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Major Goals: We propose to initiate a novel approach to studies of ultrafast laser induced high density carrier excitations in semiconductors. This research direction provides a path leading to highly localized transient as well as in some cases, permanent materials modification at an arbitrary depth. Exploring these ultrafast dynamical phenomena at the quantum level is critical for further advances in modern nanoscience. The proposed approach to laser oriented materials science goes beyond traditional investigations of optical properties and provides the means to characterize and manipulate matter in a spatially and temporally localized manner with nanometer scale accuracy far from equilibrium. Material modifications are created by localized high density excited carriers arising from a coupling between photons and coherent acoustic phonons (CAP). These studies are based on the recognition that the semiconductor band gap is transiently narrowed by the CAP wave traveling through the material. This allows highly spatially localized electronic excitation arising from photon absorption at a desired depth by properly timed laser pulses with photon energies just below the equilibrium band-gap. The ensuing femtosecond timescale dynamical excitation and relaxation processes at an arbitrary depth in the bulk of the semiconductor will be monitored using ultrafast laser pump-probe techniques, which will be no longer limited simply to measurements of material surfaces and static interfaces. The primary goal of the proposed research is to develop a theoretical and experimental understanding of these novel dynamical processes that ultimately promise to lead to the fabrication of nanometer-scale heterostructures at arbitrary depths.
The proposal is divided into three phases: (1) demonstration and characterization of localized electronic excitations at an arbitrary depth utilizing CAP spectroscopy, (2) basic studies of energy flow and relaxation dynamics of transient, highly localized excited carriers at a given depth including the effect of defects, dopants, and strain using ultrafast pump-probe techniques, and (3) studies of dynamical processes leading to permanent modification, and in situ characterization of permanently modified regions by pump-probe techniques and CAP spectroscopy. In this proposal, we explore states of matter, both transient and permanent, unobtainable by conventional methods. This pump-probe class of measurements will provide new insight into the fundamental mechanisms that control carrier relaxation and band gap modification in the transiently altered region in the host semiconductor material. In addition to its fundamental value, this research is envisioned to be widely useful and transformative in electronic and optoelectronic device applications well beyond planar technology. Indeed, the implications of this research direction are revolutionary. This approach constitutes a method to excite and ultimately pattern materials at any desired depth. This project is made possible by the use of a state of the art laser system recently acquired as a result of a DURIP award through ARO. These studies are intended not only to produce valuable scientific results, but also to substantially advance the field of nanoscale materials design consonant with the goals of the Materials Science Division of the Army Research Office.
The following experimental goals have been identified:

- Given the localized electronic excitations at an arbitrary depth as described above, detect its presence and confirm its actual depth using CAP spectroscopy.
- For these depth dependent localized excitations, use ultrafast pump-probe approaches to assess carrier decay rates, often determined by carrier-phonon interactions in the modified solid, leading to a basic understanding of the relaxation dynamics energy flow processes in the examined systems in the bulk.
- Introduce defects, stress and impurities into the system to experimentally determine how this affects the measured relaxation dynamics.
- Identify a system amenable to permanent modification, use pump-probe experiments to determine carrier and phonon decay rates leading to the permanent modification.
- Finally, use the CAP technique and other materials probes such as TEM, to characterize the permanently modified materials at a specific depth.

Accomplishments: In this final report, we present work relating to the main research thrusts supported by ARO under award W911NF-14-1-0290.
The first area of our research employs the depth-dependent coherent acoustic phonons spectroscopy, along with properly timed ultrashort photon pulses, to produce transient and localized atomic level conditions unachievable by any other means. In turn, it reveals new insights into the rates and pathways of vibrational and electronic energy flow in non-ground state condensed matter well beyond the surface. This is critical for understanding dynamical processes in solids involving electronic, optical and thermally stimulated defect and impurity reactions and migrations. The ability to directly probe these pathways and rates will stimulate theory and scaling laws for forms of matter previously unattainable. This research addresses issues of energy transfer and dissipation in solids far from equilibrium, of fundamental importance to our understanding of solid-state properties critical to energy related applications.
We showed the ability of our amplified ultrafast laser system combined with two optical parametric amplifiers to produce two CAP pulses that were send at the desired time delay/depth in a specimen. It opens opportunity for transient modification of materials using ultrafast non-degenerative experiment.
The second area of our interest covers the examination of ion implanted GaAs (direct semiconductior), SiC (indirect semiconductor), and diamond by time-domain Brillouin scattering. We have discussed recent advances in the depth profiling of optical and optoelastic properties the above mentioned specimens. The TDBS is an all optical non-destructive technique. The different optical properties obtained by TDBS can be directly related to the structural damage, and when compared to RBS/Channeling, TDBS is two orders of magnitude more sensitive.
We showed the review of TDBS applications to the study of ion-matter interactions is clearly advantageous in ion beam experiments over a wide range of ion fluences, in particular, where highly sensitive characterization cannot be accomplished by other means.
The third area of focus is a project where we studied differential transmission of graphene. We have investigated ultrafast carrier-phonon relaxation graphene dynamics using transmission pump-probe technique in the range of pump fluences that show distinct regimes of the relaxation dynamics. The main result is the observation of 10 fold faster 5 decay of the differential transmission at medium pump fluences as compared to low and high fluences. Moreover, the nature of the transmission dynamics switches from bi-exponential to single exponential decay. We further conjecture that at the critical value of the excited carrier density the hot phonon bottleneck is mitigated.
Our experimental results show the new observation in the ultrafast dynamics of supported graphene and are of importance for design of more efficient graphene based optoelectronic devices.
The fourth topic of this project is devoted to ultrafast studies of the stimulation of diamond growth on Si substrates at low temperatures. We demonstrated that prior irradiation of a silicon substrate surface with high-power ultrafast laser radiation can be used as a uniquely effective pretreatment to promote nucleation and growth at only predefined locations on the sample. It was also shown that this novel pretreatment technique allows for high-quality diamond film formation to occur on the Si substrate at significantly reduced temperatures.
Clearly, we have shown that in situ laser pretreatment exposure above a laser power damage threshold dramatically enhances diamond nucleation, growth and quality, at low-temperatures as confirmed by SEM microscopy and Raman spectroscopy.
The fifth area of our interest covers the examination of GaP using TDBS technique.
Knowledge of the spectral dependence of the photoelastic response is important both from a fundamental point of view and for applications. Particularly, it is relevant to nanoscale imaging using TDBS, where one would want to optimize and choose a probe wavelength leading to higher amplitude of Brillouin oscillations and, consequently, larger signal-to-noise ratio. We have investigated the photoelastic response of GaP as probed by time-domain Brillouin scattering. The results show order of magnitude changes in the amplitude of Brillouin oscillations with respect to probe energy which is maximized near direct optical transitions. Calculations based on the developed theoretical model are in good agreement with experimental data. The results obtained in this paper are of importance to the understanding of detection mechanisms of coherent acoustic phonons in indirect band gap

