modified in real time by the utilization of the UV light ⁴.

II. EXPERIMENTAL

An X-shaped MM topography was considered due to its relative simplicity and the ability to tailor its resonant frequency by modifying the length of the arms involved and their separation ^{5,6} (see Figure 1). The fabrication was performed employing standard lift-off photolithography process using MicroChemicals AZ 5214E as the photosensitive material. For the substrate we decided to use high resistivity silicon wafer because it shows lower absorption at these frequencies compared to other

photolithography compatible materials ⁷. The metallization was realized by evaporating 20 nm of chromium as an adhesion layer, followed by the deposition of 200 nm of silver. Then the samples were submerged in acetone bath to remove the photoresist excess of photoresist from the surface. Finally, ZnO QDs in ethanol-based colloidal solution were spin cast on the metallic array.

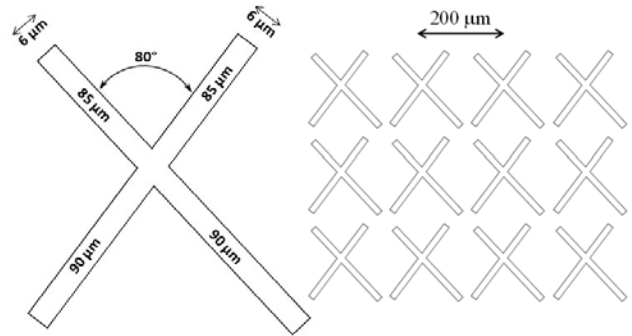


Fig. 1. An X-shaped MM geometry was employed in this exercise. The separation between each X component was 200 μm .

The synthesis of ZnO QDs was performed by making a 0.02M zinc acetate solution in pure ethanol and 0.01M lithium hydroxide in ethanol. The reaction was made by dropwise adding the LiOH solution to the ZnAc solution until a pH 12 was reached⁸⁹. Preliminary characterization of the QDs shows UV absorption from ~250 to 350 nm and an emission of ~510 nm (see Figure 2).

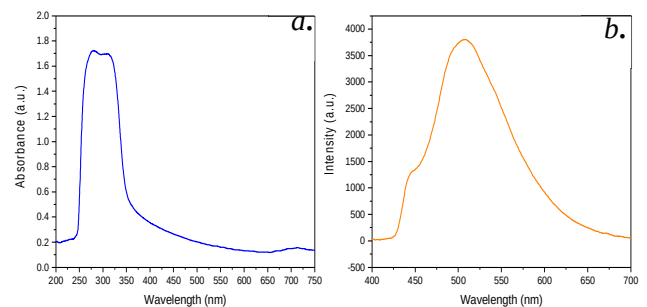


Fig. 2. a. Absorption spectra for ZnO QDs, b. Photoluminescence spectra for the synthesized QDs, exited with a wavelength of 340 nm

The characterization of the structures was conducted using THz-TDS in transmission mode employing the setup portrayed in Figure 3¹⁰. Once the samples had been prepared, several measurements were taken, including (i.) the metamaterial array without quantum dots, hereby termed the Reference sample, (ii.) the MM array with the quantum dots

deployed as well (X MM + ZnO QDs) and (iii.) the MM with quantum dots exposed to UV excitation (X MM + ZnO QDs + UV 302nm).

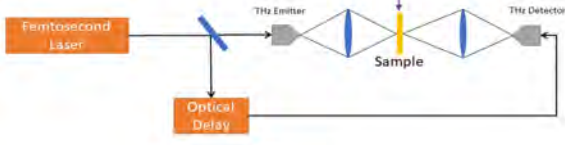


Fig. 3. THz-TDS transmission mode material characterization setup.

We observed that the MM by itself exhibit a resonant frequency at ~ 0.3 THz. As we mentioned before, without the addition of any other material, we obtained a fixed behavior for the metamaterial. In order to externally manipulate the operation of the MM, we spin coated the UV tunable QDs on the surface of the sample. The characterization of the MM with the addition of the QDs with and without UV excitation is shown in Figure 4. We observed a change in the operation amplitude with a modulation depth of $\sim 1\%$ at 0.3 THz and $\sim 4\%$ at 1 THz of the sample after being illuminated with 302 nm wavelength UV light.

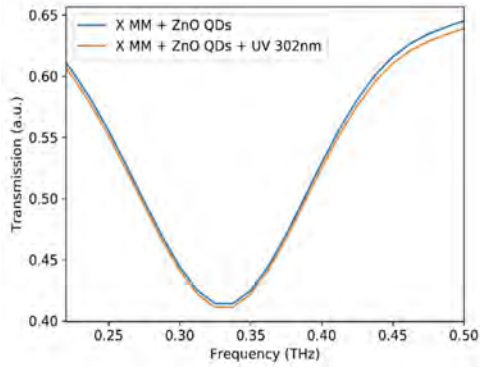


Fig. 4. THz transmission for the X shaped MM with QDs nonexcited (blue) and excited with a 302 nm wavelength (orange)

III. CONCLUSION

Our results show a resonant feature located at ~ 0.3 THz. The results also show the modulation of the amplitude of the transmitted signal upon illuminating the sample with a UV source with a wavelength of 302 nm. The experimental results will promote the demonstration of THz filters and resonators and the proliferation of devices operating in the THz regime in the near future.

ACKNOWLEDGMENTS

The authors would like to acknowledge the U.S. Army Research Office (Grant W911NF-13-1-0110), NSF (Grant 1650571) and the Department of Physics and Astronomy at the University of Texas at San Antonio, for the financial support provided for this research project.

REFERENCES

- [1] Rout, S. and Sonkusale, S., "Active Metamaterials: Terahertz Modulators and Detectors" (2017).
- [2] Padilla, W. J., Taylor, A. J., Highstrete, C., Lee, M. and Averitt, R. D., "Dynamical electric and magnetic metamaterial response at terahertz frequencies," Conf. Lasers Electro-Optics 2006 Quantum Electron. Laser Sci. Conf. CLEO/QELS 2006 **107401**(March), 1–4 (2006).
- [3] Chen, H. T., O'Hara, J. F., Azad, A. K. and Taylor, A. J., "Manipulation of terahertz radiation using metamaterials," Laser Photonics Rev. **5**(4), 513–533 (2011).
- [4] Hong, J. . T., Park, J.-Y., Lee, S. and Ahn, Y. H., "UV-induced terahertz wave modulation in free-standing ZnO nanowire films," 3751–3758 (2016).
- [5] Mirzaei, S., Green, N. G., Rotaru, M. and Pu, S. H., "Detecting and identifying DNA via the THz backbone frequency using a metamaterial-based label-free biosensor," 1010311 (2017).
- [6] Chen, K., Liu, H., Wang, Y. and Zhu, Y., "A study of trapped mode resonances in asymmetric X-shape resonator for frequency selective surface," 89090C (2013).
- [7] Dai, J., Zhang, J., Zhang, W. and Grischkowsky, D., "Terahertz time-domain spectroscopy characterization of the far-infrared absorption and index of refraction of high-resistivity , float-zone silicon," 1379–1386 (2004).
- [8] Zazueta-Raynaud, A., Pelayo-Ceja, J. E., Lopez-Delgado, R. and Ayon, A., "ZnO photoluminescent quantum dots with down-shifting effect applied in solar cells.," J. Phys. Conf. Ser. **773**(1) (2016).
- [9] Caballero, A. C., Villegas, M., Moure, C. and Ferna, J. F., "Controlled precipitation methods : formation mechanism of ZnO nanoparticles," 925–930 (2001).
- [10] Smith, R. M. and Arnold, M. A., "Terahertz time-domain spectroscopy of solid samples: Principles, applications, and challenges," Appl. Spectrosc. Rev. **46**(8), 636–679 (2011).

Computational Modeling of 3D Metamaterial Wire Arrays for Terahertz Operation

Juan Adrián Zepeda-Galvez
Department of Physics and Astronomy
The University of Texas at San Antonio
San Antonio, USA
Juanadrian.zepeda-galvez@utsa.edu

Arturo Ayón
Department of Physics and Astronomy
The University of Texas at San Antonio
San Antonio, USA
Arturo.ayon@utsa.edu

Clarissa Vazquez Colon
Department of Physics and Astronomy
The University of Texas at San Antonio
San Antonio, USA
Clarissa.VazquezColon@utsa.edu

Abstract—The computational modeling of a 3D Metamaterial beam array has been performed employing a commercially available Finite Differences Time Domain (FDTD) software package, to determine the prospective suitability of the proposed geometry in the demonstration of filters and resonators operating in the THz regime. The modeled structure comprises arrays of metallic, horizontal beams supported by vertical anchors placed on a semi-infinite silicon substrate with a refractive index of $n=3.42+i0.01$ with the boundary conditions considered periodic in the directions parallel to the beams and a Perfectly Matched Layer (PML) in the direction perpendicular to them. The simulations indicate a high pass filter behavior with a strong dependence on the unit cell length such that the cutoff frequency decreases as the length of the beams increase. Furthermore, due to the symmetry built in the system, the Metamaterial array is insensitive to the use of transverse electric (TE) or transverse magnetic (TM) polarization (Abstract)

Keywords— Terahertz, 3D Metamaterials,

I. INTRODUCTION

Metamaterials enable the possibility of manipulating Terahertz (THz) radiation in such a manner that their interaction can be tailored to fulfill prospective circuitry requirement. Suitable behavior in the THz regime is frequently difficult to obtain employing natural materials. The successful utilization of THz waves will enable applications in different fields, including astronomy and space science since about 98% of the photons created since the big bang lie in the submillimeter/far infrared range[1].

Additionally, THz radiation is non-ionizing, making them attractive for biomedical applications. In fact, the vibrational modes of many molecules, including DNA and other proteins, fall in the THz regime, thus generating a spectroscopic fingerprint, which makes the detection of those molecules relatively straightforward[2], [3]. Despite the fact that there is strong atmospheric absorption mainly due to water molecules, there are still several bands that can be used for high-speed communications. Furthermore, in the case of intra-chip communication, atmospheric absorption is effectively null [4-6] making THz signals well suited for such purposes. These promising applications underline the interest to demonstrate circuit elements to exploit the portion of the electromagnetic spectrum comprising THz frequencies.

II. DESIGN AND SIMULATION

In this work, the computational modeling of a 3D Metamaterial is reported. It consists of an array of metallic horizontal beams supported by vertical anchors placed on top of a semi-infinite silicon substrate with a refractive index of $n=3.42+0.01i$. Since most metals have their plasmonic resonance in the visible to ultraviolet regimes, it is convenient to model the metal as a Perfect Electrical Conductor. The unit cell comprises horizontal beams attached to an anchor in the

center. The width and thickness of the beams are $1.5\text{ }\mu\text{m}$ and 500nm , respectively, and separated by $5\text{ }\mu\text{m}$. The anchors are modelled as squared prisms with a side length of $6\text{ }\mu\text{m}$ and $40\text{ }\mu\text{m}$ height (see Figure 1). The simulations were carried out using the commercially available software package Lumerical based on the Finite Differences Time Domain (FDTD) method. The boundary conditions were set as periodic in the directions parallel to the beams and Perfectly Matched Layer (PML) in the direction perpendicular to them. Due to the symmetry in the system, the Metamaterial is insensitive to the use of transverse electric (TE) or transverse magnetic (TM) polarization.

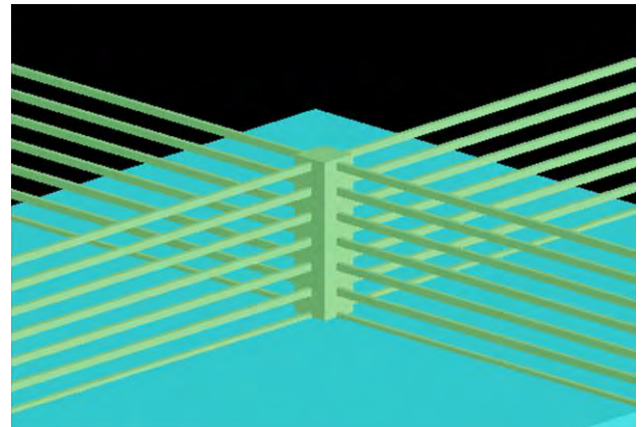


Figure 1. Schematic representation of the proposed

III. ANALYSIS

The simulations indicate a high pass filter behavior with a strong dependence on the length of the unit cell. Specifically, the cutoff frequency decreases as the length of the beams increases. Figure 2 displays the anticipated transmission behavior when considering beams of lengths of 120, 160, 200 and $240\text{ }\mu\text{m}$, respectively, with corresponding cutoff frequencies of 1.6, 1.2, 0.9 and 0.8 THz , respectively.

In order to understand the filtering mechanism, the electric and magnetic behavior at the cutoff frequency was analyzed. Figures 3a and 3b show the electric and magnetic field distribution in a plane perpendicular to the beams at the cutoff frequency. The portrayed electric and magnetic fields correspond to those of a dipole antenna evincing the modeled high-pass filtering effect.

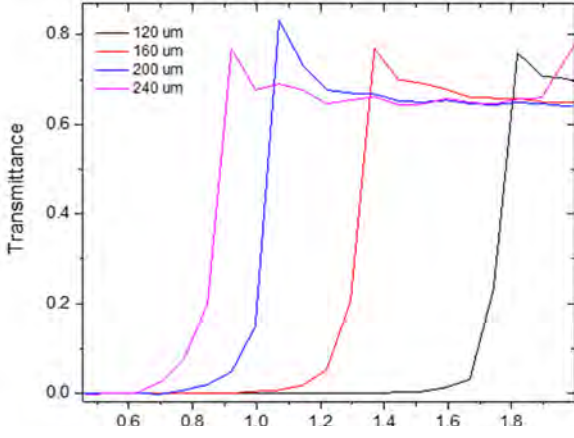


Figure 2. Transmission spectra for different unit cell lengths. The graph shows that the cutoff frequency decreases as the size of the device increases.

IV. CONCLUSIONS

A novel high-pass THz filter based on a 3D Metamaterial has been proposed and modeled computationally. In order to test the performance of the device, a commercial FDTD package was employed to perform electromagnetic simulations. The simulations indicate that the cutoff frequency has a strong dependence on the unit cell length. Furthermore, considering the symmetry of the system, the device can be used in TE or TM polarizations indistinctively.

V. ACKNOWLEDGEMENTS.

The authors would like to acknowledge the U.S. Army Research Office (Grant W911NF-13-1-0110), NSF (Grant 1650571) and the Department of Physics and Astronomy at the University of Texas at San Antonio, for the financial support provided for this research project.

- [1] D. T. Leisawitz *et al.*, "Scientific motivation and technology requirements for the SPIRIT and SPECS far-infrared/submillimeter space interferometers," no. July 2000, pp. 36–46, 2000.
- [2] J. Xu, K. W. Plaxco, and S. J. Allen, "Probing the collective vibrational dynamics of a protein in liquid water by terahertz absorption spectroscopy," *Protein Sci.*, vol. 15, no. 5, pp. 1175–1181, 2006.
- [3] A. F. Lawrence, J. C. McDaniel, D. B. Chang, and R. R. Birge, "The nature of phonons and solitary waves in alpha-helical proteins," *Biophys. J.*, vol. 51, no. 5, pp. 785–793, 1987.

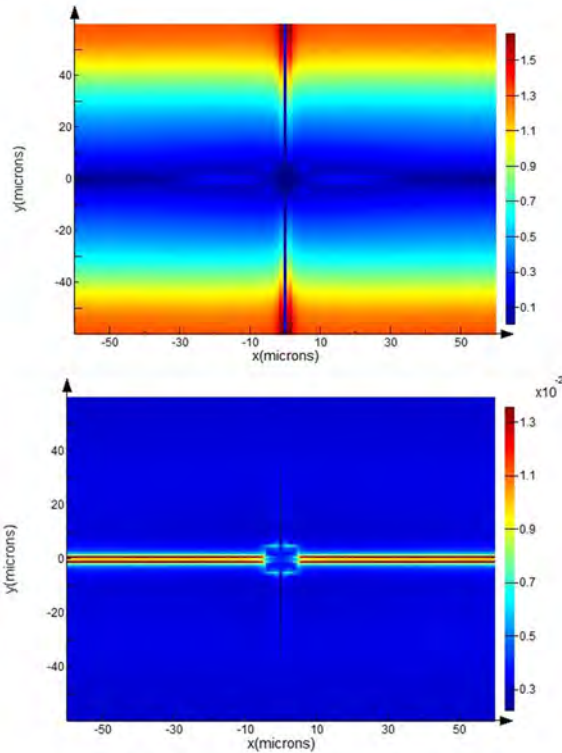


Figure 3. Simulated plots for Electric (top) and magnetic (bottom) field distributions at the cutoff frequency

EFFECT OF UV LIGHT ON SYSTEMATIC ERRORS IN THZ-TDS SPECTROSCOPY

Juan Adrián Zepeda-Galvez¹, Clarissa D. Vázquez-Colón¹, Daniel Shreiber² and Arturo Ayón¹

¹The University of Texas at San Antonio, San Antonio, TX, 78249 USA

²US Army Research Laboratory, RDRL-WMM-E, Bldg. 4600, Aberdeen Proving Ground, MD 21005-5069 USA

Abstract. Terahertz Time-Domain Spectroscopy (THz-TDS) has become an extremely important technique to determine the optical properties of materials of interest in this frequency regime. Specifically, UV photoresponsive semiconductors, including wide-bandgap semiconductors, have attracted an ever increasing attention due to their prospective application in reconfigurable devices. However, prior to their utilization it is necessary to extract from the collected THz-TDS spectra the properties of the materials under consideration. We report the observed systematic error when UV excitation of quantum dots is employed in a TDS set up, and we discuss the correction algorithms to overcome the aforementioned errors and present a preliminary explanation for the observed effect. An additional experiment employing Carbon Quantum Dots (QDs) was performed to verify the corrective method contained herein.

I. Introduction

Most of the dynamical processes in semiconductors including carrier-phonon, carrier-carrier, and carrier-photon interactions, occur in time scales from a few femtoseconds to a few picoseconds. For those time scales pump-probe experiments are considered suitable and powerful tools in the investigation of ultrafast carrier dynamics. In general, pump-probe experiments are useful in the study of photo-generated carriers, provided that the energy of the photons employed exceeds the band gap energy (E_g) of the semiconductor, i.e. $\hbar\omega \geq E_g$. [1-3]. Among the schemes employed, UV pump -THz probe experiments have been used to investigate the optical properties and the wave modulation of wide bandgap semiconductor nanomaterials [4].

Additionally, Terahertz Time-Domain spectroscopy (THz-TDS) has proven to be a powerful technique to characterize substances in the frequency domain from 30 GHz to 10 THz. The applications of THz-TDS ranges from characterization of chemical substances [5] and quality control [6, 7], to contributions in communications [8], and conservation of cultural heritage [9], and in terms of size extends from galactic to nanoscale systems [10, 11]. This wide variety of applications has led to a significant number of reports regarding methods to obtain material parameters estimation and measurement techniques [12-15]. Consequently, there has been an ever increasing number of reports in which the main topic is to study systematic errors for THz spectrometers [16, 17], including the comprehensive analysis of the aforementioned errors in measurements involving liquid samples, taking into consideration sources of error such as T-ray noise, variations of cuvette wall thicknesses, transfer function approximation, cuvette tilting, Fabry-Pérot reflections and Gouy shift, among others [18].

However, to the best of our knowledge, there are no reports addressing the influence of UV excitation in THz pump-probe measurements. In the reminder of the paper we will address this shortcoming, first indicating the origins of measurement errors and, subsequently, discussing a parameter extraction method taking into consideration the previously mentioned UV excitation. Carbon quantum dot colloidal samples will be employed to illustrate the method discussed herein.

II. Determination of optical constants

Consider a liquid sample in a quartz cuvette (see fig 1), which is mounted for THz-TDS measurements. The width of the cuvette walls is l_0 and the sample thickness will be l . Before interacting with the sample, the THz beam passes through two on-axis parabolic lenses, and two more after the interaction with the sample. An UV lamp is mounted on top of the THz-TDS setup.

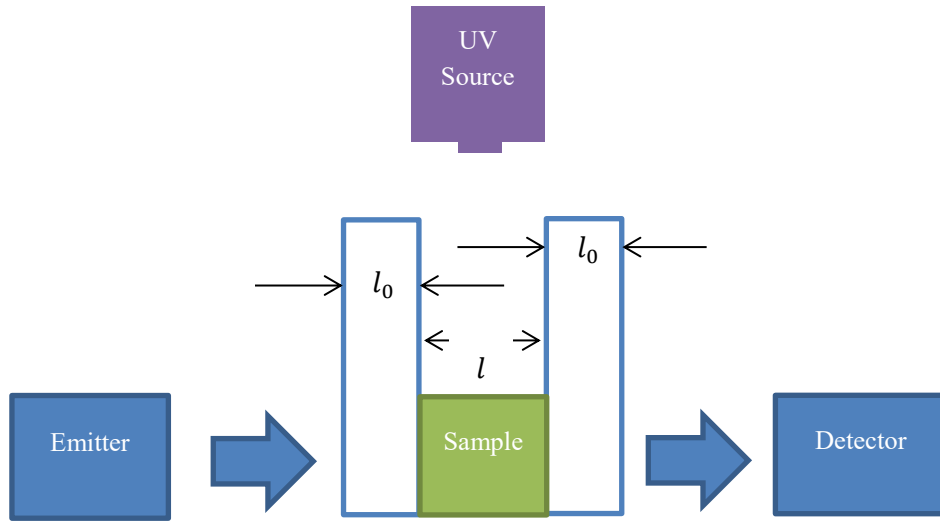


Figure 1. Sketch of the optical path that traverses the cuvette with and without sample, and with and without UV light.

In order to subtract all background influences, reference measurements are collected without the cuvette, and with the cuvette but without the colloidal sample, both in the absence and then in the presence of UV excitation, with the intent to remove said influences and determine the properties of an arbitrary colloidal sample. Figure 2a shows a typical time-domain pulse collected employing a Terahertz Time-domain spectrometer. The presence of errors is made evident by the conspicuous differences in spectra arrival times (see Figure 2b) particularly when there is no cuvette in the THz beam path. This obviates the need to define transfer function algorithms to remove systematic errors. This can be accomplished in the following fashion: let $E_{sam}(\omega)$ be the Fourier transform of the electric field of the sample, and $E_{air}(\omega)$ and $E_{cuv}(\omega)$ be the electric field of the Terahertz ray transmitted through the air, and cuvette, respectively. Throughout this article the subscripts *air*, *sam*, and *cuv* will

represent air, sample and cuvette, respectively. Employing a plane-wave approximation and following Yang's notation [18], the spectral components at a frequency ω are given by,

$$E_{air}(\omega) = E_0(\omega)P_{air}(\omega, 2l_o + l) \quad (1)$$

$$E_{cuv}(\omega) = E_0(\omega)T_{air-cuv}P_{cuv}(\omega, l_0)T_{cuv-air}P_{air}(\omega, l)T_{air-cuv}P_{cuv}(\omega, l_0)T_{cuv-air} \quad (2)$$

$$\begin{aligned} E_{sam}(\omega) \\ = E_0(\omega)T_{air-cuv}P_{cuv}(\omega, l_0)T_{cuv-sam}P_{sam}(\omega, l)T_{sam-cuv}P_{cuv}(\omega, l_0)T_{cuv-air} \end{aligned} \quad (3)$$

where E_0 is the electric field emitted by the antenna, $T_{ij}(\omega) = \frac{2\tilde{n}_i}{\tilde{n}_i + \tilde{n}_j}$ is the transmission coefficient from medium i to medium j and $P_\alpha(\omega, x) = \exp[-i\frac{\tilde{n}_\alpha x \omega}{c}]$ is the propagation coefficient in medium α , through a distance x , $\tilde{n}_\alpha(\omega) = n_\alpha(\omega) + i\kappa_\alpha(\omega)$ is the complex refractive index of medium α , as a function of frequency, and c is the speed of light in vacuum.

The transfer function of the sample is taken relative to the cuvette, and is given by the ratio between the electric field of the sample and that of the cuvette. If we assume a relatively low absorption, i.e., $\kappa \ll n$, then we can approximate the transfer function only to its real part, obtaining

$$H_{sam} = \frac{E_{sam}(\omega)}{E_{cuv}(\omega)} \approx \frac{(n_{cuv}(\omega) + n_0(\omega))^2 n_{sam}(\omega)}{(n_{cuv}(\omega) + n_{sam}(\omega))^2 n_0} \exp[-\frac{\kappa(\omega)\omega l}{c}] \exp[-i(n_{sam}(\omega) - n_0)\frac{\omega l}{c}] \quad (4)$$

where $n_0(\omega)$ is the refractive index of air. The quantities $H_{sam}(\omega)$ and $H_{cuv}(\omega)$ are obtained experimentally by applying a Fourier transform to the transmitted Time Domain pulse. It is also possible to extract the real part of the index of refraction by inverting the magnitude of the transfer function. Similarly, we can deduce the absorption coefficient by inverting the argument in the equation.

$$n_{sam}(\omega) = n_0 - \frac{\arg[H_{sam}(\omega)] c}{\omega l} \quad (5)$$

$$\kappa = \frac{c}{l\omega} \left\{ \ln \left[\frac{(n_{cuv}(\omega) + n_0(\omega))^2 n_{sam}(\omega)}{(n_{cuv}(\omega) + n_{sam}(\omega))^2 n_0(\omega)} \right] - \ln[|H_{sam}|] \right\} \quad (6)$$

In order to determine the complex refractive index of the cuvette, we employ a similar transfer function but this time the electric field of the cuvette is compared to the one in air, and then the weak absorption approximation is employed. The transfer function becomes

$$\begin{aligned}
H_{cuv} &= \frac{E_{cuv}(\omega)}{E_{air}(\omega)} \\
&\approx \frac{16n_{cuv}^2(\omega)n_0^2(\omega)}{(n_{cuv}(\omega) + n_0(\omega))^4} \exp\left[-\frac{2\kappa_{cuv}(\omega)\omega l_0}{c}\right] \exp\left[-i\left(n_{cuv}(\omega) - n_0(\omega)\right)\frac{2\omega c}{l_0}\right]
\end{aligned} \tag{7}$$

This expression can also be inverted, to yield

$$n_{cuv}(\omega) = n_0(\omega) - \frac{\arg[H_{cuv}(\omega)] c}{\omega l_0} \tag{8}$$

$$\kappa_{cuv} = \frac{c}{l_0 \omega} \left\{ \ln \left[\frac{16n_{cuv}^2(\omega)n_0^2(\omega)}{(n_{cuv}(\omega) + n_0(\omega))^4} \right] - \ln[|H_{cuv}|] \right\} \tag{9}$$

The overall error in the index of refraction induced by the error sources investigated in his paper, is on the order of 10^{-2} and varies inversely with the frequency [18]. It is necessary, however, to take into consideration yet another source of error when dealing with UV pumping, which is demonstrated in figure 2b. It shows the relatively small but noticeable shift in the THz pulse between air and UV-illuminated air. Furthermore, the observed shift becomes more noticeable as the energy of the UV photons employed increases. This shift propagates to a variation in the phase when the Fourier transform is made. As shown in equation 5, the phase is necessary to compute the index of refraction (see figures 3a and 3b)

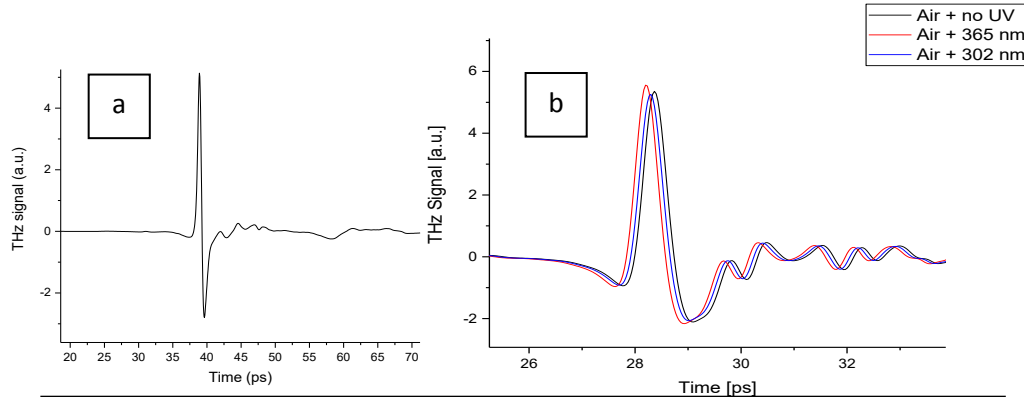


Figure 2. (a) Typical time domain spectra. (b) Time trace of transmission through air (black), air plus UV excitation, $\lambda=302$ nm and $\lambda=365$ nm (blue and red, respectively).

III. Results

When the approximation $E_i(\omega) \approx E_{iUV}(\omega)$, where i stands for cuvette or air, is made, an error in the optical parameters of the material is introduced presumably due to the interaction between the silicon dioxide lenses and UV radiation applied. To avoid this error it is required to measure air and cuvette

transfer functions under UV excitation, namely $H_{samUV}(\omega)$ and $H_{cuvUV}(\omega)$, in order to calculate and perform a similar treatment as it was used before to deduce equation 5 and equation 6. The corrected optical parameters become

$$n_{samUV}(\omega) = n_0(\omega) - \frac{\arg[H_{samUV}(\omega)] c}{\omega l} \quad (10)$$

$$\kappa_{samUV} = \frac{c}{l\omega} \left\{ \ln \left[\frac{(n_{cuvUV}(\omega) + n_{0UV}(\omega))^2 n_{samUV}(\omega)}{(n_{cuvUV}(\omega) + n_{samUV}(\omega))^2 n_{0UV}(\omega)} \right] - \ln[|H_{samUV}|] \right\} \quad (11)$$

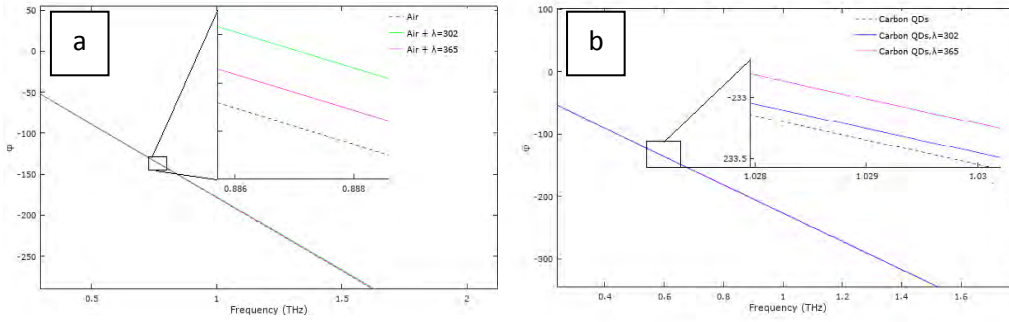


Figure 3. (a) Phase of the Fourier transform (FT) for air without and with UV exposure (b) phase of the FT for the QD sample without and with UV exposure.

To demonstrate the application of the suggested method, THz-TDS measurements were performed on a Carbon quantum dot colloidal sample, diluted in ethanol, under exposure to two different UV excitation wavelengths, namely, $\lambda=302 \text{ nm}$ and $\lambda=365 \text{ nm}$. The UV lamp was mounted above the THz-TDS system, as pictured in figure 1. The colloidal solution was transferred into a 1 mm quartz cuvette using a plastic pipette and was placed at the focal point between the parabolic lenses.

Figure 4a displays the uncorrected and figure 4b the corrected refractive index of the colloidal solution. It can be observed that as the excitation wavelength, the error also increases. It is thought that the underlying reason for this shift is due to the interaction of the UV photons with the parabolic mirrors, which are made of silicon dioxide, and under UV exposure experience a change in their conductivity, however, further investigation is needed to verify this argument.

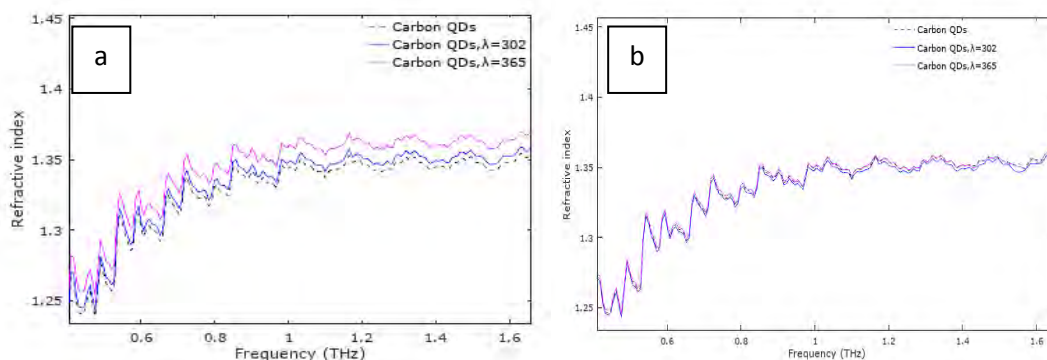


Figure 4. . (a) Refractive index of colloidal Carbon quantum dots in ethanol computed using free air as a reference. (b) Refractive index of Carbon quantum dots computed using Air+UV as a reference.

IV Conclusion

A new source of error in THz-TDS which could contribute inaccuracies in the extraction of optical parameters of materials under UV pump- THz probe experiments has been investigated, and a correction algorithm based on measuring air and cuvette under UV excitation and therefore deducing a new transfer function has been derived and discussed. The proposed correction was validated by applying the proposed methodology to data obtained from a THz-TDS experiment in a colloidal solution of Carbon Quantum dots diluted in ethanol. The determination of the source of the delay in the air waveform when UV radiation is present requires further experimentation.

V Acknowledgements

This work was co-funded by the Army Research Office (ARO) and the Air Force Office of Scientific Research (AFOSR) Grant W911NF-15-1-0297.

V References

- [1] F. Rossi, "Theory of ultrafast phenomena in photoexcited semiconductors " *Reviews of modern physics* vol. 74, p. 5, 08/2002 2002
- [2] P. D. Cunningham and L. M. Hayden, "Carrier dynamics resulting from above and below gap excitation of P3HT and P3HT/PCBM investigated by optical-pump terahertz-probe spectroscopy," *Journal of Physical Chemistry C*, vol. 112, pp. 7928-7935, May 29 2008.
- [3] M. Rahm, *et al.*, "THz Wave Modulators: A Brief Review on Different Modulation Techniques," *Journal of Infrared Millimeter and Terahertz Waves*, vol. 34, pp. 1-27, Jan 2013.

