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Simultaneous Electronic and Lattice Characterization Using Coupled Femtosecond Spectroscopic Techniques

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Simultaneous Electronic and Lattice Characterization Using Coupled Femtosecond Spectroscopic Techniques

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Abstract

High-power electronics are central in the development of radar, solid-state lighting, and laser systems. Large powers, however, necessitate improved heat dissipation as heightened temperatures deleteriously affect both performance and reliability. Heat dissipation, in turn, is determined by the cascade of energy from the electronic to lattice system. Full characterization of the transport then requires analysis of each. In response, this four-month late start effort has developed a transient thermorefectance (TTR) capability that probes the thermal response of electronic carriers with 100 fs resolution. Simultaneous characterization of the lattice carriers with this electronic assessment was then investigated by equipping the optical arrangement to acquire a Raman signal from radiation discarded during the TTR experiment. Initial results show only tentative acquisition of a Raman response at these timescales. Using simulations of the response, challenges responsible for these difficulties are then examined and indicate that with outlined refinements simultaneous acquisition of TTR/Raman signals remains attainable in the near term.

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NOMENCLATURE

A	Total Raman intensity
BS	Beam splitter
BW	Bandwidth
CW	Continuous wave
DLC	Diamond like carbon
EOM	Electro-optical modulator
fs	Femtosecond
FWHM	Full width at half maximum
I	Intensity [W/cm^2]
LLF	Laser line filter
NA	Numerical aperture
PBS	Polarizing beam splitter
S	Raman Scattering efficiency [$\text{cm}^{-1}\text{sr}^{-1}$]
TBC	Thermal boundary conductance [$\text{GW}/\text{m}^2\text{K}$]
TBP	Time-bandwidth product
Ti: Al_2O_3	Titanium:Sapphire Laser
TTR	Transient thermoreflectance
DOE	Department of Energy
SNL	Sandia National Laboratories
ν	Frequency [cm^{-1}]
Ω_R	Raman frequency [cm^{-1}]
Γ	Linewidth [cm^{-1}]

1. INTRODUCTION

The performance and reliability of many microsystems ranging from high-power electronics utilized in radar and satellites to MEMS serving in sensory and actuating applications is directly linked to the device's operational temperature [1, 2]. Consequently, optimization and even realization require that the mechanisms governing the thermal dissipation be clearly understood. Due to the electronic nature of these devices, thermal dissipation occurs via energetic transfer from the electrical to lattice environments thus inherently coupling these systems (See Figure 1). Despite these systems being implicitly linked, device characterization has continually focused on singularly probing either the (i) electronic or (ii) lattice (phonon) carriers, making it impossible to directly observe their coupling and hence the full nature of the thermal transport.

In response, this study provides an initial step in spanning the gap between operation and investigation, while in conjunction providing a paradigm shift in device characterization, by seeking to analyze each energetic carrier concurrently. Specifically, the project attempts to prove the viability of such a concurrent approach through the first observation of simultaneously acquired, sub-picosecond resolved, thermoreflectance (TTR) and Raman signals with the long term goal of developing a tool that is uniquely suited to probe the cascade of thermal energy in microdevices from “cradle to grave.”

As the four-month project is intrinsically a “proof of concept” endeavor, effort focused not on the analysis of this thermal cascade, but rather on acquiring the appropriate equipment and optical arrangement allowing for the acquisition of a simultaneous TTR/Raman signal. Although each technique is frequently utilized to examine thermal phenomena [3], a proof of concept approach is pertinent as the development of ultrafast methods remain challenging in their own right. Combination of two different techniques thus adds complexity to an already sensitive arrangement in which one of the signals (Raman) is implicitly weak due to its statistical nature. To address these challenges and our approaches to their mitigation, the subsequent sections are arranged in the following form. First, the methods themselves are examined from a theoretical point of view in order to explore their applicability as complementary probes in thermal transport and to address the particular complications that arise in their analysis at small time scales. Using this knowledge, the following section describes the utilized optical arrangement, the acquired signals, and simulations demonstrating the challenges of ultrafast Raman. The study then concludes with a series of recommendations on refinement of the experimental arrangement.

Figure 1. Schematic representation of the energy cascade in microelectronic devices. Energy is initially inserted via the application of a potential whence electrons begin to accelerate. As the electrons gain energy, they transfer energy to the lattice environment (phonons), whereby the phonons diffuse allowing for thermal equilibration. The current work focuses on the development of a tool capable of seeing the evolution of this process as it occurs within both the lattice and electrical environments.

2. THEORY

Both thermoreflectance and Raman techniques are well established in their capabilities of interrogating thermal transport in a range of materials and systems including both MEMS and high-power electronics [4]. Specifically, each method has been utilized to not only perform thermometry but to also observe the underlying mechanisms governing the transport of the energy carriers in which they probe [5, 6]. Yet while similarities are apparent in the manner in which each technique has been leveraged, it is the subtle, but significant, differences in the information provided by each method that provides both the promise for the current combined approach and highlights why heretofore each technique solely incorporated is incapable of seeing the entirety of the salient processes at play in thermal dissipation.

2.1 Raman Spectroscopy

In solid state Raman analysis, relevant thermal information is deduced through analysis of the inelastic energy transfer between light (photons) and lattice vibrations (phonons). This process occurs upon impingement of incident radiation to a surface in which a photon with energy ε_i is absorbed by either an electron or, in a dramatically more unlikely case, a phonon. This process causes the absorbing species (i.e. the electron) to be promoted from its equilibrium energy, ε_g , to a virtual state of energy, ε_L . As the virtual state is in non-equilibrium, the absorbing species almost simultaneously relaxes back to its equilibrium state. In the vast majority of instances, this occurs in a direct fashion causing the re-emission of a photon of energy equal to that which was incident ($\varepsilon_L - \varepsilon_g = \varepsilon_i$) in a process known as Rayleigh scattering.