semiconductors and GaP based optoelectronic devices. Information obtained from these types of studies can be used for optimizing the optical response for a wide variety of materials.
The sixth topic covers systematic studies on the influence of doping in GaAs on Brillouin oscillations using time domain Brillouin scattering. The amplitude of Brillouin oscillations changes with respect to dopant concentration while the change in their frequency is negligible. our results indicate that TDBS can be used to measure dopant concentrations but more importantly they pave the way to measure specific dopant concentration as a function of depth.
We have provided a proof-of-principle demonstration that CAP wave can allow us to accurately measure depth-dependent optical and optoelastic constants in a way not possible by any other technique. The above points provide a roadmap for making the technique a competitive characterization method, with great potential for industrial application.
This new approach constitutes a totally new approach to measure any strain, dopants, impurities, interfaces and interfacial strain arising from lattice deformation as a function of depth. This is a capability that is of great importance to the semiconductor device community as it provides a means of in-situ quality control.

Training Opportunities: During the period of this grant four graduate students were trained to effectively carry out the experiments required to accomplish the goals of our ARO supported projects. The names of the graduate students are:
-Andrey Baydin, graduate student
-Rustam Gatamov, graduate student
-Adam Dodson, graduate student
-Hongrui Wu, graduate student

During the period covered by our ARO grant. Rustam Gatamov and Andrey Baydin graduated and received PhD degree. Andrey Baydin remained in our group as a postdoctoral fellow.

Results Dissemination: During the period of the grant, the list of publications are shown below:
1. R. Gatamov, A. Baydin, H. Krzyzanowska, N. Tolk, “Fluence and wavelength dependent ultrafast differential transmission dynamics in graphene” Materials Research Express 7, 095601, 2020.
2. K. Hallman, K. Miller, A. Baydin, S. Weiss, N. Tolk, R. Haglund, Jr. “Ultrafast switching of 1550 nm pulses in a hybrid VO2 silicon waveguide” Advanced Optical Materials 9 (4), 2001721 2020.
3. A. Baydin, R. Gatamov, H. Krzyzanowska, C.J. Stanton, and N. Tolk “Energy-dependent am-plitude of Brillouin oscillations in GaP” Phys. Rev. B 99, 165202, 2019.
4. A. Baydin, H. Krzyzanowska, L. Feldman, and N. Tolk “Post-implantation depth profiling usingtime-domain Brillouin scattering” Nucl. Instrum. Meth. B 440, 36, 2019.
5. A. Dodson, A. Baydin, H. Wu, H. Krzyzanowska, N. Tolk, “Influence of doping level on Brillouin oscillations in GaAs” Physical Review Applied, 12 (5), 054006, 2019
6. H. Krzy?anowska, W. Paxton, M. Yilmaz, A. Mayo, J. Kozub, M. Howel, J. Gregory, J. Butler, W. Poo Kang, R. Mu, J. Davidson, and N. Tolk,” Low temperature diamond growth arising from ultrafast pulsed-laser,” submitted to Carbon 131 (2018) 120-126; https://doi.org/10.1016/j.carbon.2018.01.083
7. A. Baydin, H. Krzyzanowska, R. Gatamov, J. Garnett, N. Tolk, "The photoelastic coefficient P12 of H+ implanted GaAs as a function of defect density", Scientific Reports 7 (2017) 15150; DOI:10.1038/s41598-017-14903-x
8. A Baydin, V Henner, G Sumanasekera, “Mechanisms of fast coherent magnetization inversion in ferronanomagnets”, Journal of Magnetism and Magnetic Materials 441, 604-608, 2017

During the period of the grant, the list of invited and oral presentations are shown below:

1. A. Baydin, “Depth dependent modification of optical constants arising from H+ implantation in n-type 4H-SiC measured using coherent acoustic phonons”, 63rd AVS international exhibition and symposium, 2016, Nashville, TN
2. N. Tolk NSF CAREER review panel, Alexandria, VA, October 22-24, 2017
3. N. Tolk, Invited Talk “Graphene and the Path to Commercialization” Graphene Innovation Summit and Expo, October 29-31, 2017, Nashville Tennessee
4. N. Tolk, Invited Talk, “Depth-Dependent Studies of Electron and Phonon Ultrafast Dynamics in Femtosecond Laser Induced Transient States of Matter” ULTRAFAST DYNAMICS AND METASTABILITY WORKSHOP, Georgetown University, Washington D.C., 13 - 15 November 2017
5. N. Tolk, Invited Talk, “Depth-Dependent Studies of Electron and Phonon Ultrafast Dynamics in Femtosecond Laser Induced Transient States of Matter”, SPIE CONFERENCE-ULTRAFAST BANDGAP PHOTONICS III, Gaylord Palms Resort & Convention Center, Orlando, Florida United States, 15 - 19 April 2018
6. N. Tolk, Two Invited Talks, “Studies of Ultra-Fast Phonon/Carrier Dynamics and E-Field Induced Second Harmonic Generation” Part I and Part II, EPIOPTICS 12, International School of Solid State Physics Erice, Sicily, Italy, 24-29 July 2018
7. H. Krzyzanowska, Invited/Colloquium, Department of Physics, University of Alabama in Huntsville, March 6th, 2018 Towards a Si-based laser efficient infrared emission from Er-doped SiO2/nc-Si multilayers,
8. H. Krzyzanowska, Invited Talk, Efficient infrared emission from Er-doped SiO2/nc-Si multilayers for all-silicon on chip application, Energy Materials Nanotechnology (EMN) Greece Meeting 2018, May 14-18, 2018 Heraklion, Greece
9. H. Krzyzanowska, A. Baydin, L. C. Feldman, N. H. Tolk, Invited Talk, Depth dependent optical and elasto-optical effects of ion implantion studied by time-domain Brillouin scattering, XII-th International Conference ION IMPLANTATION AND OTHER APPLICATIONS OF IONS AND ELECTRONS, Kazimierz Dolny, Poland, June 18-21, 2018,
10. A. Wolska, H. Krzy?anowska, M. T. Klepka, Poster presentation, EXAFS and photoluminescence study on the Er-doped SiO2/nc-Si multilayers 17th International Conference on X-ray Absorption Fine Structure XAFS 2018, 22–27 July 2018 in Kraków, Poland
11. N. Tolk, Invited Talk, “The Interaction of Directed Energy Beams of Ultrafast-Laser Photon Pulses with Material Systems”, Army Futures Command Meeting, Vanderbilt University, Nashville TN, United States, 19 December, 2018
12. A. Baydin, Apr 2019 “Depth-dependent studies of electron and phonon ultrafast dynamics in femtosecond laser-induced transient states of matter” invited talk at International Symposium on Ultrafast Dynamics and Metastability & Ultrafast Bandgap Photonics, Georgetown University, Washington, DC
13. A. Baydin, Mar 2019“Optoacoustic spectrum of GaP: experiment and theory” contributed talk at APS March Meeting, Boston, MA
14. A. Baydin, Feb 2019“Ultrafast hot carrier and phonon dynamics in supported graphene” contributed talk at