- [4] J. T. Hong, *et al.*, "UV-induced terahertz wave modulation in free-standing ZnO nanowire films," *Optical Materials Express*, vol. 6, pp. 3751-3758, Dec 1 2016.
- [5] K. Ajito and Y. Ueno, "THz Chemical Imaging for Biological Applications," *Ieee Transactions on Terahertz Science and Technology*, vol. 1, pp. 293-300, Sep 2011.
- [6] N. Karpowicz, *et al.*, "Compact continuous-wave subterahertz system for inspection applications," *Applied Physics Letters*, vol. 86, Jan 31 2005.
- [7] S. Wietzke, *et al.*, "Terahertz imaging: a new non-destructive technique for the quality control of plastic weld joints," *Journal of the European Optical Society-Rapid Publications*, vol. 2, 2007.
- [8] A. Barh, *et al.*, "Specialty Fibers for Terahertz Generation and Transmission: A Review," *Ieee Journal of Selected Topics in Quantum Electronics*, vol. 22, Mar-Apr 2016.
- [9] A. M. Gomez-Sepulveda, *et al.*, "History of Mexican Easel Paintings from an Altarpiece Revealed by Non-invasive Terahertz Time-Domain Imaging," *Journal of Infrared Millimeter and Terahertz Waves*, vol. 38, pp. 403-412, Apr 2017.
- [10] C. Kulesa, "Terahertz Spectroscopy for Astronomy: From Comets to Cosmology," *Ieee Transactions on Terahertz Science and Technology*, vol. 1, pp. 232-240, Sep 2011.
- [11] P. Kuzel and H. Nemec, "Terahertz conductivity in nanoscaled systems: effective medium theory aspects," *Journal of Physics D-Applied Physics*, vol. 47, Sep 17 2014.
- [12] O. S. Ahmed, *et al.*, "Efficient Material Parameters Estimation with Terahertz Time Domain Spectroscopy," *Terahertz Technology and Applications Iv*, vol. 7938, 2011.
- [13] T. D. Dorney, *et al.*, "Material parameter estimation with terahertz time-domain spectroscopy," *Journal of the Optical Society of America a-Optics Image Science and Vision*, vol. 18, pp. 1562-1571, Jul 2001.
- [14] L. Duvillaret, *et al.*, "A reliable method for extraction of material parameters in terahertz time-domain spectroscopy," *Ieee Journal of Selected Topics in Quantum Electronics*, vol. 2, pp. 739-746, Sep 1996.
- [15] L. Duvillaret, *et al.*, "Highly precise determination of optical constants and sample thickness in terahertz time-domain spectroscopy," *Applied Optics*, vol. 38, pp. 409-415, Jan 10 1999.
- [16] H. W. Hubers, *et al.*, "Terahertz Spectroscopy: System and Sensitivity Considerations," *Ieee Transactions on Terahertz Science and Technology*, vol. 1, pp. 321-331, Sep 2011.
- [17] M. Naftaly, "Metrology Issues and Solutions in THz Time-Domain Spectroscopy: Noise, Errors, Calibration," *IEEE Sensors Journal*, vol. 13, Jan 2013.
- [18] F. Yang, *et al.*, "Uncertainty in Terahertz Time-Domain Spectroscopy Measurement of Liquids," *Journal of Infrared Millimeter and Terahertz Waves*, vol. 38, pp. 229-247, Feb 2017.

Reconfigurable Behavior of CdTe Quantum Dots at Terahertz Frequencies employing UV excitation

Clarissa D. Vázquez-Colón^{1*}, Juan Adrián Zepeda-Galvez¹, Daniel Shreiber², Arturo Ayón¹

¹Department of Physics and Astronomy, The University of Texas at San Antonio, Texas, USA

² US Army Research Laboratory, Aberdeen Proving Ground, Aberdeen, Maryland USA

* Corresponding author: clarissa.vazquezcolon@utsa.edu, 210-458-6562

Abstract

We report the synthesis and characterization of cadmium-telluride (CdTe) quantum dots (QDs) and their performance at Terahertz frequencies employing THz time-domain spectroscopy (THZ-TDS). The data was analyzed using Fast Fourier Transform (FFT) to obtain the optical characteristics of the aforementioned CdTe QDs colloidal solutions. Additional measurements were collected while exposing the synthesized QDs to UV excitation with wavelengths of 302 nm and 365 nm, respectively. A noticeable variation in both the real and imaginary components of the index of refraction was observed, that could prove crucial in the demonstration of reconfigurable devices operating in the THz regime.

Keywords: Terahertz; Quantum dots; CdTe; Time Domain Spectroscopy

1 Introduction

In recent years the possibility of operating with THz frequencies has captured the attention of scientists and technologists due to the relative lack of availability of systems for THz signal generation and detection. The interest in the THz gap region extending from 300 GHz to 10 THz is mostly driven by the attractive characteristics of THz radiation, including its ability to be transmitted through most materials, and being non-ionizing and, therefore, considered to be nonhazardous to humans or the environment. Signal generation, detection and modulation in this region of the electromagnetic spectrum could enable the demonstration of ground breaking applications in large market segments, namely, medical, security, imaging, and communications. In order to address the perceived needs for THz devices and schemes, the effort discussed herein, focused on the study and characterization of CdTe quantum dots (QDs) at THz frequencies. QDs are semiconductor nanostructures, typically crystalline, that confine charge carriers to a nanoscale region, and are described by quantum mechanical laws. QDs exhibit a different behavior compared to bulk materials because the large surface to volume ratio of QDs affect their physical and chemical properties (Amelia et al. 2012). In fact, their electronic properties are strongly determined by their size (Trindade et al. 2001), although those characteristics are essentially due to the aforementioned confinement effect of charge carriers. Considering that a variety of QDs exhibit photoluminescent Stokes shift effects (Petryayeva et al. 2013), they have been identified as suitable for biolabeling, LEDs, lasers, and solar cells (Moreels et al. 2009), among others. However, the utilization of QDs in the THz region of the electromagnetic spectrum remains largely underexplored at a time when there is an observed need to develop materials and techniques that could address the needs of resonators, filters and other circuitry elements with a satisfactory Terahertz performance, to satisfy the anticipated requirements in electronics, optics, analytical science, biological imaging including spectroscopy, and medical therapy (Ferguson and Zhang 2002; Dragoman and Dragoman 2004; Dexheimer 2008; Mantsch and Naumann 2010; Guillet et al. 2014). Therefore, we discuss the synthesis and characterization of CdTe QDs at THz frequencies, including their prospective utilization for amplitude modulation when exposed to UV excitation of different wavelengths, specifically 302 nm and 365 nm. The utilization of THz time domain spectroscopy (THz-TDS) permits the extraction of the real and imaginary parts of their effective index of refraction, as well as their attenuation, and conductivity as a function of frequency.

2 Methods

2.1 Synthesis of CdTe QDs

CdTe QDs were chemically synthesized employing a water-based procedure (Murray et al. 1993; Zou et al. 2008; Wu et al. 2012a; Yuan et al. 2012; Pelayo et al. 2016). This procedure involves the preparation of three preliminary mixtures. The first mixture was prepared in an Erlenmeyer flask in which 0.2 mmol of cadmium acetate dihydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99.5%) is added to 50 ml of deionized (DI) water, and subsequently, 18 μl of thioglycolic acid (TGA, 90%) was also added. The second solution consists of 1 M of sodium hydroxide (NaOH) that was employed to adjust the pH of the first solution. When a pH between 10.5 and 11 was obtained the solution was stirred for an additional 5 min. A third solution was made containing 0.04 mmol of potassium telluride hydrate (K_2TeO_3 , 95%) dissolved in 50 ml of DI water, and stirred for 5 min. The solution of potassium telluride was added to the first solution of cadmium acetate, and finally 80 mg of sodium borohydride (NaBH_4 , 99.99%) was added and the solution stirred for a further 5 min. The solution was then transferred to a single-neck round-bottom flask that was attached to a Liebig condenser. The flask containing the solution was submerged in laboratory oil at a constant temperature of 100 °C and stirred at 500 rpm while being refluxed. The size of the synthesized CdTe QDs is controlled by the refluxing time (Wu et al. 2012b). The solution used for the THz-TDS characterization corresponded to the dilution of 1 ml of the final CdTe QD solution to 10 ml of ethanol as well as 1:10 in water. This project involved the preparation of CdTe QD colloidal solutions with a synthesis time of 1 hr and 8 hr, respectively.

2.2 Absorbance and bandgap measurements

Material band gaps were determined by using a graphic procedure (Kar and Chaudhuri 2005) based on the following expression:

$$\frac{d \ln(\alpha h f)}{d(h f)} = \frac{m}{h f} - E_g \quad \text{Eq. 1}$$

derived from

$$\alpha = \frac{A}{h f} (h f - E_g)^m \quad \text{Eq. 2}$$

where α is the absorbance spectra of the quantum dots, hf is the incident photon energy, E_g is the band gap and m is a parameter related to the nature of the exciton optical transition which can only take the values of 0.5, 2, 3/2 and 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively.

2.4 Terahertz characterization

Upon completion of QD synthesis, the THz amplitude modulation experiments were performed using a Menlo Systems TERA K15 Time-Domain THz Spectrometer in transmission mode (see Figure 1). Measurements were made at room temperature and air, cuvette, and solvent reference measurements were collected in order to extract the influence of the aforementioned QDs. The CdTe QDs colloidal solutions were dispensed in quartz cuvettes (High precision Cell HellmaAnalytics) with a reservoir width of 1 mm and wall thickness of 1.25 mm. The samples were also exposed to two different UV excitations with wavelength of 302 nm and 365 nm. The THz time domain data obtained from the equipment was processed employing a standard Fast Fourier Transform (FFT).

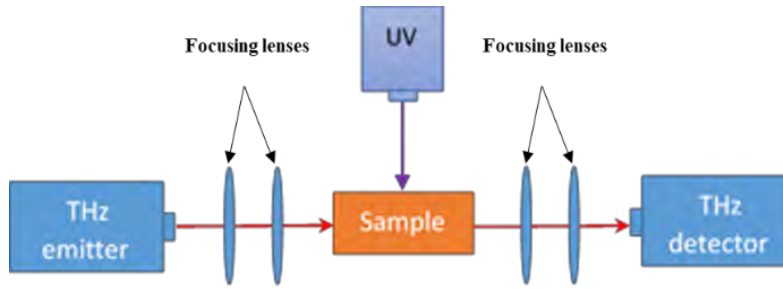


Fig 1. THz-TDS experiment setup

3 Results and discussions

3.1 Absorbance and bandgap

The absorbance and calculated bandgaps for the synthesized quantum dots are shown in Figure 2. For the 1 hr and 8 hr QD solutions, the extracted bandgaps were 3.57 eV and 2.82 eV (347 and 440 nm), respectively. The extracted bandgaps are significantly shifted from the bulk value for CdTe (~1.5 eV). Similar behavior has also been observed in other CdTe QDs (Abd El-Sadek et al. 2009).

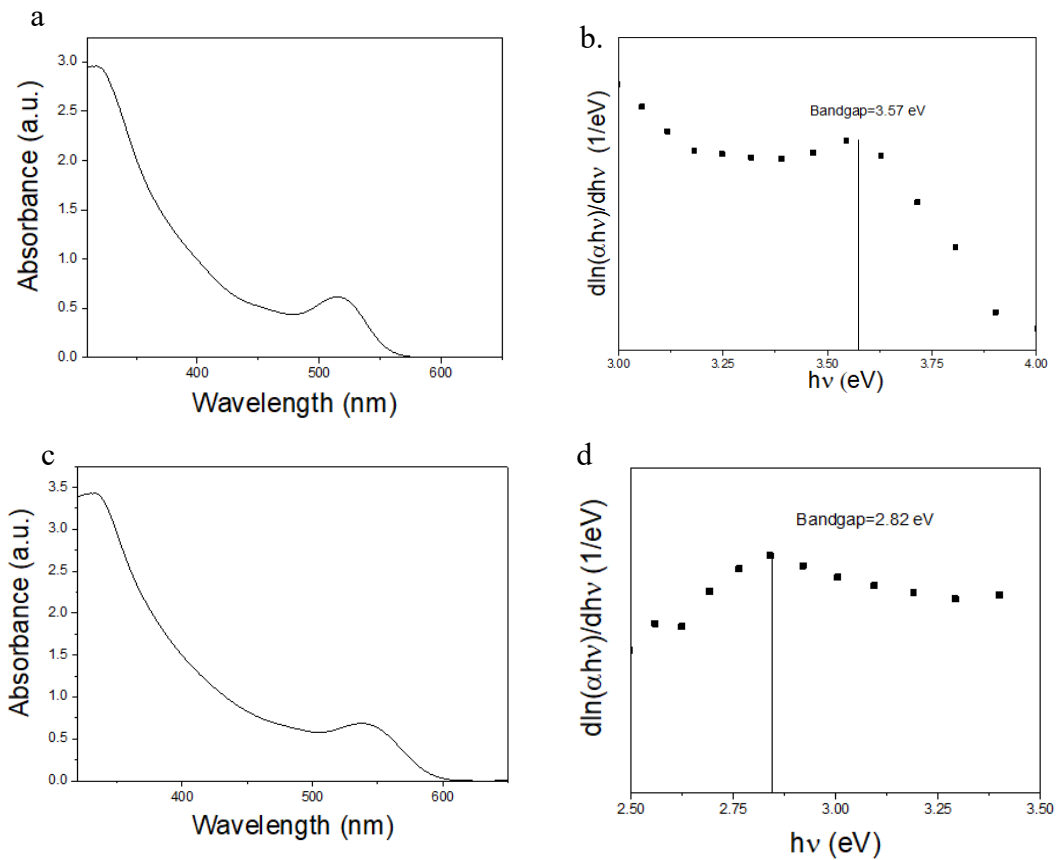


Figure 2. (a.) Absorbance spectrum and (b.) Bandgap calculation of CdTe QDs with a synthesis time of 1 hr, (c.) Absorbance spectrum and (d.) Bandgap calculation of CdTe QDs with a synthesis time of 8 hr.

Size of quantum dots

The size of CdTe quantum dots can be estimated by employing the empirical equation $D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - (194.84)$, where λ corresponds to the wavelength of the first exciton absorption peak (Yu et al. 2003). Based on the aforementioned expression we estimated the radii of the prepared CdTe quantum dots to be 2.62 nm and 3.10 nm for the synthesis times of 1 hr and 8 hr, respectively.

3.2 Terahertz characterization

3.2.1 Modulation depth

The extracted THz time domain amplitude variation before and after exposing the sample to UV illumination is shown in Figure 3. A relatively small, but not negligible, time delay is discernible between the sample without UV excitation and the sample exposed to UV. This effect is thought to be due to an increased conductivity of the colloidal solution. The fact that the shift increases as the energy of the excitation signal increases seems to corroborate the aforementioned assumption. The modulation depth induced by the UV exposure can be calculated employing the equation: $\left| \frac{T_{UV} - T_{noUV}}{T_{UV}} \right|$ (Sensale-Rodriguez et al. 2012; Hong et al. 2016), where T_{UV} and T_{noUV} are the corresponding normalized transmittances. In the case of CdTe QDs with a synthesis time of 1 hr, the extracted modulation depth at 1 THz is approximately 30% with an UV excitation of 302 nm, and 10% for an UV excitation of 365 nm, respectively (see Figure 4). Figure 4 also shows the transmittances and modulation depths for the 8 hr solutions.

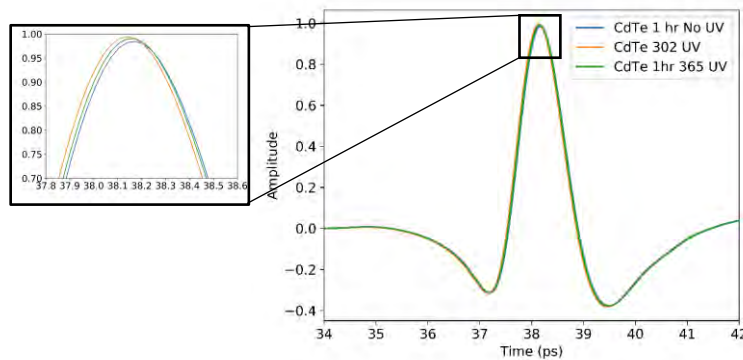


Figure 3. THz time domain amplitude for CdTe QDs solution 1 hr of synthesis without UV excitation and with UV excitation of 302 nm of wavelength.

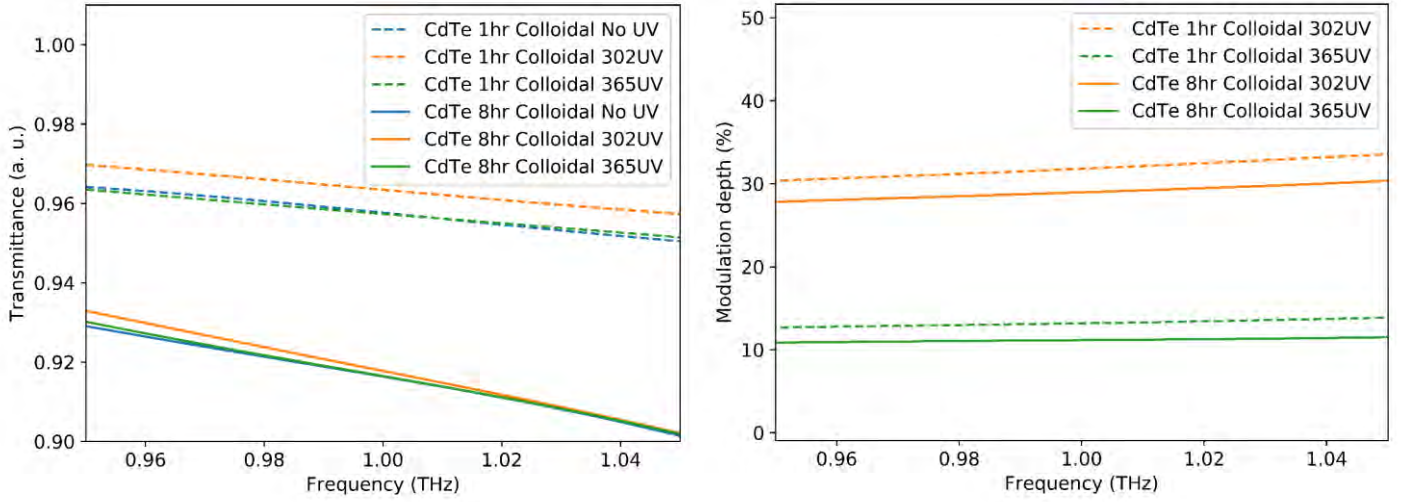


Figure 4. (a) Transmittance normalized to solvent for the different UV excitations. (b) Modulation depth induced by exposing CdTe QDs of synthesis time 1 hr (dashed) and 8 hours (solid) to UV excitation with wavelength of 302 nm and 365 nm.

3.2.2 Optical properties

The refractive index of the colloidal solutions can be calculated by calculating the Fourier transforms of the time-series data and employing the following equations: $\tilde{n} = n + ik$ where $n = 1 + \left(\frac{c}{\omega d}\right) \Delta\phi$ and $k = -\left(\frac{c}{\omega d}\right) \ln \rho$, where ω is the angular frequency, c is the speed of light in vacuum, d is the cuvette light (in this case is 1 mm), ρ is the transmission amplitude that is defined as follows: $\rho(\omega) = \tilde{E}(\omega)_{sample} / \tilde{E}(\omega)_{reference}$ and $\Delta\phi$ is the phase shift between $\tilde{E}(\omega)_{sample}$ and $\tilde{E}(\omega)_{reference}$ (Withayachumnankul and Naftaly 2014). Figure 5 shows the index of refraction of the synthesized CdTe colloidal solution as a function of frequency with no UV excitation, and with UV excitations with wavelengths of 302 nm and 365 nm, respectively. We speculate that a higher value of refractive index after exposing the sample to a 365 nm (3.4 eV) UV light is observed because the excitation in these QDs occurs at a wavelength of around 347 nm (3.57 eV) (Figure 2). Figure 2 also shows a rapid decline in the absorption spectrum past the bandgap energy (increase in transparency), which potentially explains the decrease in the index of refraction when the QDs are exposed to the higher UV excitation of 302 nm (4.1 eV). There is also a small difference between the two different synthesis times (dashed vs. solid lines), which we attribute to the difference in size of the QDs. Figure 6 shows the calculated extinction coefficients k for the solutions. We also calculated the conductivity of the CdTe nanoparticles using the equation $\sigma =$

$\epsilon_0 \omega \epsilon_i$, where ϵ_0 is the permittivity of free space and ϵ_i is the imaginary part of the complex permittivity of the material, the results of the calculations are shown in Figure 7.

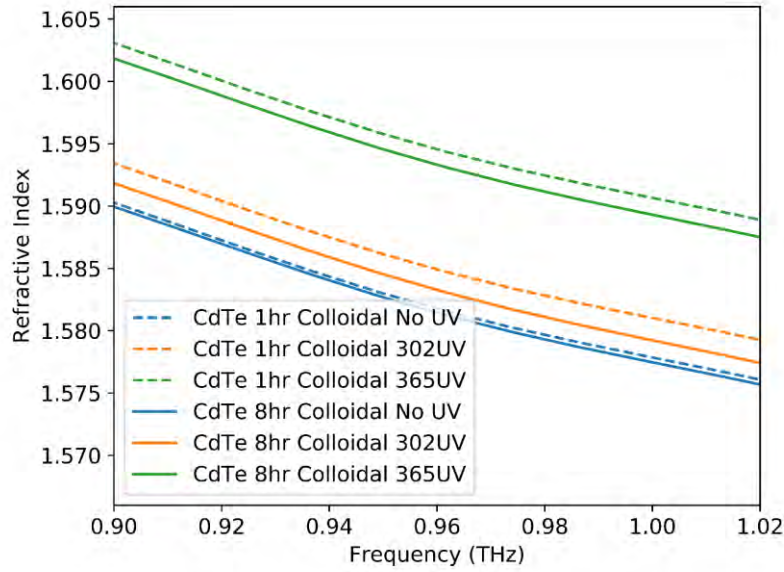


Figure 5. Refractive index for CdTe QDs 1hr (dashed) and 8hr (solid) of solution synthesis without UV exposure (blue line), 302 nm UV exposure (yellow line) and 365 nm UV exposure (green line)

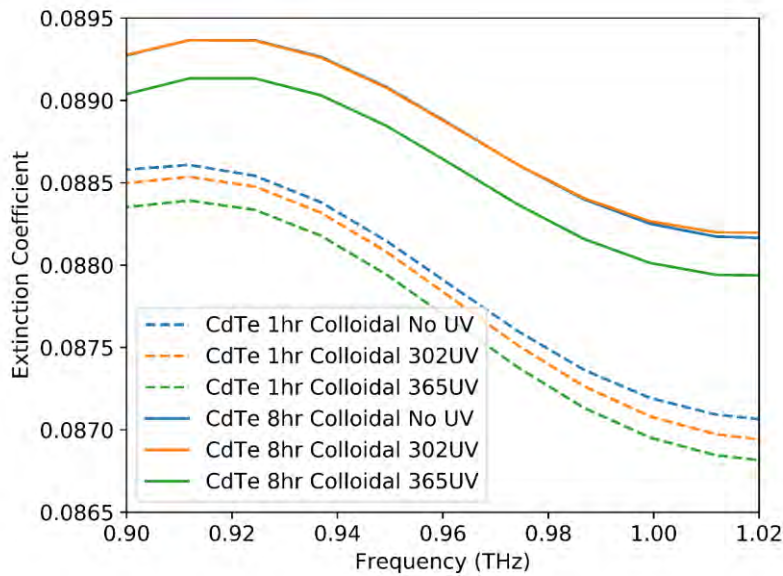


Figure 6. Extinction coefficient for CdTe QDs 1hr (dashed) and 8hr (solid) of solution synthesis without UV exposure (blue line), 302nm UV exposure (yellow line) and 365nm UV exposure (green line)

The increase in conductivity when the sample is exposed to 365 nm UV light is consistent with the increase in absorbance at 365 nm versus 302 nm (Figure 2). Since 365 nm is closer to our estimated bandgap energy, it is likely the carrier density of the QDs is increasing when exposed to this UV wavelength.

It is thought that the increase in the conductivity after exposing the sample to UV of 365 nm is due to the increase in the carrier density of the QDs. The transmittance, modulation depth, refractive index and conductivity were also calculated for the solution of CdTe 8 hr of synthesis and they show the same trend.

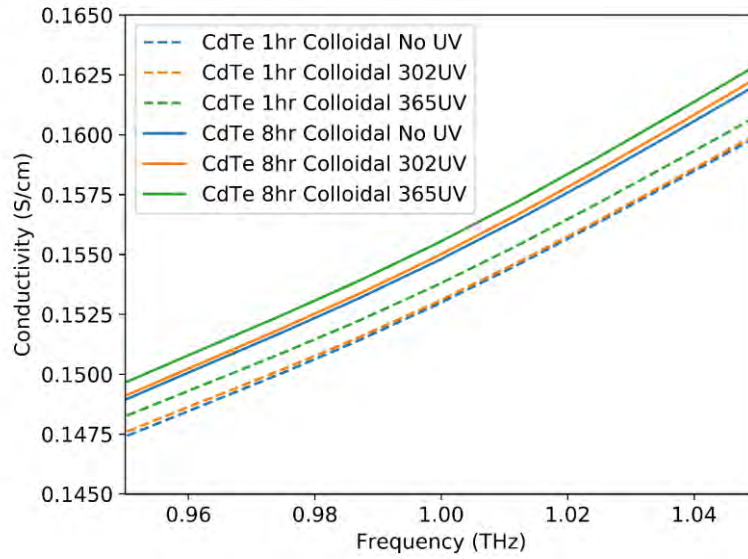


Figure 7. Conductivity for CdTe QDs 1hr (dashed) and 8hr (solid) without UV exposure (blue trace), 302 nm UV exposure (orange trace) and 365 nm UV exposure (green trace).

The measured indices were fitted using a two-term Sellmeier equation (Eq. 3) and also the Herzberger equation (Eq. 4). In both cases reasonably good fits were obtained (see Figure 8).

$$n^2 - 1 = \frac{A_1 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{A_2 \lambda^2}{\lambda^2 - \lambda_2^2} \quad (\text{Eq. 3})$$

$$n = A + BL + CL^2 + D\lambda^2 + E\lambda^4 \quad (\text{Eq. 4})$$

where $L = (\lambda - 0.028)^{-1}$

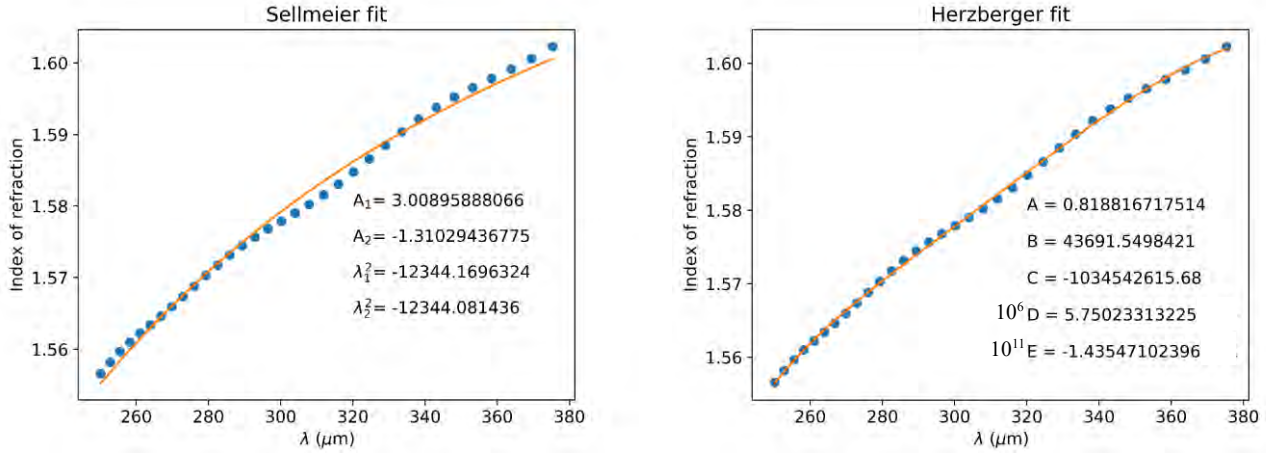


Figure 8. Model fits for the 1hr no UV exposure CdTe solution refractive index. Similar fits were obtained for other

4 Conclusions

Synthesis of CdTe QDs of 1hr and 8hr of duration was made. The bandgap and sizes of the nanoparticles were estimated using the method explained above. The estimated bandgap for CdTe QDs 1hr and 8hr of synthesis are the following 3.57 eV and 2.82 eV respectively. The estimated values of size are the following 2.62 and 3.10 nm respectively. We characterized our solutions in the THz regime and found that using UV excitation we can modulate the behavior of our material at THz frequencies. The index of refraction was higher when exposed to UV light of 365 vs 302 nm. We attribute this to 365 being closer to bandgap wavelength we estimated from UV-Vis.

Acknowledgements

This work was co-funded by the Army Research Office (ARO) and the Air Force Office of Scientific Research (AFOSR) Grant W911NF-15-1-0297.

References

Abd El-Sadek MS, Kumar JR, Moorthy Babu S (2009) Optical properties of thiol-stabilised CdTe nanoparticles. *Int J Nanoparticles* 2:20–29.

- Amelia M, Lincheneau C, Silvi S, Credi A (2012) Electrochemical properties of CdSe and CdTe quantum dots. *Chem Soc Rev* 41:5728–5743. doi: 10.1039/c2cs35117j
- Dexheimer SL (2008) Terahertz spectroscopy: principles and applications . 131:
- Dragoman D, Dragoman M (2004) Terahertz fields and applications. *Prog Quantum Electron* 28:1–66. doi: [http://dx.doi.org/10.1016/S0079-6727\(03\)00058-2](http://dx.doi.org/10.1016/S0079-6727(03)00058-2)
- Ferguson B, Zhang X-C (2002) Materials for terahertz science and technology. *Nat Mater* 1:26–33.
- Guillet JP, Recur B, Frederique L, et al (2014) Review of Terahertz Tomography Techniques. *J Infrared, Millimeter, Terahertz Waves* 35:382–411. doi: 10.1007/s10762-014-0057-0
- Hong J. T, Park J-Y, Lee S, Ahn YH (2016) UV-induced terahertz wave modulation in free- standing ZnO nanowire films. 6:3751–3758.
- Kar S, Chaudhuri S (2005) Synthesis and optical properties of single and bicrystalline ZnS nanoribbons. *Chem Phys Lett* 414:40–46. doi: <http://dx.doi.org/10.1016/j.cplett.2005.08.021>
- Mantsch HH, Naumann D (2010) Terahertz spectroscopy: The renaissance of far infrared spectroscopy. *J Mol Struct* 964:1–4. doi: <http://dx.doi.org/10.1016/j.molstruc.2009.12.022>
- Moreels I, Lambert K, Smeets D, et al (2009) Size-Dependent Optical Properties of Colloidal PbS Quantum Dots. *ACS Nano* 3:3023–3030. doi: 10.1021/nn900863a
- Murray CB, Norris DJ, Bawendi MG (1993) Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites. *J Am Chem Soc* 115:8706–8715. doi: 10.1021/ja00072a025
- Pelayo JE, Zazueta A, Lopez-delgado R, et al (2016) Silicon solar cell efficiency improvement employing the photoluminescent , down- shifting effects of carbon quantum dots. *Mater Renew Sustain Energy* 5:2–5. doi: 10.1007/s40243-016-0070-4
- Petryayeva E, Algar WR, Medintz IL (2013) Quantum Dots in Bioanalysis: A Review of Applications across Various Platforms for Fluorescence Spectroscopy and Imaging. *Appl Spectrosc* 67:215–252. doi: 10.1366/12-06948
- Sensale-Rodriguez B, Yan R, Kelly MM, et al (2012) Broadband graphene terahertz modulators enabled by intraband transitions. 3:780.
- Trindade T, O'Brien P, Pickett NL (2001) Nanocrystalline Semiconductors: Synthesis, Properties, and Perspectives. *Chem Mater* 13:3843–3858. doi: 10.1021/cm000843p
- Withayachumnankul W, Naftaly M (2014) Fundamentals of measurement in terahertz time-domain spectroscopy. *J Infrared, Millimeter, Terahertz Waves* 35:610–637. doi: 10.1007/s10762-013-0042-z
- Wu S, Dou J, Zhang J, Zhang S (2012a) A simple and economical one-pot method to synthesize high-quality water soluble CdTe QDs. *J Mater Chem* 22:14573. doi: 10.1039/c2jm31409f
- Wu S, Dou J, Zhang J, Zhang S (2012b) A simple and economical one-pot method to synthesize high-quality water soluble CdTe QDs. *J Mater Chem* 22:14573–14578. doi: 10.1039/C2JM31409F
- Yu WW, Qu L, Guo W, Peng X (2003) Experimental Determination of the Extinction Coefficient of CdTe , CdSe , and CdS Nanocrystals Experimental Determination of the Extinction Coefficient of CdTe , CdSe , and CdS Nanocrystals. *Chem Mater* 15:2854–2860. doi: 10.1021/cm034081k
- Yuan Z, Yang P, Cao Y, et al (2012) Time-Resolved Photoluminescence Spectroscopy Evaluation of CdTe and CdTe/CdS Quantum Dots. *ISRN Spectrosc* 2012:1–8. doi: 10.5402/2012/894385
- Zou L, Gu Z, Zhang N, et al (2008) Ultrafast synthesis of highly luminescent green- to near infrared-emitting CdTe nanocrystals in aqueous phase. *J Mater Chem* 18:2807–2815. doi: 10.1039/B801418C

Computational Modeling of 2D Metamaterial Wire Arrays in the Terahertz Regime

Clarissa Vázquez Colón and Arturo A. Ayón

Department of Physics and Astronomy, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249

*Corresponding author: clarissa.vazquezcolon@utsa.edu

Abstract

Metamaterials are artificial materials engineered to exhibit certain properties not existing in nature, that are comprised of arrays of elements from readily available materials such as metals. In this work we concentrated in the study of 2D metallic arrays because there is a special interest on the behavior of such structures at terahertz (THz) frequencies as a function of geometrical parameters. It is anticipated that this type of structure will enable the demonstration of novel THz lenses, filters, beam splitters, resonators, waveguides, antennas, hyperlenses, sensors, Fabry-Perot interferometers, metamaterials and reflectors, among others. Therefore, we report the computational modeling of transmission of electromagnetic waves through a 2D silver (Ag) nanowire array. Modifying the geometric parameters such as the lattice constant and wire radius enable us to predict the propagation at THz frequencies. Additionally, by judiciously removing selected wires in the geometry we also anticipate waveguiding effects through the aforementioned 2D array. The dimensions of the structures range from micrometers to nanometers permitting the propagation of frequencies from 1 THz to 3 THz and from 100 THz to 1,000 THz, respectively.

Keywords: COMSOL, Metamaterials, Terahertz

1. Introduction

Recently there has been an interest in the study of artificially structured electromagnetic (EM) materials because of the distinct possibility of exhibiting novel electromagnetic responses not available in naturally occurring materials (1). Specifically, it is expected that these artificial materials will exhibit a negative refractive index and enable superlensing, cloaking and other selected EM behaviors (2). In particular there is a special interest in the investigation of 2D and 3D nanowire arrays because of their potential application in different bands of the electromagnetic spectrum. In fact, these structures have been analytically studied because of their prospective application in the microwave, infrared and optical frequencies (3) (4) (5). Of particular interest is the reported fact that these structures typically produce narrowband emission spectra with near 100% efficiency and varying the permittivity of the medium enables the tuning of the associated narrowband emissions. Furthermore, these structures have to be impedance-matched with the environment and must possess low-loss constituent materials in order to minimize the absorption and in order to achieve nearly perfect emission (6). As far as the practical applications are concerned, the study of the THz regime is particularly attractive for the detection of concealed or obscure objects due to their relatively large penetration capabilities in non-metallic materials. The wavelength in this regime is sufficiently small to obtain high-quality image resolution and to detect the location of threatening or otherwise

identifying objects of interest. Additionally, THz radiation is not hazardous to biological tissue since it is non-ionizing and is, therefore, considered safe for human exposure. In naturally conducting materials electric responses normally occur at high frequencies. Considering an infinitely long array of wires, if the objective is to have this behavior to take place at lower frequencies then the plasma frequency needs to be taken into consideration and for guidance to achieve the sought results. The plasma frequency is given by,

$$\omega_{ep}^2 = \frac{ne^2}{\epsilon_0 m_{eff}} \quad (1)$$

where n is the electron density, e is the electron charge, ϵ_0 is the vacuum permittivity and m_{eff} is the electron effective mass (7). Ostensibly in order to lower the frequency response either the effective mass must increase or the electron density must decrease (7). A possible way to change these parameters is by using thin metallic wires (8). Due to the structural organization and the low amount of metal in a unit cell, the electron density of these metallic wires is lower and in this case the plasma frequency equation becomes,

$$\omega_{ep}^2 = \frac{2\pi c^2}{a^2 \ln\left(\frac{a}{r}\right)} \quad (2)$$

where r is the radius of the wires in the array, a is the lattice spacing and c is the velocity of light in vacuum. Furthermore, due to the force created on the electrons by the mutual inductance of the wires the electron effective mass is intensified. Thus, considering wires whose length tends to infinity, the effective permittivity of the structure is given by,

$$\epsilon_{eff}(\omega) = 1 - \frac{\omega_{ep}^2}{\omega^2 + j\Gamma\omega} \quad (3)$$

where Γ is responsible for the propagation loss. In the case of $\omega < \omega_{ep}$ the permittivity becomes negative. It is anticipated that employing well-established nanofabrication techniques will enable the demonstration of structures comparable to those depicted herein, and that are compatible with a mass production environment. The flexibility of the prospective process would allow us to vary various geometric parameters and, more importantly, would permit to reliably and repeatedly collect data over extended segments of the electromagnetic spectrum. Those arrays would enable technologists to collect the much needed data as a function of spatial and crystalline structure and will promote the further development of THz devices.