Figure 2. In Raman scattering, 3 separate events give rise to the detected inelastic scattering. Through observation of the change in radiation incident and emitted from the surface, deductions can be made with respect to the interaction of the light with the crystal lattice and hence its thermal characteristics.

In approximately 1 out of every 10^7 of these instances, however, the relaxation process from the virtual state does not take place in a direct fashion. In this case, the absorbing electron may either absorb additional energy or emit a portion of its energy to the lattice in the form of a phonon (See Figure 2). On account of the indirect event, the excited species moves to a secondary non-equilibrium virtual state of energy ε_m that is unequal to either its original ground (ε_g) or excited level (ε_L). Thus, upon relaxing from this secondary virtual state the electron will emit a photon of energy that is unequal to that which was originally incident ($\varepsilon_m - \varepsilon_g \neq \varepsilon_i$). The emission of this unequal, or inelastically scattered, radiation is the origin of the Raman effect. If the inelastic scattering occurs from an emission event, the scattered radiation is of lower energy and is termed Stokes Raman scattering. Complementary to that, if the scattering results from an absorption event, the resultant radiation is of higher energy and is named anti-Stokes Raman scattering. Due to this emission and absorption, the relative strength of each one of these signals then arises from the population distribution of the phonons. As there are more empty states than those occupied near room temperature, the strength of the Stokes signal is more than an order of magnitude greater than that of the anti-Stokes signal under ambient conditions.

Owing to the incident light's invariance with the lattice's temperature, all deductions of the Raman process are based on changes in the phonon behavior of the crystal. Thus, any aspect of the phonon that changes with temperature, i.e., its population, lifetime, or energy, can then be used to probe the thermal state of the investigated material [7]. This information is not only valuable as a tool to measure temperature but may also be utilized to trace the rate and mechanisms by which the analyzed phonons scatter and decay thereby providing insight into the cascade of energy through the vibratory lattice [8]. The information provided, however, is exclusive to the energy transport of the phonons. As such, Raman methods are incapable of determining the manner and rate in which this energy originally entered into the phononic environment. During microelectronic operation this insertion occurs through the coupling of the electronic and lattice carriers, consequently full characterization of the thermal dissipation mechanisms then necessitates investigation of both environments in tandem.

2.1.1 Challenges to Ultrafast Raman Spectroscopy

As the Raman effect is literally a one-in-a-million occurrence, the signal strength is inherently weak whether continuous wave (CW) or ultrafast applications are explored. In ultrafast applications, this weakness becomes exacerbated by two main effects related to the nature of the incident radiation. First, the majority of sub-picosecond lasers have at their material base a titanium/sapphire (Ti:Al₂O₃) crystal that emits at the near infrared (NIR) wavelength of 785 nm. Raman scattered light will then have wavelengths shifted relative to this central incident beam. As mentioned previously, the strongest portion of the Raman scattered light stems from the Stokes process which, at room temperature, has a peak magnitude at least one order of magnitude greater than the complementary anti-Stokes component. Stokes scattered light, however, is red-shifted relative to the incident beam. Unfortunately, most spectral detectors (PMT's, CCD's) have efficiencies that become greatly reduced in the spectral region above 900 nm. This reduction effectively dampens an already small signal and limits the region of observable "strong" Stokes scattering to less than $\sim 1650 \text{ cm}^{-1}$ from the laser line as shown in Figure 3. Unfortunately, many materials have pertinent Raman bands above this cut-off

Figure 3. Raman shift as a function of its absolute spectral location for a 785 nm incident laser. Standard detector efficiencies reduce the range of observable signal to less than ~900 nm thereby limiting the collection of Stokes signals to shifts of less than 1650 cm^{-1} .

frequency including, most notably, carbon based materials such as diamond, graphene, carbon nanotubes, etc. [9]. Thus, it is for this reason, along with additional thermal considerations not enumerated here, that the weaker anti-Stokes signal is most often utilized in ultrafast Raman analysis [10, 11].

In addition to the limitations imposed by the NIR wavelength of the $\text{Ti:Al}_2\text{O}_3$ laser, the pulsed

Figure 4. Spectral broadening of a laser that occurs with shorter pulse lengths. This broadening can extend to regions of interest for Raman analysis and effectively block the signal.

nature of the source also induces complications in the acquisition of a signal. Specifically, unlike in CW Raman, a pulsed laser is an inherently broadened spectral source. This fact arises as a ramification of the Heisenberg uncertainty principle and inversely relates the temporal pulse length to the spectral distribution of the source (See Figure 4). Optimally, the purest “tone” of a pulsed source is bandwidth-limited (i.e., has the narrowest spectral distribution for a given pulse duration) and relates the spectral FWHM to the temporal FWHM via the time-bandwidth product (TBP). This spectral spread in the incident radiation, in turn, reduces the peak intensity of the Raman response while simultaneously expanding the FWHM of the signal. More importantly, at small temporal pulse lengths, the spectral broadening of the laser source may extend to wavelengths where the Raman signal is expected. Since the Raman signal is of such smaller intensity in comparison to the incident radiation, when the signals intersect spectrally, resolution of the Raman intensity becomes nearly impossible. The significance of these points is further addressed in the following section.