SPIE Photonics West, San Francisco, CA
15. A. Baydin, Workshop; Mar 2019 The 2019 GERA Energy Research Workshop at March Meeting, Boston, MA (selective)

Honors and Awards: Ph. D. Defenses
1. Rustam Gatamov, Ultrafast pump-probe fluence and wavelength dependent relaxation dynamics in graphene, December 8, 2020.
2. Andery Baydin, Depth Dependent Optical and Elastooptical Effects of Ion Implantation Studied by Time-domain Brillouin Scattering", March 21, 2018,

Awards:
- A. Dodson, University Graduate Fellowship - Akunuri V. Ramayya Award Russell G. Hamilton Scholar, 2020
- A. Baydin, Travel Grant (Vanderbilt University Graduate School) Jan 2018 (APS March Meeting 2018, Los Angeles, CA)
- DOE BES travel grant for IBMM 2018 conference June 2018 (IBMM 2018, San Antonio, Texas)

Protocol Activity Status:

Technology Transfer: Patent:
1. Z. Jarrahi, N. Tolk, J. Bers, J. Davidson, H. Krzyzanowska, A. Baydin; “Direct Growth and High Resolution Patterning of Graphene on Ultra nanoCrystalline Diamond (UNCD) using Lasers, Invention Disclosure, U.S. Patent and Trademark Office Jan 28, 2018 (S/N 62/623,294)

PARTICIPANTS:

Participant Type: PD/PI
Participant: Norman H. Tolk
Person Months Worked: 3.00 **Funding Support:**
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Participant Type: Co PD/PI
Participant: Halina Krzyzanowska
Person Months Worked: 12.00 **Funding Support:**
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Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Andrey Baydin
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Rustam Gatamov
Person Months Worked: 6.00 **Funding Support:**
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Participant Type: Graduate Student (research assistant)

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Participant: Hongrui Wu
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Article Title: Post-implantation depth profiling using time-domain Brillouin scattering
Authors: Andrey Baydin, Halina Krzyzanowska, Leonard Feldman, Norman Tolk
Keywords: Ion implantation, GaAs, SiC, Diamond, Depth profiles, Refractive index, Photoelastic coefficient, Optical properties, Time domain Brillouin scattering
Abstract: The unique capabilities of time domain Brillouin scattering (TDBS) for studying post-implantation effects on optical and opto-elastic properties of semiconductors are discussed. This method utilizes coherent acoustic phonons to measure depth-dependent optical and opto-elastic changes arising from structural damage caused by ion implantation. This non-destructive technique is shown to be two orders of magnitude more sensitive than Rutherford backscattering spectrometry. Results are presented for silicon carbide (SiC), gallium arsenide (GaAs) and diamond. Using the TDBS approach, we have obtained depth-dependent profiles of the complex refractive index in hydrogen implanted 4H-SiC, and of the photoelastic coefficient in hydrogen implanted GaAs. In helium implanted diamond samples, both the complex refractive index and the photoelastic coefficient have been determined. A comparison between indirect (4H-SiC, diamond) and direct (GaAs) band gap semiconductors shows the sensitivity of TDBS t
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Article Title: Low temperature diamond growth arising from ultrafast pulsed-laser pretreatment
Authors: Halina Krzy?anowska, William F. Paxton, Mesut Yilmaz, Anthony Mayo, John Kozub, Mick Howell, Justi
Keywords: Diamond, Diamond-like coatings
Abstract: At temperatures significantly lower than normal growth temperatures using the hot filament chemical vapor diamond deposition approach, we have observed growth of high quality diamond films resulting from the application of in situ ultrafast pulsed-laser irradiation as a pretreatment step, on a conventionally abraided Si substrate surface. Low-temperature growth is seen to occur only where the sample was pretreated by laser irradiation. This effect is correlated with the formation, above a particular laser fluence threshold, of laser induced periodic nanostructures on the silicon substrate surface, with characteristic lengths significantly less than the laser wavelength, l. The origin of these previously observed features will be discussed. Diamond growth samples were characterized using scanning electron microscopy and micro-Raman spectroscopy. This work strongly indicates that appropriate ultrafast-laser pretreatment shows promise as a means of promoting high-quality low-temperature C
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Article Title: Influence of Doping Level on Brillouin Oscillations in
Authors: Adam Dodson, Andrey Baydin, Hongrui Wu, Halina Krzyzanowska, Norman Tolk
Keywords: molecular beam epitaxy, Time-domain Brillouin scattering (TDBS)
Abstract: Time-domain Brillouin scattering is a unique tool for determining depth-dependent material properties. Here, we show the influence of doping level in GaAs on Brillouin oscillations. Measurements are performed on intrinsic, n-type, and p-type GaAs samples. The results show high sensitivity of the amplitude of Brillouin oscillations to the doping concentration. Theoretical calculations are in good agreement with experimental data. This work provides an insight into specific dopant profiling as a function of depth.
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Article Title: Energy-dependent amplitude of Brillouin oscillations in GaP
Authors: Andrey Baydin, Rustam Gatamov, Halina Krzyzanowska, Christopher J. Stanton, Norman Tolk
Keywords: photoelastic response of GaP as probed by time-domain Brillouin scattering
Abstract: Gallium phosphide is an important indirect band gap material with a variety of applications in optics ranging from LEDs to applications in GaP/Si based solar cells. We investigated GaP using ultrafast, pump-probe coherent acoustic phonon spectroscopy (time-domain Brillouin scattering). We measured the dependence of the amplitude of the differential reflectivity as modulated by coherent acoustic phonons (CAPs) as a function of laser probe energy and found that the amplitude of the coherent phonon oscillations varies nonmonotonically near the direct gap transition at the G point. A theoretical model is developed which quantitatively explains the experimental data and shows that one can use coherent phonon spectroscopy to provide detailed information about the electronic structure, the dielectric function, and optical transitions in indirect band gap materials. Our calculations show that the modeling of experimental results is extremely sensitive to the wavelength dependent dielectric fun
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Article Title: The photoelastic coefficient $${P}_{12}$$P12 of H+ implanted GaAs as a function of defect density
Authors: Andrey Baydin, Halina Krzyzanowska, Rustam Gatamov, Joy Garnett, Norman Tolk
Keywords: photoelastic effect describing coupling between light and sound
Abstract: The photoelastic phenomenon has been widely investigated as a fundamental elastooptical property of solids. This effect has been applied extensively to study stress distribution in lattice-mismatched semiconductor heterostructures. GaAs based optoelectronic devices (e.g. solar cells, modulators, detectors, and diodes) used in space probes are subject to damage arising from energetic proton (H+) irradiation. For that reason, the effect of proton irradiation on photoelastic coefficients of GaAs is of primary importance to space applied optoelectronics. However, there yet remains a lack of systematic studies of energetic proton induced changes in the photoelastic properties of bulk GaAs. In this work, the H+ energy and fluence chosen for GaAs implantation are similar to that of protons originating from the radiation belts and solar flares. We present the depth-dependent photoelastic coefficient P12 profile in non-annealed H+ implanted GaAs obtained from the analysis of the time-domain Bri
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Partners