2. Computational Modeling

In order to study the electromagnetic (EM) properties of silver wire arrays we employed the commercially available RF module encountered in COMSOL Multiphysics (9), which is a finite element analysis based software package. The first geometry to be modeled comprised a 2D array of silver rods in vacuum, with a lattice constant of 400 nm (center to center) and wire radius of 50 nm (system 1) (10) as shown in Fig. 1. We also simulated a system with lattice constant of 100 μm (center to center) and wire radius of 5 μm (system 2) (see Fig. 5). The experimental optical data of permittivity of silver was taken from (11), on which we applied an interpolation function to obtain the real and imaginary components of Ag's dielectric function. Additionally, we employed COMSOL's EM Waves sub-module to incorporate the dielectric losses option. Perfect electric conductor boundary conditions were assumed at the top and bottom of the structure, and two ports

were used in the long sides of the rectangular structures in order to launch the wave from one side of the structure and detect it on the other side (see Fig. 2). The wave was set as a rectangular transverse electric (TE) wave. The frequency was varied from 100 THz to 1,000 THz in steps of 1 THz for system 1, and from 1 THz to 3 THz in steps of 0.01 THz for system 2. Subsequently, the geometry was modified by the removal of selected metallic wires to obtain an L-shaped waveguide in the structure (see Figs. 3 and 7). The ultimate goal of said geometry alteration was to demonstrate a waveguide at high and low frequencies in the THz regime (see Figs. 4 and 8). Subsequently, in order to understand the contribution of the length in the proposed geometry we created a 3D geometry by using COMSOL's EM 3D module that comprised an array of silver wires embedded in silicon and of radius of 1 μm (see Fig. 10). The center to center distance between wires in the z direction is 4 μm and the distance in the y direction was modeled with values of 4, 8, 12, and 20 μm , respectively. In terms of the length (in the x direction) the values considered included 20, 40, and 100 μm . The relevant axis directions are indicated in the same Fig. 10.

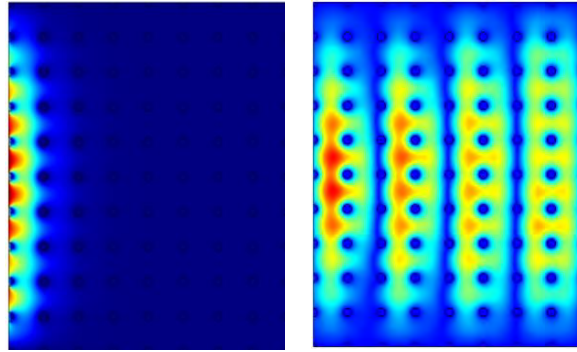


Fig. 1: Electric field propagation at 250 THz (left) and 350 THz (right). The center-to-center distance of the wires is 400 nm and their radii is 50 nm.

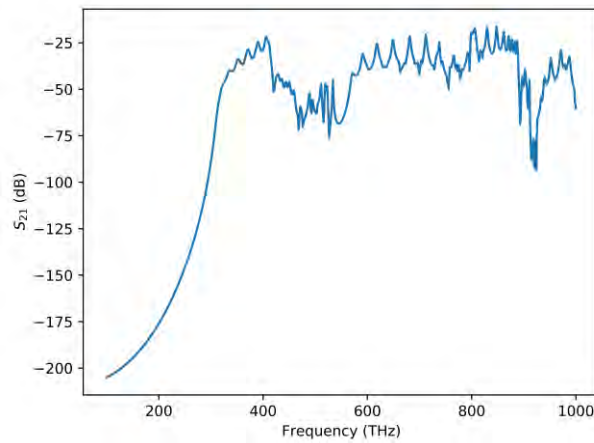


Fig. 2: Transmission spectra for the structure in Fig. 1.

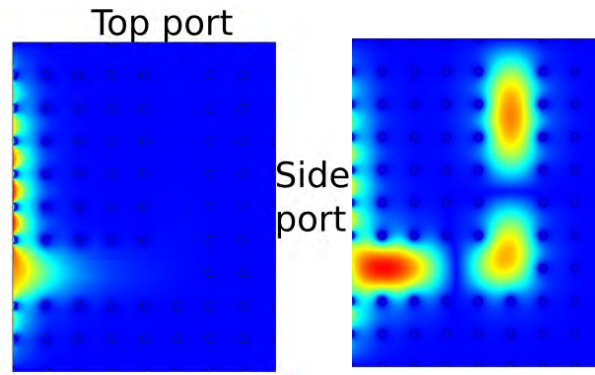


Fig. 3: Electric field propagation at 150 THz (left) and 200 THz (right). The center-to-center distance of the wires is 400 nm and their radii is 50 nm.

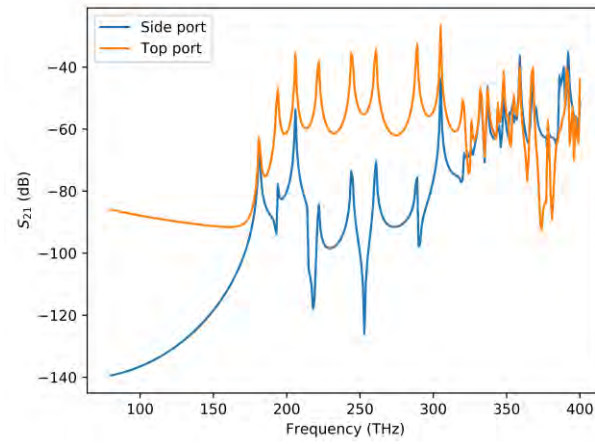


Fig. 4: Transmission plot for the waveguide in Fig. 3. The orange line represents the reading of the top port and the blue line represents the transmission plot for the side port.

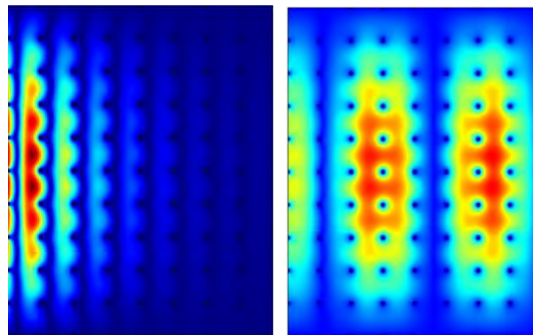


Fig. 5: Electric field propagation at 1.75 THz (left) and 1 THz (right). The center-to-center distance of the wires is 100 μm and their radii is 5 μm .

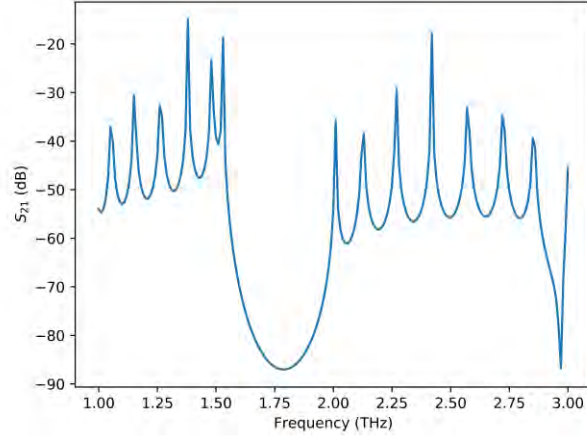


Fig. 6: Transmission spectra for the structure in Fig. 5. The bandgap at 1.75 THz is consistent with the electric field propagation shown in Fig. 5, left.

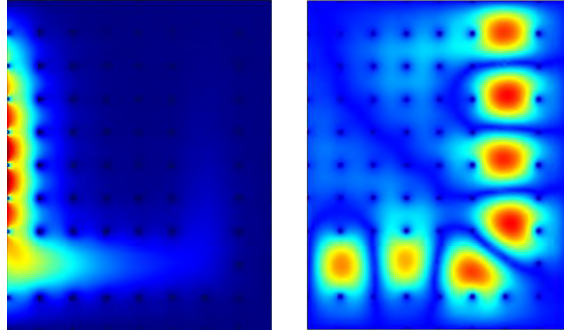


Fig. 7: Electric field propagation at 0.6 THz (left) and 1 THz (right). The center-to-center distance of the wires is $100\text{ }\mu\text{m}$ and their radii is $5\text{ }\mu\text{m}$.

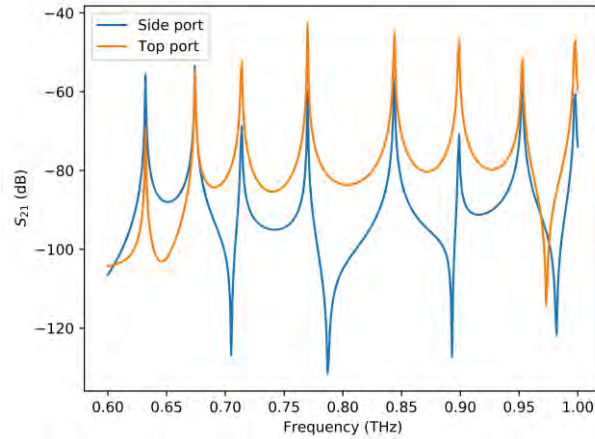


Fig. 8: Transmission plot for the waveguide in Fig. 7. The orange line represents the reading of the upper port and the blue line represents the transmission plot for the side port, as defined in Fig. 3.

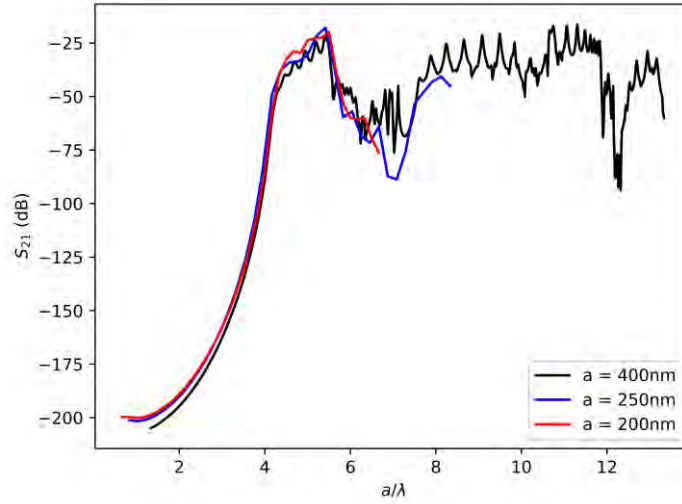


Fig. 9: Comparison between 3 different structures with the same a/r ratio. This highlights the critical frequency's dependence on the geometrical parameters

3. Discussions and Results

Fig. 1 shows the geometry of the 2D silver pillar array with the selected values of $a = 400$ nm and $r = 50$ nm (a/r ratio of 8). These values were chosen to ensure operation in the high (100 – 1,000) THz regime. The simulation was performed using the parameters described above. Our results are shown in Fig. 1, which is a plot of the electric field (E-field) normal to the surface in which red represents a higher E-field intensity, and blue the opposite. The results portrayed in Fig. 1, left (right) show the E-field propagation at 250 (350) THz. Fig. 2 shows the transmission spectra for this structure, which are consistent with the propagation results in Fig. 1. In order to demonstrate the waveguide effect, several pillars were removed from the original geometry (see Fig. 3). Two different ports were defined in this structure, as shown in Fig. 3, left, in order to calculate the transmission spectra for both boundaries separately. Fig. 4 shows the transmission spectra for Fig. 3. The optimal range of operation can be seen to be around 200 – 300 THz, which is the frequency range where the propagation at the side port is minimal and the propagation at the top port is maximal, neglecting the frequency range of 100 – 200 THz, in which no propagation is seen. In order to study the effect of scaling-up in frequency, we constructed two additional systems with the same a/r ratio, but with values chosen to operate at higher frequencies. This is shown in Fig. 9, with the transmission spectra plotted against scaled coordinates (a/λ), where λ is the wavelength of the incoming wave. The transmission spectra plotted against frequency is shown in Fig. S1. Note that the spectra for $a = 400$ nm is the same as shown in Fig. 6.

Additionally, the size and separation of the rods were also varied in order to ensure operation in the low THz regime. In this case the selected values were $r = 5$ μ m and $a = 100$ μ m (a/r ratio of 20) as shown in Fig. 5. The transmission spectra for this structure is shown in Fig. 6, which shows a gap at 1.75 THz. This gap is also shown in Fig. 5, left. This gap is consistent with the Bragg condition, since $\lambda/2$ is on the order of the lattice constant $a = 100$ μ m. An L-shaped waveguide was also made with the latter sizes, and wave propagation was also observed in the low THz regime (see Figs. 7 and 8).

Once we obtained promising results with the 2D models, we turned our attention to fully 3D systems. A 3D wire array embedded in silicon was modeled, and the radii and wire separation adjusted seeking

transmission in the 1 to 3 THz range. These dimensions were also guided by experimental fabrication considerations. To this end, we considered an array of silver wires immersed in silicon and of radius of $1\ \mu\text{m}$. We selected Si due to its mass production compatibility and low-loss properties. The distance between wires in the z direction was of $4\ \mu\text{m}$, the distance in the y direction was changed between $4\ \mu\text{m}$, $8\ \mu\text{m}$, $12\ \mu\text{m}$, and $20\ \mu\text{m}$. The length (in the x direction) was also changed between $20\ \mu\text{m}$, $40\ \mu\text{m}$ and $100\ \mu\text{m}$. Fig. 10 shows the geometry under study, and indicates the different directions (x, y, z) mentioned previously. Our results indicate that the frequency of operation is inversely proportional to the wire length (see Fig. 11). The size and density of our structures support multiple local resonances, generally leading to broadband transmission. In addition, our computed critical frequencies are in good agreement with the estimates based on Eq. 2. These observations constitute practical guidance for the experimental phase. Experimental verification of the computed results will be presented in a future article.

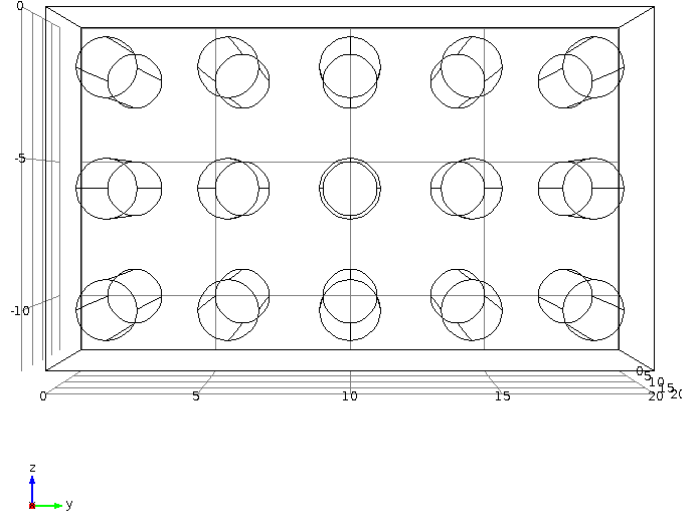


Fig 10: Geometry of 3D silver rods array in a silicon substrate. The distance in the z direction (vertical) was fixed to $4\ \mu\text{m}$, the distance in the y direction (horizontal) was varied between $4\ \mu\text{m}$, $8\ \mu\text{m}$, $12\ \mu\text{m}$ and $20\ \mu\text{m}$, and the length (x direction, into the page) was varied $20\ \mu\text{m}$, $40\ \mu\text{m}$ and $100\ \mu\text{m}$.

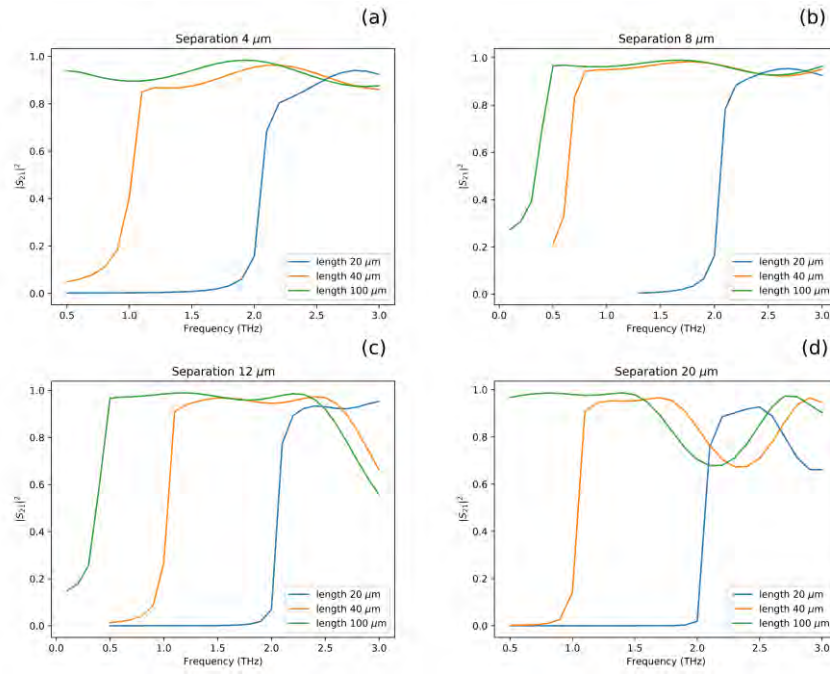


Fig 11: This figure shows transmission plots that illustrate the effect of changing the values in the x direction (length of the rods). Each plot shows constant separation values in the y and z direction. The length of the rods was varied with values of 20 μm , 40 μm and 100 μm .

4. Conclusions

The computer simulations reveal that metallic arrays can support electromagnetic transmission at THz frequencies. By modifying the wire diameter as well as the separation between the wires it is possible to determine the operational frequency of the array. Transmission is therefore predicted between 1 THz to 3 THz for a geometry defined by $r = 5 \mu\text{m}$ and $a = 100 \mu\text{m}$ (a/r ratio of 20) and between 300 THz to 1,000 THz for a geometry of $r = 50 \text{ nm}$ and $a = 400 \text{ nm}$ (a/r ratio of 8). Furthermore, we also anticipate the possibility of using a wire array as a waveguide by modifying its topographical distribution. Finally, we have modeled the high-pass filtering effects of 3D metallic arrays embedded in a silicon substrate and anticipate that the cutoff frequency can be tailored by selecting the length of the wires involved. An effort is presently underway to fabricate the modeled structures and validate the simulated results with experimental observations.

Acknowledgements.

This work was co-funded by the Army Research Office (ARO) and the Air Force Office of Scientific Research (AFOSR) Grant W911NF-15-1-0297

Supplementary information

Plots showing transmission spectra for two additional 2D systems tailored to operate at different frequencies, power flow along the output ports, and an additional 3D structure are included in the Supplementary Information.

References

1. G. Oliveri, D. H. Werner, A. Massa, Reconfigurable Electromagnetics Through Metamaterials -- A Review. *Proceedings of the IEEE* **103**, 1034-1056 (2015).
2. H. Tao, W. J. Padilla, X. Zhang, R. D. Averitt, Recent Progress in Electromagnetic Metamaterial Devices for Terahertz Applications. *IEEE Journal of Selected Topics in Quantum Electronics* **17**, 92-101 (2011).
3. J. B. Pendry, A. J. Holden, D. J. Robbins, W. J. Stewart, Magnetism from conductors and enhanced nonlinear phenomena. *Ieee Transactions on Microwave Theory and Techniques* **47**, 2075-2084 (1999).
4. J. B. Pendry, A. J. Holden, W. J. Stewart, I. I. Youngs, Extremely low frequency plasmons in metallic mesostructures. *Phys Rev Lett* **76**, 4773-4776 (1996).
5. J. B. Pendry, A. J. Holden, D. J. Robbins, W. J. Stewart, Low frequency plasmons in thin-wire structures. *Journal of Physics-Condensed Matter* **10**, 4785-4809 (1998).
6. M. Diem, T. Koschny, C. M. Soukoulis, Wide-angle perfect absorber/thermal emitter in the terahertz regime. *Physical Review B* **79**, 4 (2009).
7. W. Withayachumnankul, D. Abbott, Metamaterials in the Terahertz Regime. *IEEE Photonics Journal* **1**, 99-118 (2009).
8. J. B. Pendry, A. J. Holden, W. J. Stewart, I. Youngs, Extremely low frequency plasmons in metallic mesostructures. *Physical Review Letters* **76**, 4773-4776 (1996).
9. <https://www.comsol.com/>.
10. H. Butt, Q. Dai, T. D. Wilkinson, G. A. J. Amaratunga, PHOTONIC CRYSTALS & METAMATERIAL FILTERS BASED ON 2D ARRAYS OF SILICON NANOPILLARS. *Progress in Electromagnetics Research-Pier* **113**, 179-194 (2011).
11. H. J. Hagemann, W. Gudat, C. Kunz, Optical constants from the far infrared to the x-ray region: Mg, Al, Cu, Ag, Au, Bi, C, and Al₂O₃. *J. Opt. Soc. Am.* **65**, 742-744 (1975).

interferometers, metamaterials and reflectors. In this work we report the computational modeling of transmission of electromagnetic waves through a silver (Ag) nanowire array. The geometrical parameters such as the lattice constant and radius enable us to demonstrate propagation at THz frequencies. Also, by creating a 90° defect in the geometry, we demonstrate the ability of the structure to behave as a waveguide at those frequencies. The sizes of the structures are in the micro and nanometers ranges in order to propagate 4 THz and 100 THz to 400 THz, respectively. The study was performed using the RF module of the finite element analysis based software, COMSOL Multiphysics.

Introduction

- Metamaterials are made of arrays of elements from composite materials such as metals or plastics
- Highly dense periodic arrays of metal nanowires can be used to produce metamaterials
- These arrays can be engineered to exhibit certain values of permittivity and permeability
- They possess mutual plasmonic coupling effects
- They have lower plasma frequency than a comparable bulk metal
- They exhibit filtering response at different frequencies
- THz frequencies have been historically underexplored, since conventional materials have weak electromagnetic responses at these frequencies
- Common materials do not exhibit strong electromagnetic response between 1 THz to 3 THz
- THz metamaterial devices are expected to have novel applications in medicine, astronomy, security, communications, and biochemistry

Methodology

- Finite element analysis program COMSOL Multiphysics
- Radio frequency (RF) module was used to study the electromagnetic
- The geometry is a 2D array of silver rods in vacuum of lattice constant 50nm
- Experimental values of permittivity were used and interpolation function was used for different optical parameters
- COMSOL EM Waves sub-module was used in the top and bottom of the structure
- Two ports were used in the long sides of the rectangular structures to inject the wave from one side of the structure and receive it in the other side
- The wave was set as a rectangular transverse electric (TE) wave
- The frequency was also varied from 100 THz to 400 THz in steps of 10 THz
- The frequency was also varied from 1 THz to 4 THz in steps of 0.1 THz
- Defects in the structure were created to demonstrate waveguide effects

Results

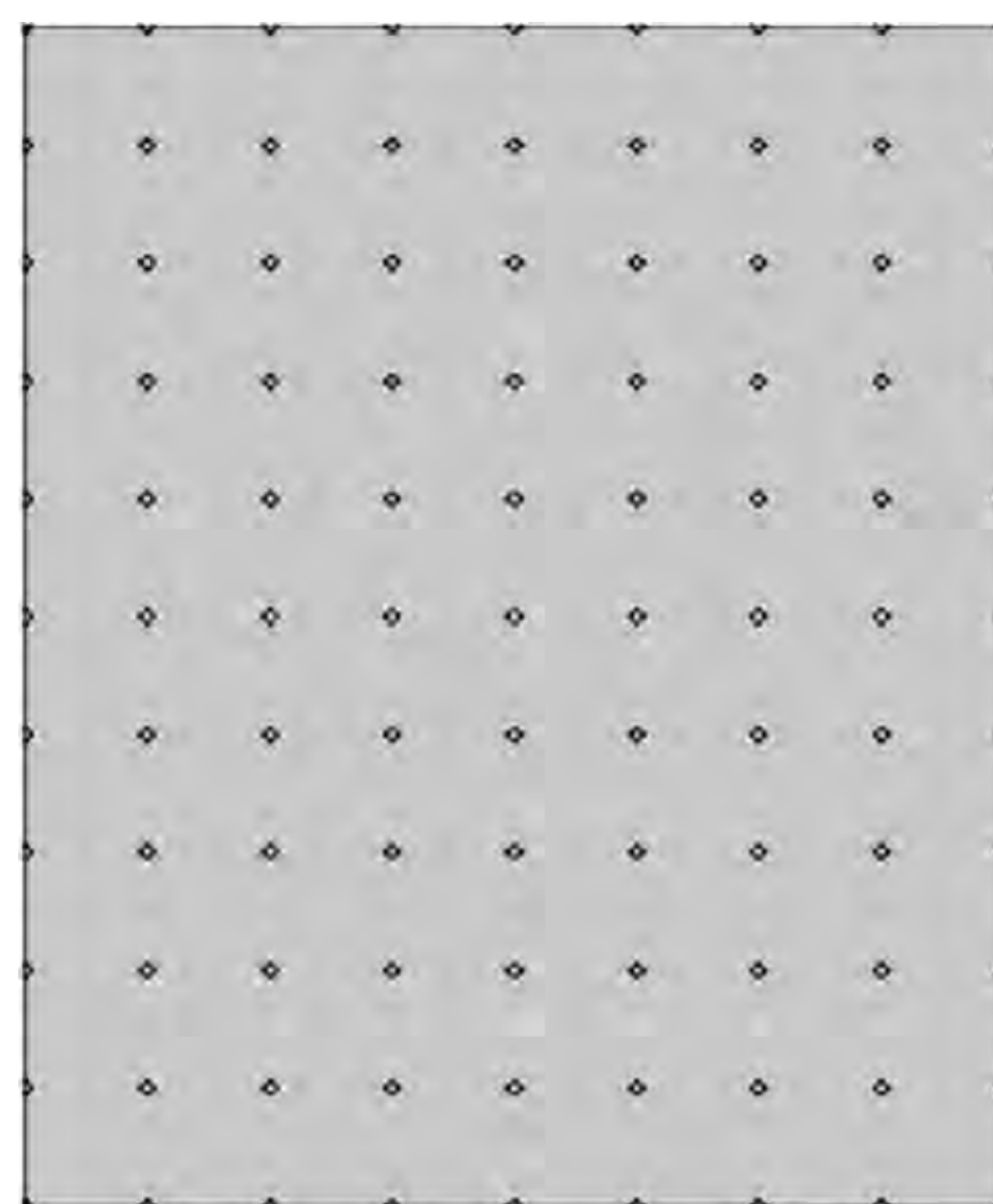


Fig 1. Geometry of a 2D array of silver pillars with $a=100\mu\text{m}$ and $r=5\mu\text{m}$