2.1.2 Estimating Raman Signals in Ultrafast Raman Spectroscopy

In light of the outlined challenges to ultrafast Raman, the following mathematical construct is used to examine the expected nature of the signal emerging from the sample. First, consider a bandwidth-limited femtosecond pulse of duration, τ , having Gaussian temporal and spectral profiles. The Gaussian spectral distribution can be described by:

$$I_p(\nu) = I_o \exp\left(-\frac{4 \ln(2)(\nu - \nu_L)^2}{BW^2}\right), \quad (1)$$

where ν_L is the main frequency of the laser in cm^{-1} , I_o is the intensity at ν_L , and BW is the bandwidth or FWHM of the distribution. Eq. 1 can also be recast in terms of the Raman shift, or frequency difference from the laser line as:

$$I_p(\omega) = I_o \exp\left(-\frac{4 \ln(2)\omega^2}{BW^2}\right), \quad (2)$$

where $\omega = \nu - \nu_L$. Figure 4 shows spectral profiles of laser pulses of various durations, and hence different bandwidths. BW is, in turn, related to the pulse duration through TBP as:

$$BW = \frac{\text{TBP}}{3 \times 10^{10} \tau[s]} = \frac{0.44}{3 \times 10^{10} \tau[s]} = \frac{14,667}{\tau[fs]} [\text{cm}^{-1}]. \quad (3)$$

Considering then a highly-ordered crystalline sample with Raman frequency, Ω_R , and neglecting any signal convolution due to the measurement equipment, the resulting Raman spectrum for a given incident probe frequency, ω_i , has a Lorentzian distribution that can be described as:

$$L_i(\omega) = \frac{2A_i}{\pi} \frac{\Gamma}{4(\omega - \omega_i^R)^2 + \Gamma^2}. \quad (4)$$

In Eq. 4, the Raman line shape is centered at a frequency shift $\omega_i^R = \omega_i + \Omega_R$, and has a linewidth, Γ , and total intensity, $A_i = \int_{-\infty}^{\infty} L_i(\omega) d\omega$. The total intensity, however, is related to the incident probe intensity, $I_p(\omega_i)$, by the scattering efficiency, S , as $A_i = SI_p(\omega_i)$. Utilizing silicon as an example, $S = 3.05 \times 10^{-6} \text{ cm}^{-1} \text{ sr}^{-1}$ [12], and considering the use of a collection objective with a 0.28 numerical aperture (NA) and 33.5 mm working distance (Edmund Optics 5X Infinity-corrected objective), the conversion efficiency is estimated as $2.56 \times 10^{-7} \text{ cm}^{-1}$.

The Raman intensity at any frequency shift, ω_n , resulting from the broadband probe is then the sum of all individual Lorentzian distributions over the frequency space covered by the incident broadband probe:

$$I_R(\omega_n) = \sum_i L(\omega_n, \omega_i^R) = \sum_i \frac{2SI_p(\omega_i)}{\pi} \frac{\Gamma}{4(\omega - \omega_i^R)^2 + \Gamma^2} = \sum_i \frac{2SI_o}{\pi} \frac{\Gamma}{4(\omega - \omega_i^R)^2 + \Gamma^2} \exp\left(-\frac{4\ln(2)\omega_i^2}{BW^2}\right). \quad (5)$$

In integral form, Eq. 5 can be expressed as:

$$I_R(\nu_n) = \frac{1}{2\pi} \frac{SI_o}{BW} \int_{-\infty}^{\infty} \frac{\Gamma}{4(\omega_n - \omega_i - \Omega_R)^2 + \Gamma^2} \exp\left(-4\ln 2 \frac{\omega_i^2}{BW^2}\right) d\omega_i \quad (6)$$

where the limits of integration cover the range of frequencies of the probe laser pulse, and can be taken from $-2BW$ to $2BW$ without loss in accuracy of the numerical calculation.

As shown in Figure 5, the Raman signal is as broad spectrally as the probe laser pulse. Additionally, because of the low efficiency of the Raman process, there is a high likelihood for the signal to be completely occluded by the elastically-scattered probe beam depending on the Raman frequency band of the material under study. This is demonstrated in Figure 5b & c, where non-transform-limited pulses were considered, causing the examined Si peak to completely “disappear” under the much stronger probe intensity.

A significant finding from this analysis is the ability to establish a lower limit on the frequency range available for study under femtosecond Raman spectroscopy without the need for additional experimental controls. Specifically, it is found that frequency shifts below approximately 3 BW have a strong likelihood of being irresolvable due to the elastically-scattered light from the sample. As a consequence, exploration of frequencies below this threshold necessitates a narrower bandwidth and therefore longer pulse duration. This fact is demonstrated in Figure 6 for a 0.6 ps pulse where the 520 cm^{-1} shifted line of Si, unobservable at 90 fs pulses, is now clearly observable. Alternatively, femtosecond laser pulses could be used for Raman spectroscopy of materials with Raman frequencies above the 3 BW limit, such as SiC ($\Omega_R \sim 960 \text{ cm}^{-1}$), as shown in Figure 7.

Figure 5. (a) Simulated Stokes Raman signal for silicon ($\Omega_R = 520 \text{ cm}^{-1}$) considering a transform-limited 90 fs ($TBP = 0.44$; $BW = 163 \text{ cm}^{-1}$), 785 nm laser probe pulse. (b) Simulated Raman signal for a “near transform-limited” 90 fs ($TBP = 0.57$; $BW = 211 \text{ cm}^{-1}$) pulse. Intensity is normalized to the peak intensity of the probe laser. (c) Simulated Raman signal for a transform-limited 90 fs pulse which has a 325 cm^{-1} -wide broadband “pedestal” that makes up 0.01% of the probe intensity.

Figure 6. Simulated Raman signal for a transform-limited 0.6 ps pulse ($TBP=0.44$; $BW = 24 \text{ cm}^{-1}$) case.

Figure 7. Simulated Raman for SiC ($\Omega_R \sim 960 \text{ cm}^{-1}$), considering a transform-limited 90 fs ($TBP = 0.44$; $BW = 163 \text{ cm}^{-1}$), 785 nm laser probe pulse.