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I certify that the information in the report is complete and accurate:
Signature: Norman H Tolk
Signature Date: 10/22/21 12:41PM

Final Report

September 15-th, 2017 – December 14-th, 2020

Depth-Dependent Transient and Permanent Materials Modification Arising from Ultrafast Laser Induced Carrier and Phonon Excitations

Norman Tolk, PI

Halina Krzyzanowska, co-PI

Andrey Baydin, postdoctoral fellow

Rustam Gatamov, graduate student

Adam Dodson, graduate student

Hongrui Wu, graduate student

Table of Contents

1. Abstract

The Final Report of the Depth-Dependent Transient and Permanent Materials Modification Arising from Ultrafast Laser Induced Carrier and Phonon Excitations Project shows our activity in 6 research areas.

Topic 1

The first topic is related to depth-dependent transient materials modification arising from ultrafast laser induced carrier and phonon excitations.

The major scientific objective of this research is to experimentally demonstrate and subsequently characterize ultrafast laser induced spatially localized transient states in the materials of interest. Implementing this program requires utilizing the concept of transient modification (narrowing/broadening) of the band gap in host materials by ultrafast laser-induced transient strain pulse (CAP), followed by intense ultrafast photo-excitation pulse at appropriate wavelengths to locally, at a specific depth, excite carriers in the material. Central to our approach is the creation of a propagating coherent acoustic wave, which locally alters the host material and in particular results in a spatial and temporally localized band-gap narrowing which, when coupled with properly timed excitation laser pulse, results in the desired transient state.

We employed a unique ultrafast optical probe system to test the ultrafast system for three beam experiment. We successfully created second CAP pulse after the desired time delay, which means the desired depth in a specimen.

Topic 2

The second area of our studies covers the unique capabilities of the time domain Brillouin scattering (TDBS) technique for studying post-implantation effects on optical and optoelastic properties of semiconductors.

This method utilizes coherent acoustic phonons to measure depth-dependent optical and optoelastic changes arising from structural damage caused by ion implantation. This non-destructive technique is shown to be two orders of magnitude more sensitive than Rutherford backscattering spectrometry. Results are presented for silicon carbide (SiC), gallium arsenide (GaAs) and diamond. Using the TDBS approach, we have obtained depth-dependent profiles of the complex refractive index in hydrogen implanted 4H-SiC, and of the photoelastic coefficient in hydrogen implanted GaAs. In the helium implanted diamond samples, both the complex refractive index and the photoelastic coefficient have been measured. A comparison between indirect (4H-SiC, diamond) and direct (GaAs) band gap semiconductors shows the sensitivity of TDBS to the particular optical properties of different semiconductors. These studies provide basic insight into the dependence of optical properties on defect densities created by ion implantation, which is of relevance to the fabrication photonic and optoelectronic devices. Further development of TDBS shows promise for measuring the depth dependent positioning of specific defects (color centers) in wide band gap semiconductors.

This work was published in Nuclear Instruments and Methods B **440**, 36 (2019).

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Topic 3

The third chapter of this report is focused on ultrafast pump-probe transmission studies of graphene.

Understanding the ultrafast carrier dynamics of graphene on a substrate is a fundamental step in the development of graphene based optoelectronic devices. Graphene is a single layer material of carbon atoms with high carrier mobility and unique optoelectronic properties which make it useful for a wide range of applications.

In this research, we study ultrafast carrier and phonon dynamics in CVD graphene on a quartz substrate using pump-probe spectroscopy in transmission geometry. We cover a range of pump fluences that allows us to observe probe dynamics governed by both intra- and interband transitions. At low pump fluences, after initial interband transition bleaching, the differential transmission crosses zero and becomes negative due to prevailing intraband absorption processes. At high pump fluences, the differential transmission always stays positive due to predominant interband transitions. The response at low and high fluences has already been observed and discussed in previous papers. To the best of our knowledge, there are no published papers showing or discussing the response of graphene at interm ediate pump fluences, when the type of response changes. More specifically, F. Kadi et al. [Kadi, F. et al. Microscopic description of intraband absorption in graphene: The occurrence of transient negative differential transmission. Phys. Rev. Lett. 113, 035502, DOI: 10.1103/PhysRevLett. 113.035502 (2014)] discusses microscopic description of intraband absorption in graphene. The paper microscopically explains the occurrence of transient negative differential transmission, i. e. a zero-crossing of the differential transmission at about 300 fs, by including intraband transitions to their model. The authors did not discuss or hypothesize about the fact that the interplay could lead to a faster relaxation at intermediate pump fluences. They did not do any calculations nor experiments in that direction. R. J. Suess et al. [Suess, R. J. et al. Role of transient reflection in graphene nonlinear infrared optics. ACS photonics 3, 1069 (2016)] demonstrates various responses of graphene depending on the pump fluence and explains them within the model of the inter- and intraband processes. Similar to our work, they also observe two qualitatively different responses of graphene. However, they do not discuss and do not show what happens when you use pump fluences, at which the ultrafast response changes from one type to another. Moreover, they say that “temperature at which the conductivity contributions from interband and intraband processes achieve parity was not reached in our experiment". The novelty of our work is to study the transition from intraband to interband dominated response of graphene. Therefore, our work completes the picture of the influence of inter- and intraband processes on the pump-probe response of graphene, if not theoretically, at least experimentally. Thus, at medium fluences, we observe an order of magnitude faster decay of the differential transmission that can be explained by the competitive interplay between intra- and interband transitions. In addition, we show that electron temperature relaxes approximately ten times longer than the differential transmission at these medium fluences.

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https://doi.org/10.1088/2053-1591/abb5f2

Topic 4

The fourth area of our interest is a project assessing to use ultrafast laser to stimulate diamond growth on silicon.

We have observed growth of high quality diamond films resulting from the application of in situ ultrafast pulsed-laser irradiation as a pretreatment step, on a conventionally abraided Si substrate surface. Low-temperature growth (temperatures significantly lower than 800^{o}C) is seen to occur only where the sample was pretreated by laser irradiation. This effect is correlated with the formation of laser induced periodic nanostructures on the silicon substrate surface, with characteristic lengths significantly less than the laser wavelength. Diamond growth samples were characterized using scanning electron microscopy and micro-Raman spectroscopy. This work strongly indicates that appropriate ultrafast-laser pretreatment shows promise as a means of promoting high-quality low-temperature CVD diamond growth in predetermined patterns, thus, demonstrating potential as a technique for the fabrication of diamond-based devices and selective diamond growth on semiconductor substrates.