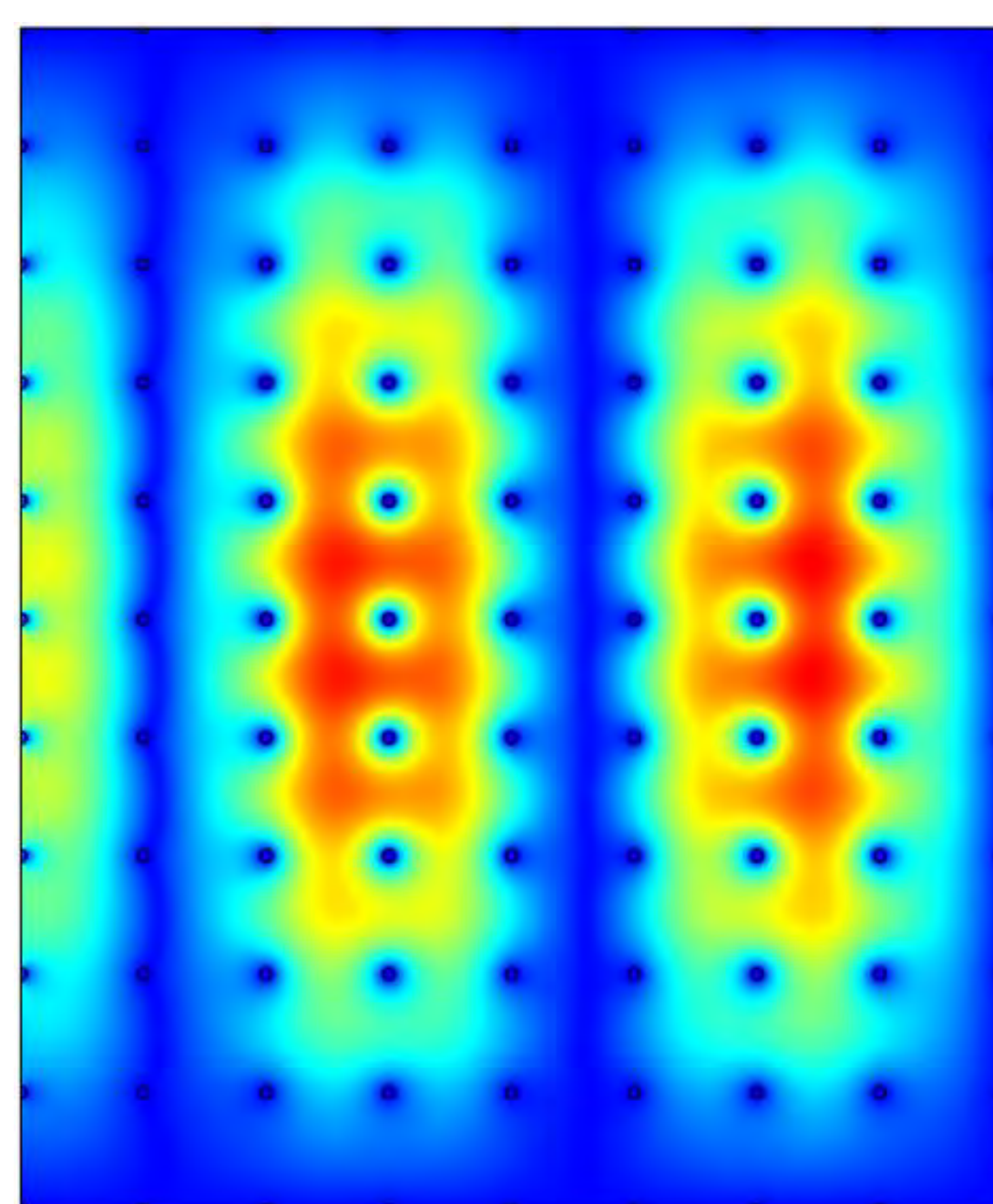


Fig 2. Electric field propagation at 1 THz

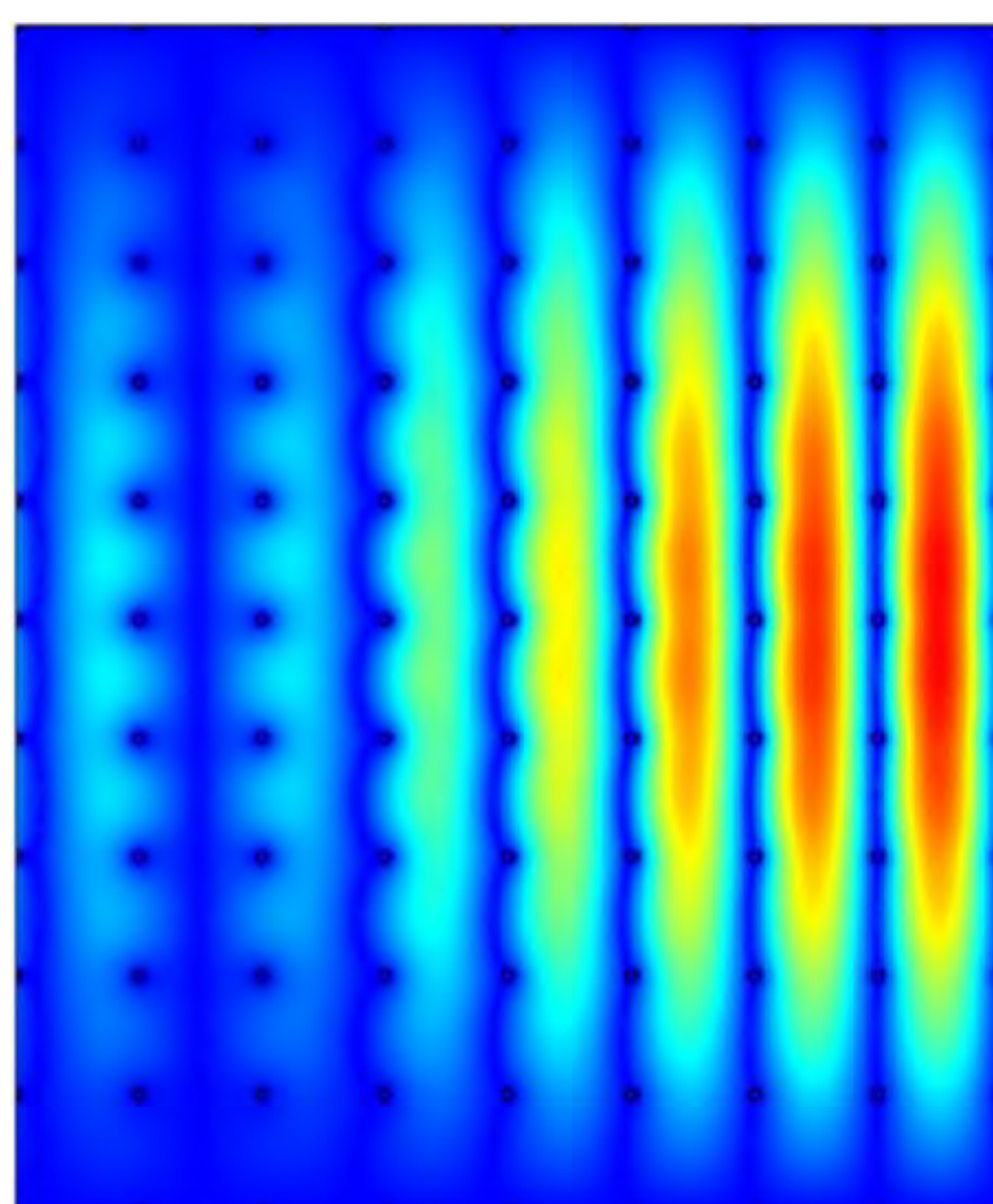


Fig 3. Electric field propagation at 1.5 THz

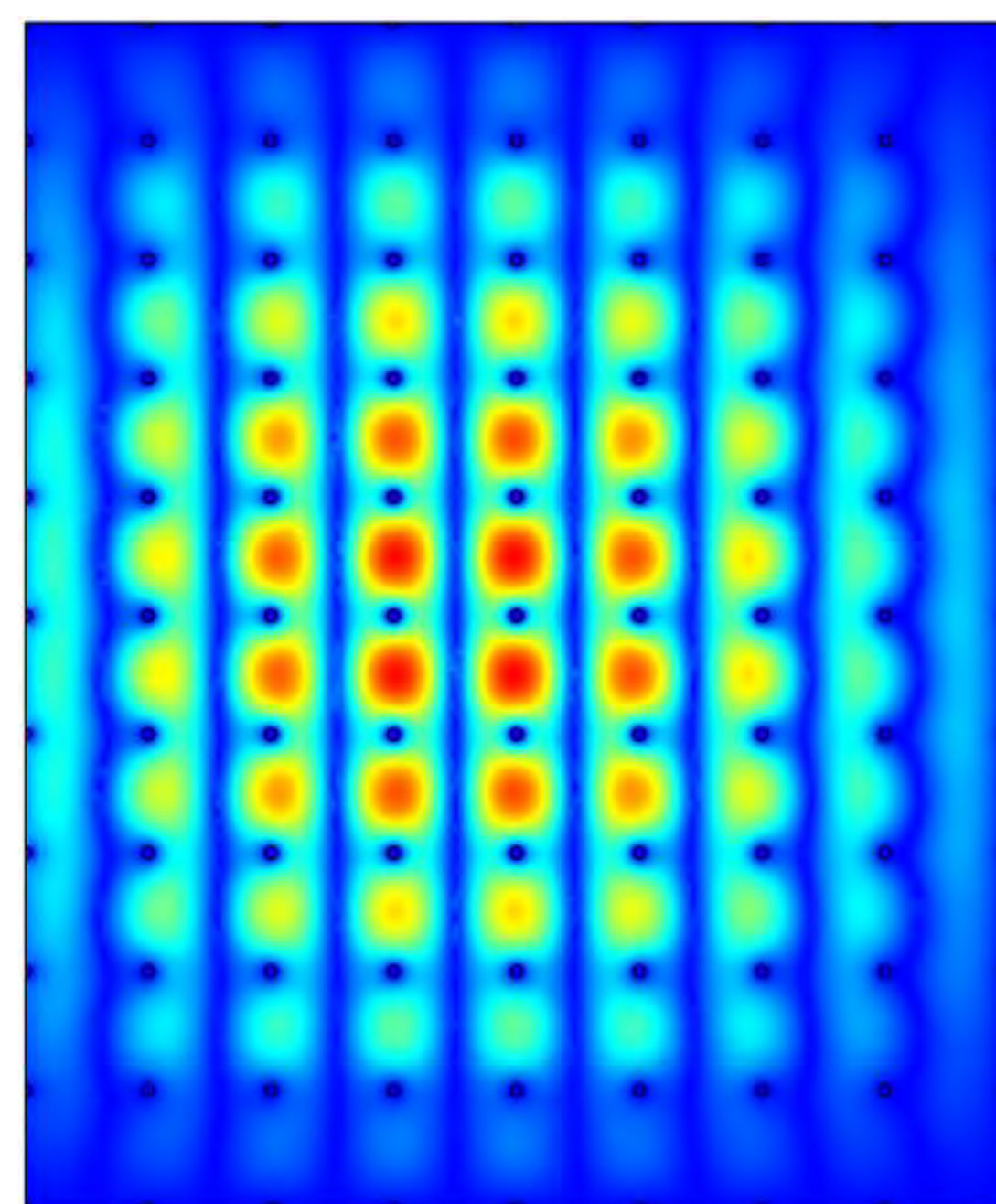


Fig 3. Electric field propagation at 2 THz

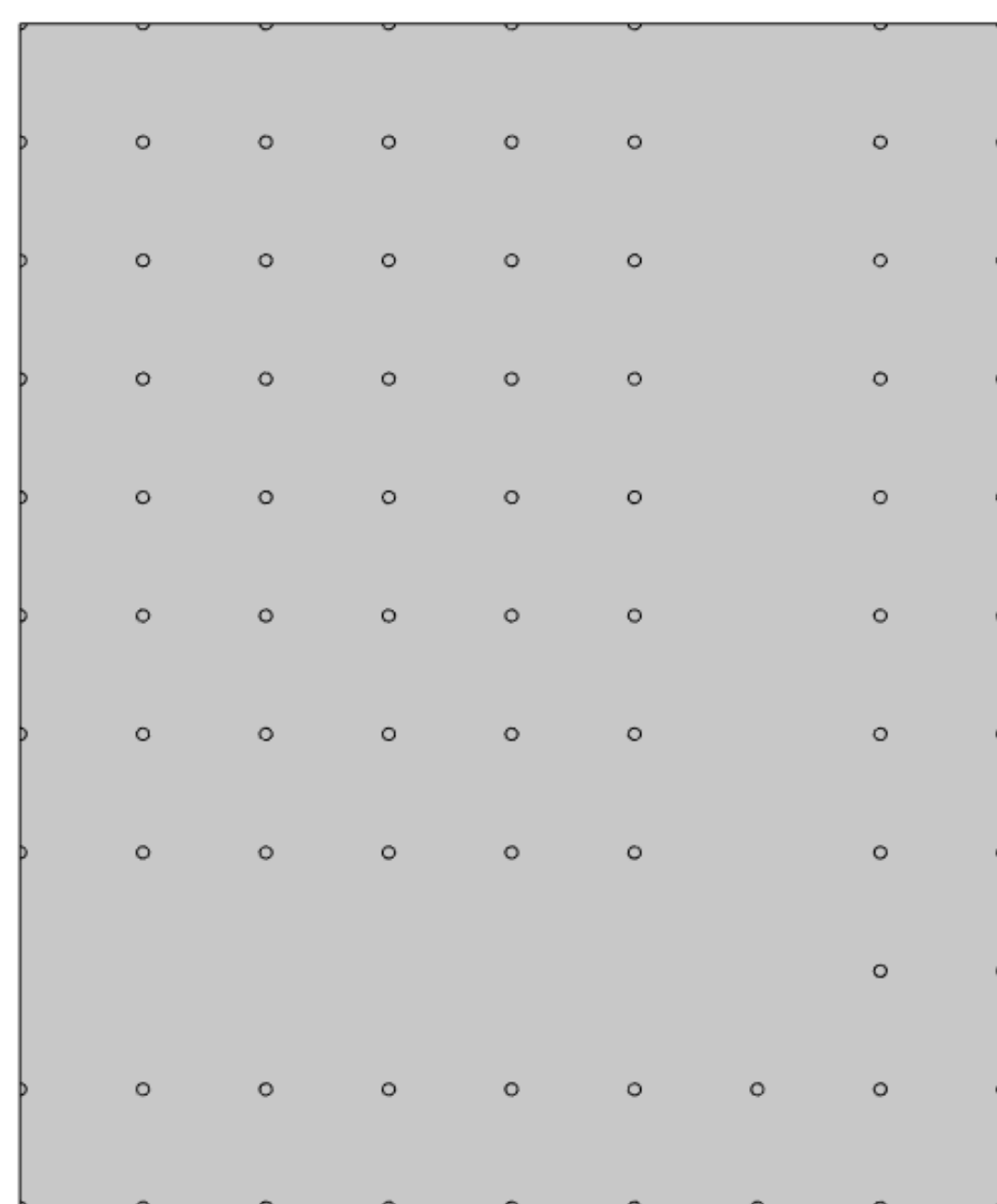


Fig 5. Geometry of 90 degree defect of a 2D array of silver pillars with $a=100\mu\text{m}$ and $r=5\mu\text{m}$

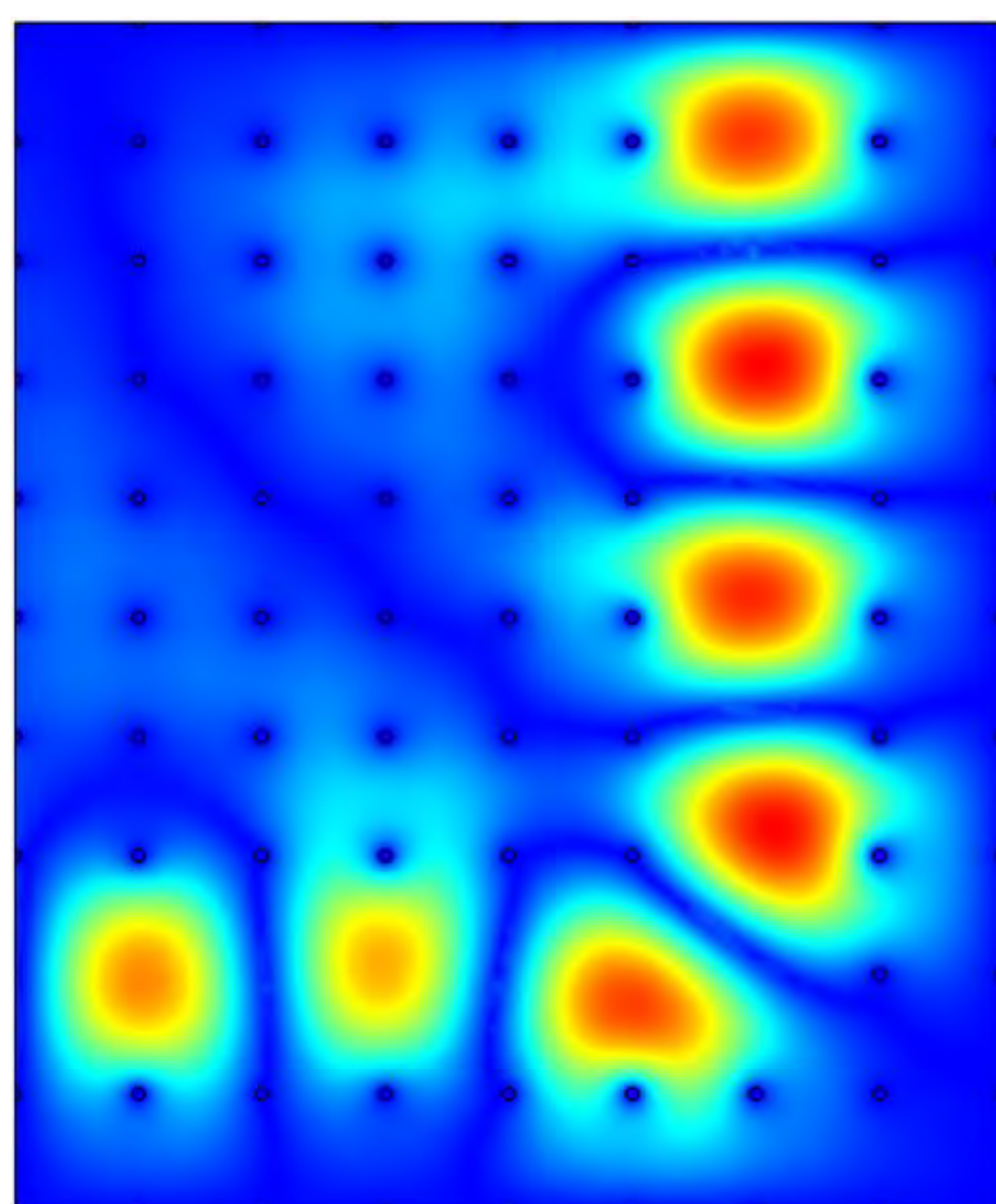


Fig 6. Waveguide electric field propagation at 1 THz

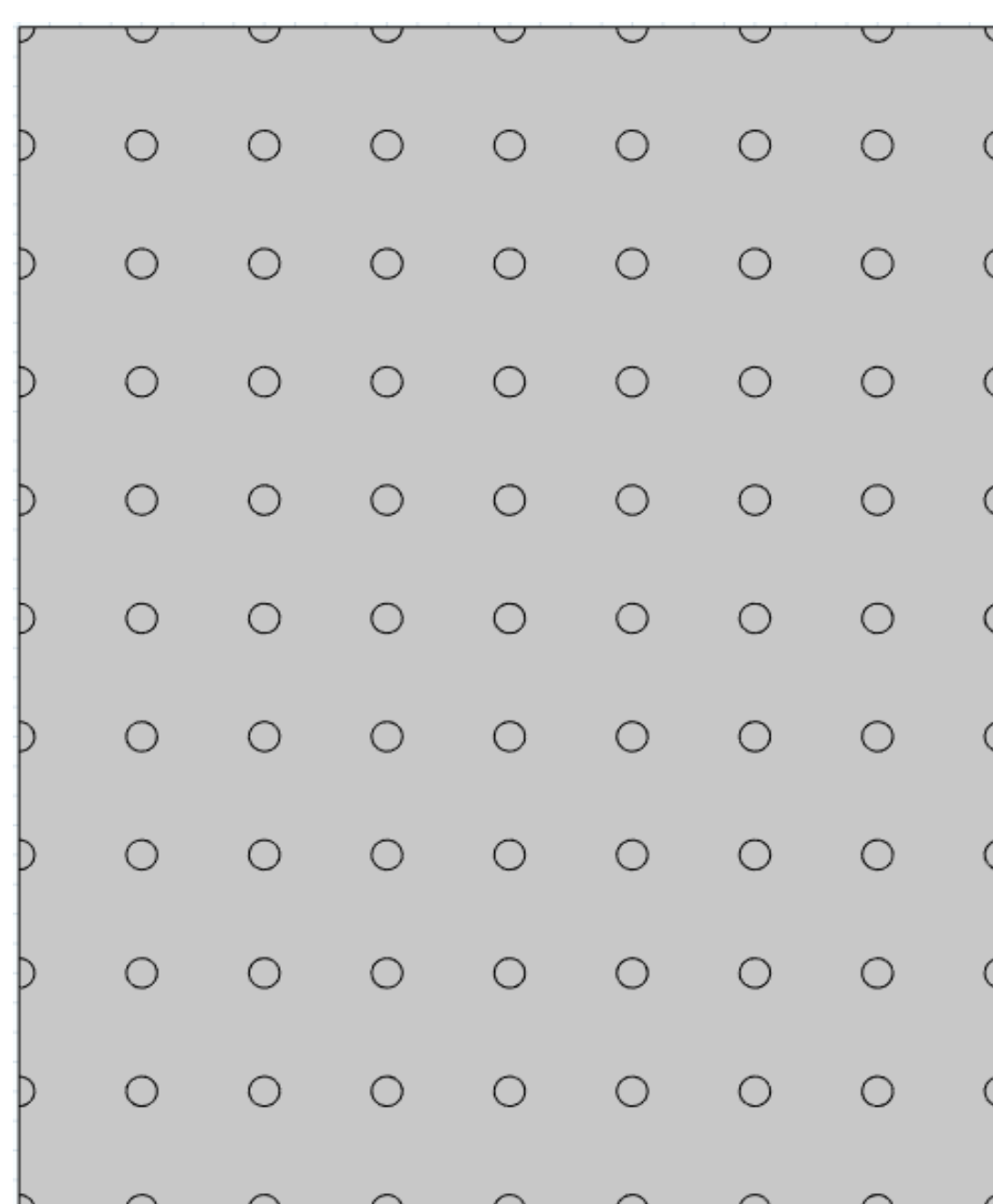


Fig 7. Geometry of a 2D array of silver pillars with $a=400\text{nm}$ and $r=50\text{nm}$

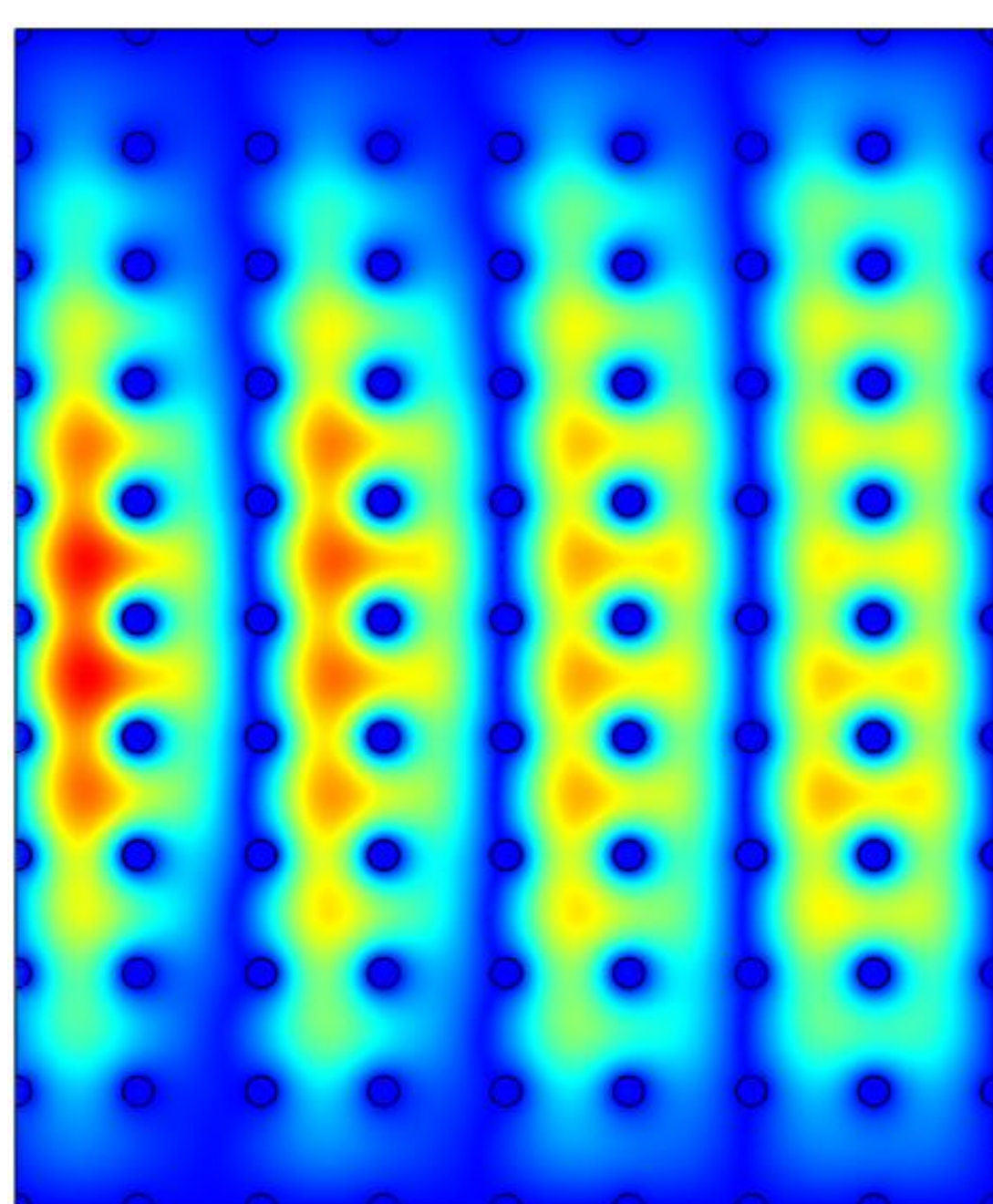


Fig 8. Electric field propagation at 350 THz

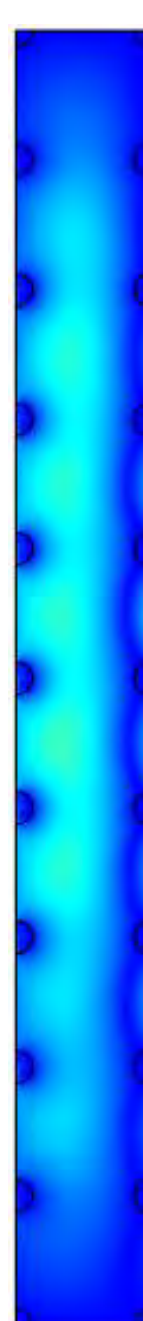


Fig 9. Electric field propagation at 350 THz

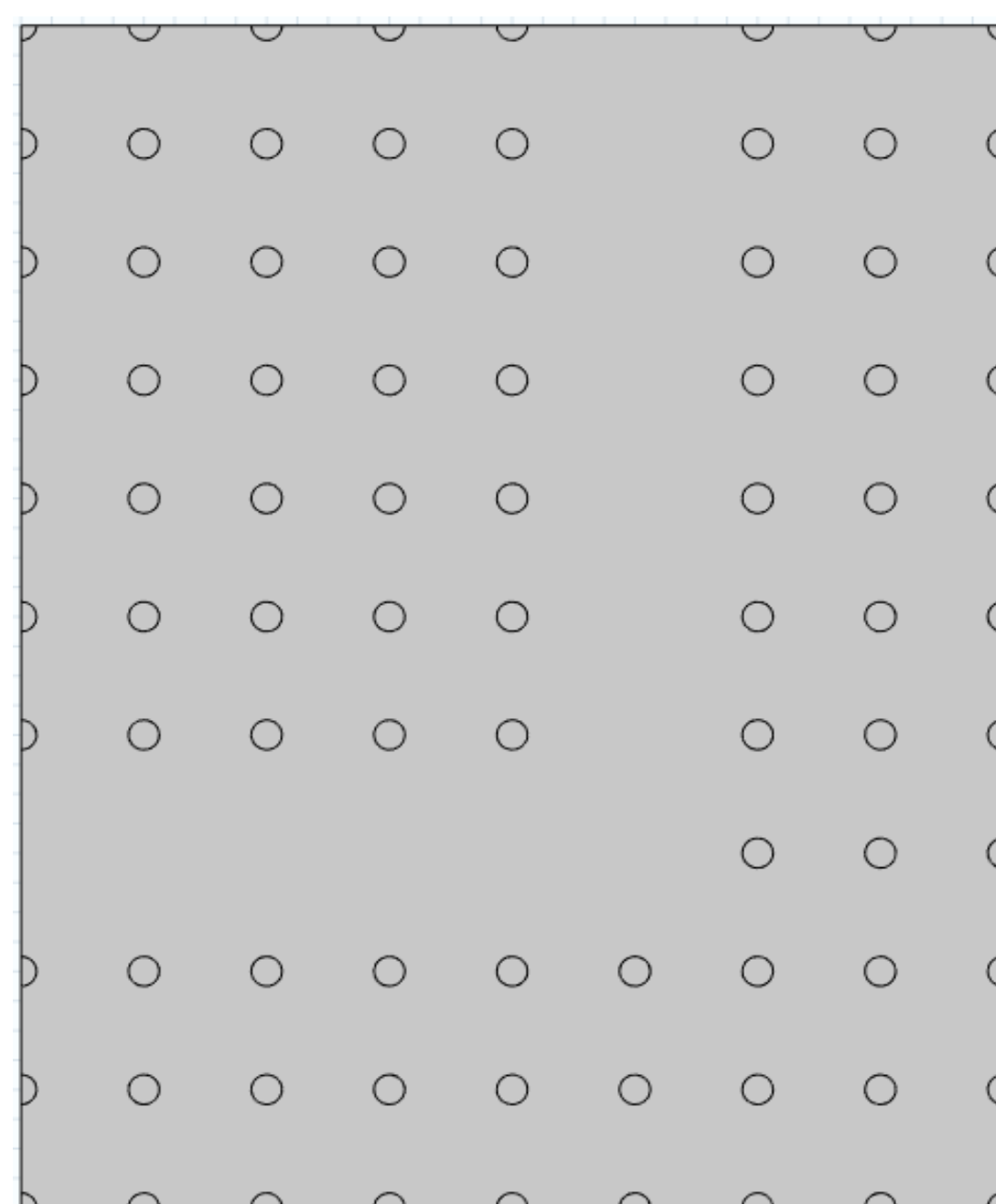


Fig 10. Geometry of 90 degree defect of a 2D array of silver pillars with $a=400\text{nm}$ and $r=50\text{nm}$

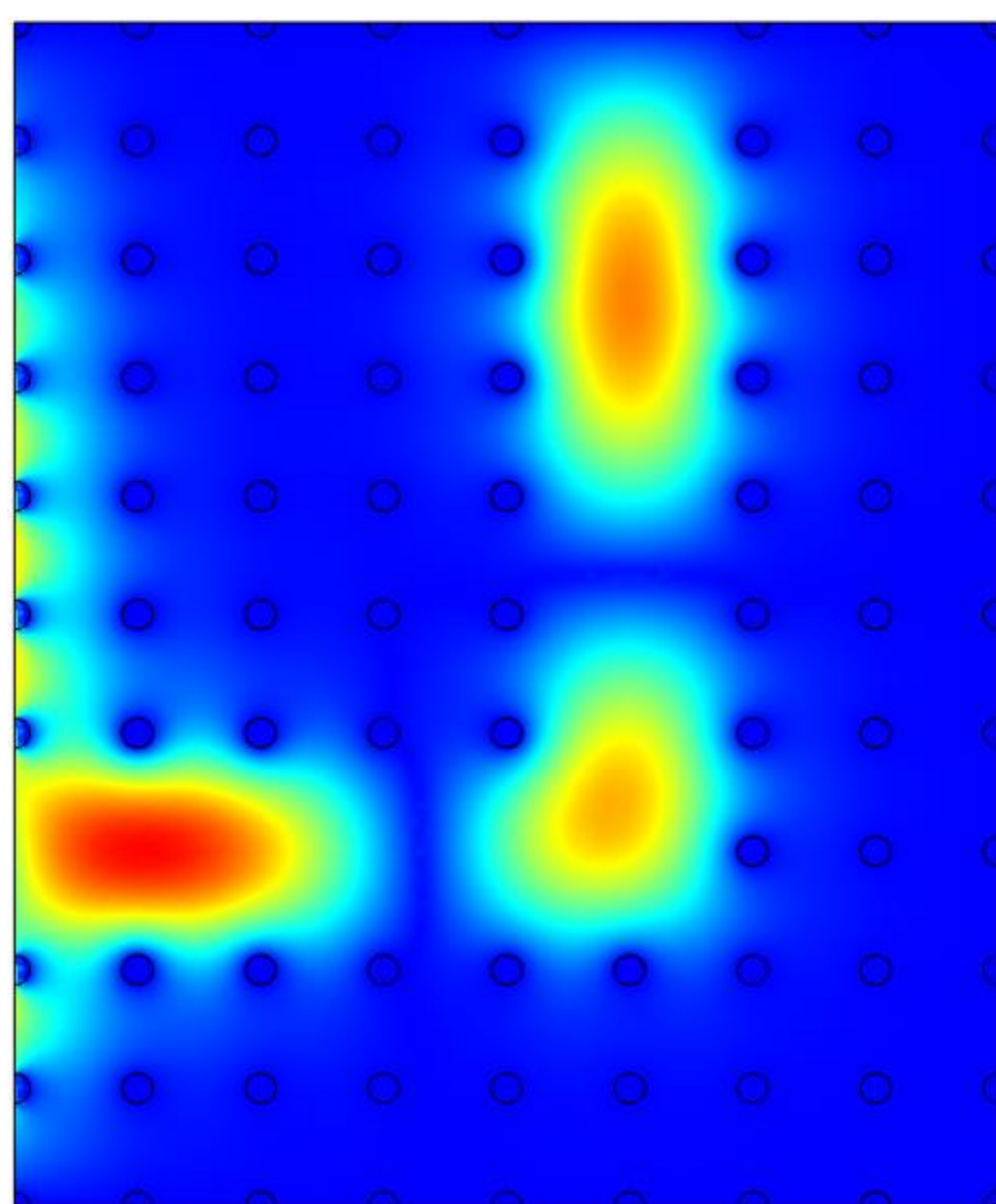


Fig 11. Waveguide electric field propagation at 200 THz

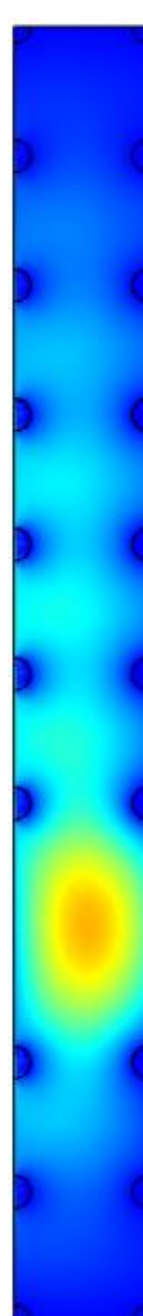


Fig 12. Waveguide electric field propagation at 300 THz

Conclusions

- Our simulation demonstrates that we can have electromagnetic transmission at THz frequencies through metallic arrays
- We were able to demonstrate transmission between 1 THz to 4 THz
- We also demonstrated transmission between 100 THz to 400 THz
- Transmission was confirmed and waveguide effect was demonstrated by making defects in the simulation geometry
- It was also demonstrated that we can change its operational frequency by changing its geometry size and distance

References

1. Butt, H., et al., *PHOTONIC CRYSTALS & METAMATERIAL FILTERS BASED ON SILICON NANOPILLARS*. Progress in Electromagnetics Research-Pier
2. W. Withayachumnankul, and D. Abbott, "Metamaterials in the Tera-*Photonics Journal*, vol. 1, no. 2, pp. 99-118, 2009.

Acknowledgements

This work was co-funded by the Army Research Office (ARO) and the Air Force Office of Sponsored Research (AFOSR) Grant W911NF-15-1-0297

Metamaterials are artificial materials engineered to exhibit certain properties not existing in nature. These artificial materials are made of arrays of elements from composites such as metals or plastic. In this work we are interested in the study of 2D metal arrays because there is a special interest on the behavior of these 2D arrays at terahertz frequencies and the function of geometrical parameters. It is anticipated that this type of structure will enable us to demonstrate novel THz lenses, filters, beam splitters, resonators, hyperlenses, sensors, Fabry–Perot interferometers, metamaterials and reflectors. In this work we report the computational modeling of transmission of electromagnetic waves through a silver (Ag) nanowire array. Changing the geometrical parameters such as the lattice constant and radius enable us to demonstrate propagation at THz frequencies. In the case of a defect in the geometry we were also able to demonstrate the ability of the structure to behave as a waveguide at those frequencies. The sizes of the structures are in the nanometers range in order to propagate frequencies of 1 THz to 4 THz and 100 THz to 400 THz, respectively. The study was performed using the RF module of the COMSOL Multiphysics software.

Introduction

- Metamaterials are made of arrays of elements from composite materials such as metals or plastics
- Highly dense periodic arrays of metal nanowires can be used to produce metamaterials
- These arrays can be engineered to exhibit certain values of permittivity and permeability
- They possess mutual plasmonic coupling effects
- They have lower plasma frequency than a comparable bulk metal
- They exhibit filtering response at different frequencies
- THz frequencies have been historically underexplored, since conventional materials have weak electromagnetic responses at these frequencies
- Common materials do not exhibit strong electromagnetic response between 1 THz to 3 THz
- THz metamaterial devices are expected to have novel applications in medicine, astronomy, security, communications, and biochemistry

Methodology

- Finite element analysis program COMSOL Multiphysics
- Radio frequency (RF) module was used to study the electromagnetic response
- The geometry is a 2D array of silver rods in vacuum of lattice constant of 50nm
- Experimental values of permittivity were used and interpolation function was used for different optical parameters
- COMSOL EM Waves sub-module was used in the top and bottom of the structure
- Two ports were used in the long sides of the rectangular structures in order to send the wave from one side of the structure and receive it in the other side
- The wave was set as a rectangular transverse electric (TE) wave
- The frequency was also varied from 100 THz to 400 THz in steps of 10 THz
- The frequency was also varied from 1 THz to 4 THz in steps of 0.1 THz
- Defects in the structure were created to demonstrate waveguide effect at different frequencies