2.2 Transient Thermoreflectance (TTR)

The reflectivity of a sample is primarily determined by the electronic energy bands of the material that define the allowable states of the electron. The manner and extent to which the states of these bands are filled is dependent upon the electrons' statistical distribution. Due to the

Figure 8. Electrons and holes populate the energy bands of the crystal lattice with a distribution heavily influenced by the thermal environment. During a TTR experiment, incident radiation (arrows) probes this distribution, and in turn the thermal environment, as the likelihood of reflection (R) is heavily affected by the ease of transition from a lower to higher energy band. The probability of such a transition, in turn, is determined by the number of filled and empty electronic states thereby making the reflectivity a measure of electronic temperature.

anharmonicity of the crystal lattice, these bands are modified both in shape and occupation with changes in temperature. These changes, in turn, induce the associated alterations in the reflectivity of the sample that may be measured to monitor the thermal environment.

During a TTR experiment, a perturbation in the environment is most often induced by a high intensity, ultrafast, “pump” laser source. Upon impinging with the surface, this pump energy is transferred to the electrons, which move from an initial equilibrium state to a higher energy non-equilibrium state. Following closely behind this pump pulse is an additional radiation source of lower intensity that serves to “probe” the sample. The reflectivity of the probe pulse will change based upon the occupation of the electron’s energy bands (See Figure 8). This occupation, in turn, continually changes with time relative to the pump pulse based upon the material’s relaxation back to equilibrium. Thus, by monitoring the probe’s reflectivity as a function of time relative to the initial perturbation, a host of thermal effects related to the relaxation may be investigated. These effects include not only a measurement of electron temperature but also the coupling strength between the electrons and phonons.

Similar to Raman spectroscopy in its isolation, however, thermoreflectance directly probes only the electronic environment. It cannot, therefore, observe the thermal transport once energy has left this specific system and begun to be dissipated within the crystal lattice. As such, full view of the thermal transport as it moves from the electronic and into the crystal lattice then requires that both environments be sampled simultaneously to observe the entire energetic cascade through the material.

2.3 Combination of Ultrafast Raman and TTR for Thermal Analysis

Our approach attempts to provide a fuller view of thermal transport by simultaneous application of thermoreflectance and Raman spectroscopy through use of a novel pump/probe experimental set-up. The purpose for combining the two optical techniques stems from their selective probing of the different energy carriers as outlined above. Raman capitalizes upon the inelastic energy transfer between the probing radiation and the phonons of the material. Thus, any change of a Raman active phonon mode—i.e., population, lifetime, or energy—may be probed with the technique. The resulting signal can then be used to measure not only the lattice temperature but also utilized to trace the rate and mechanisms by which the analyzed phonons evolve, scatter, and decay. The information provided, however, is exclusive to the transport of the phonon system. In response, TTR must also be implemented in order to analyze the electronic transport, and the manner that energy initially enters the lattice, through its capability to monitor the electronic temperature. The sum of each technique’s information, in turn, allows for observation into the interplay by which energy enters and exits each environment.

$$\begin{aligned}
C_E \frac{\partial T_e}{\partial t} &= -k_E \nabla^2 T_e - g_{Lo} [\tau_{e-Lo}] * (T_e - T_{Lo}) - g_{La} [\tau_{e-La}] * (T_e - T_{La}) + E_{in} \\
C_{Lo} \frac{\partial T_{Lo}}{\partial t} &= -k_{Lo} \nabla^2 T_{Lo} + g_{Lo} [\tau_{e-Lo}] * (T_e - T_{Lo}) - g_{ph} [\tau_{ph-ph}] * (T_{Lo} - T_{La}) \\
C_{La} \frac{\partial T_{La}}{\partial t} &= -k_{La} \nabla^2 T_{La} + g_{ph} [\tau_{ph-ph}] * (T_{Lo} - T_{La}) + g_{La} [\tau_{e-La}] * (T_e - T_{La})
\end{aligned}$$

Figure 9. Three temperature (electron- T_e , non-equilibrium “hot” phonon- T_{Lo} , and lattice temperature- T_{La}) model describing the cascade of energy (See Figure 1) utilized to analyze the temporal TTR and Raman signals. Terms in black are material constants while those in red are acquired from TTR and those in green from the Raman signal.

The nature of Raman lends itself to combination with other techniques as the method utilizes less than 1% of the scattered radiation. The remaining signal, normally thrown away, can then be utilized in the thermoreflectance analysis through spectrally specific filtering of the scattered radiation. Furthermore, by use of the femtosecond pulsed laser, observation may take place on a time scale relevant to the interrogated carriers (i.e., electrons and phonons) interaction and scattering. Specifically these mechanisms will be interrogated by injecting hot carriers into the material via an optical “pump” pulse and, in later stages, with an electric field. With this perturbation, the carriers are driven out of equilibrium with their subsequent thermalization causing emission of phonons into the lattice. To analyze these processes, a subsequent “probe” pulse will interrogate the state of the energy carriers at time intervals of ~ 200 fs after this seeding event. The resulting Raman and TTR signals will be collected simultaneously allowing for the direct measurement of: the rate of phonon emission (τ_{e-ph}), the non-equilibrium and equilibrium lattice temperatures, electron temperature, and most importantly the electron-phonon coupling rates that determine the mechanisms and efficiency by which energy returns to equilibrium.

Mechanically, these parameters are acquired by tracking their temporal evolution in the framework of a so called “3-temperature model” shown in Figure 9 [13]. The model is derived from conservation of energy considerations between the three relevant systems at play, namely; the electrons, the preferred—and as a consequence oftentimes non-equilibrium—lattice modes into which they decay, and then finely the lattice as a whole. By then utilizing the model to fit the time evolution of the directly measured values of the electron, non-equilibrium, and lattice temperatures, higher fidelity assessments of electron phonon coupling along with specification of the energy decay mechanisms may be acquired in a more rigorous fashion without the need for assumptions typically employed (See Table 1). Without the need for these assumptions, new phenomena may be analyzed as is outlined in the following sub-sections.