This work was published in *Carbon* **131** (2018) 120.

https://doi.org/10.1016/j.carbon.2018.01.083

Topic 5

The fifth topic is related to both experimental and theoretical studied of gallium phosphide that is an important indirect band gap material with a variety of applications in optics ranging from LEDs to applications in GaP/Si based solar cells.

We investigated GaP using ultrafast, pump-probe coherent acoustic phonon spectroscopy (time-domain Brillouin scattering). We measured the dependence of the amplitude of the differential reflectivity as modulated by coherent acoustic phonons (CAPs) as a function of laser probe energy and found that the amplitude of the coherent phonon oscillations varies non-monotonically near the direct gap transition at the □ point. A theoretical model is developed which quantitatively explains the experimental data and shows that one can use coherent phonon spectroscopy to provide detailed information about the electronic structure, the dielectric function, and optical transitions in indirect band gap materials. Our calculations show that the modeling of experimental results is extremely sensitive to the wavelength dependent dielectric function and its derivatives.

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DOI: 10.1103/PhysRevB.99.165202

Topic 6

The fourth chapter of this report is focused on systematic ultrafast pump-probe reflection studies of the influence of doping level on Brillouin oscillations in GaAs.

Our studies show the influence of doping level in GaAs on Brillouin oscillations. The experiment was carried out at probe energies near the band gap of GaAs for three samples: intrinsic, n-type and p-type. The experimental results are also compared to theoretical calculations developed in the previous study. Previously published research on the influence of doping profiles on CAP detection and generation shows that the doping profile, the position of the interface between the differently doped regions and the thickness of the transition region can be determined. Contrary to that report, we investigate the probe energy region near the band gap of GaAs and show qualitatively different way of determining doping concentrations. Moreover, we discuss that TDBS can be sensitive both to the doping concentration and the type of doping.

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DOI: 10.1103/PhysRevApplied.12.054006

2. **Depth-dependent transient materials modification arising from ultrafast laser induced carrier and phonon excitations**

In the second phase of this proposal, we generate CAP waves in GaAs, which travel through the material with the attendant transient band gap narrowing. In order to generate 1% strain CAP waves, we have investigated the effect of the various transducer types and thicknesses on generation of the CAP waves. Although, the field of nonlinear picosecond ultrasonics is mature, no systematic studies have been made to date, especially, for thin transducer layers on GaAs. The sample examined in this phase was fabricated by Chris Palmstrom group from UC Santa Barbara. It consists of 1 μm GaAs layer deposited on a sapphire wafer and schematically is shown in Figure 1. Two different thicknesses of Ti and Al transducers have been deposited on the GaAs/sapphire sample.

Figure 2 shows change in reflectivity $\Delta R/R_0$, as a function of time delay, Δt, for Ti and Al at two different thicknesses. The change in reflectivity is representative of the strain profile. As it can be seen the shapes and amplitudes of the reflectivity data is different for different transducers. It is interesting that the pulses for 20 nm Ti and Al have the highest amplitude. The code to solve Korteweg de Vries equation explain nonlinear propagation of acoustic waves is being developed.

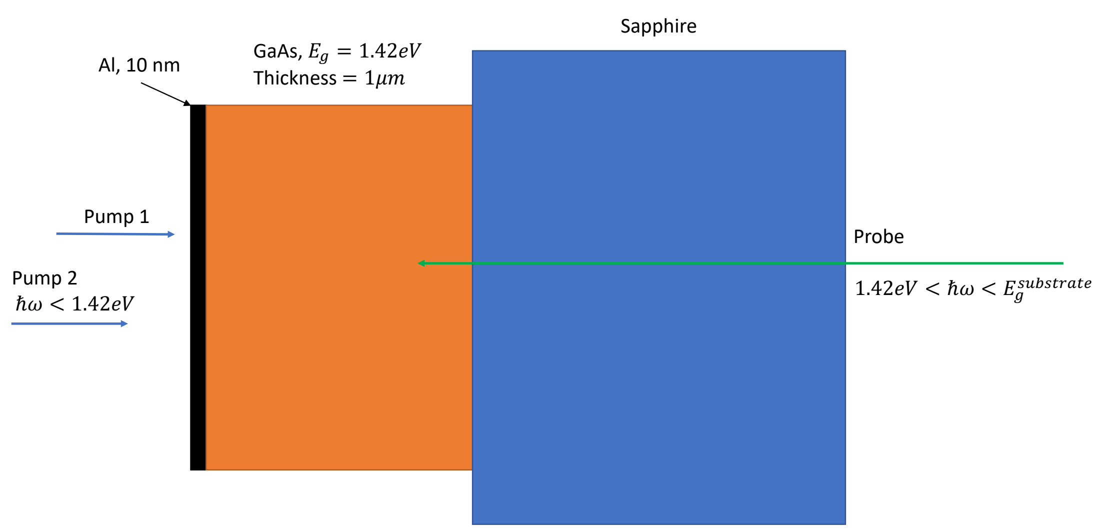


Fig. 1. Current experimental configuration. The probe pulse comes 200 ps after the CAP pump pulse (800 nm). The probe beam wavelength was set as 400 nm.