Results

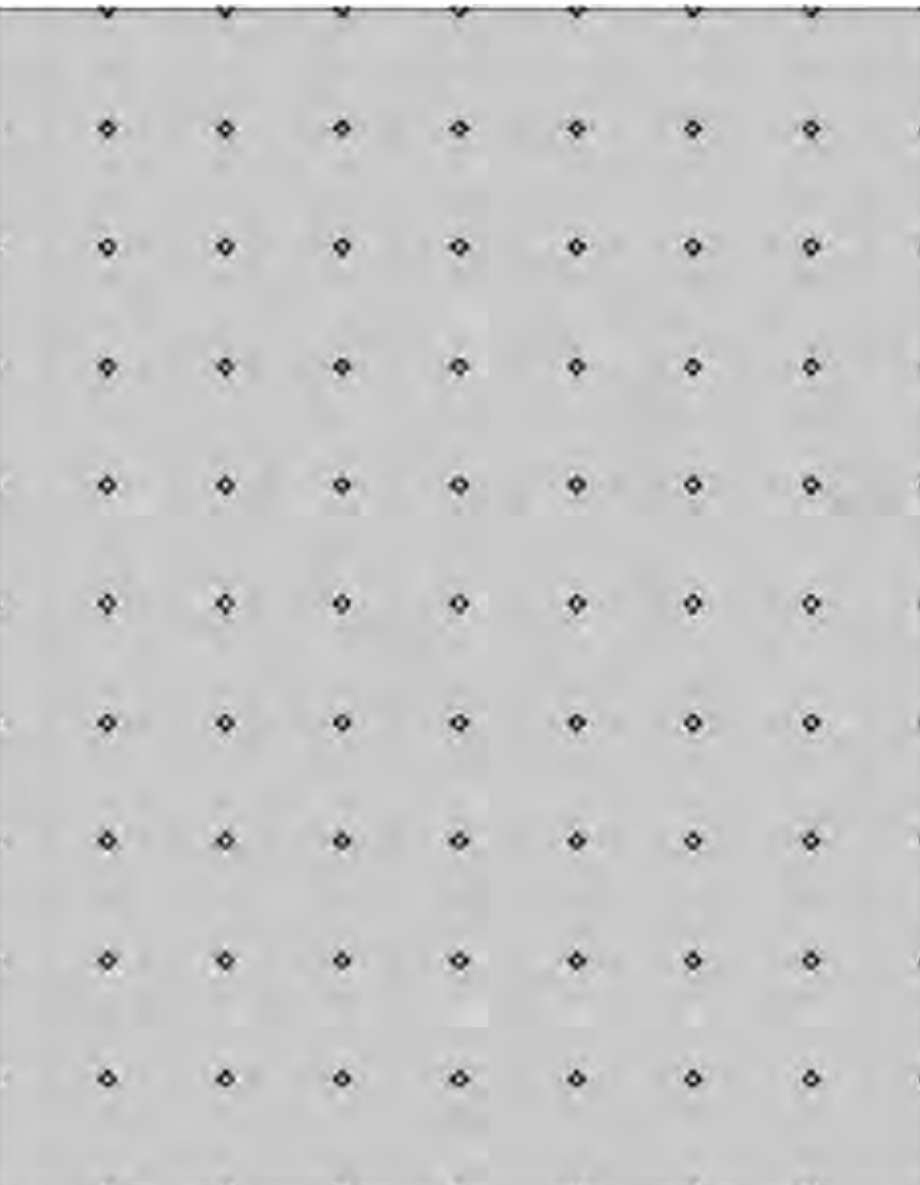


Fig 1. Geometry of a 2D array of silver pillars with a=100µm and r = 5µm

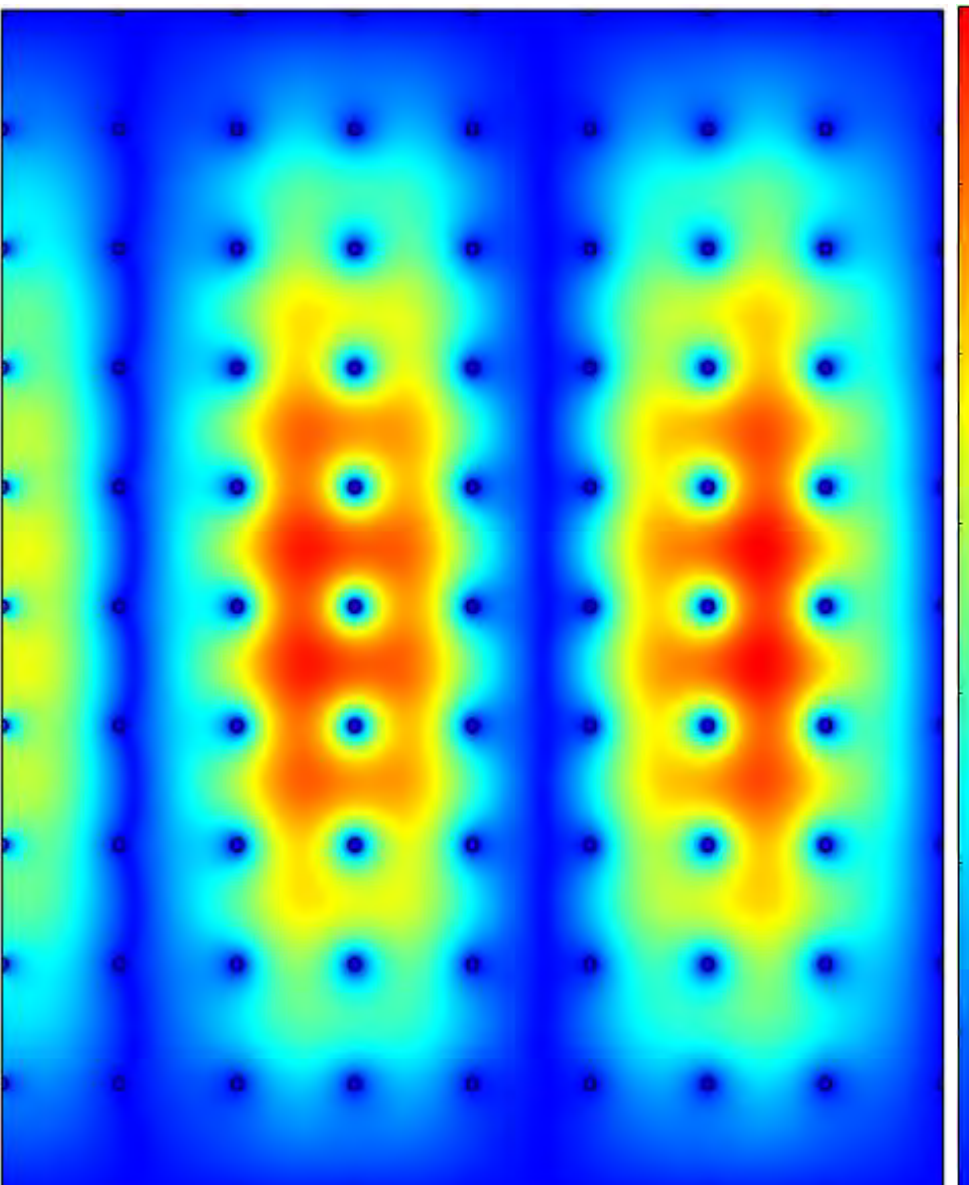


Fig 2. Electric field propagation at 1 THz

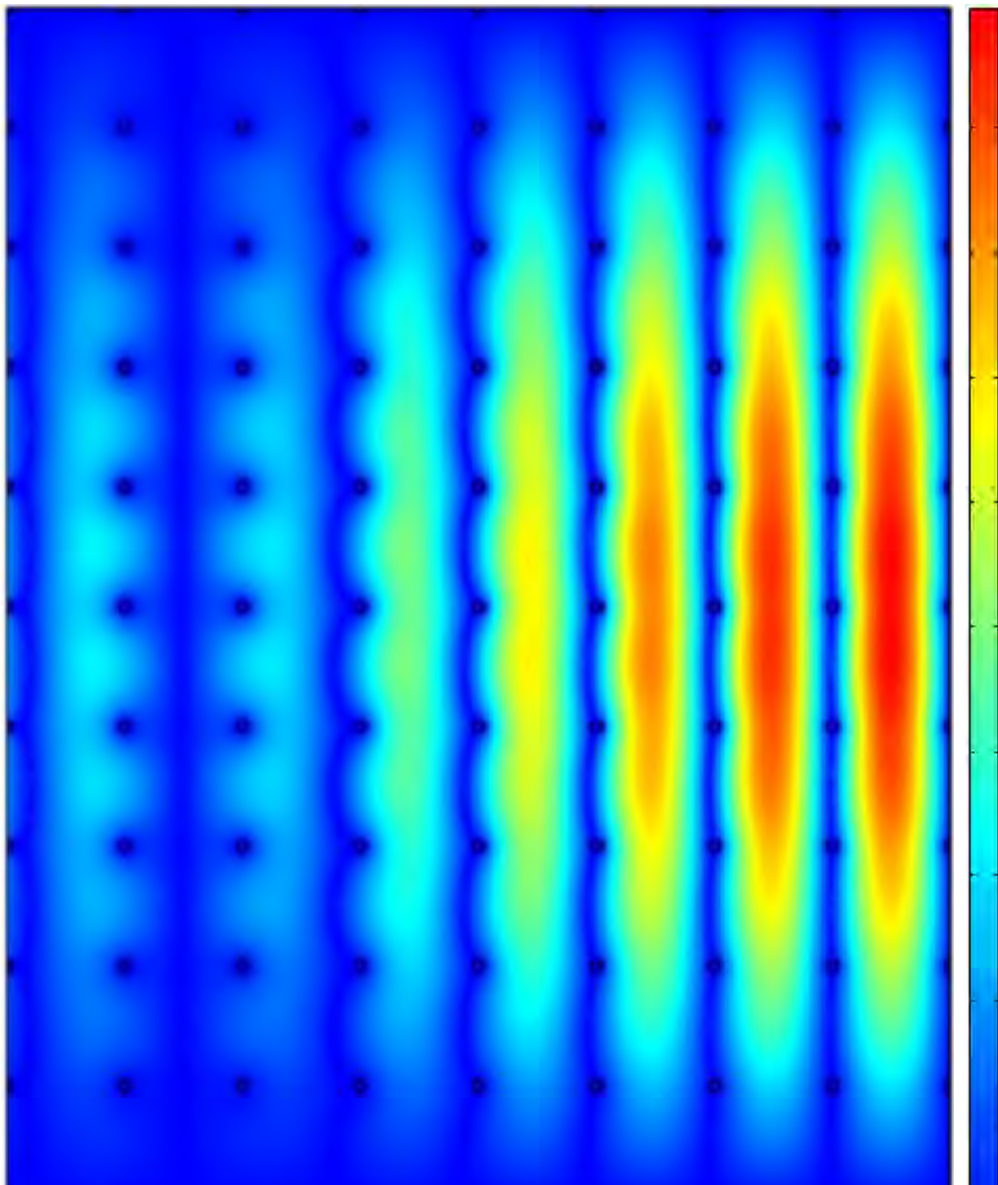


Fig 3. Electric field propagation at 1.5 THz

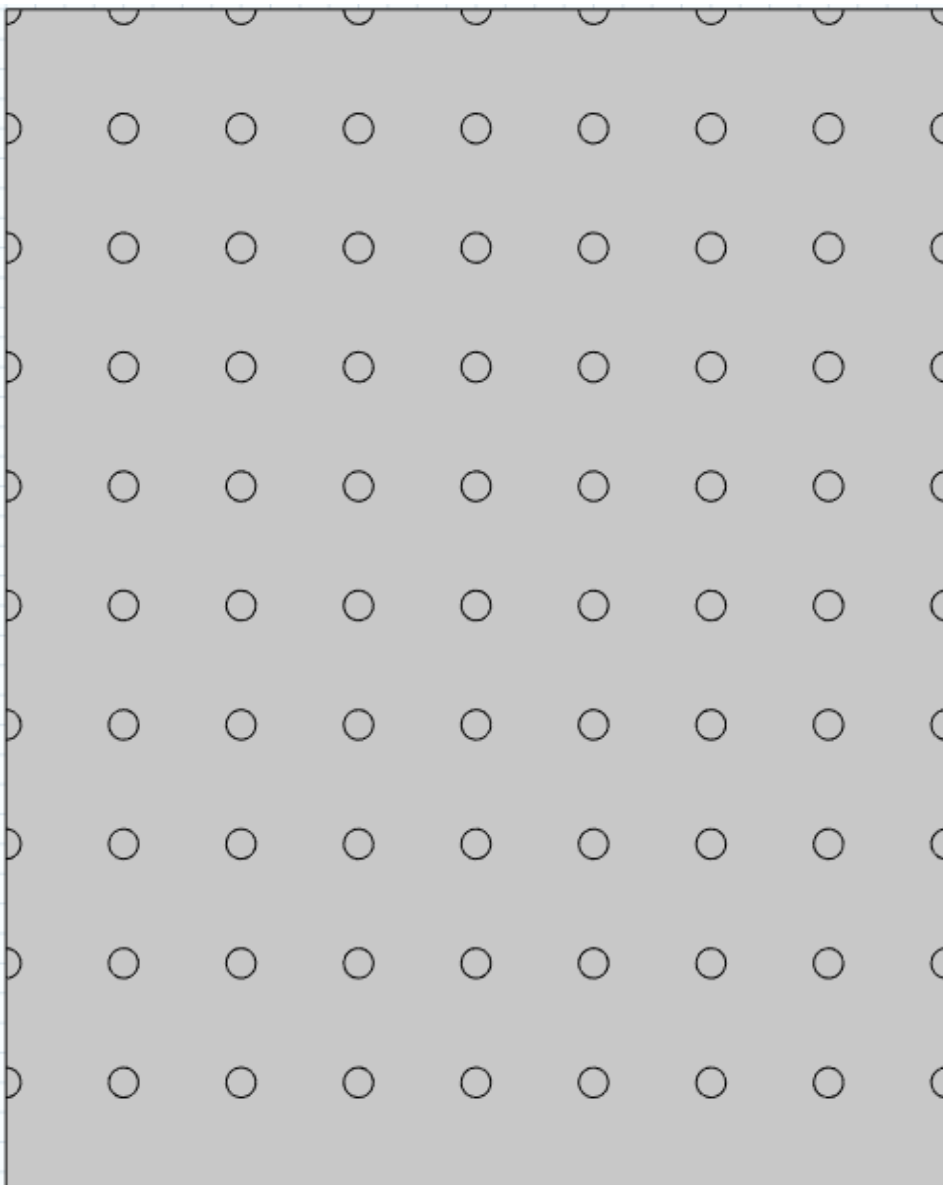


Fig 7. Geometry of a 2D array of silver pillars with a=400nm and r = 50nm

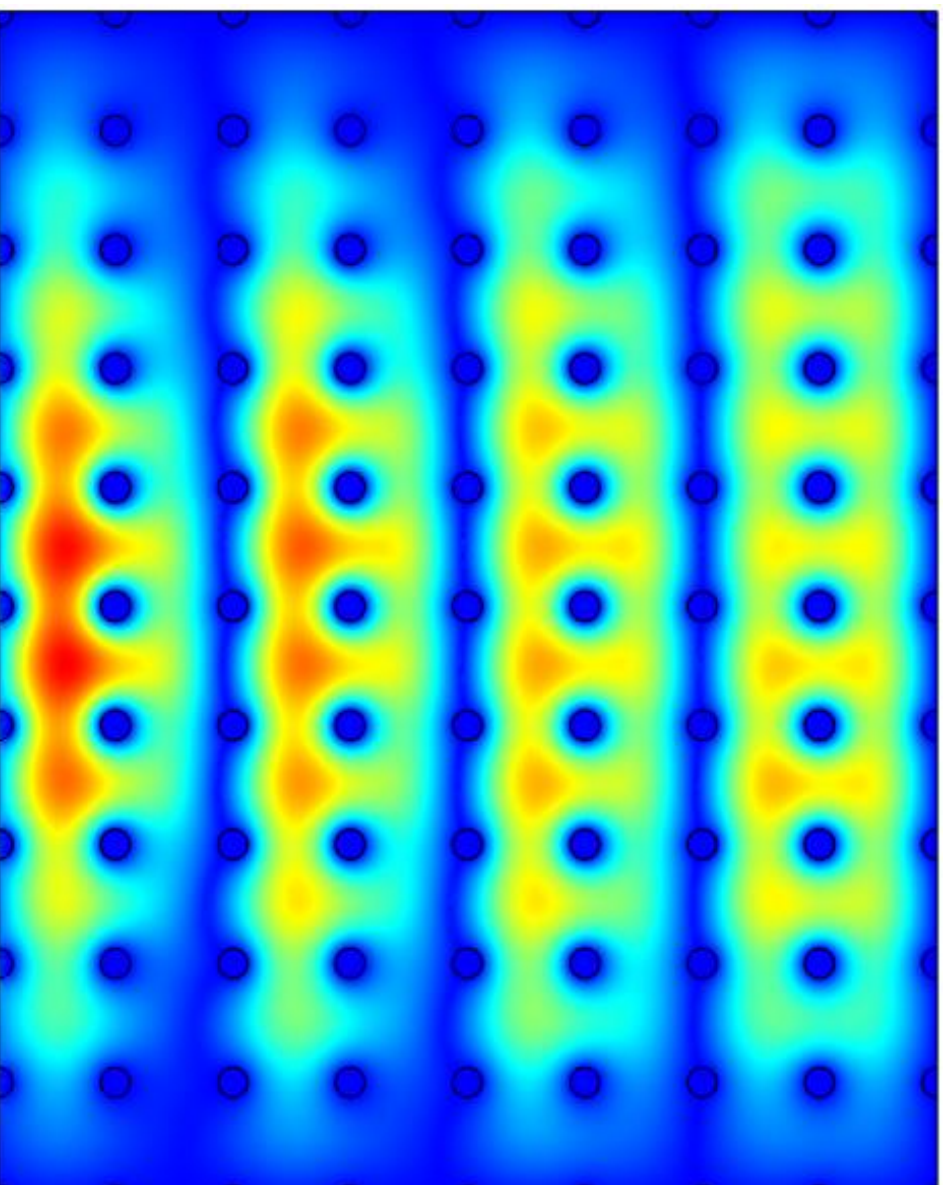


Fig 8. Electric field propagation at 350 THz

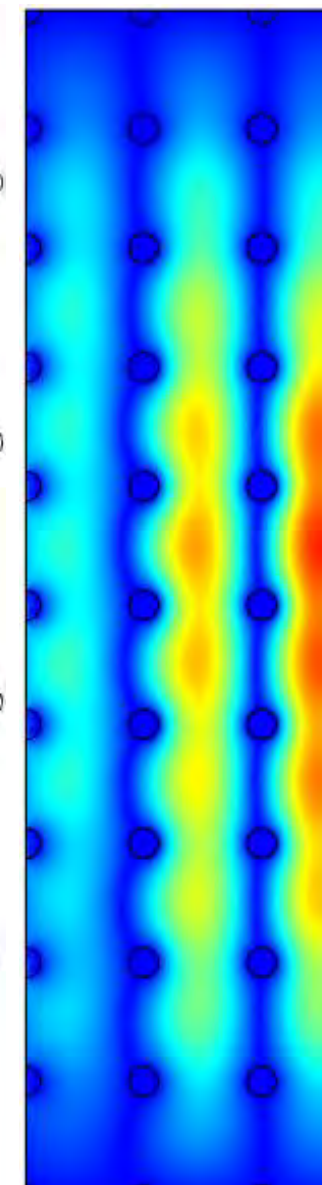


Fig 9. Electric field propagation at 400 THz

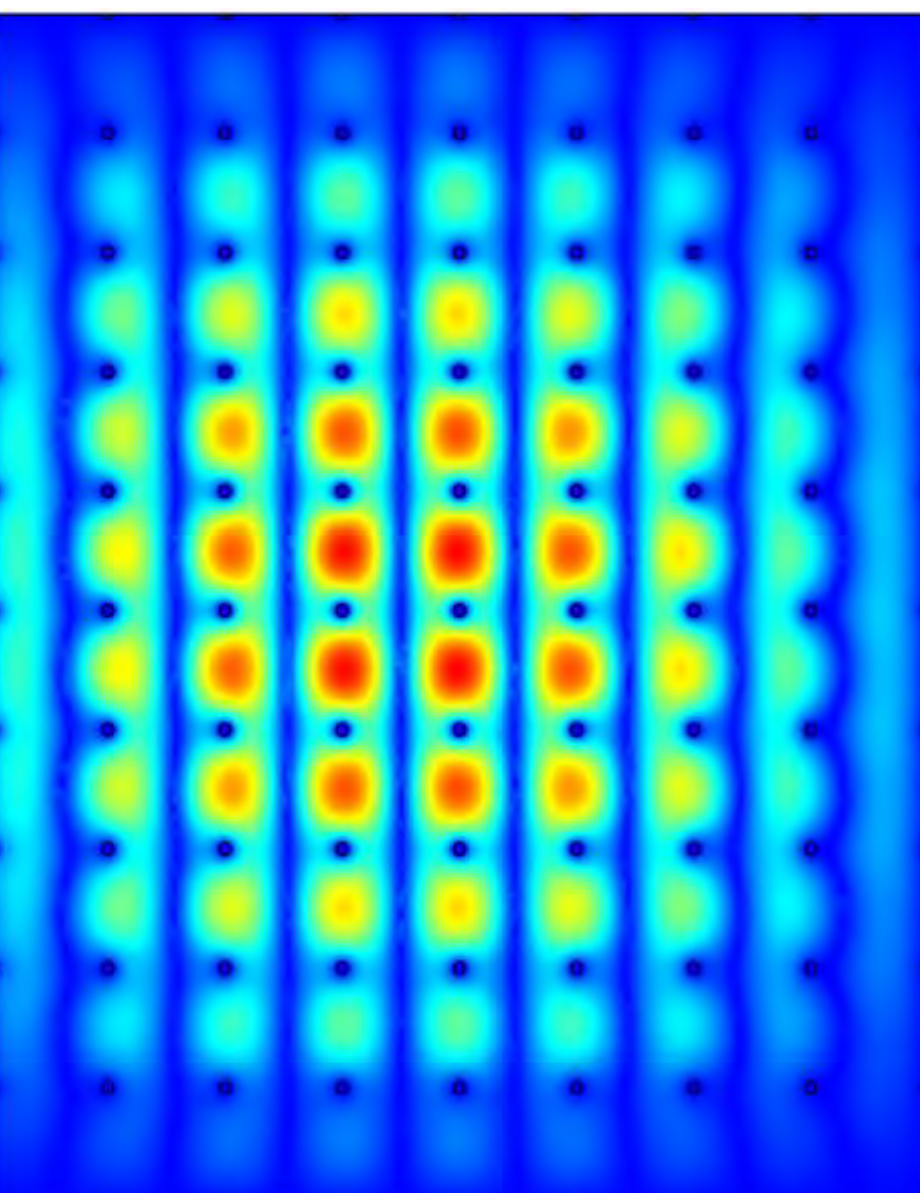


Fig 4. Electric field propagation at 2 THz

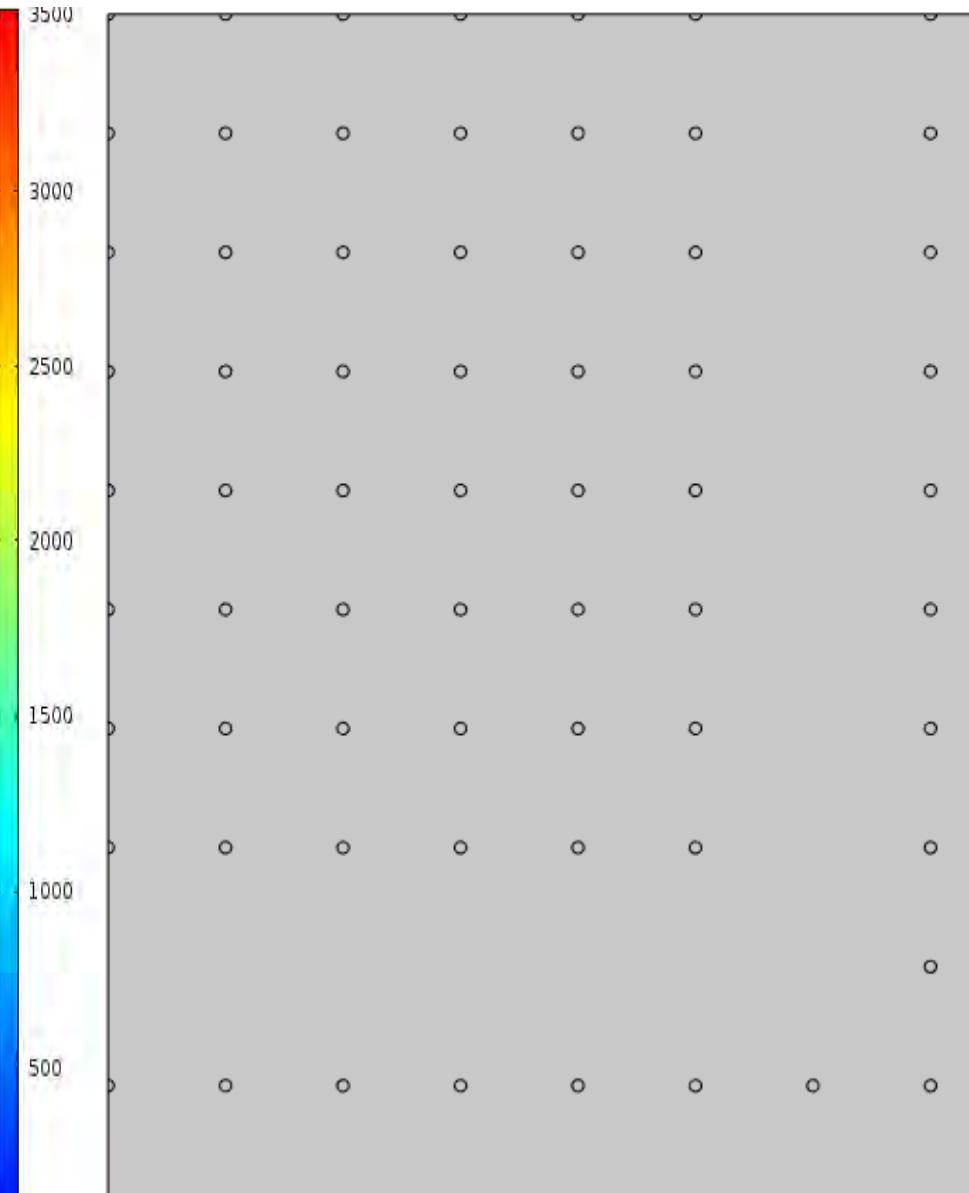


Fig 5. Geometry of 90 degree defect of a 2D array of silver pillars with a=100µm and r = 5µm

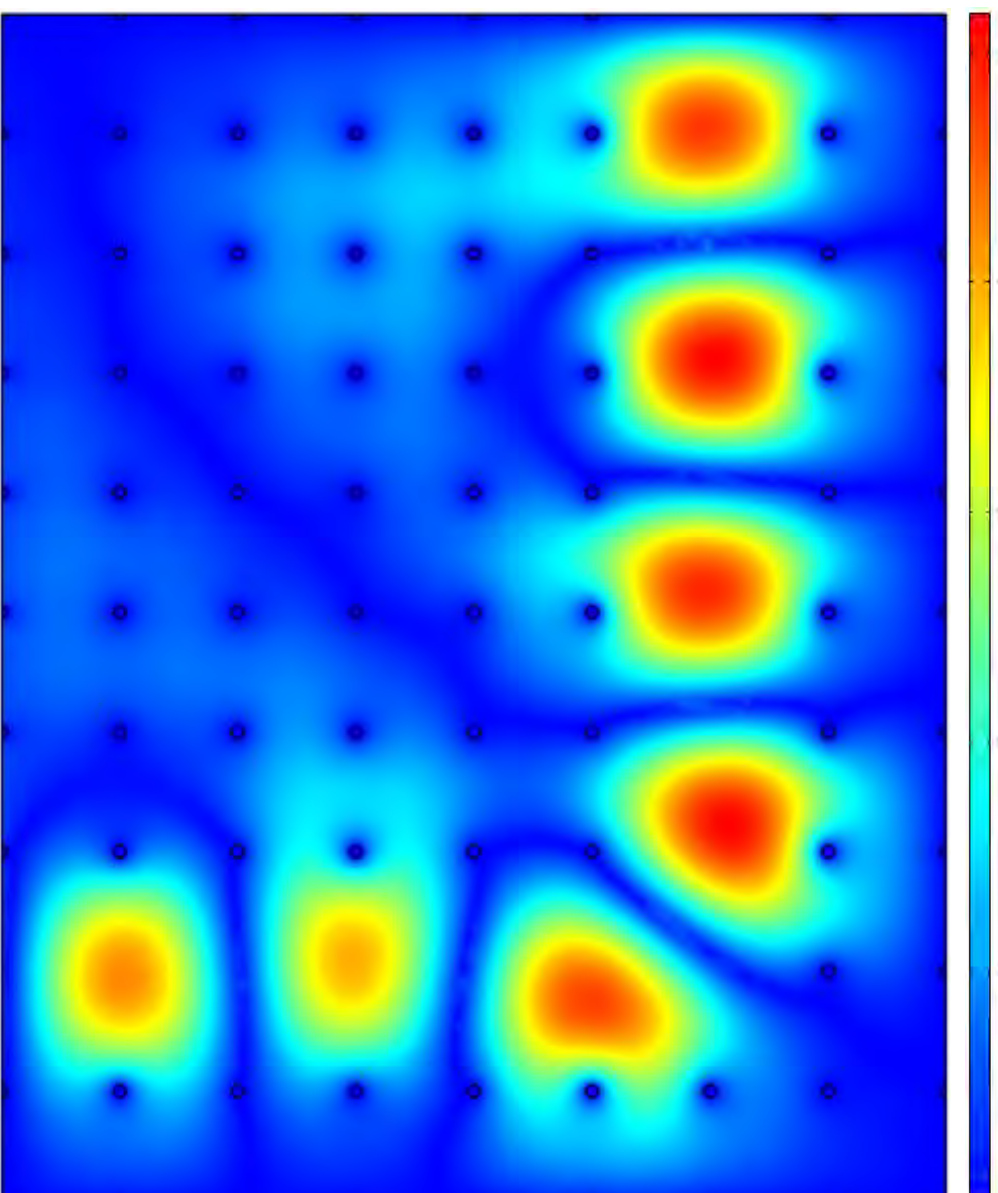


Fig 6. Waveguide electric field propagation at 1 THz

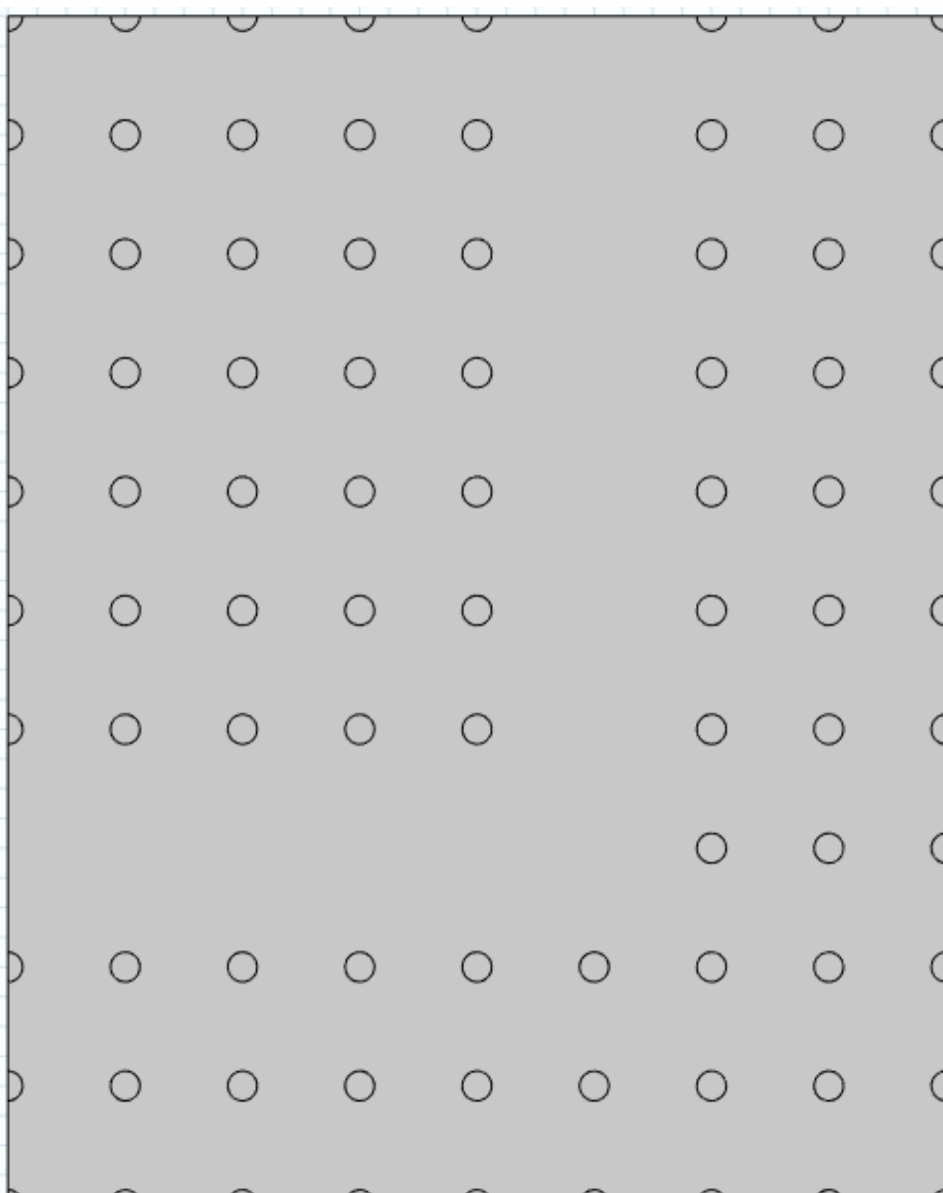


Fig 10. Geometry of 90 degree defect of a 2D array of silver pillars with a=400nm and r = 50nm

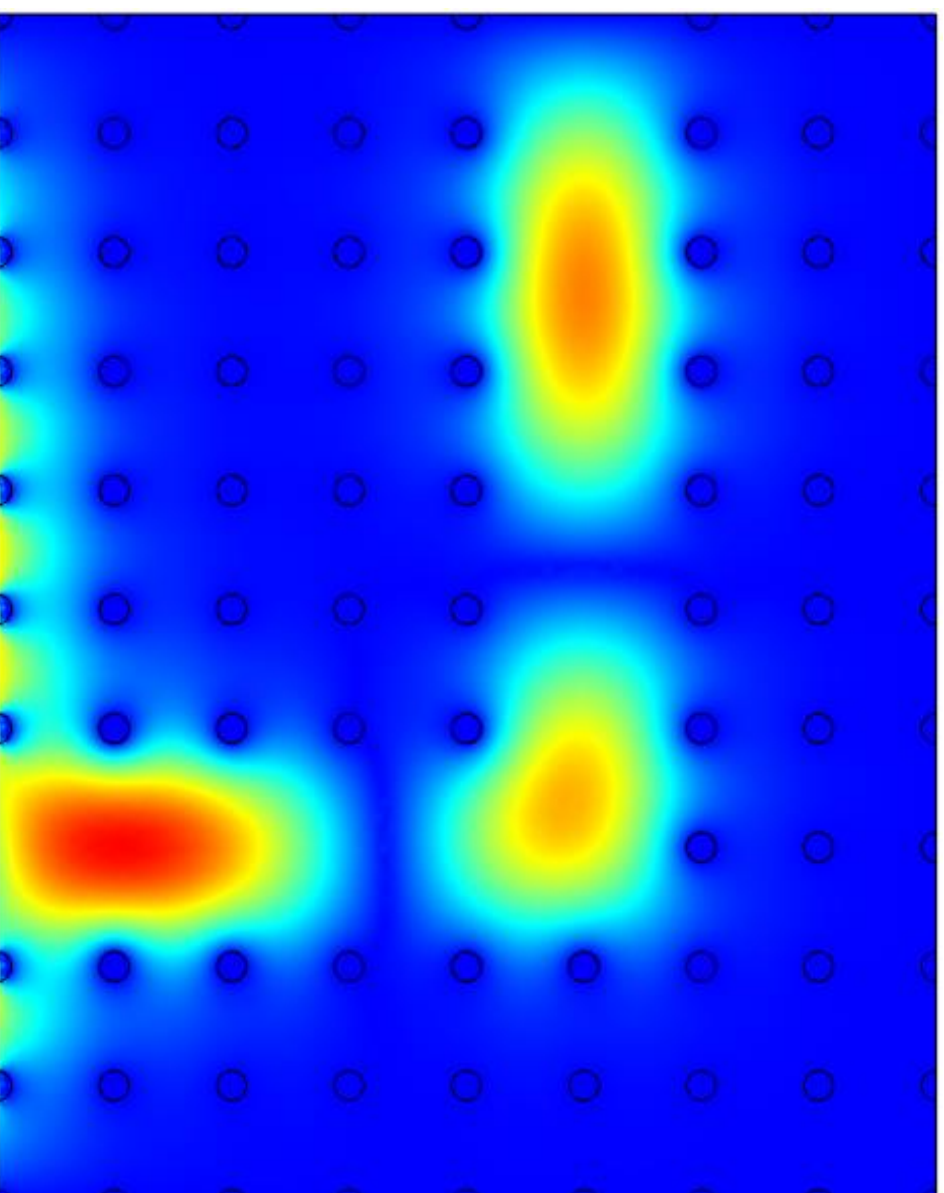


Fig 11. Waveguide electric field propagation at 200 THz

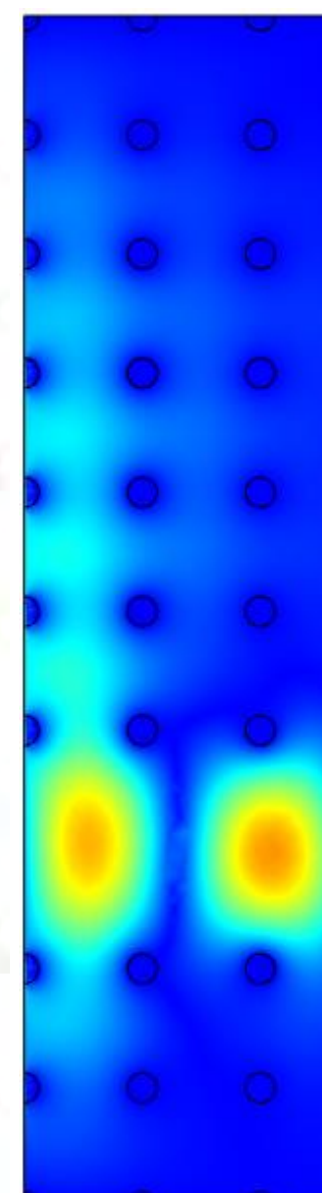


Fig 12. Waveguide electric field propagation at 300 THz

Conclusions

- Our simulation demonstrates that we can have electromagnetic transmission at THz frequencies through metallic arrays
- We were able to demonstrate transmission between 1 THz to 4 THz
- We also demonstrated transmission between 100 THz to 400 THz
- Transmission was confirmed and waveguide effect was demonstrated by making defects in the simulation geometry
- It was also demonstrated that we can change its operational frequency by changing its geometry size and distance

References

1. Butt, H., et al., *PHOTONIC CRYSTALS & METAMATERIAL FILTERS BASED ON SILICON NANOPILLARS*. Progress in Electromagnetics Research–Pier, 2009.
2. W. Withayachumnankul, and D. Abbott, “Metamaterials in the Terahertz Frequency Range,” *Journal*, vol. 1, no. 2, pp. 99–118, 2009.

Acknowledgements

This work was co-funded by the Army Research Office (ARO) and the Air Force Office of Scientific Research (AFOSR) Grant W911NF-15-1-0297

Abstract

We report the synthesis and characterization of cadmium–telluride (CdTe) quantum dots (QDs) and their performance at Terahertz (THz) frequencies employing THz time–domain spectroscopy (THz–TDS). The data was analyzed using a combination of Fast Fourier Transform (FFT) and effective medium theory to obtain the optical characteristics of the aforementioned CdTe QDs. Additionally, we performed similar measurements while exposing the QDs to a UV excitation with wavelengths of 302 nm and 365 nm and observed a noticeable variation in both the real and imaginary components in the index of refraction that could prove crucial in the demonstration of reconfigurable devices operating in the THz regime.

Introduction

- THz region of submillimeter range is located at 300 GHz to 3 THz in the electromagnetic spectrum (EM)
- Materials and devices in this region of the EM spectrum are mostly leading applications on security, imaging and communications
- THz–TDS allows us to obtain real and imaginary part of optical properties as a function of frequency
- The materials that we will be studying are CdTe QDs, which are nanoscale semiconductor structures that in this case exhibit photoluminescent effects
- The prospective utilization of QDs for THz applications remains relatively underexplored

Experimental

- The synthesis of the QDs was performed following the steps in Figure 1.