Table 1. Measurable parameters acquired using each of the methods. Combining the techniques increases the number of direct measurements allowing for determination of the factors driving transport as well as the analysis of “new” phenomena.

Mtd. [Ref.]	T_e	T_{Lo}	$T_{La.}$	τ_{e-ph}/G_{e-ph}	τ_{ph-ph}/G_{ph-ph}
TTR [14]					
Raman [15, 16]					
Combined					
Direct Measurement	Indirectly deduced from complementary measurements and transport assumptions.				

2.3.1 Energy Cascade of III-V Materials

Employing the coupled analysis is particularly salient in the analysis of polar semiconductors (GaAs, ZnO) and especially group III-nitrides (GaN, InN, AlN) where cooling of the electronic system takes place through concentrated emission of longitudinal-optical (LO) phonons. Efficient transport, both from an electrical and thermal perspective, requires that these low-velocity phonons rapidly decompose into faster moving acoustic modes. The rate of this decomposition (~ 1 ps), however, is over an order of magnitude slower than the source of their creation—i.e., emission—leading to a non-equilibrium distribution of the population and the presence of so called “hot phonons.” These hot phonons are deleterious to device performance as their presence reduces both thermal transport as well as electron drift velocity, thus making the mechanisms by which they decay imperative for further device improvement [17].

While several studies have identified that both the population and lifetime of the hot phonons are dependent upon the electrical carriers, the mechanisms by which the energy contained in these phonon modes eventually equilibrates with the surroundings is a subject of intense debate [6]. Although differing decay routes have been proposed, specification, and the associated ramifications on device design, has remained elusive as techniques characterizing the phenomenon have either focused on the electronic or vibratory environments, necessitating deductions in the analysis of the complementary milieu. Hence, direct characterization of the coupling between the electrons, high energy LO phonons, and the modes into which they decompose has been impossible leading to uncertainty with respect to the major factors affecting energy dissipation. The current approach allows for the removal of these assumptions thereby allowing for definitive answers concerning the formation and eventual dissipation of these modes central to the energy transport in these devices.

2.3.2 Interfacial Transport Processes

The transport of thermal energy across material interfaces is becoming increasingly relevant in the performance of thin-film and nanostructured devices. Thermal boundary conductance (TBC), which describes the efficiency of heat flow at material interfaces, is a concept that must be

understood in order to optimize the capability of systems such as thermoelectrics and thermal interface materials. While atomistic calculations and analytical models accurately describe the nature of the heat transfer in these regions, questions remain concerning the exact processes by which energy carriers transmit heat across the material boundaries. Specifically, the interfacial scattering mechanisms involved with electron and phonon transport—such as elastic, inelastic, or coupled processes—have not been physically observed leaving unexplained phenomena in the transport. Responding to these core deficiencies is central to the understanding and exploitation of interfacial heat transfer.

Experimentally observing the scattering processes of electrons and phonons at solid material interfaces permits direct specification, rather than simple deduction, of the exact pathways of energy transmission across the interface. To ascertain these pathways, in turn, it is necessary to simultaneously probe both the electronic and lattice environments as their transport is inextricably linked. For example, in semiconductor materials, conduction band electrons near an interface may transport their energy through scattering with electrons and phonons both within their own material as well as that of the interfacial complement. Similarly, phonons participate in energy transfer through scattering both with other phonons as well as electrons on either side of the boundary. Specification of the interfacial heat transfer then relies on the accurate monitoring of not only electrons and phonons, but their interaction as well. In the coupled approach, this is possible through the measurement of both the electron and lattice temperatures on either side of the boundary. Furthermore, as Raman is mode specific, the coupled approach allows for the determination of what modes, and hence what processes, are most capable of participating in the transport.

3. EXPERIMENT AND RESULTS

Due to the relatively short time span of the project (4 months), the chief objectives of the study centered on the realization of an experimental set up capable of resolving both sub-picosecond TTR and Raman signals and, if time allowed, to acquire each simultaneously. As such, the thermal analysis described previously is to be viewed as a longer term goal for which the current project serves as a “proof of concept” endeavor. The following sections highlight the efforts undertaken as part of this viability effort. Specifically, the optical arrangement is first described with considerations of its capability in the acquisition of TTR and ultrafast Raman subsequently considered.

3.1 Optical Arrangement

Building on several nearly identical arrangements that have been utilized in the analysis of both TTR and Raman, a coaxial pump-probe geometry is utilized for all measurements (See Figure 10 and Figure 11) [3, 18-20]. The laser pulse emanates from a Spectra Physics Mai Tai oscillator outputting 350 mW of power at a repetition rate of 80 MHz with pulse widths of 90 fs at a central wavelength of 785 nm. The pulse first passes through a pair of collimating lenses in order to minimize any probe divergence at the sample surface that may be induced due to the variable delay stage. The pulse train then passes through an adjustable half-wave plate before being split into the pump and probe paths by a polarizing beam splitter cube (PBS). Such a setup fixes the pump and probe path as orthogonally polarized to one another. With such an arrangement, adjustment of only the wave plate allows for easy control between the pump and probe powers.

To properly map the temporal evolution of the signals of interests, the probe beam is delayed relative to the pump beam by means of a variable delay stage that allows up to 4 ns of delay. The probe is then sent towards the sample using a 50/50 beam splitter. On the pump path, the beam is modulated by a ConOptics M350-160 electro-optic modulator (EOM) and sent to a PBS which coaxially aligns the pump and probe beams before interacting with the sample surface. Focusing of the beams is accomplished by a 10X Edmund Optics objective (0.28 NA). Procedurally, focus of the probe beam is realized through adjustment of the objective relative to the sample surface. The quality of the focus is assessed by characterizing the beam using a sweeping knife edge [21]. Using such a method, the probe beam radius at minimum pump-probe delay is $\sim 20\ \mu\text{m}$ and exhibits less than $1\ \mu\text{m}$ divergence at the maximum time delay.