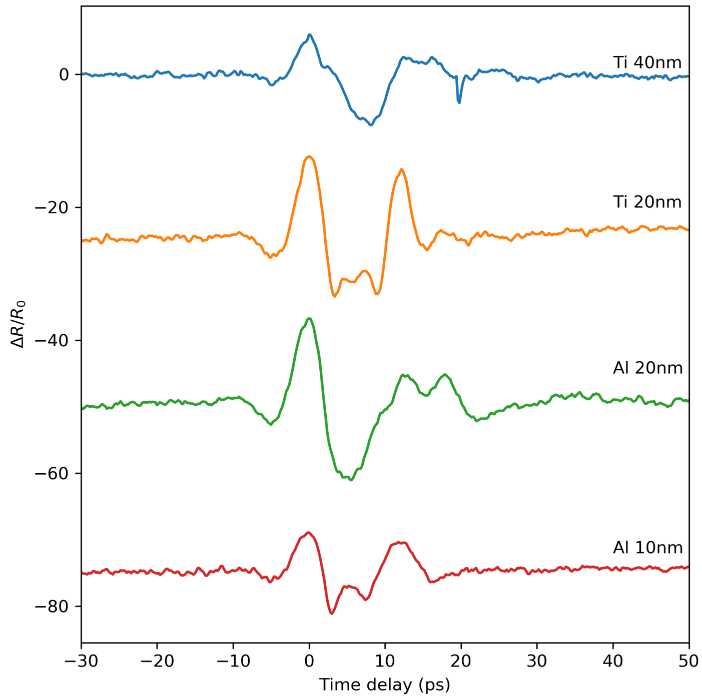
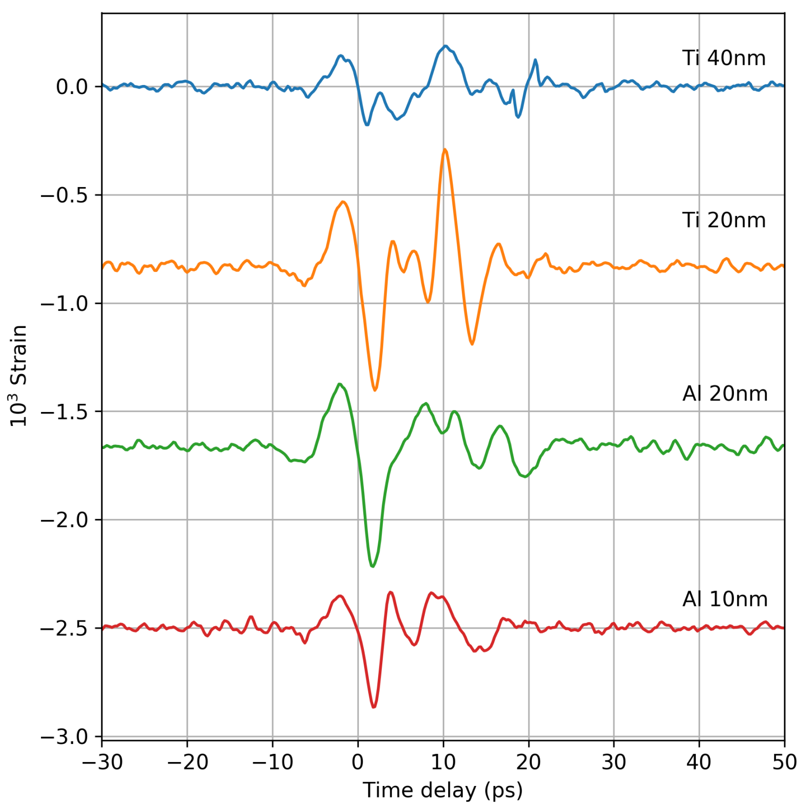


Fig. 2. CAP spectrum from GaAs/sapphire sample. experiment. The pump pulse was set as 800 nm and the probe beam wavelength was 400 nm.



We estimate the magnitude of the CAP generated strain and extracted its depth profile for examined transducers. The profiles are depicted in Figure 3. We are able to generate 0.5 % of the strain wave. However, the work to optimize the strain created by CAP for the level of 1% is ongoing.

Fig. 3. Strain depth dependent profiles for Al and Ti transducers from GaAs/sapphire sample.

3. Post-implantation depth profiling using time-domain Brillouin scattering

Essential to the basic understanding of the ion-matter interaction is the experimental determination of depth profiles of implanted species and the damage produced during the implantation process. This can provide information about the electronic and nuclear stopping mechanisms, and their coupled effects involving defect dynamics. There are various depth profiling techniques in use e.g: Rutherford backscattering, elastic recoil detection, secondary ion mass spectrometry, particle induced X-ray emission, X-ray fluorescence, and others. In this section of the report, we review advances in the time-domain Brillouin scattering technique as applied to ion implanted semiconductors and show examples of depth profiling for GaAs, 4H-SiC, and diamond. TDBS, known as picosecond ultrasonics or coherent acoustic phonon (CAP) spectroscopy, is completely nondestructive technique and offers markedly high depth resolution for all materials under study. It is an ultrafast optical pump-probe technique and has been thoroughly reviewed by Matsuda *et. al*. and Gusev *et. al*. In short, an optical pump pulse absorbed in a thin transducer generates a strain wave (coherent acoustic phonons or CAP) that traverses a material. The reflection and transmission of the optical probe pulse is then modulated by the travelling CAP wave which results in a signal containing Brillouin oscillation as light scatters from acoustic phonons due to Brillouin scattering. The amplitude and frequency of the Brillouin oscillations depend on the material elastic, optical and optoelastic properties that, in general, can be depth dependent.

To date, TDBS has been widely used to access depth dependent material properties such as elastic and optical inhomogeneities in disordered films, ion implantation induced modification of interfacial bonding, textures in materials compressed at megabar pressures, doping profiles, depth-dependent stress, imaging of grain microstructure, and determination of laser-induced temperature gradients in liquids.

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https://doi.org/10.1016/j.nimb.2018.11.033

4. Fluence and wavelength dependent ultrafast differential transmission dynamics in graphene

Graphene is a single layer material of carbon atoms with high carrier mobility and unique optoelectronic properties which make it useful for a wide range of applications. The use of the advantageous properties of graphene in application to optoelectronic devices inevitably entails generation of hot carriers with energies significantly exceeding the Fermi energy. Therefore, carrier relaxation dynamics plays a central role in many proposed graphene based devices. Especially with the scale of devices continuing to shrink, power capabilities being pushed to the limit and efficient heat removal becoming an issue it is hard to underestimate the importance of the enhanced understanding of carrier relaxation dynamics in graphene. There has been going on an enormous effort by many groups to study the graphene related relaxation dynamics using various techniques such as photocurrent measurements, ultrafast pump-probe spectroscopy, time resolved Raman spectroscopy, etc. Ultrafast pump-probe spectroscopy has been particularly fruitful in providing valuable insights into electron-electron, electron-phonon and phonon-phonon interactions. Typically, after electrons and holes are excited into a non-thermal distribution by an ultrafast laser pulse, they thermalize into a Fermi-Dirac distribution through Coulomb interactions in tens of femtoseconds. The cooling of the hot thermal population of carriers occurs through the emission of optical phonons. At the point when the temperatures of the electron and phonon systems equilibrate, the hot phonon bottleneck occurs, which significantly lessens the cooling rate. Subsequent cooling results primarily from the hot optical phonons undergoing anharmonic decay into acoustic phonons. However, in the case of supported graphene, direct coupling of the charge carriers to surface phonons in the polar substrates is a possible cooling channel. As predicted by theories and measured by experiments, the time constant of the hot optical phonon decay in graphene is of the order of a few picoseconds. The hot phonon bottleneck bears far reaching implications for device performance, in particular the photoresponse of optoelectronic devices. Hence, full understanding of cooling pathways of excited carrier and hot phonons are necessary for device applications. In the previous ultrafast pump-probe studies of the hot phonon dynamics in graphene as a function of pump fluence the behavior of the relaxation time constant was found to be nearly monotonic consistent with the standard electron-phonon model. We report measurements of the strong nonlinearity of the relaxation time constant with respect to the density of photo-excited carriers as obtained from the ultrafast pump-probe measurements in the transmission geometry of the CVD graphene on a quartz substrate. More specifically, the differential transmission relaxation time has been found to be about 10 times smaller at a medium pump fluence compared to low and high pump fluences used in the experiment. Moreover, the decay type of the differential transmission switches from bi-exponential to single-exponential. Such fast relaxation (165 fs) at a medium pump fluence indicates the mitigation of the hot phonon bottleneck.