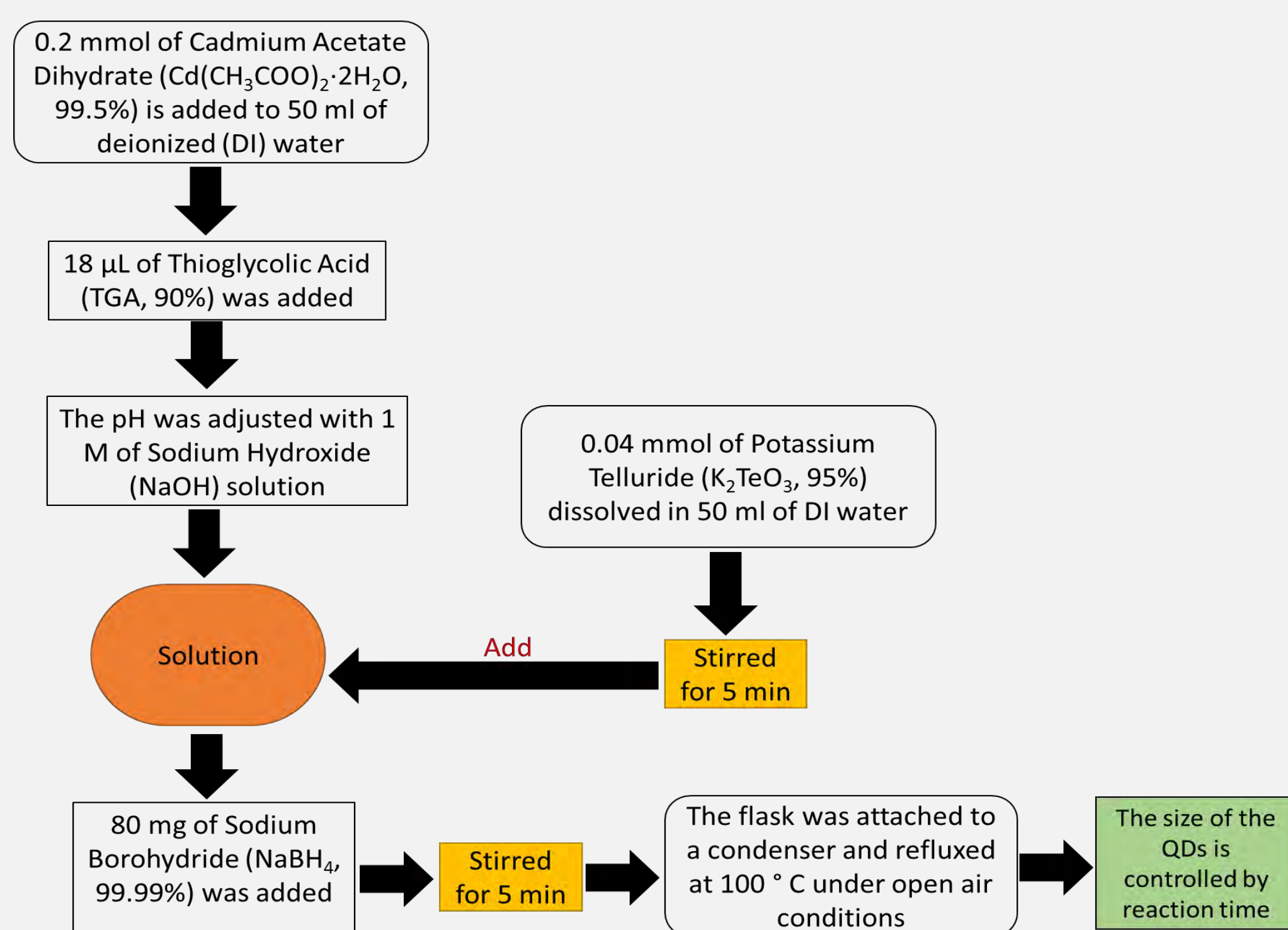


Figure 1: CdTe QDs synthesis

- THz–TDS technique was used in transmission mode (Figure 2)

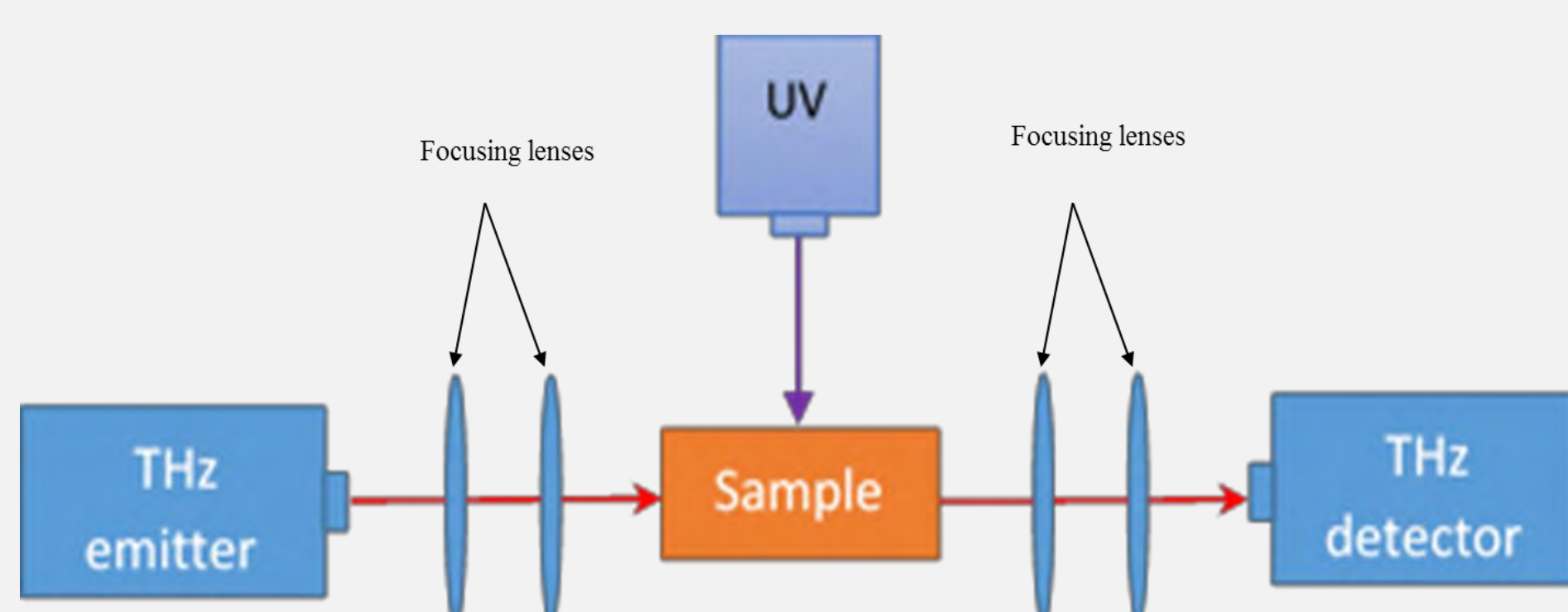


Figure 2: THz–TDS Setup

- The time domain data was processed using Fast Fourier Transform (FFT) and effective medium theory to obtain the optical properties.

Results and Discussion

- The experimental value of band gap is 3.64 eV and transition was obtained to be allowed direct bandgap
- The sizes of the CdTe QDs (1hr of synthesis) are around 2–3 nm

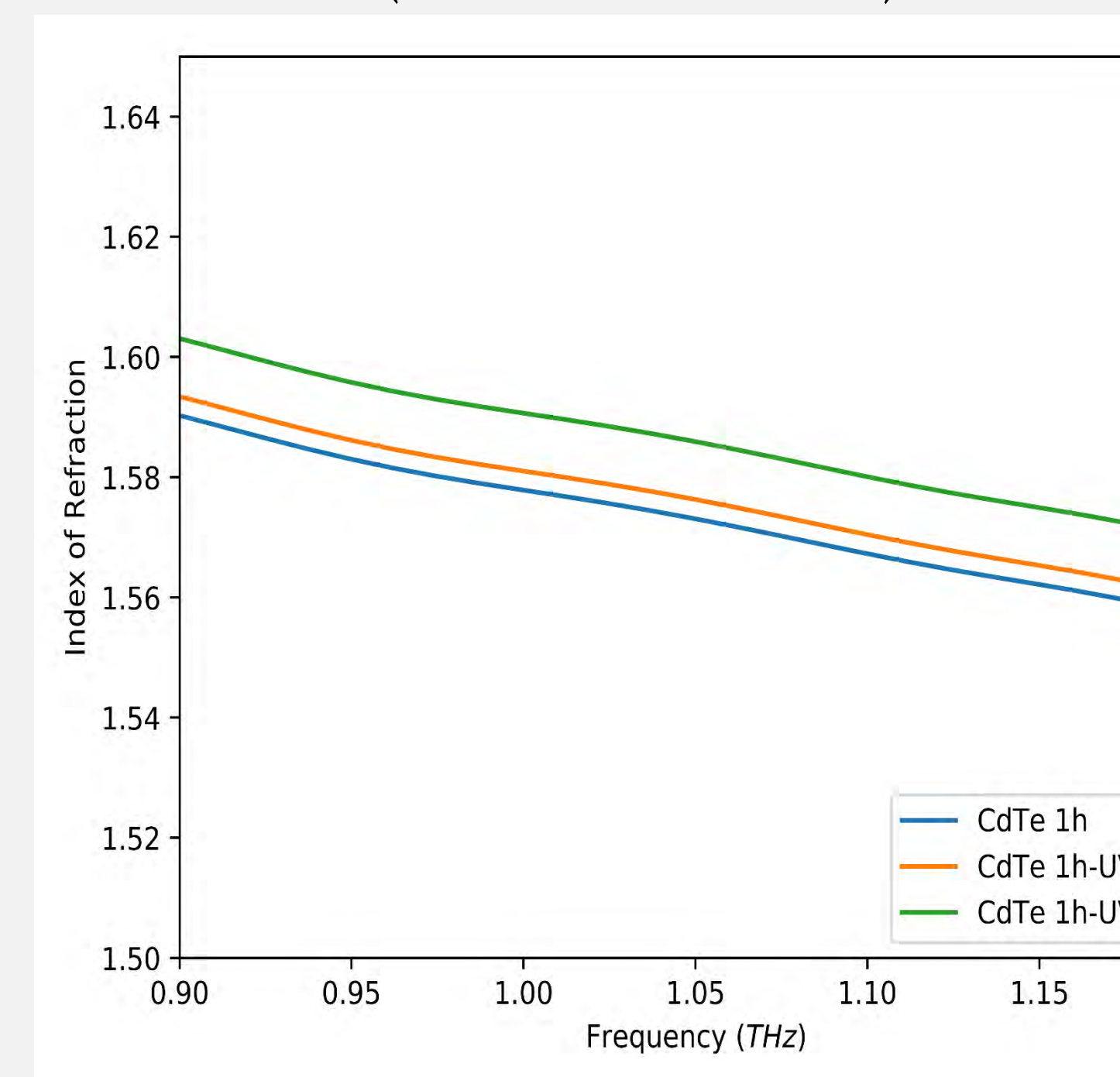


Figure 3: Extracted refractive index as a function of frequency of colloidal 1 hr synthesis CdTe QDs.

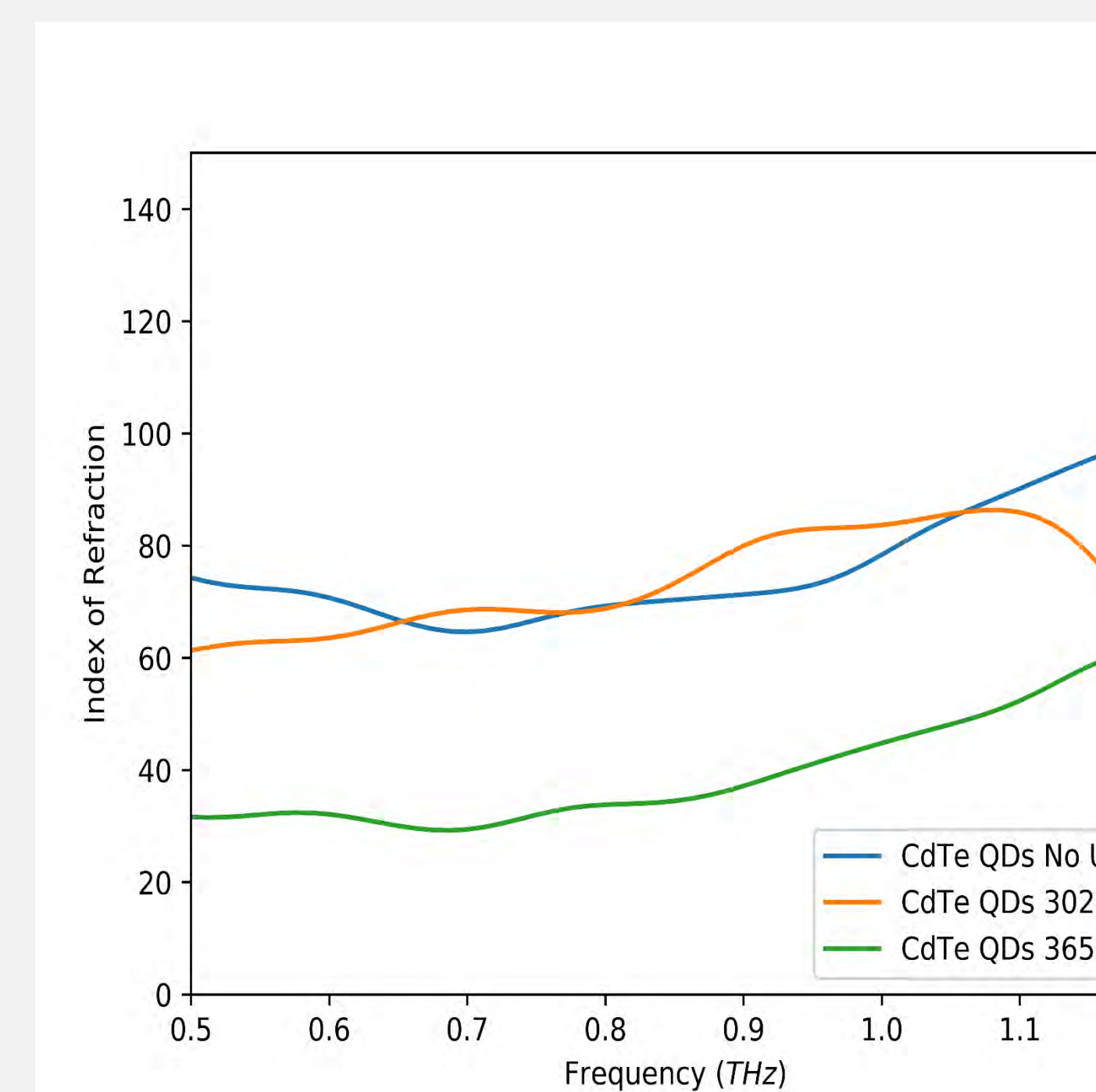


Figure 4: Extracted refractive index as a function of frequency for the 1 hr synthesis CdTe QDs using effective medium theory.

Conclusions

- We demonstrated a shift in the index of refraction of light at THz frequencies.
- We applied effective medium theory to obtain the optical properties of the QDs from the colloidal solutions.
- We speculate that the shift is due to optical nonlinearities.

References

- C. A. Schmuttenmaer, “Exploring Dynamics in the Far-Infrared with Terahertz Spectroscopy,” *Phys. Rev. Lett.*, vol. 104, no. 4, pp. 1759–1780, Apr. 2004.
- M. Hangyo, M. Tani, and T. Nagashima, “Terahertz Time-Domain Spectroscopy of Infrared Millimeter Waves,” vol. 26, no. 12, pp. 1661–1690, 2005.
- T. Trindade, P. O’Brien, and N. L. Pickett, “Nanocrystalline Semiconductor Quantum Dots: Perspectives,” *Chem. Mater.*, vol. 13, no. 11, pp. 3843–3858, Nov. 2001.
- E. Petryayeva, W. R. Algar, and I. L. Medintz, “Quantum Dots in Bioanalysis: A Review of Various Platforms for Fluorescence Spectroscopy and Imaging,” *Appl. Spectrosc. Rev.*, vol. 48, no. 3, pp. 201–220, Mar. 2013.
- S. Wu, J. Dou, J. Zhang, and S. Zhang, “A simple and economical one-pot method for the synthesis of water soluble CdTe QDs,” *J. Mater. Chem.*, vol. 22, no. 29, pp. 14573–14578, 2012.

Acknowledgements

This work was co-funded by the Army Research Office (ARO) and the National Science Foundation (NSF) Grant W911NF-15-1-0297

frequencies under UV excitation. Experiments were performed using the THz time-domain spectroscopy (THz-TDS) technique, and the collected data was analyzed utilizing Fast Fourier Transform (FFT) to obtain the optical characteristics of the aforementioned CdTe QDs. The wavelengths of the UV excitations employed in this experiment were 302nm and 365nm. Our results indicate a noticeable variation in both the real and imaginary components of the index of refraction and an inverse relationship between the wavelength of exposure and the index of refraction with and without UV exposure that could prove crucial in the demonstration of reconfigurable devices operating in the THz regime.

Introduction

- The THz gap region is located between the infrared and microwave light of the electromagnetic spectrum (approximately from 300 GHz to 10 THz)
- Detection, generation and modulation in this frequency range could enable the demonstration of applications in medical, security, imaging and communications
- THz-TDS allows us to obtain real and imaginary part of optical properties as a function of frequency
- This work presents the study of CdTe QDs at these frequencies
- QDs are nanoscale semiconductor structure that in this case exhibit photoluminescent effects
- These structures are relatively underexplored at THz frequencies and could lead to various applications in the semiconductor field including consumer electronics.

Experimental

- Colloidal QDs were synthesized employing the following procedure:

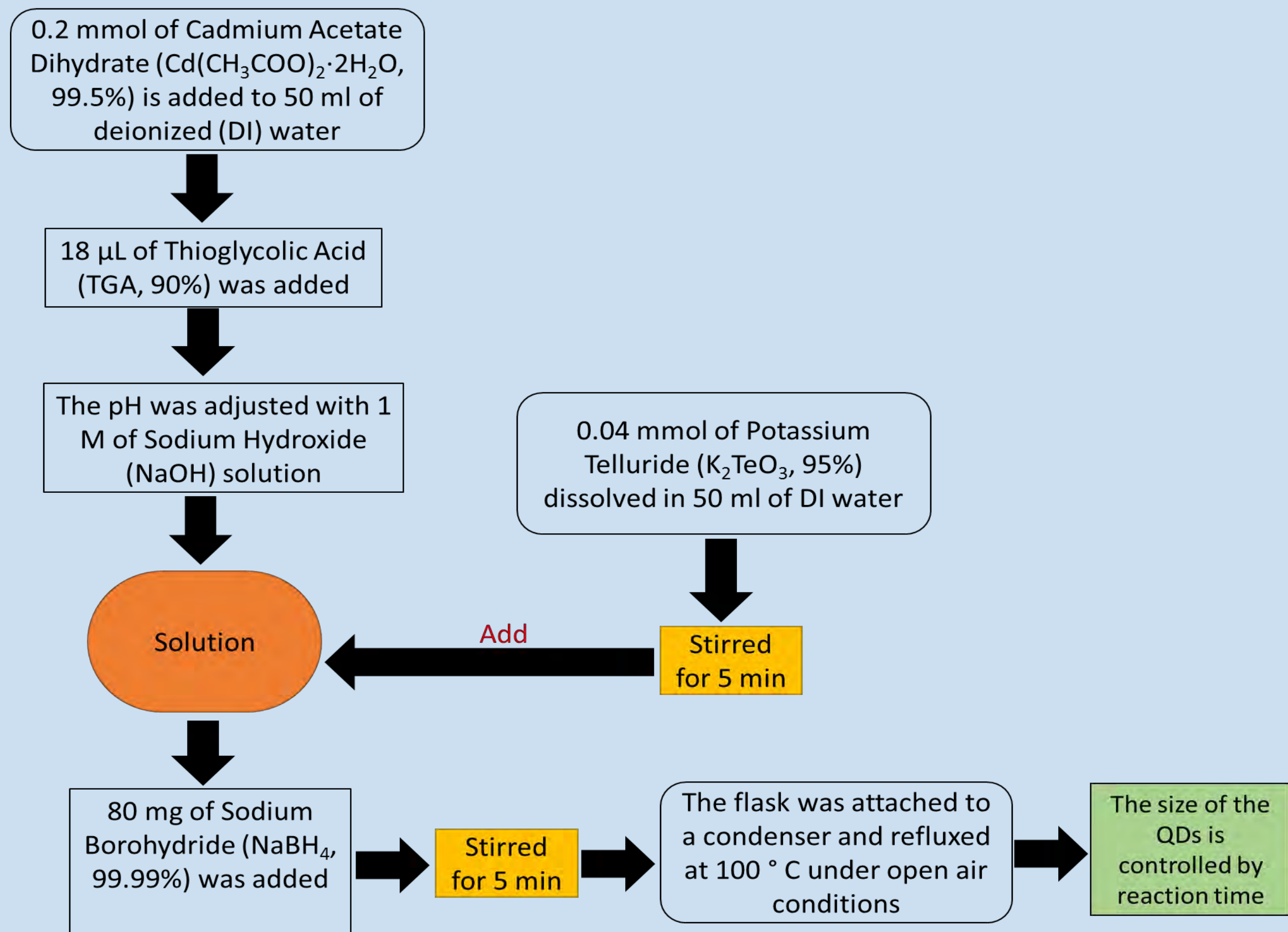


Figure 1: CdTe QDs synthesis

- The optical properties at THz frequencies was studied using THz-TDS technique in transmission mode (Figure 2).

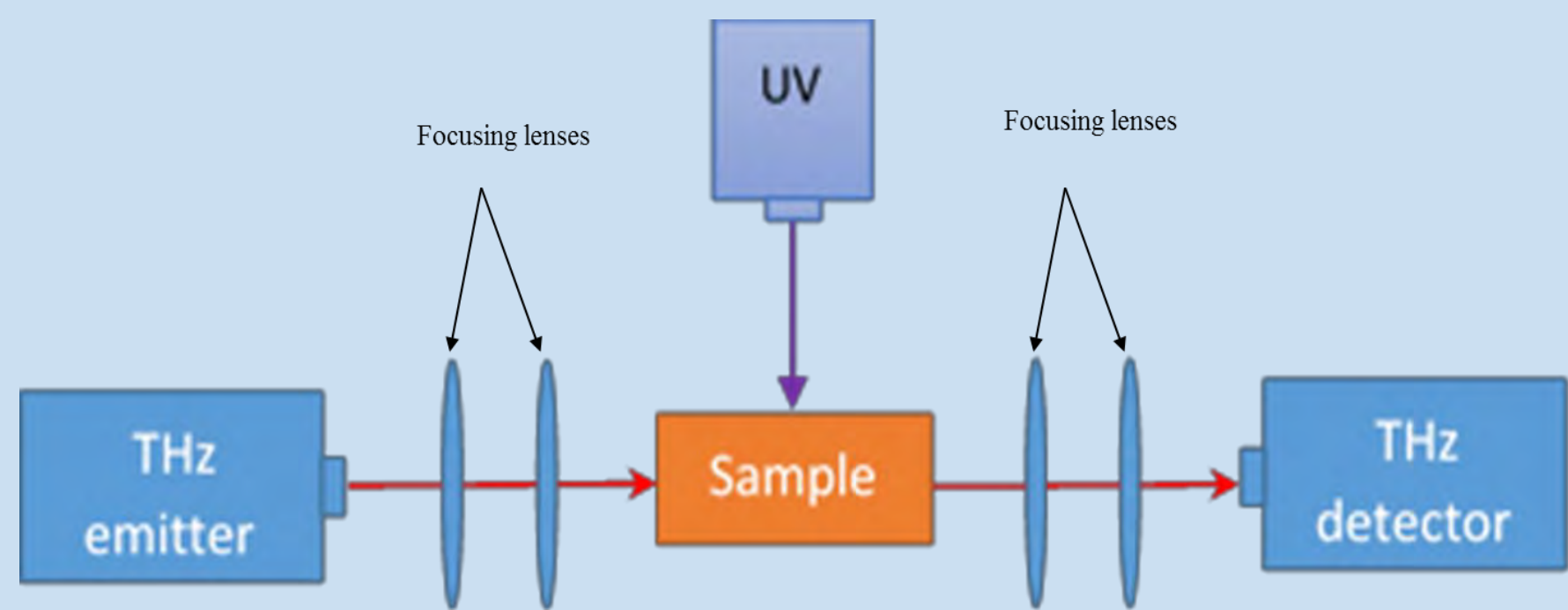


Figure 2: THz-TDS Setup

- The THz time domain data (Figure 3) obtained from the THz-TDS was processed using Fast Fourier Transform (FFT) to extract the optical properties of the colloidal CdTe QDs.

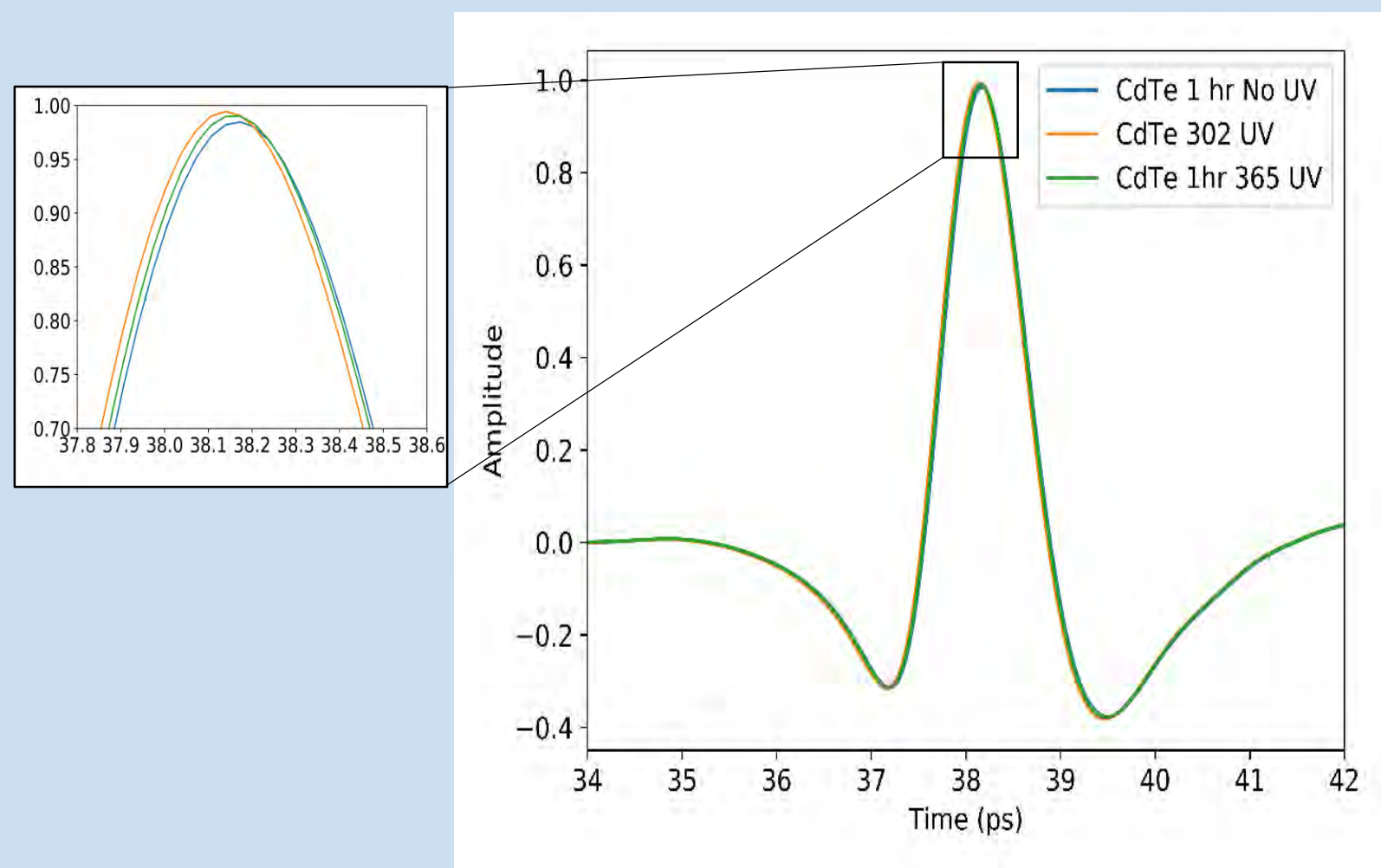


Figure 3: THz time domain amplitude for CdTe QDs solution 1 hr of synthesis without UV excitation and with UV excitation of 302 nm and 365 nm of wavelength.

Acknowledgements

This work was co-funded by the Army Research Office (ARO) and the Air Force Office of Scientific Research (AFOSR) Grant W911NF-15-1-0297

$$\frac{d(\ln \alpha(\nu))}{d\nu} = \frac{m}{h\nu - E_g}$$

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - (19$$

Figure 4 shows the plots for the absorbance and bandgap calculations for colloidal CdTe QDs with synthesis times

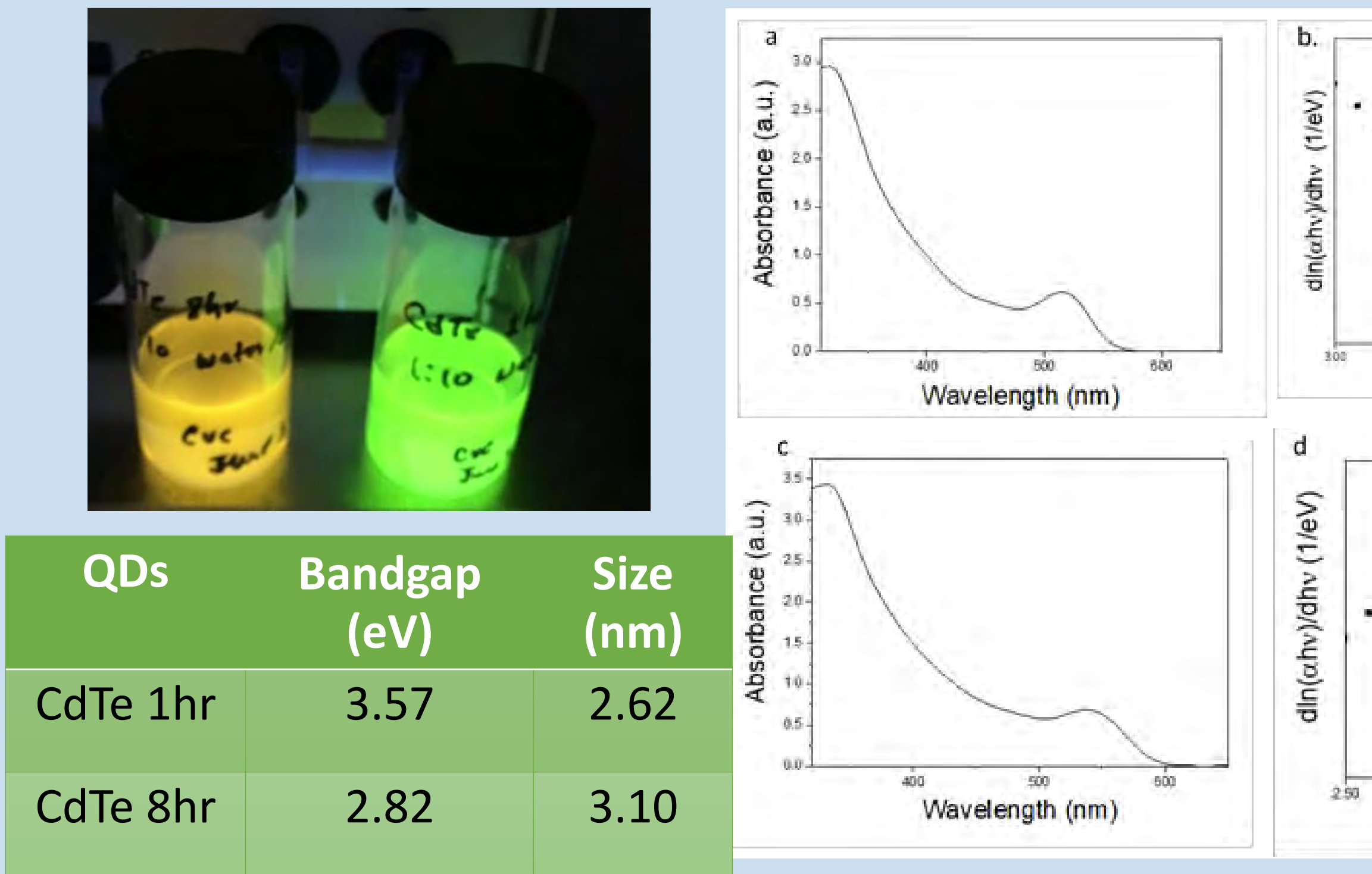


Figure 4: (a.) Absorbance spectrum and (b.) Bandgap calculation of CdTe QDs with a synthesis time of 1 hour. (c.) Absorbance spectrum and (d.) Bandgap calculation of CdTe QDs with a synthesis time of 8 hours.

- Plots of the THz time domain data are shown in Figure 3. There is a discernible shift when switching from no UV exposure to 302 nm and 365 nm UV exposure.
- After processing the time domain data using the FFT optical properties were calculated for the two different UV exposures.

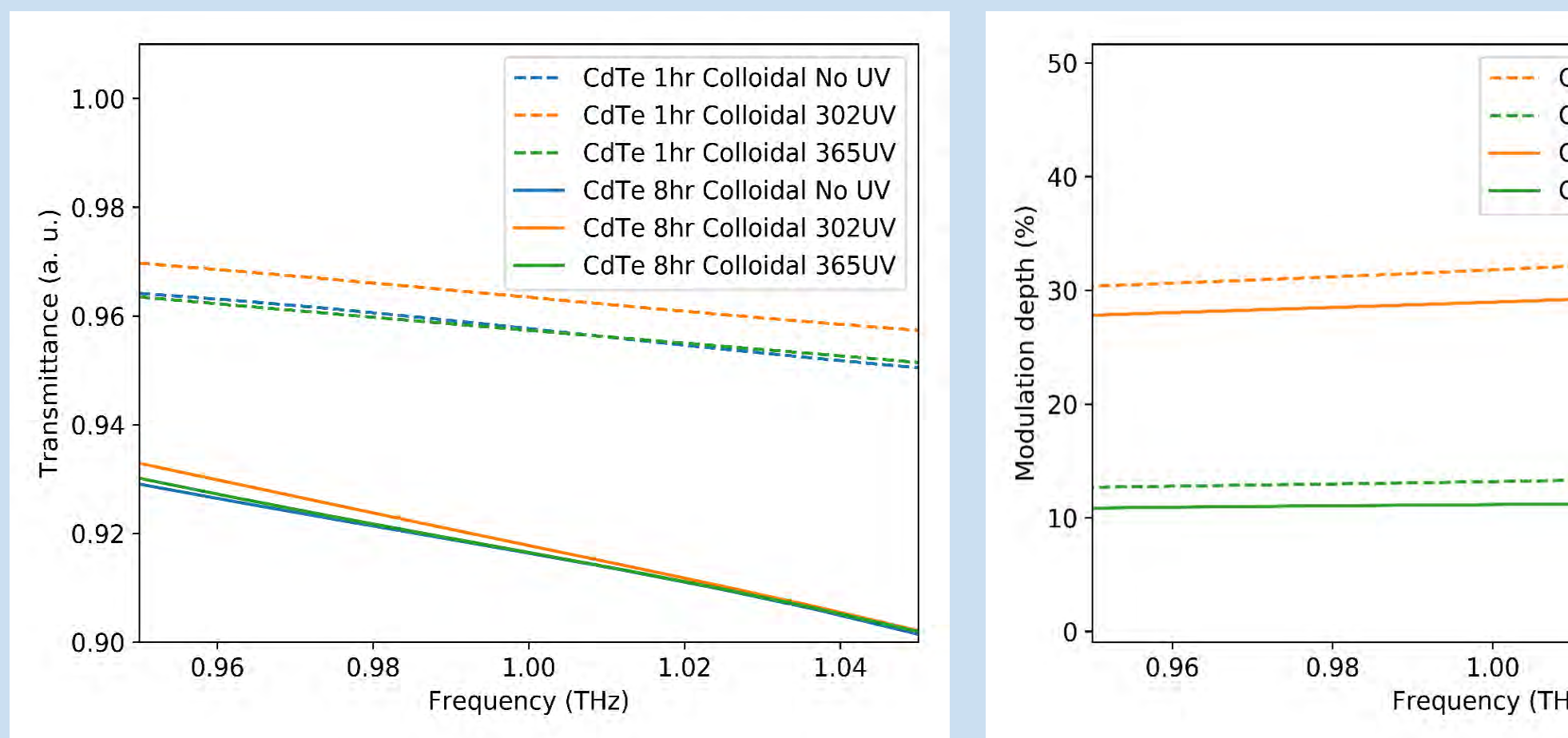


Figure 5: (a) Transmittance normalized to solvent for the different UV excitations. (b) Modulation depth induced by exposing CdTe QDs to UV excitation with wavelength of 302 nm and 365 nm. (dashed) and 8 hours (solid) to UV excitation with wavelength of 302 nm and 365 nm.