To collect the TTR signal, the reflected probe beam is transmitted back through the PBS and 50/50 beam splitter. The reflected pump, in contrast, is blocked by the PBS as; again, it is polarized orthogonally to the probe. After the 50/50 beam splitter, the signal is focused onto a photodiode (ThorLabs DET 10A) connected to a SRS 844 lock-in amplifier that monitors the baseline voltage and the change in the voltage due to the thermorefectance signal. To image the sample surface before analysis, an additional 50/50 beam splitter is utilized in tandem with a CCD camera. This beam splitter is removed, however, before analysis in order to maximize the amount of acquired signal.

Figure 10. Transient thermoreflectance (TTR) set up utilized to analyze the thermal response of electronic system.

To acquire a Raman signal, the optical arrangement is modified only slightly as shown in Figure 11. First, in an effort to reduce the spectral bandwidth of the laser, a laser line filter (Semrock 785 MaxLine, 3 nm bandwidth) is placed after the collimating lenses. At the cost of some incident power and temporal resolution, this filter reduces the spectral bandwidth of both the pump and the probe allowing for Raman shifts closer to the laser line of 785 nm to be acquired. An additional laser line filter rotated such that the beam intersects it at a non-normal angle ($<20^\circ$) further shapes the probe pulse after it has proceeded past the delay stage. This second filter not only further reduces the band edges of the laser pulse but also allows for the probe to be at a different wavelength than that of the pump, as shown in Figure 12. Such an approach is analogous to the “Two-Tint” measurements of Kang *et al.* [3] and ensures that the Raman signal arising from the pump does not become convoluted with that stimulated by the probe.

Further alterations in the original TTR arrangement arise due to differences in the collection of the signal for a Raman versus thermoreflectance analysis. These changes begin with the placement of a kinematic mirror after the 50/50 BS that directs the entirety of the probe towards

Figure 11. Optical arrangement for the acquisition of an ultrafast Raman signal used to analyze the thermal response of the lattice.

a fiber optic coupler (ThorLabs F230SMA-B). It is of note that use of the mirror inhibits the possibility of acquiring TTR and Raman simultaneously. The current approach is utilized, however, as it allows for an examination into the feasibility of performing incoherent Raman with 90 fs pulses in a manner that maximizes the amount of available signal. In addition, the arrangement nearly mirrors that utilized by Kang *et al.* in their examination of non-concurrent Raman and TTR [3]. To acquire both signals simultaneously, the arrangement must only be slightly altered as is shown in Figure 17. Due to the time constraints of this project, however, this was not attempted and the details of such a modification are left for the descriptions of future effort (See Section 4.1).

Figure 12. Spectral profile of the laser with no filtering and with the various arrangements of filters. For combined TTR/Raman studies, both filters are used on the probe path, while only the normal incidence filter is used on the pump path.

Analysis of the Raman scattered light, meanwhile, takes place by transporting the light to the spectrometer (Horiba Jobin Yvon iHR320) using a 120 μm core broadband fiber optic. Radiation emerges from the fiber and is then focused onto the 75 μm -wide entrance slit of the spectrometer using an additional fiber optic coupler and a beam expander. To remove any elastically scattered light, a notch filter (Semrock NF01-785-25) is placed directly in front of the spectrometer. The spectrally-resolved signal is measured using a back-illuminated CCD camera (Princeton Instruments Pixis 1024B) which gives a spectral resolution of $0.42 \text{ cm}^{-1}/\text{pixel}$. Finally, it is of note that as all probe light that reaches the CCD has passed through the polarizing beam splitter both on its incident and scattered path, the resulting Raman signal will be observed only if a mode's selection rules allow for this equal polarization. As such, the current arrangement requires Raman signals to be active in the $z(xx)\bar{z}$ orientation or some derivative thereof (i.e., $x(yy)\bar{x}$, $y(zz)\bar{y}$, etc.).

3.2 Acquisition of Sub-Picosecond TTR Signals

Prior to attempting the acquisition of both TTR and Raman signals simultaneously, the initial effort concentrated on demonstrating the capability of either acquisition system individually. To that effect, the thermoreflectance capability was assessed by acquiring a TTR signal from a bare silicon surface. While the setup described above and shown in Figure 10 has been successfully

Figure 13. *Transient thermoreflectance (TTR) signal acquired from a wafer of silicon at a pump fluence of 1.59 J/m^2 .*

used to analyze metal-coated samples to extract thermal conductivity and thermal boundary conductance, a non-metallized surface was chosen instead [22]. Demonstrating the technique on a bare semiconductor surface ensures future compatibility with the Raman acquisition technique described above.

The data acquired from the silicon surface, shown in Figure 13, exhibits the typical the response observed in ultrafast thermoreflectance signals. The observed signal is indicative of the change in reflectance of the sample as a result of the temperature increase induced by the pump laser pulse, which is, in turn, proportional to the electron and lattice temperatures of the sample. Thus, the reflectance signal exhibits a sharp increase upon the arrival of the pump laser pulse. Given that the duration of the pulse is on the order 100 femtoseconds, the laser energy is absorbed by the electronic system of the sample. The excited electronic system decays into equilibrium with the silicon lattice on a timescale on the order of ~ 1 ps. The temperature of the sample then decays further owing to phonon-phonon scattering mechanisms. By fitting the acquired data to an appropriate thermal model (e.g., Figure 9 or some such) pertinent information about the energy cascade within the electronic system of the material could be extracted.