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https://doi.org/10.1088/2053-1591/abb5f2

5. Ultrafast laser pretreatment of silicon surfaces leading to selective placement of diamond nucleation and growth at low temperatures

Substantial enhancement of the growth of diamond films is observed by applying in situ ultrafast pulsed-laser irradiation on a Si substrate surface as a pretreatment step in preparation for hot filament chemical vapor diamond deposition. Beyond a particular laser intensity threshold, periodic nanostructures with characteristic lengths significantly less than the laser wavelength, λ are observed to be formed on the silicon substrate surface. The origin of these features will be discussed but remains controversial. Such surface modification is shown to strongly influence the diamond growth initiation, i.e., nucleation process. Subsequent chemical vapor deposition (CVD) diamond growth, performed at a significantly lower temperature than normal growth temperatures, is shown to strongly correlate with the intensity of the incident laser beam prior to growth. Our diamond growth samples were characterized using scanning electron microscopy and micro Raman spectroscopy. Our work strongly suggests that ultrafast laser pretreatment shows promise as a means of promoting high-quality low-temperature CVD diamond growth in predetermined patterns, thus, demonstrating significant potential as a technique for the fabrication of diamond-based devices and selective diamond growth on semiconductor substrates.

To prepare for growth on non-diamond materials and substrates, a pretreatment technique is often employed to enhance the nucleation process. Commonly, this nucleation process consists of abrading and/or ‘seeding’ the substrate surface to create microstructures to locally enrich the surface with carbon, which assists in the nucleation of diamond, or depositing diamond particles directly which promotes diamond growth at favorable sites and/or speed the coalescence of the films. Various other methods have been explored to stimulate (nucleate) diamond growth on silicon substrates. Among them are: C+ implantation into a Si substrate, modification of the Si substrate by C^{60} and C^{70}, and pulsed (excimer) laser deposition (pretreatment) of amorphous carbon or crystalline tungsten carbide layer. The excitation and decomposition of molecules of reaction gases by pulsed laser excitation has also been employed during high-temperature (above 700^{o}C) CVD growth.

Our studies report on a novel approach to enhance diamond nucleation and growth at lower than normal growth temperatures using an ultrafast laser pretreatment procedure. This treatment has been shown to overcome many hurdles associated with diamond deposition and promises to bring electronic uses of diamond materials closer to device applications. More specifically, in this study, diamond growth was greatly facilitated by applying in situ a stream of ultrafast laser pulses to prepare the silicon substrate surface prior to hot filament chemical vapor deposition (HF-CVD). It is shown that the incident femtosecond-laser pulses modify the substrate surface under vacuum to create favorable nucleation and growth conditions including surface dangling bonds and/or surface nanostructures which during the CVD process, facilitate the bonding of carbon species. This in turn is shown to result in markedly enhanced diamond nucleation and growth at significantly reduced temperatures, down to at least 530^{o}C, as observed in this study. In this work, the ultrafast laser pretreatment of the Si substrate was performed over a relatively short time scale (a matter of a few minutes). The significantly enhanced growth was observed and documented using scanning electron microscopy (SEM) and Raman spectroscopy. Such an approach to materials science goes beyond traditional surface preparation recipes of the Si substrate prior to CVD diamond deposition. Clearly, the laser pretreatment described here enables low-temperature selective diamond deposition on semiconductor wafers and thus promises to be an important tool for diamond-writing applications.

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6. Experimental and theoretical studied of gallium phosphide using time-domain Brillouin scattering

Gallium phosphide (GaP) is a compound semiconductor with an indirect band gap of 2.26 eV with a zinc blende crystal structure. GaP is an ideal candidate for optical/photonic structures in the visible range due to its high refractive index and low absorption coefficient. Most commonly it is used in manufacturing low-cost red, orange, and green light-emitting diodes (LEDs) with low to medium brightness. In addition, GaP is a nearly perfectly lattice matched to Si and has a conduction band minimum near the X point like in Si. This allows to grow high quality layers of GaP on top of Si for possible use in Si-based hybrid optoelectronic devices including high efficiency photovoltaics. Recently, the generation of broadband THz pulses by optical rectification in GaP waveguides was demonstrated. The dispersion of the GaP emitter and the peak frequency of the emitted THz radiation are tunable. Also, the use of a waveguide for the THz emission offers scalability to higher power and represents the highest average power for a broadband THz source pumped by fiber lasers.

Our work reports experimental studies of probe energy dependence of the amplitude of Brillouin oscillations arising from CAPs in bulk GaP and compare with theoretical calculations. While normally one might use CAPs to study the quality of interfaces and antiphase domains in heterostructures such as GaP films on Si, recently Ishioka *et al.* [K. Ishioka, A. Rustagi, U. Höfer, H. Petek, and C. J. Stanton, Phys. Rev. B 95, 035205 (2017)] studied the energy dependence of coherent phonons in bulk GaP with 400 nm (3.1 eV) pump pulses and probe pulses ranging in energy from 2.0 to 2.6 eV. With a change in energy of the probe pulse, one usually sees a shift in the frequency of oscillation given by $f = 2nv/\lambda$ where n is the index of refraction, λ is the wavelength of the probe, and v is the sound velocity. In addition to a change in frequency, Ishioka *et al.* also surprisingly saw that the amplitude of the oscillations increased significantly (by a factor of 5–7) as one approached 2.6 eV. They however could not quantitatively explain these experimental results. In this current study we extend the range of the probe energy from the Ishioka *et al.* study from below the indirect band gap (2.26 eV) to well above the direct band gap (2.78 eV) of GaP. Our results show a nontrivial energy dependence (i.e., the change is *nonmonotonic*) of the amplitude of Brillouin oscillations above 2.6 eV. Our experiments show that the complicated structure in the energy dependence of the amplitude arises from both direct and indirect contributions to the dielectric function of GaP. We develop a theoretical model taking into account the indirect and direct gaps, which shows good agreement with the experimental results, provided we use an experimentally derived dielectric function for GaP *with a very small grid size*. We find that dielectric function experimentally obtained by Aspnes and Studna [D. E. Aspnes and A. A. Studna, Phys. Rev. B 27, 985 (1983)] and used by Ishioka *et al.* in their model, does not have an appropriately small spacing between data points to accurately calculate the derivative in the region of interest.