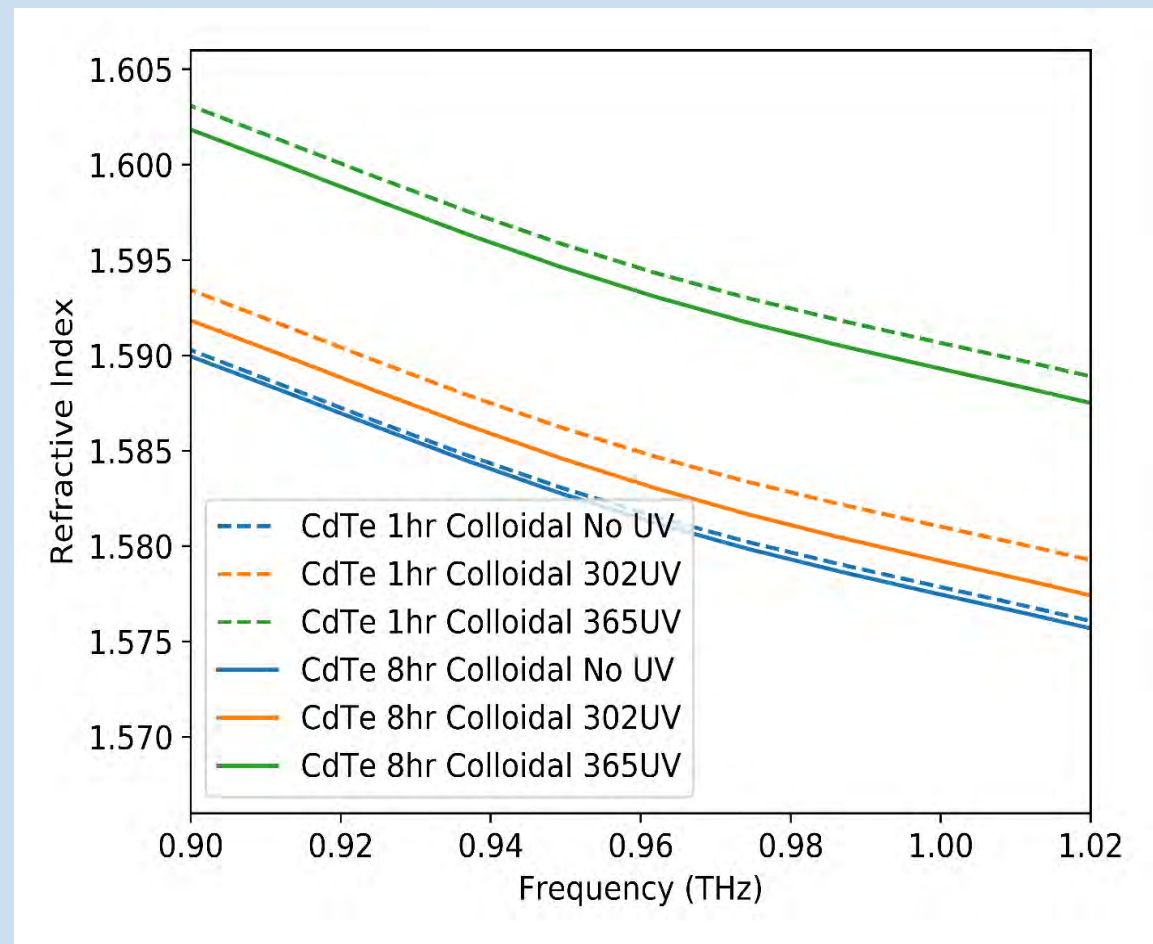


Figure 6: Refractive index for CdTe QDs 1hr (dashed) and 8hr (solid) of solution synthesis without UV exposure (yellow line) and 365 nm UV exposure (green line).

- Transmittance results (Figure 5a) indicate that by increasing the excitation energy the transmittance is higher. The modulation depth in Figure 5b.
- Figure 6 shows the refractive index for the colloidal QDs of 1hr and 8hr with and without UV excitation.

Conclusions

- We calculated the THz transmittance for the colloidal CdTe 1hr and CdTe 8hr of synthesis showing a variation in the transmittance with UV light.
- THz modulation was also calculated and is consistent with the transmittance results.
- We demonstrated a shift in the real part of the index of refraction at THz frequencies when exposing the sample to UV light.
- We speculate that the shift in the index of refraction is due to the electron polarizability.

References

- [1] S. Kar and S. Chaudhuri, "Synthesis and optical properties of single and bicrystalline ZnS nanoribbons," Chem. Phys. Lett., vol. 414, no. 1, pp. 40–46, 2005.
- [2] W. W. Yu, L. Qu, W. Guo, and X. Peng, "Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals," Chem. Mater., vol. 15, no. 14, pp. 2854–2860, 2003.
- [3] J. E. Pelayo, A. Zazueta, R. Lopez-delgado, E. Saucedo, and R. Ruelas, "Silicon solar cell efficiency improvement employing the photoluminescent, down-conversion layer," Renew. Sustain. Energy, vol. 5, no. 2, pp. 2–5, 2016.
- [4] H. H. Mantsch and D. Naumann, "Terahertz spectroscopy: The renaissance of far infrared spectroscopy," J. Mol. Struct., vol. 964, no. 1, pp. 1–4, 2010.

Important notes:

Do **NOT** write outside the grey boxes. Any text or images outside the boxes **will** be deleted.

Do **NOT** alter the structure of this form. Simply enter your information into the boxes. The form will be automatically processed – if you alter its structure your submission will not be processed correctly.

Do not include keywords – you can add them when you submit the abstract online.

Title:

Characterization of CdTe quantum dots for terahertz applications

Authors & affiliations:

Clarissa D. Vázquez-Colón¹, Juan Adrián Zepeda-Galvez¹, Daniel Shreiber², and Arturo Ayón¹

¹The University of Texas at San Antonio, USA, ²US Army Research Laboratory, Aberdeen Proving Ground, USA

clarissa.vazquezcolon@utsa.edu

Abstract: (Your abstract must use **Normal style** and must fit in this box. Your abstract should be no longer than 300 words. The box will 'expand' over 2 pages as you add text/diagrams into it.)

Preparation of Your Abstract

1. The title should be as brief as possible but long enough to indicate clearly the nature of the study. Capitalise the first letter of the first word **ONLY** (place names excluded). No full stop at the end.

2. Abstracts should state briefly and clearly the purpose, methods, results and conclusions of the work.

Introduction: Clearly state the purpose of the abstract

Methods: Describe your selection of observations or experimental subjects clearly

Results: Present your results in a logical sequence in text, tables and illustrations

Discussion: Emphasize new and important aspects of the study and conclusions that are drawn from them

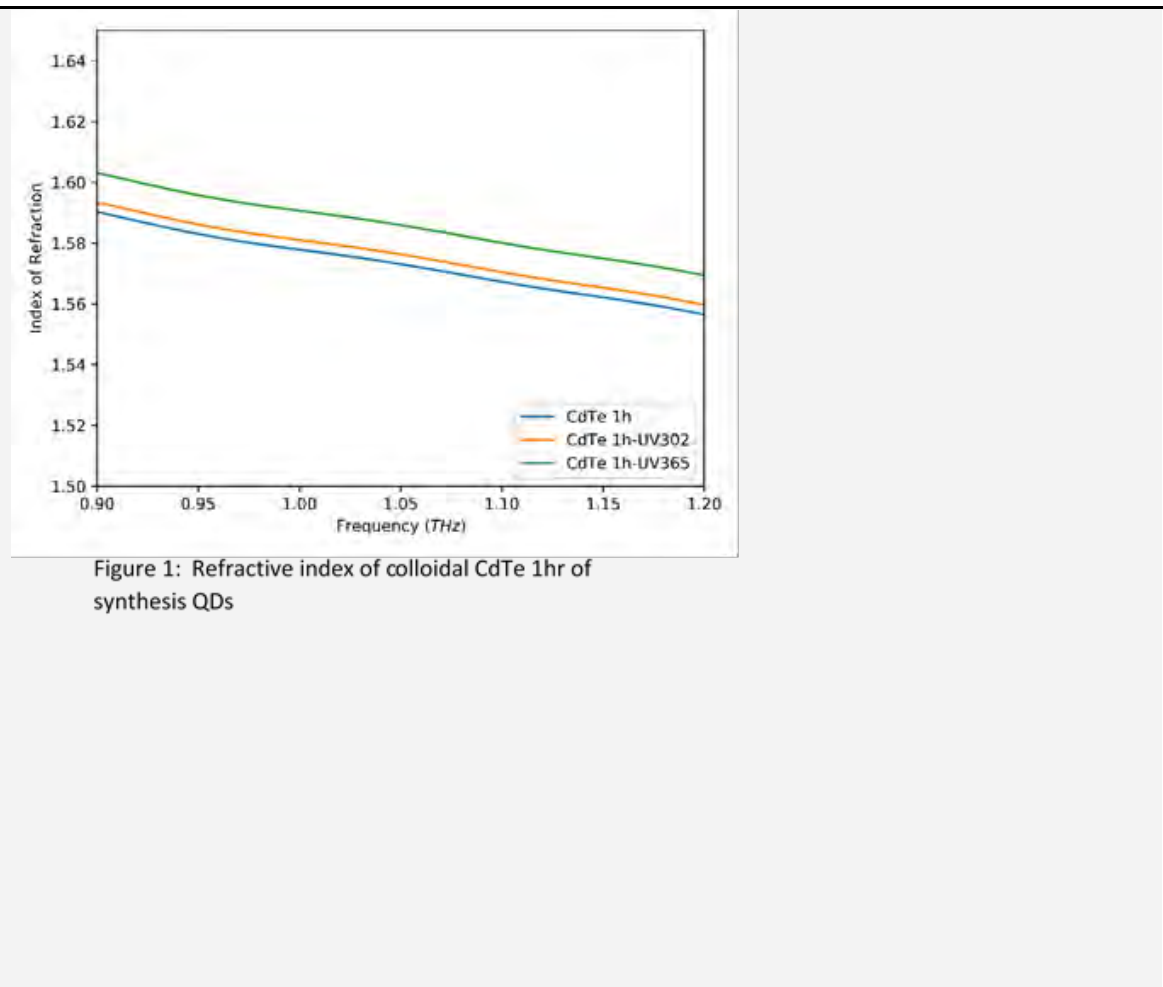
Recently, there is a special interest in the study of materials at Terahertz (THz) frequencies due to the lack of technological applications at this frequency range. THz region comprises the region of 0.1 to 10 THz of the electromagnetic spectrum. In this work we report the synthesis and characterization of CdTe quantum dots (QDs) at these frequencies. QDs in general are structures described by quantum mechanical laws and exhibit different behaviors compared to bulk materials because the large surface to volume ratio of QDs affect their physical and chemical properties. The prospective utilization of QDs for Terahertz applications remains an unexplored research area at the time when there is a perceived need to develop materials and techniques that could address the needs for resonators, filters and other circuitry elements with a satisfactory THz performance. The characterization of the CdTe QDs was performed using a THz time-domain spectroscopy (THz-TDS) technique, which allows to obtain optical properties such as index of refraction, dielectric constant and conductivity. The data was analyzed using a combination of Fast Fourier Transform and effective medium theory to obtain the optical characteristics of CdTe QDs solutions of 1 hr and 8 hrs of synthesis. In order to verify the prospective tunable behavior when exposed to UV photons we performed measurements with a UV excitation source with wavelengths of $\lambda=302\text{nm}$ and $\lambda=365\text{nm}$. Our results shows a higher index of refraction of the QDs solution without UV than those exposed to UV photons. The data also shows a change in the index of refraction between the exposures of the two different UV wavelengths. The observed results indicate an inverse relationship between the energy of exposure and the index of refraction at THz frequencies that could prove crucial in the demonstration of reconfigurable devices (see fig1).

Important notes:

Do **NOT** write outside the grey boxes. Any text or images outside the boxes **will** be deleted.

Do **NOT** alter the structure of this form. Simply enter your information into the boxes. The form will be automatically processed – if you alter its structure your submission will not be processed correctly.

Do not include keywords – you can add them when you submit the abstract online.



compared to bulk materials because the large surface to volume ratio of QDs affect their physical and chemical properties. In fact, their electronic properties are strongly d although the aforementioned characteristics are essentially due to the confinement effect on charge carriers. However, the prospective utilization of QDs for Terahertz appl unexplored research area at the time when there is a perceived need to develop materials and techniques that could address the needs for resonators, filters and other circuit satisfactory Terahertz performance in order to satisfy the anticipated requirements in electronics, optics, analytical science, biological imaging including spectroscopy, and Therefore, we report the characterization of cadmium-telluride (CdTe) QDs of sizes ranging from 2 nm to 18 nm and their performance at Terahertz frequencies employing spectroscopy (THz-TDS)[3].

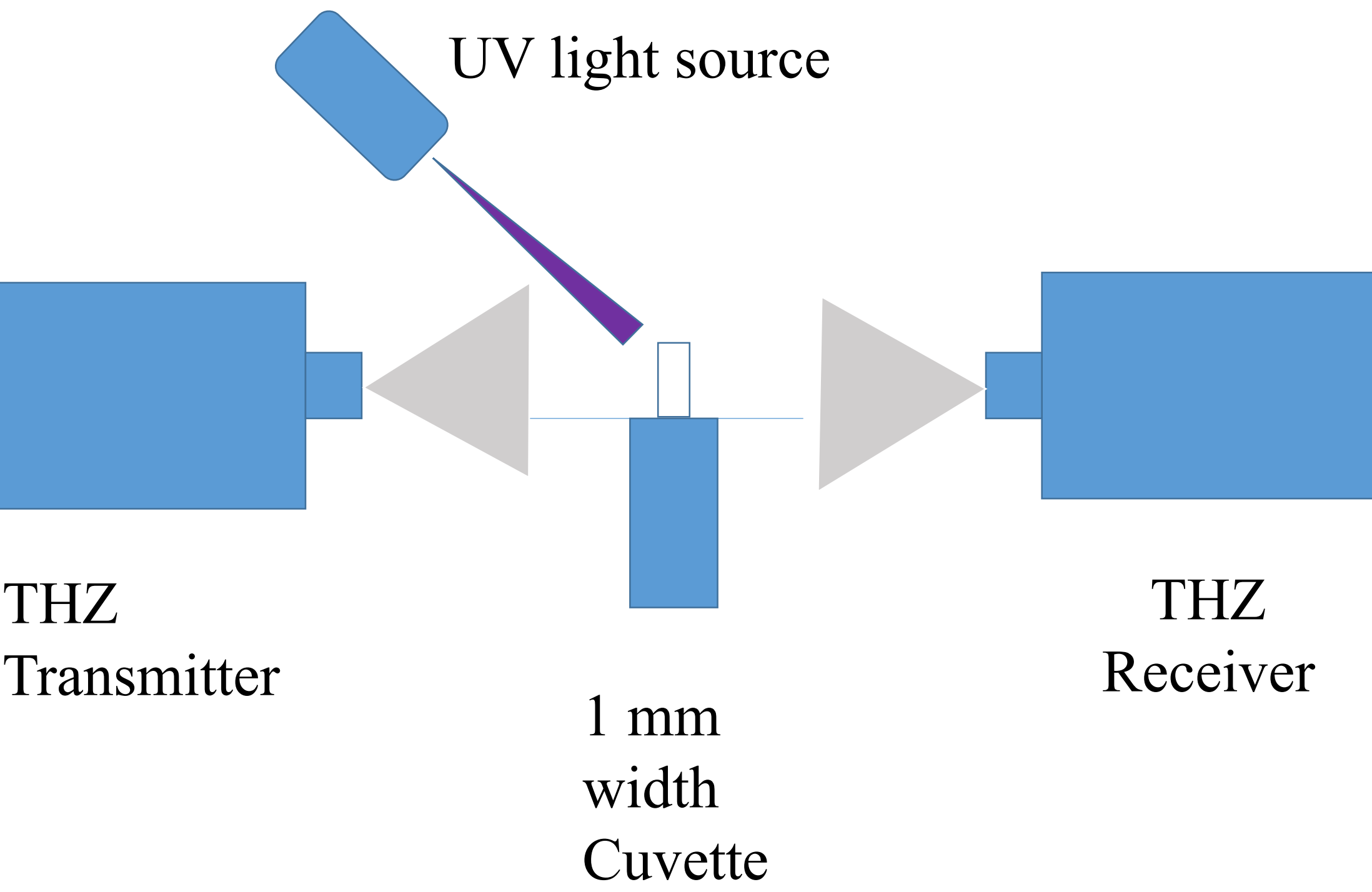
Introduction

- THz frequencies been historically underexplored.
- THz metamaterial devices are expected to have novel applications in medicine, astronomy, security, communications, and biochemistry
- Terahertz Time Domain Spectroscopy (THz-TDS) has proven to be the best technique to study the Terahertz behavior from 1-10 THz
- QDs have attracted extensive attention due to their high number of possible applications.
- Optical and electrical properties can be tailored by manipulating the size and concentration of QDs
- The sizes of CdTe QDs are related to the time of synthesis

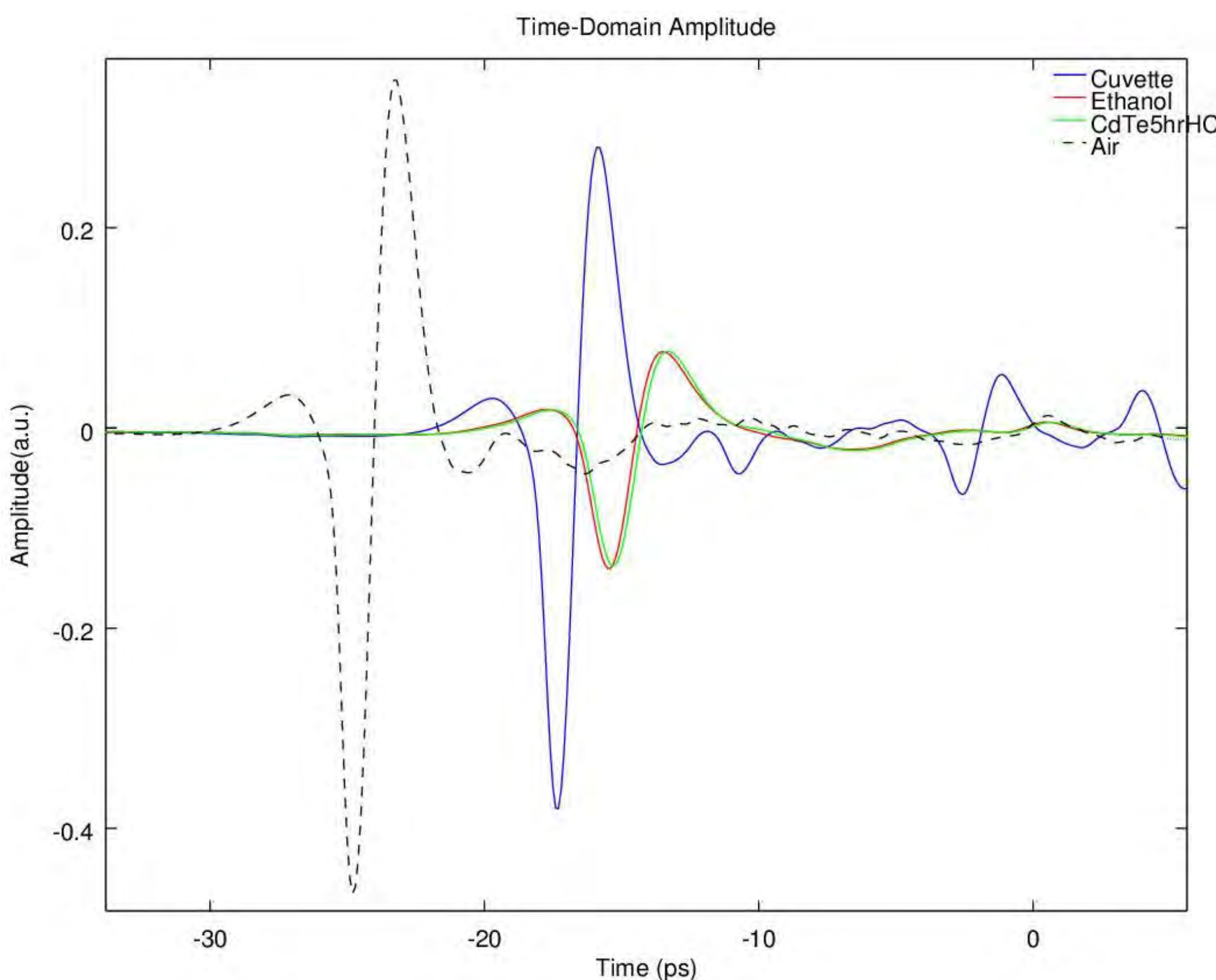
Methodology

- CdTe Quantum dots were synthesized following [4]
- Colloidal CdTe QDs were initially synthesized in aqueous solution and then transferred to ethanol solvent to ethanol
- By diluting a portion of the solutions we obtained 2 different concentrations of CdTe QDs
- A commercial THz-TDS (Picometrix T-Ray® 5000 Transmitter and Receiver) was used.
- The Time Domain pulses were then transformed to the frequency domain using the Fast Fourier Transform (FFT)
- UV light were applied using a commercial UV lamp

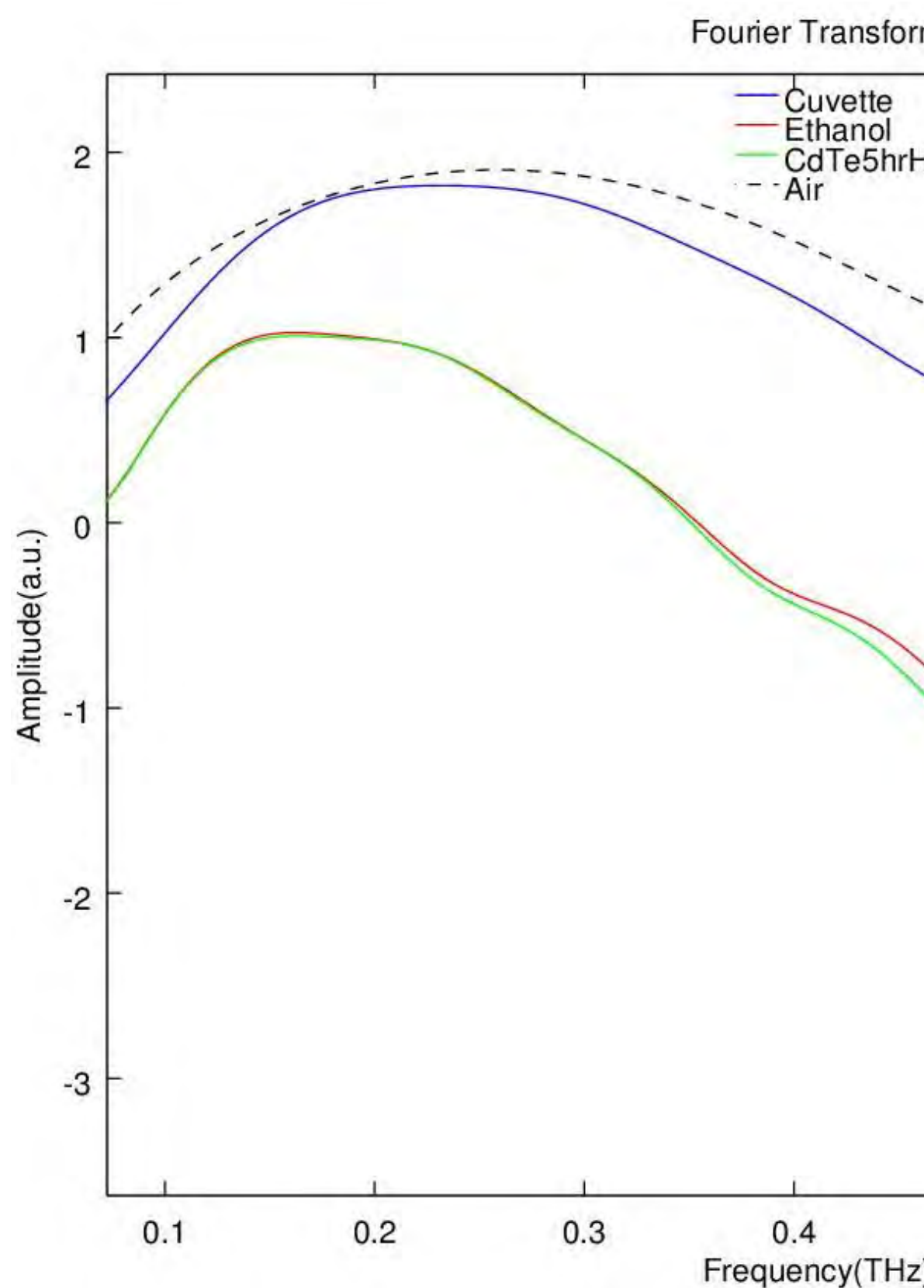
Results



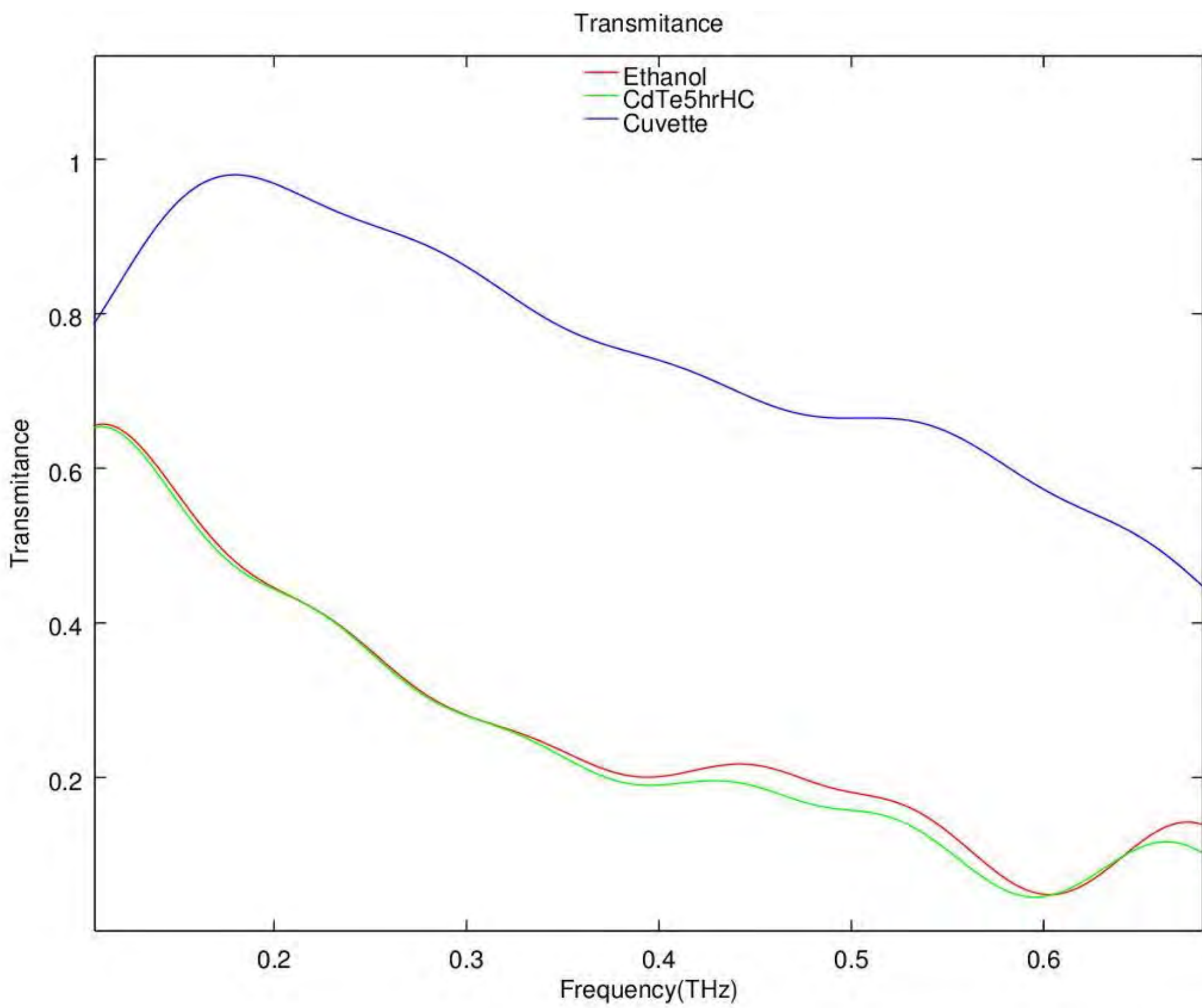
Typical setup for THz-TDS spectroscopy



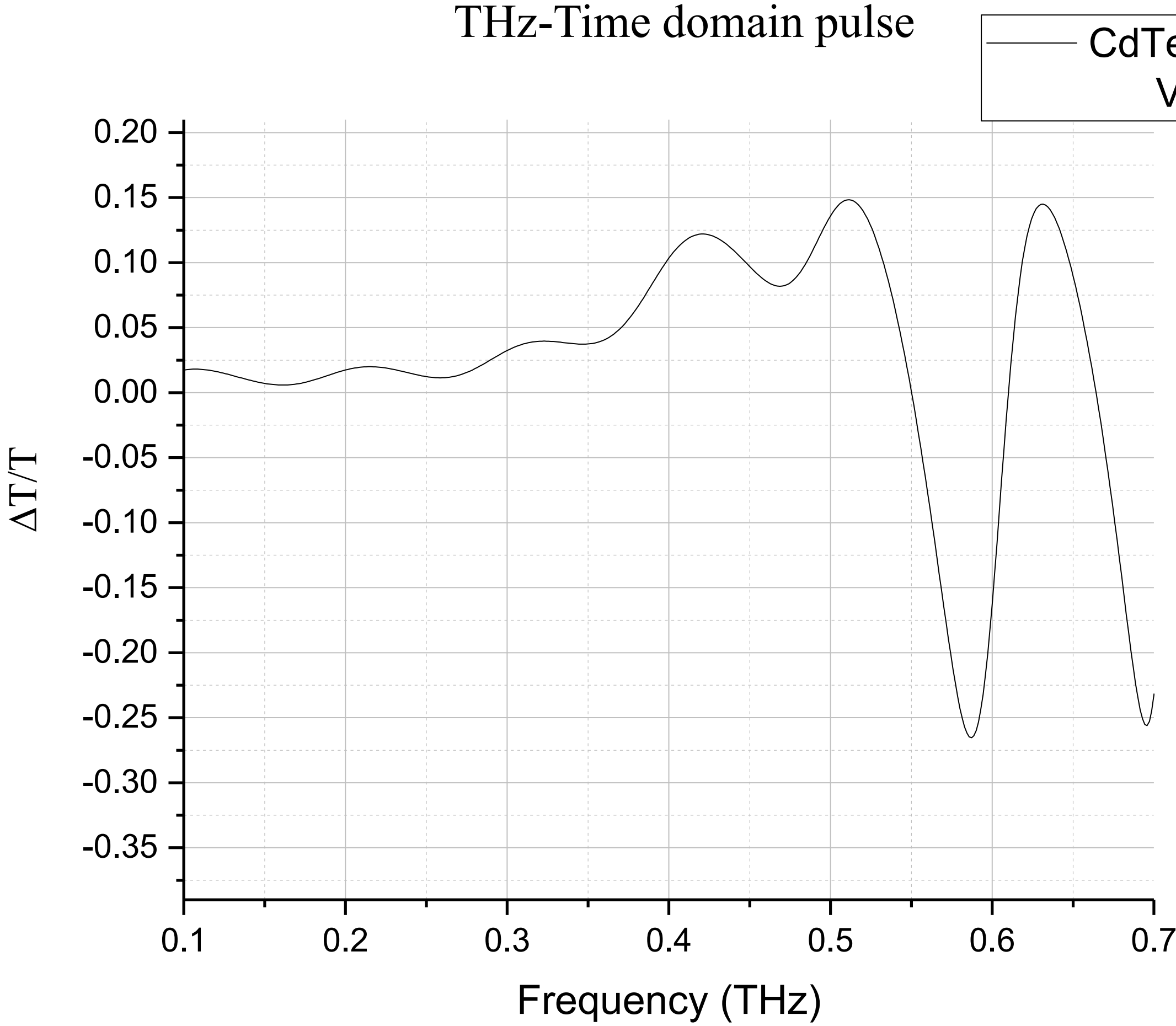
THz-Time domain pulse



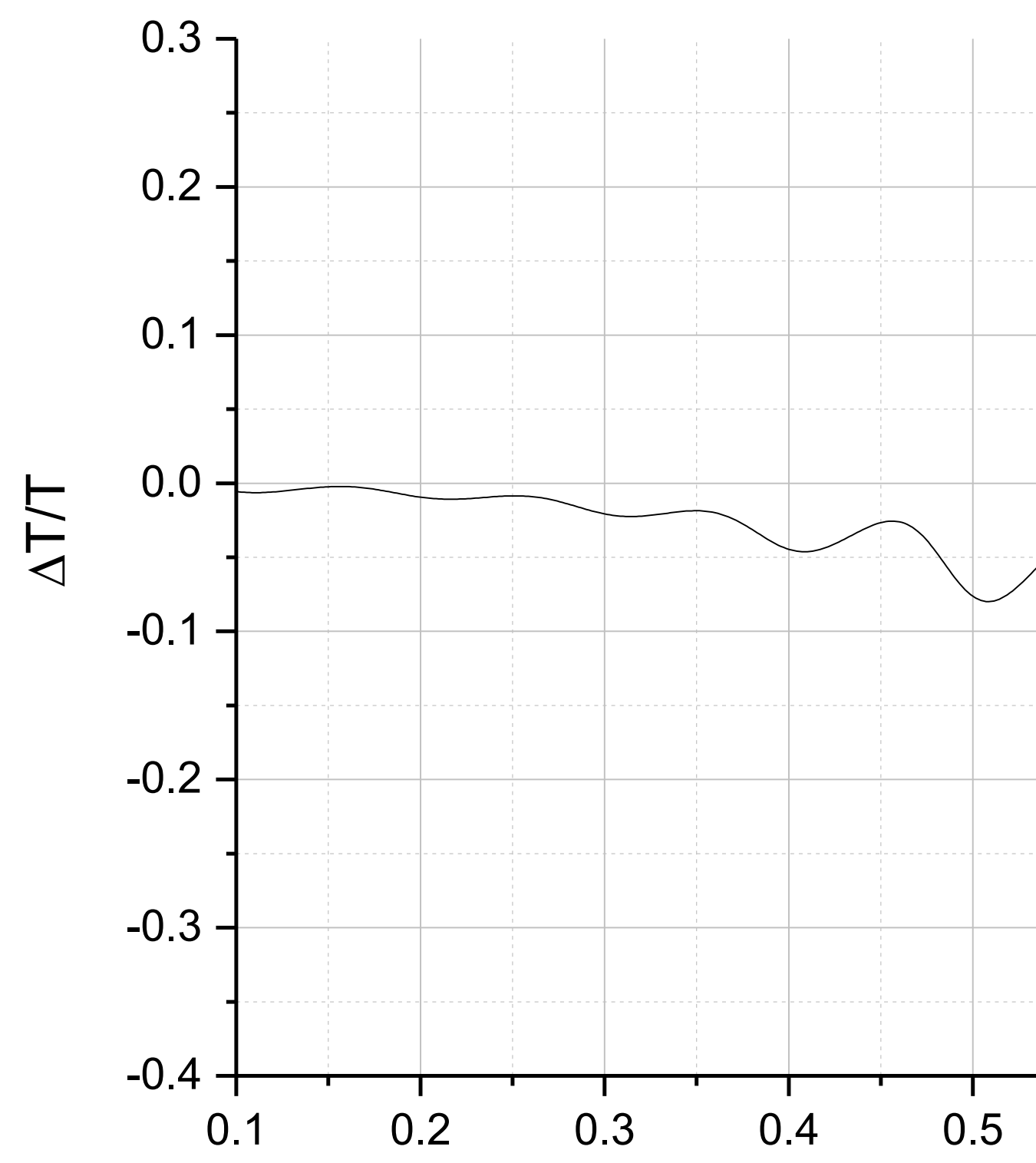
Frequency Domain Amplitude



Transmittances. The green line represents the colloidal solution with QDs.