3.3 Acquisition of Ultrafast Raman Signals

The second objective of the project centered on the acquisition of a Raman signal from silicon at sub-picosecond time scales. Silicon exhibits a Raman shift at 520 cm^{-1} relative to the incident laser wavelength due to the triply degenerate optical mode at the Brillouin zone center. For a 785 nm incident laser pulse, the 520 cm^{-1} shifted Raman signal is present at the absolute spectral wavelengths of 818.4 nm and 754.2 nm for the Stokes and anti-Stokes contributions, respectively. These signals are only $\sim 35 \text{ nm}$ away from the incident laser line, however, leading to concerns that their small magnitudes may be completely obscured by the tails of spectrally broadened laser pulse (See Figure 5). For example, in Section 2.1.2 Raman signals were shown to be observable only when the shift was at least 3 times that of BW. From the perspective of

silicon, this limit necessitates a temporal pulse width of at least 85 fs and, in all likelihood, a time significantly greater as the actual pulse is most likely *not* bandwidth limited.

With these considerations in mind, initial efforts commenced through utilization of a Coherent Mira Ti:Al₂O₃ laser employed to pump a Coherent RegA regenerative amplifier resulting in a temporal pulse width of 200 fs. The 200 fs pulse width was chosen as it allows for both the temporal resolution needed to observe the transport properties themselves while also offering sufficient spectral purity to allow for the observation of Raman signals at less than 350 cm⁻¹ away from the laser line. Unfortunately, however, after investing 2 months of the project to setting up the optical arrangement using this 200 fs pulse, the power supply of the laser failed before any data could be acquired relegating this set up of no use for the effort's remaining duration.

In response, the optical arrangement described in Section 3.1 (See Figure 11) was developed and employed in an effort to acquire ultrafast Raman signals. The Mai Tai laser utilized in this arrangement, in contrast to the Mira, has a pulse length of only 90 fs and, as such, a bandwidth of ~15 nm (See Figure 12). Due to this large bandwidth, acquisition of the silicon Raman signal was found to be irresolvable as is shown in Figure 14. In this case, the large spectral tail of the incident laser overwhelms the Si Raman signal resulting in a response that is indistinguishable from that of a Raman silent aluminum (Al) film. We attribute the difficulty to the laser pulse's tail as the employed optical arrangement is virtually identical to that employed by Letcher *et al.* to analyze Si's ultrafast Raman response in all aspects except the pulse length of the incident probe [23, 24]. Furthermore, the observed response is similar to that predicted in Section 2.1.2 assuming a non-bandwidth limited pulse (See Figure 5). Therefore, it is concluded that the 90 fs pulses limit the acquisition of Raman signals to wavenumber further from the laser line that of

Figure 14. Signal acquired from a wafer of (111) silicon and that of aluminum in a spectral range where the Si Raman signal is expected. Due to the large spectral tail of the 90 fs laser pulse, the Raman signal of Si is not observed as it is indistinguishable from that of a Raman silent Al film.

Figure 15. CW Raman response of a thin film of diamond like carbon (DLC). Although the CW Raman response shows both a diamond (left) and graphitic (right) peak, selection rules dictate that due to the polarization of both the incident and scattered beam in the ultrafast arrangement only the graphitic peak will be observable.

Si's 520 cm^{-1} . Analysis of Si should then take place with either longer pulse lengths or with a shorter pulse length sufficiently shaped using laser line filters to limit the extent of the tail. Efforts are currently underway using the latter approach.

To further investigate whether the tail of the incident laser line was obscuring the Si Raman response, a thin heterogeneous film of diamond like carbon supplied by T. Friedman (1112) was investigated. Diamond like carbon (DLC) is chosen as it has exhibits several Raman active modes shifted relative to the laser line at much greater magnitude than that of Si. Specifically, the examined film when examined using non-polarized CW Raman exhibited peaks at both 1332 cm^{-1} , a diamond feature, and 1580 cm^{-1} due to the presence of graphite (See Figure 15). As the analysis of Section 2.1.2 predicts that features beyond 960 cm^{-1} are resolvable even using 90 fs pulse lengths (See Figure 7), the DLC film was examined using the arrangement described in Figure 11.

Shown in Figure 16 is the resulting Raman spectrum of the DLC film as acquired using the ultrafast set up. Unlike that seen in the CW response, the characteristic diamond peak at 1332 cm^{-1} was not observed. This is possible, however, due to the equal polarization of both the incident and scattered radiation in the ultrafast arrangement. Selection rules, in turn, exclude the presence of the diamond peak when light propagates perpendicular to the (100) face of the lattice with this equal polarization [25]. As the diamond is expected to grow mainly in this orientation, its absence from the Raman spectrum, while surprising due to the high heterogeneity observed in the film, is not prohibited.

In contrast, a distinct spectral feature was observed near a Raman shift of 1580 cm^{-1} where the graphite peak is expected. To ensure that the observed signal arose from the material and not from a random light source, all ambient radiation was removed to the fullest extent possible. Additionally, several spectra were acquired to remove the possibility of the signal arising from noise within the optical detector. In each case, the signal remained nearly identical to that shown in Figure 16. It was then concluded that the spectral feature arose from the Raman effect, and as

Figure 16. Suspected graphitic peak observed from DLC film using ultrafast Raman arrangement. The spectral location of the peak is similar to that observed from CW Raman lending confidence to the validity of the signal.

such, an ultrafast Raman signal had been acquired. Subsequent measurements after moving and remounting the sample, however, did not exhibit this same feature. Therefore, the acquired Raman signal was not repeatable. It is not clear whether the unrepeatability stems from the high heterogeneity of the film or rather if the observed signal was spurious and not a consequence of the Raman effect. As such, current work is underway to acquire a homogeneous graphite sample to analyze with the current optical arrangement.

In summary, work commenced on the development of an ultrafast Raman capability through incorporation of a laser source having 200 fs laser pulses that would allow for examination of Si. Due to the unexpected breakdown of this source, a Mai Tai laser having a 90 fs pulse was implemented despite the fact that its spectral bandwidth was both predicted and observed to overwhelm the Si Raman signal making it irresolvable. To minimize the effects of the spectrally broad laser line, a diamond like carbon film was analyzed in the ultrafast arrangement. Although a spectral feature that corresponds to graphite was observed, its acquisition was not found to be repeatable. Therefore, future work is needed to fully realize the ultrafast Raman capability. The following section outlines the future strategy for rigorously accomplishing this task.