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DOI: 10.1103/PhysRevB.99.165202

Topic 6

7. **Systematic ultrafast pump-probe reflection studies of the influence of doping level on Brillouin oscillations in GaAs**

Time-domain Brillouin scattering has proved to be a unique tool for determining depth dependent material properties. Here, we show the influence of doping level in GaAs on Brillouin oscillations. The results show high sensitivity of the amplitude of Brillouin oscillations to the doping concentration. This study provides an insight into the specific dopant profiling as a function of depth.

TDBS has proven to be invaluable tool to study different depth dependent properties of materials such as elastic and optical inhomogeneities in disordered films, ion implantation induced modification of interfacial bonding, sub-µm textures in materials compressed at megabar pressures, doping profiles, depth-dependent stress, imaging of grain microstructure, and determination of laser-induced temperature gradients in liquids. It has been shown that TDBS is sensitive to ion implantation induced damage in gallium arsenide, diamond and silicon carbide at low fluences.

The amplitude of Brillouin oscillations changes drastically near the band edge and is maximized at the band gap (Γ point). Such dependence can be explained by the sharpness of the band edge. It has been shown in case of GaP that the energy dependence of the amplitude of the dielectric function agrees well with the derivative of the dielectric function. Therefore, when one takes the derivative of the dielectric function, it is maximized near the band gap energy as the slope in this region is steep.

For n-type GaAs sample, the peak in the amplitude of Brillouin oscillations shifts to higher energies (shorter wavelengths) and broadens. While, for p-type GaAs sample, no dependence of the amplitude of Brillouin oscillations on probe energy is observed in the probe energy region. Note, that in our case, p-type sample has higher concentration of carriers than the n-type sample. The response of the n-type and p-type samples also agrees well with predicted energy dependence based on the derivative of the dielectric function. As dopants are added to the GaAs lattice, donor or acceptor states depending on the type of doping form near the conduction or valence bands, respectively. This formation of dopant states results in the changes in the dielectric function such as smearing of the band edge for the imaginary part of the dielectric function and shifting and broadening of the peak associated with the band gap for the real part of the dielectric function. Our results demonstrate that TDBS can be used to distinguish between different dopant concentrations. While, there are other techniques to measure doping levels, TDSB can uniquely provide depth resolution simultaneously with doping concentration.

This work was published in Physical Review Applied **12,** 054006 (2019).

DOI: 10.1103/PhysRevApplied.12.054006

8. Summary

In this final report, we presented work relating to six main research thrusts supported by ARO under award W911NF-14-1-0290.

The first area of our research employs the depth-dependent coherent acoustic phonons spectroscopy, along with properly timed ultrashort photon pulses, to produce transient and localized atomic level conditions unachievable by any other means. In turn, it reveals new insights into the rates and pathways of vibrational and electronic energy flow in non-ground state condensed matter well beyond the surface. This is critical for understanding dynamical processes in solids involving electronic, optical and thermally stimulated defect and impurity reactions and migrations. The ability to directly probe these pathways and rates will stimulate theory and scaling laws for forms of matter previously unattainable. This research addresses issues of energy transfer and dissipation in solids far from equilibrium, of fundamental importance to our understanding of solid-state properties critical to energy related applications.

We showed the ability of our amplified ultrafast laser system combined with two optical parametric amplifiers to produce two CAP pulses that were send at the desired time delay/depth in a specimen. It opens opportunity for transient modification of materials using ultrafast non-degenerative experiment.

The second area of our interest covers the examination of ion implanted GaAs (direct semiconductior), SiC (indirect semiconductor), and diamond by time-domain Brillouin scattering. We have discussed recent advances in the depth profiling of optical and optoelastic properties the above mentioned specimens. The TDBS is an all optical non-destructive technique. The different optical properties obtained by TDBS can be directly related to the structural damage, and when compared to RBS/Channeling, TDBS is two orders of magnitude more sensitive.

We showed the review of TDBS applications to the study of ion-matter interactions is clearly advantageous in ion beam experiments over a wide range of ion fluences, in particular, where highly sensitive characterization cannot be accomplished by other means.

The third area of focus is a project where we studied differential transmission of graphene. We have investigated ultrafast carrier-phonon relaxation graphene dynamics using transmission pump-probe technique in the range of pump fluences that show distinct regimes of the relaxation dynamics. The main result is the observation of 10 fold faster 5 decay of the differential transmission at medium pump fluences as compared to low and high fluences. Moreover, the nature of the transmission dynamics switches from bi-exponential to single exponential decay. We further conjecture that at the critical value of the excited carrier density the hot phonon bottleneck is mitigated.

Our experimental results show the new observation in the ultrafast dynamics of supported graphene and are of importance for design of more efficient graphene based optoelectronic devices.

The fourth topic of this project is devoted to ultrafast studies of the stimulation of diamond growth on Si substrates at low temperatures. We demonstrated that prior irradiation of a silicon substrate surface with high-power ultrafast laser radiation can be used as a uniquely effective pretreatment to promote nucleation and growth at only predefined locations on the sample. It was also shown that this novel pretreatment technique allows for high-quality diamond film formation to occur on the Si substrate at significantly reduced temperatures.

Clearly, we have shown that *in situ* laser pretreatment exposure above a laser power damage threshold dramatically enhances diamond nucleation, growth and quality, at low-temperatures as confirmed by SEM microscopy and Raman spectroscopy.

The fifth area of our interest covers the examination of GaP using TDBS technique.

Knowledge of the spectral dependence of the photoelastic response is important both from a fundamental point of view and for applications. Particularly, it is relevant to nanoscale imaging using TDBS, where one would want to optimize and choose a probe wavelength leading to higher amplitude of Brillouin oscillations and, consequently, larger signal-to-noise ratio. We have investigated the photoelastic response of GaP as probed by time-domain Brillouin scattering. The results show order of magnitude changes in the amplitude of Brillouin oscillations with respect to probe energy which is maximized near direct optical transitions. Calculations based on the developed theoretical model are in good agreement with experimental data. The results obtained in this paper are of importance to the understanding of detection mechanisms of coherent acoustic phonons in indirect band gap semiconductors and GaP based optoelectronic devices. Information obtained from these types of studies can be used for optimizing the optical response for a wide variety of materials.

The sixth topic covers systematic studies on the influence of doping in GaAs on Brillouin oscillations using time domain Brillouin scattering. The amplitude of Brillouin oscillations changes with respect to dopant concentration while the change in their frequency is negligible. our results indicate that TDBS can be used to measure dopant concentrations but more importantly they pave the way to measure specific dopant concentration as a function of depth.

We have provided a proof-of-principle demonstration that CAP wave can allow us to accurately measure depth-dependent optical and optoelastic constants in a way not possible by any other technique. The above points provide a roadmap for making the technique a competitive characterization method, with great potential for industrial application.

This new approach constitutes a totally new approach to measure any strain, dopants, impurities, interfaces and interfacial strain arising from lattice deformation as a function of depth. This is a capability that is of great importance to the semiconductor device community as it provides a means of *in-situ* quality control.