Relative Transmission of high (HC) to low (LC) concentration of CdTe Quantum Dots



Relative Transmission of high (HC) to low (LC) concentration of CdTe Quantum Dots under UV light

Conclusions

- We have observed that the transmission of colloidal QDs can be tailored by varying the concentration and size of the QDs employed.
- By exposing the sample to a UV source, a relatively small but not negligible increment in transmission was observed.
- The data collected to date indicate that the frequencies of interest extend from 0.4 to 0.8 THz .

References

1. T. Trindade, P. O'Brien, N.L. Pickett, Chemistry of Materials, 13 (2001) 1743-1748.
2. M. Amelia, C. Lincheneau, S. Silvi, A. Credi, Chemical Society Reviews, 34 (2005) 5743.
3. C.A. Schmuttenmaer, Chem. Rev., 104 (2004) 1759-1779.
4. Tronco-Jurado, U., Saucedo-Flores, E., Ruelas, R., López, R., Alvarado, A. A. *Microsystem Technologies*, (2015) 1-9

Acknowledgements

This work was co-funded by the Army Research Office (ARO) and the Air Force Office of Scientific Research (AFOSR) Grant W911NF-15-1-0297

unmentioned errors and present a preliminary explanation for the observed effect.

An additional experiment employing Carbon Quantum Dots (QDs) was performed to verify the corrective method contained herein.

Introduction

- Pump-probe experiments are useful in the study of photo-generated carriers, provided that the energy of the photons employed exceeds the band gap energy (E_g) of the semiconductor [1].
- Terahertz Time-Domain spectroscopy (THz-TDS) has proven to be a powerful technique to characterize substances in the frequency domain from 30 GHz to 10 THz and its applications ranges from characterization of chemical substances[2] and quality control[3] to contributions in communications [4], and in terms of size extends from galactic to nanoscale systems[5,6].
- Consequently, there has been an ever increasing number of reports in which the main topic is to study systematic errors for THz spectrometers [7,8].

Determination of the optical constants

The transmission of the cuvette will be

$$\tilde{T}_{cuv,0} = \frac{\tilde{E}_{cuv,0}(\omega)}{\tilde{E}_{air,0}(\omega)} = \frac{16\tilde{n}_{air,0}(\omega)\tilde{n}_{cuv,0}(\omega)}{(\tilde{n}_{air,0}(\omega) + \tilde{n}_{cuv,0}(\omega))^4} e^{-2i\frac{\omega d}{c}(\tilde{n}_{cuv,0}(\omega) - \tilde{n}_{air,0}(\omega))}$$

Similarly, the transmission of the cuvette and the sample

$$\begin{aligned} \tilde{T}_{sam,0} &= \frac{\tilde{E}_{sam,0}(\omega)}{\tilde{E}_{air,0}(\omega)} \\ &= \frac{\tilde{n}_{sam,0}(\omega)}{\tilde{n}_{air,0}(\omega)} \frac{(\tilde{n}_{sam,0} + \tilde{n}_{air,0})^2}{(\tilde{n}_{sam,0} + \tilde{n}_{cuv,0})^2} e^{-i\frac{\omega s}{c}(\tilde{n}_{sam,0}(\omega) - \tilde{n}_{air,0}(\omega))} \end{aligned}$$

Correction Algorithm

The optical parameters of the material are those that satisfy the equations

$$\tilde{T}_{cuv,0}(\omega) = \frac{\tilde{E}_{cuv,0Exp}(\omega)}{\tilde{E}_{air,0Exp}(\omega)}$$

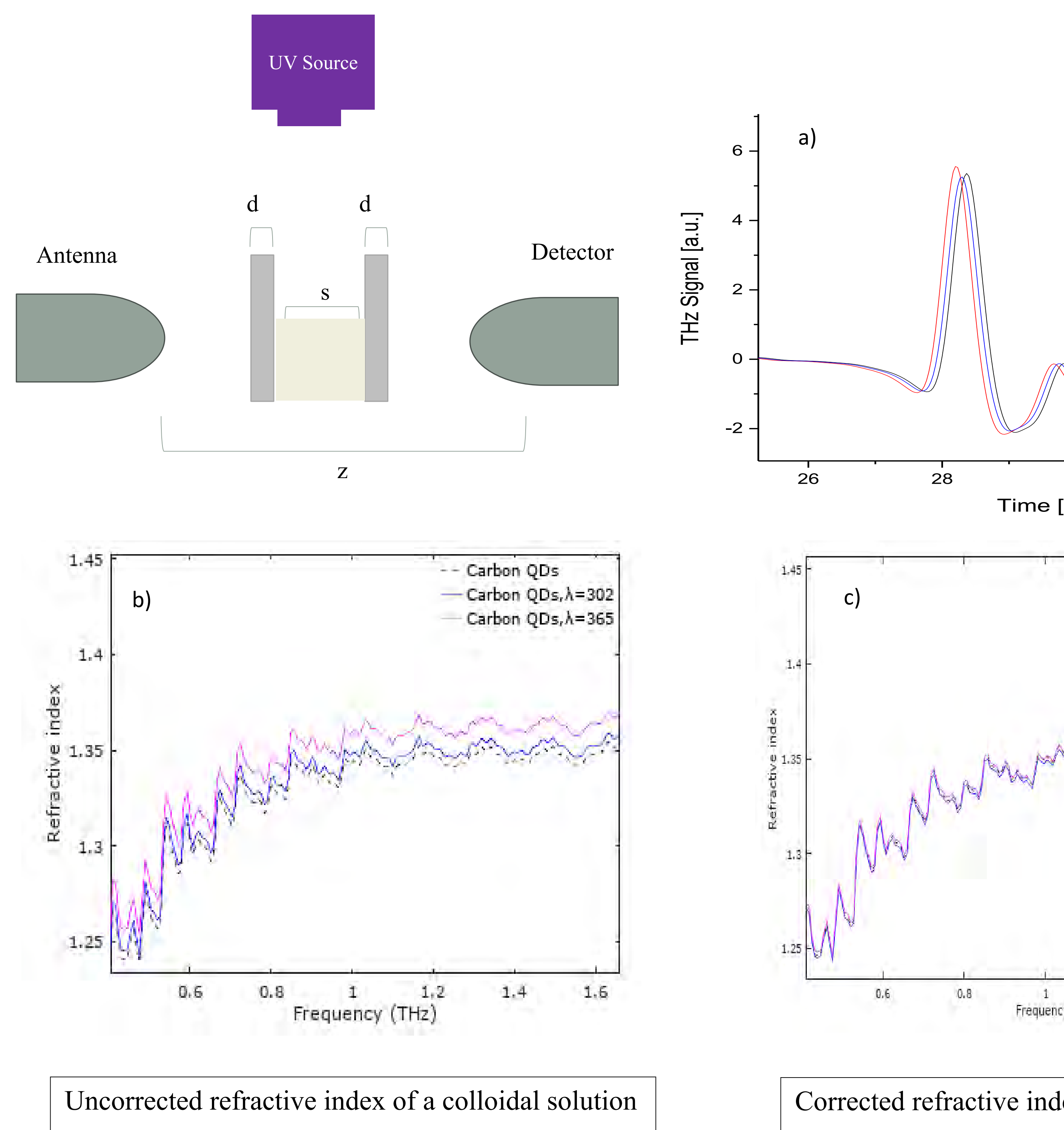
$$\tilde{T}_{sam,0}(\omega) = \frac{\tilde{E}_{sam,0Exp}(\omega)}{\tilde{E}_{cuv,0Exp}(\omega)}$$

- A small but noticeable difference in the time domain waveforms when the UV excitation was observed.
- To avoid this error it is required to measure air and cuvette Transmissions under UV excitation, namely $\tilde{T}_{samExp,\lambda}(\omega)$ and $\tilde{T}_{cuvExp,\lambda}(\omega)$, and perform a similar treatment as it was used before to obtain $\tilde{T}_{i,0}(\omega)$.
- The optical parameters are then the ones that satisfy

$$\tilde{T}_{cuv,\lambda}(\omega) = \frac{\tilde{E}_{cuv,\lambdaExp}(\omega)}{\tilde{E}_{air,\lambdaExp}(\omega)}$$

$$\tilde{T}_{sam,\lambda}(\omega) = \frac{\tilde{E}_{sam,\lambdaExp}(\omega)}{\tilde{E}_{cuv,\lambdaExp}(\omega)}$$

- THz-TDS measurements were performed on a Carbon quantum dot colloidal sample, diluted in ethanol to demonstrate the application of the suggested method



Conclusions

- A new source of error in THz-TDS which could contribute inaccuracies in the extraction of optical parameters of materials under UV pump- THz probe experiments has been investigated, and a correction algorithm based on measuring air and cuvette under UV excitation and therefore deducing a new theoretical Transmission has been derived and discussed.
- The proposed correction was validated by applying the proposed methodology to data obtained from a THz-TDS experiment in a colloidal solution of Carbon Quantum dots diluted in ethanol.
- It is thought that the underlying reason for this shift is due to the interaction of the UV photons with the parabolic mirrors, which are made of silicon dioxide, and under UV exposure experience a change in their conductivity, however, further experimentation is required.

References

- F. Rossi, "Theory of ultrafast phenomena in photoexcited semiconductors " *Reviews of Modern Physics*, vol. 54, pp. 1077-1090, 1982.
- K. Ajito and Y. Ueno, "THz Chemical Imaging for Biological Applications," *Ieee Transactions on Terahertz and Technology*, vol. 1, pp. 293-300, Sep 2011.
- S. Wietzke, *et al.*, "Terahertz imaging: a new non-destructive technique for the quality control of joints," *Journal of the European Optical Society-Rapid Publications*, vol. 2, 2007.
- A. Barh, *et al.*, "Specialty Fibers for Terahertz Generation and Transmission: A Review," *Topics in Quantum Electronics*, vol. 22, Mar-Apr 2016.
- C. Kulesa, "Terahertz Spectroscopy for Astronomy: From Comets to Cosmology," *Journal of Terahertz Science and Technology*, vol. 1, pp. 232-240, Sep 2011.
- P. Kuzel and H. Nemec, "Terahertz conductivity in nanoscaled systems: effective medium theory," *Journal of Physics D-Applied Physics*, vol. 47, Sep 17 2014.
- M. Naftaly, "Metrology Issues and Solutions in THz Time-Domain Spectroscopy," *Sensors Journal*, vol. 13, Jan 2013.
- F. Yang, *et al.*, "Uncertainty in Terahertz Time-Domain Spectroscopy Measurements," *Millimeter and Terahertz Waves*, vol. 38, pp. 229-247, Feb 2017.

Acknowledgements

This work was co-funded by the Army Research Office (ARO) and the Air Force Office of Scientific Research (AFOSR) Grant W911NF-15-1-0297

excitation with wavelengths of $\lambda=302\text{nm}$ and $\lambda=365\text{nm}$.

Introduction

- Carbon QDs stand out from their semiconductor counterparts due to their biocompatibility and prospective application in biosensing, bioimaging, electro-optical and photonic materials, energy harvesting, and others[1].
- Terahertz Time-Domain spectroscopy (THz-TDS) has proven to be a powerful technique to characterize substances in the frequency domain from 30 GHz to 10 THz and its applications ranges from characterization of chemical substances[2] and quality control[3] to contributions in communications [4], and in terms of size extends from galactic to nanoscale systems[5,6].
- Additionally, THz frequencies are also compatible with cellular telephone devices and are anticipated to be able to enhance the performance of other structures including laser diodes, semiconductor optical amplifiers and infrared detectors[7]

Determination of the optical constants

The transmission through the cuvette will be

$$\tilde{T}_{cuv,0} = \frac{\tilde{E}_{cuv,0}(\omega)}{\tilde{E}_{air,0}(\omega)} = \frac{16\tilde{n}_{air,0}(\omega)\tilde{n}_{cuv,0}(\omega)}{(\tilde{n}_{air,0}(\omega) + \tilde{n}_{cuv,0}(\omega))^4} e^{-2i\frac{\omega d}{c}(\tilde{n}_{cuv,0}(\omega) - \tilde{n}_{air,0}(\omega))}$$

Similarly, the transmission of the cuvette and the sample

$$\begin{aligned}\tilde{T}_{sam,0} &= \frac{\tilde{E}_{sam,0}(\omega)}{\tilde{E}_{cuv,0}(\omega)} \\ &= \frac{\tilde{n}_{sam,0}(\omega)}{\tilde{n}_{air,0}(\omega)} \frac{(\tilde{n}_{sam,0} + \tilde{n}_{air,0})^2}{(\tilde{n}_{sam,0} + \tilde{n}_{cuv,0})^2} e^{-i\frac{\omega s}{c}(\tilde{n}_{sam,0}(\omega) - \tilde{n}_{air,0}(\omega))}\end{aligned}$$

Terahertz Characterization of Carbon Quantum Dots

The optical parameters of the material are those that satisfy the equations

$$\tilde{T}_{cuv,\lambda}(\omega) = \frac{\tilde{E}_{cuv,\lambda Exp}(\omega)}{\tilde{E}_{air,\lambda Exp}(\omega)}$$

$$\tilde{T}_{sam,\lambda}(\omega) = \frac{\tilde{E}_{sam,\lambda Exp}(\omega)}{\tilde{E}_{cuv,\lambda Exp}(\omega)}$$

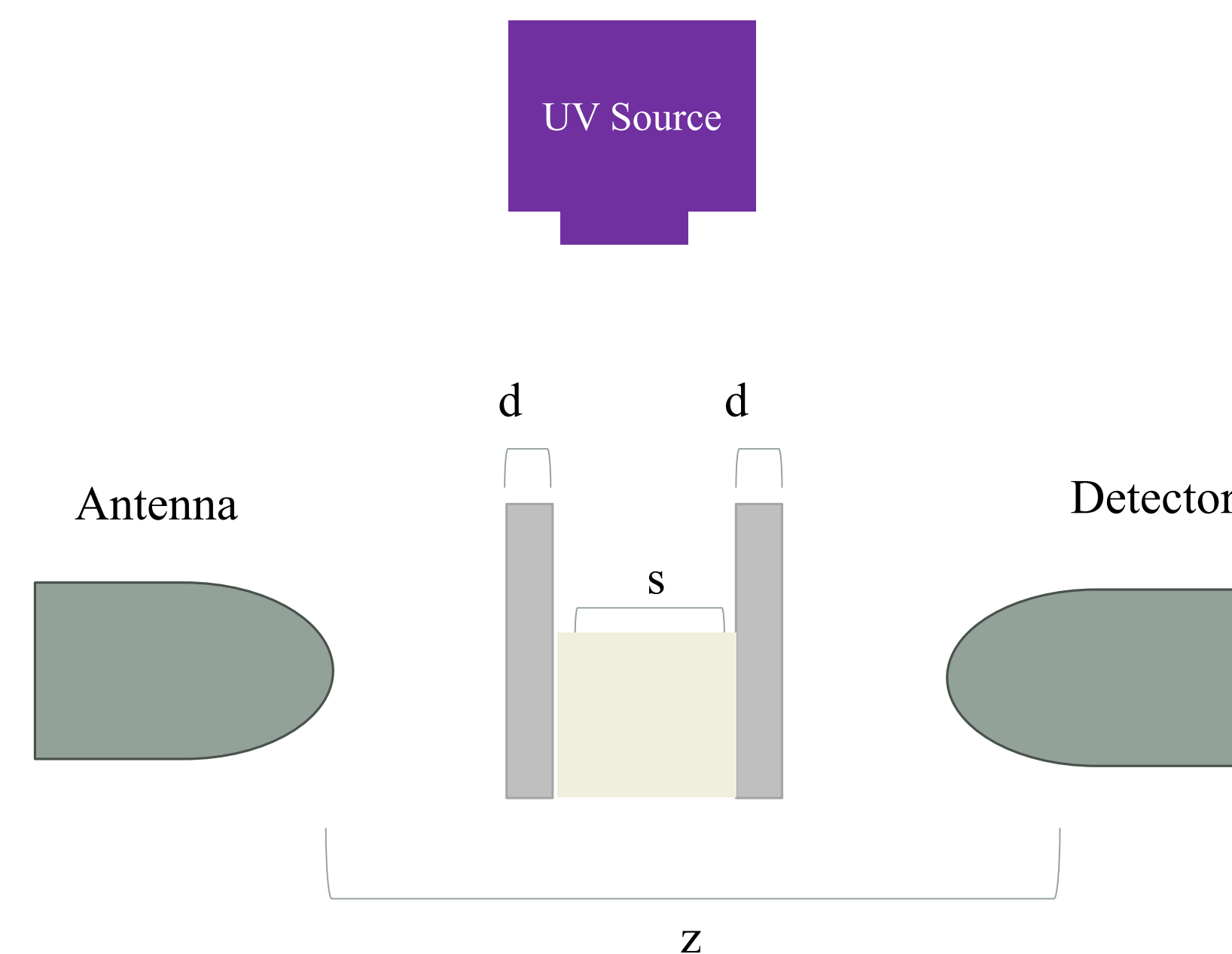
Once we obtain the complex index of refraction, the permittivity is easily calculated

$$\tilde{\epsilon} = \tilde{n}^2$$

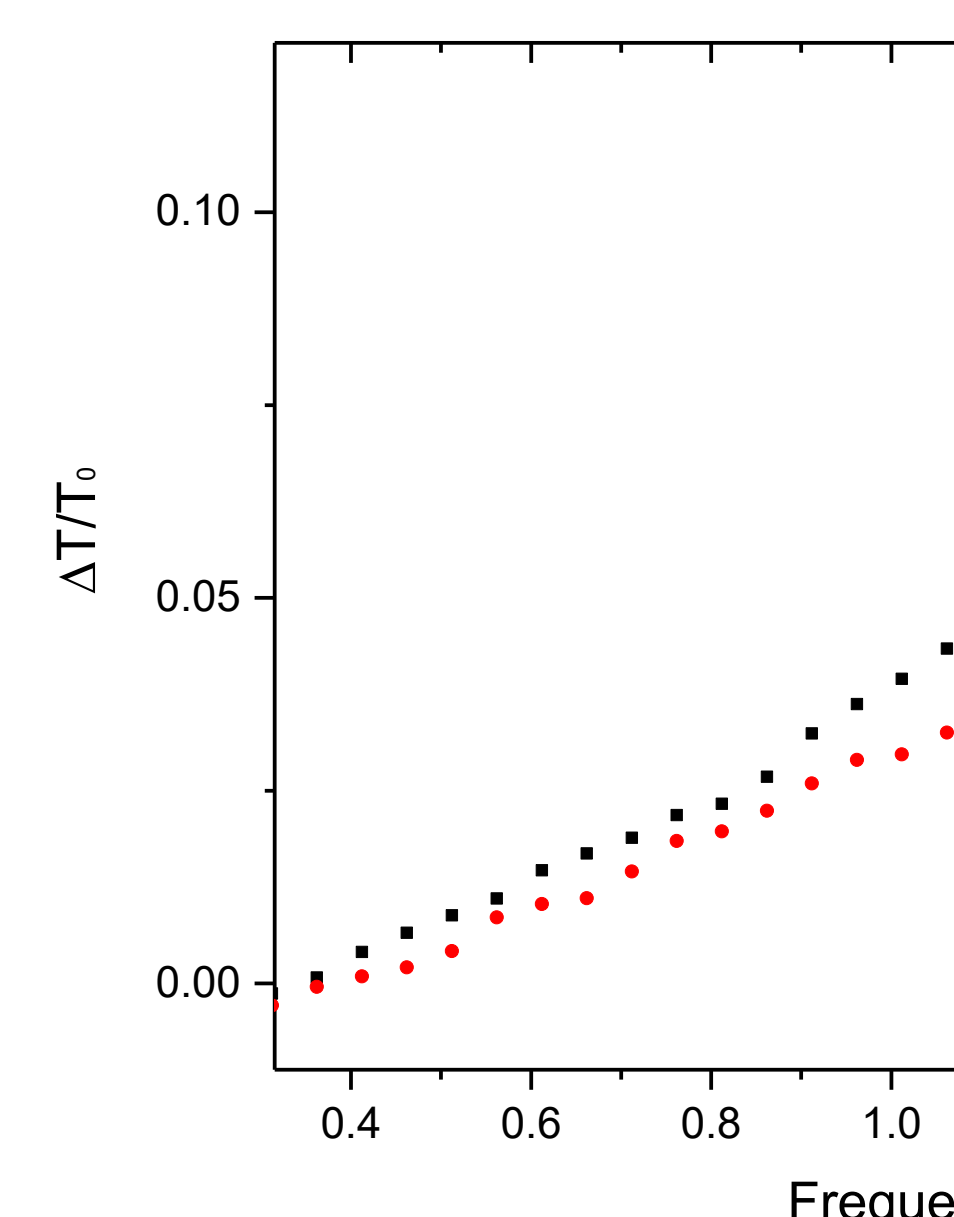
The change in the conductivity upon photoexcitation is given by

$$\Delta\sigma = -i\omega\epsilon_0\Delta\epsilon(\omega)$$

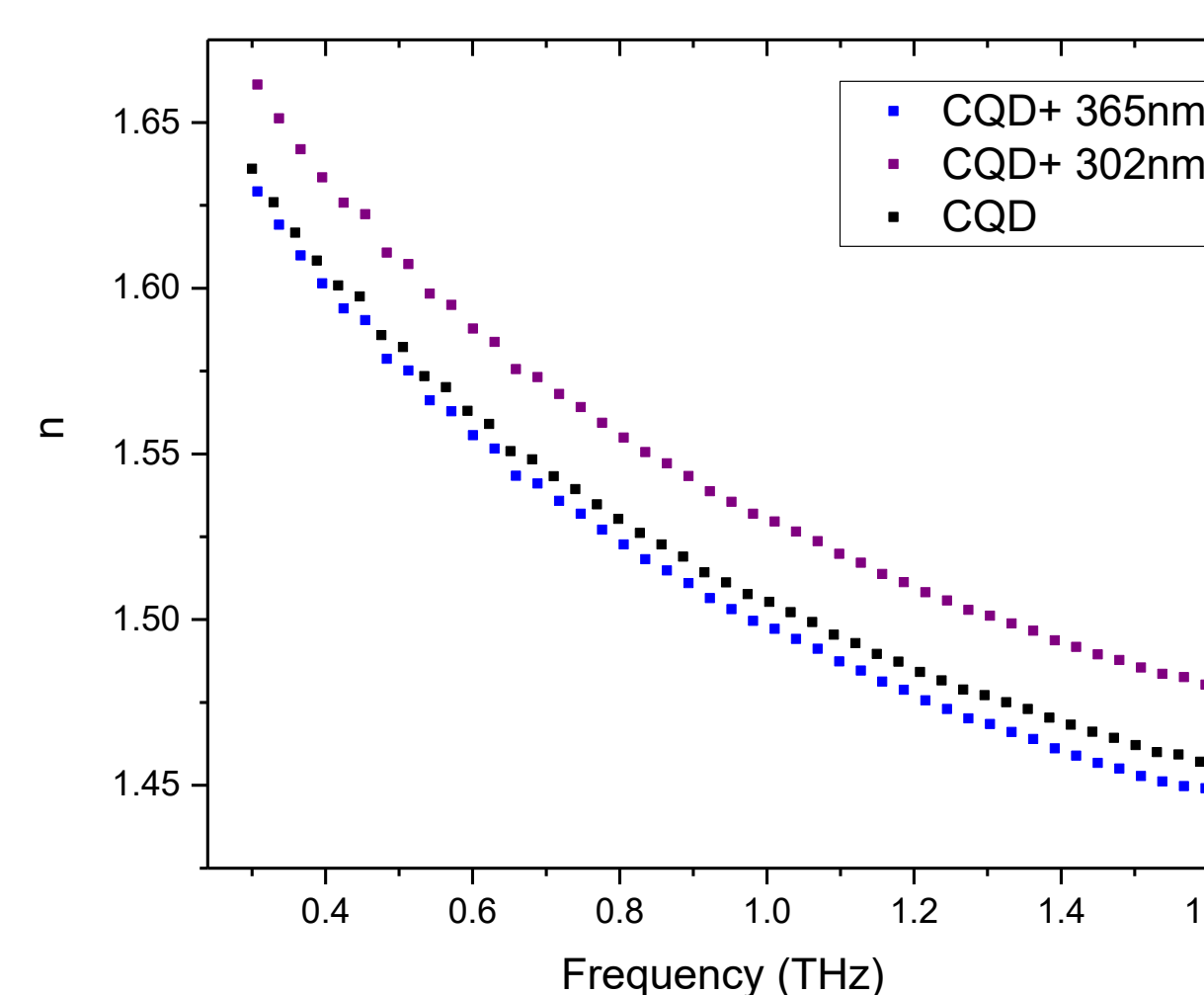
- Carbon Quantum Dots were synthesized following an alkali-assisted electrochemical fabrication method and the size were tailored by varying the applied current.



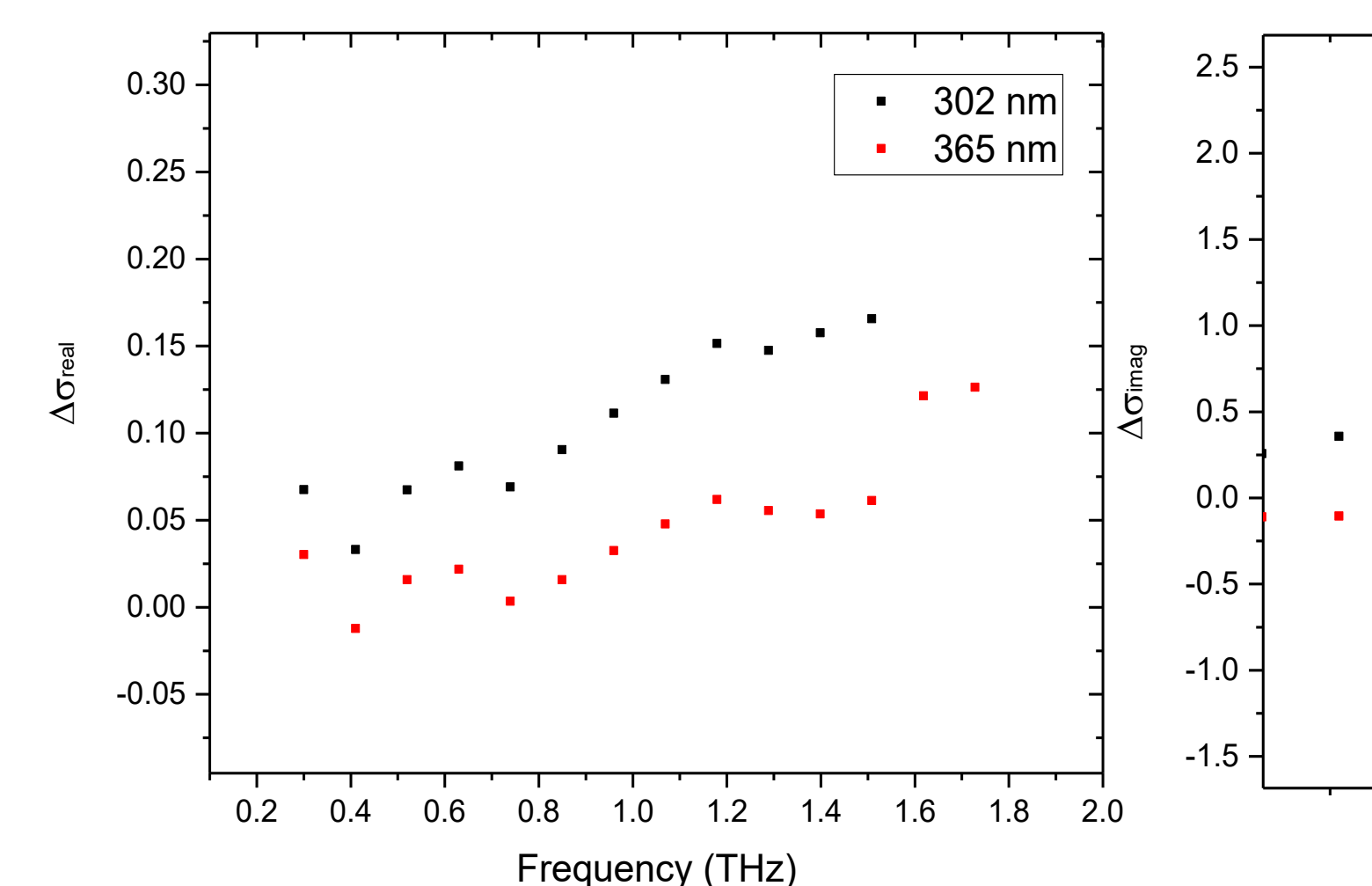
Sketch of a typical THz-TDS setup



A modulation of around 5% in the transmission is achieved by illuminating the sample with UV light.



Index of refraction of Carbon quantum dots, diluted in ethanol at different UV excitations.



Real and imaginary parts of the change of conductivity at different frequencies.

Conclusions

- Carbon Quantum Dots were characterized for Terahertz frequencies, employing Time-Domain spectroscopy.
- We demonstrated a shift in the real part of the index of refraction as a response of UV excitation
- It was shown the modulation potential of around 5% in Transmission and 15% in photoconductivity at 1 THz.
- We speculate that the modulation is related to a polarization of the nanoparticles, although further investigation is required.

References

- 1) Jelinek, R. (2016). *Carbon Quantum Dots: Synthesis, Properties and Applications*. Springer, pp. 1-10.
- 2) S. Wietzke, *et al.*, "Terahertz imaging: a new non-destructive technique for the detection of plastic weld joints," *Journal of the European Optical Society-Rapid Communications*, vol. 1, pp. 293-300, Sep 2011.
- 3) A. Barh, *et al.*, "Specialty Fibers for Terahertz Generation and Transmission," *Journal of Selected Topics in Quantum Electronics*, vol. 22, Mar-Apr 2016.
- 4) C. Kulesa, "Terahertz Spectroscopy for Astronomy: From Comets to Planets," *Transactions on Terahertz Science and Technology*, vol. 1, pp. 232-240, 2011.
- 5) P. Kuzel and H. Nemec, "Terahertz conductivity in nanoscaled systems: a review," *Journal of Physics D-Applied Physics*, vol. 47, Sep 17 2014.
- 6) M. Amelia, C. Lincheneau, S. Silvi, A. Credi, *Chemical Society Reviews*, vol. 45, pp. 5743-5760, 2016.

Acknowledgements

This work was co-funded by the Army Research Office (ARO) and the Air Force Office of Scientific Research (AFOSR) Grant W911NF-15-1-0297

Important notes:

Do **NOT** write outside the grey boxes. Any text or images outside the boxes **will** be deleted.

Do **NOT** alter the structure of this form. Simply enter your information into the boxes. The form will be automatically processed – if you alter its structure your submission will not be processed correctly.

Do not include keywords – you can add them when you submit the abstract online.

Title:

Determination of the Optical Properties under UV excitation of Carbon Quantum Dots in the Terahertz Regime

Authors & affiliations:

Juan Adrian Zepeda-Galvez¹, Clarissa D. Vazquez-Colon¹, Daniel Shreiber² and Arturo A. Ayon¹
¹University of Texas at San Antonio, USA; ²US Army Research Laboratory, Aberdeen Proving Ground, USA

Juanadrian.zepeda-galvez@utsa.edu

Abstract: (Your abstract must use **Normal style** and must fit in this box. Your abstract should be no longer than 300 words. The box will 'expand' over 2 pages as you add text/diagrams into it.)

Preparation of Your Abstract

1. The title should be as brief as possible but long enough to indicate clearly the nature of the study. Capitalise the first letter of the first word ONLY (place names excluded). No full stop at the end.

2. Abstracts should state briefly and clearly the purpose, methods, results and conclusions of the work.

Introduction: Clearly state the purpose of the abstract

Methods: Describe your selection of observations or experimental subjects clearly

Results: Present your results in a logical sequence in text, tables and illustrations

Discussion: Emphasize new and important aspects of the study and conclusions that are drawn from them

The tuneable fluorescent properties of Quantum Dots (QDs) have inspired numerous research efforts as well as scientific reports in the past decade. The key features that make Carbon QDs particularly attractive are their nontoxicity and abundance. In fact, carbon is one of the components of living tissue itself, thereby allowing its consideration for utilization in areas where toxicity represents a significant risk, for instance invasive applications. Part of the interest in the utilization of the THz regime lies in the fact that these are non-ionizing frequencies, thus there is a potential application in bio-compatible electronics devices. Additionally, THz frequencies are also compatible with cellular telephone devices and are anticipated to be able to enhance the performance of other structures including laser diodes, semiconductor optical amplifiers and infrared detectors.

To obtain the THz spectra, a commercial THz Time-Domain Spectrometer was employed. Fig 1 shows a schematic of the setup chosen for the experiments. Utilizing THz-Time Domain Spectra in combination with Fast Fourier Transformations (FFT), the dielectric functions of the colloidal Carbon Quantum Dots and the solvent were obtained. Once these quantities were known, we extracted the dielectric function of the nanoparticles making use of the Landau-Lifshitz-Looyenga dielectric mixture expression, which relates the cubic root of the dielectric function of the solution to the cubic root of the dielectric function of the solute and the solvent, weighted by their concentrations. We also employed Quartz Crystal Microgravimetry (QCM) to determine the nanoparticle concentration in the colloidal solution.

Fig 2 shows the index of refraction of the Carbon quantum Dots with and without UV light. As observed, the refracted index is affected by UV excitation with wavelengths of 302nm and 365 nm. This result demonstrates that the optical properties refraction can be tuned by the application of an external UV excitation.

We anticipate the ability to tailor the properties of carbon quantum dots employing UV excitation will prove crucial in the demonstration of reconfigurable devices operating at THz frequencies.

Important notes:

Do **NOT** write outside the grey boxes. Any text or images outside the boxes **will** be deleted.

Do **NOT** alter the structure of this form. Simply enter your information into the boxes. The form will be automatically processed – if you alter its structure your submission will not be processed correctly.

Do not include keywords – you can add them when you submit the abstract online.