4. RECCOMENDATIONS AND FUTURE WORK

Sandia is a proven leader in the thermal behavior of microsystems due to significant investments in the modeling (Enhanced Molecular Dynamics for Simulating Thermal and Charge Transport Phenomena in Metals and Semiconductors, LDRD-117786), measurement (Noncontact Surface Thermometry for Microsystems, LDRD-67067), and control (Phonon Engineering for Nanostructures, LDRD-105906) of the phenomena determining the cascade of energy from initial insertion to eventual equilibration. The present study takes the first step in the development of a “first of its kind” tool that with its realization would further the laboratory’s world class proficiency in this area. With this initial investment, proficiency has been achieved in the acquisition and analysis of TTR while difficulties remain in attaining a robust, rigorous, and repeatable ultrafast Raman signal. In response, the following sections leverage the significant understanding gained in this study concerning the limitations of ultrafast Raman to outline the steps that will enable the realization of the simultaneous femtosecond capability.

4.1 Simultaneous Capability Via 150 Fs Pulses and 45° Beam Splitter

A chief obstacle during the current project arose from the use of a 90 fs pulsed laser source that is inherently broadband. The broadband nature of the laser pulse, as stated previously, effectively masks much of the resulting Raman spectra (See Figure 5). The use of a longer laser pulse, meanwhile, largely circumvents this difficulty. As such, future work will implement 150 fs pulses produced by a Spectra Physics Tsunami Laser that is currently in the process of being brought back on line. Using a conservative 4.5 times BW limit, these 150 fs pulses are anticipated to allow for observation of Raman shifts above 440 cm^{-1} and hence the analysis of most semiconductor materials: silicon (520 cm^{-1}), GaN (568 cm^{-1} & 734 cm^{-1}), SiC (789 cm^{-1} & 969 cm^{-1}) and graphene (1350 cm^{-1} , 1580 cm^{-1} , and 2700 cm^{-1}). Additionally, this Tsunami laser is of higher power than that of the Mai Tai reported earlier and thus should produce a heightened level of signal. Maximization of the probe signal will also take place through the incorporation of a Semrock 45° ultrasteep beam splitter (LPD01-785RU-25) as shown in Figure 17. The use of a 45° beam splitter effectively “turns” the probe beam onto the same path as that of the pump without reducing the power of the incident radiation. This is in contrast to the arrangement incorporated in Figure 11 in which a 50/50 beam splitter is utilized in the same capacity albeit with an associated halving of the incident probe intensity. Implementing the 45° beam splitter, however, allows for measurement of only the Stokes signal as it transmits only light on the red side of the laser line.

The arrangement described in Figure 17 is nearly equivalent for the TTR experiment to that utilized in the current study and depicted in Figure 10. The only alteration stems from the use of the 45° beam splitter, which reflects over 98% of the incident and reflected TTR signal. Therefore, it is anticipated that the optical arrangement will allow for the simultaneous acquisition of the Raman signal at the expense of only ~4% of the TTR signal. Furthermore, the arrangement will also allow for the use of either technique to be utilized independent to the other without the need to remove any optical components.

Figure 17. Combined Raman and TTR set up utilizing a 150 fs pulse and a 45° beam splitter to acquire each signal simultaneously. The 150 fs pulse allows for measurement at spectral locations closer to the laser line while the higher power source and use of the 45° beam splitter will increase signal.

In addition, the use of laser line filters to shape the incident pulse and probe beams will be quantified as the current study has employed, but not optimized, their utility (See Figure 12). Consequently, in the developing of the optical set up shown in Figure 17, both laser line filters will be tuned independently with the goal of maximizing the total power of incident light reaching the sample from both the pump and probe while concurrently insuring that each of these beams is as spectrally distinct as possible. In this manner, the signal strength will be maximized while in conjunction minimizing the effect of the pump beam on the measured TTR or Raman signals. Such an approach has been utilized previously in the “Two-Tint” measurements of Kang *et al.* with good success and hence its incorporation is merited here [3].

4.2 Coupled Capability Incorporating Polarization Control

The Raman activity of a given material—or mode within such a material—is determined, in part, by the polarization of the incident and scattered radiation. To then maximize both the flexibility and capability of the technique, it is imperative that this polarization be in some way controlled. The majority of ultrafast TTR and Raman arrangements, however, utilize a co-linear pump/probe arrangement in which the two beam paths are separated and recombined via polarizing beam splitters as has been shown in Figure 10, Figure 11, and Figure 17. Such an arrangement requires that the incident and measured radiation be identically polarized. Identical polarization, in turn, severely limits the range of materials and individual phonon modes that may be

Figure 18. Simultaneous Raman and TTR arrangement in which polarization is controlled via removable half-wave plates along the incident and collection paths. As such, polarizing beam splitters cannot be utilized to steer and recombine the pump and probe beams, requiring spectral shaping of each path to allow for their separation and analysis. 50/50 Beam splitters are utilized in concert with a laser line filter to obtain the TTR signal while a 45° beam splitter reflects the incident probe but transmits the resulting Stokes shifted radiation allowing for the Raman analysis.

observed. Hence, arrangements will be examined in which the polarization is controlled rather than being mandated as part of the beam steering process.

Figure 18 describes one such arrangement in which the polarization is controlled both along the incident and scattered paths using removable half-wave plates. As the polarization is no longer utilized to distinguish the pump and probe beams, a 50/50 beam splitter is incorporated first to spatially divide the paths. Further beam separation then occurs in a spectral fashion via shaping of the pump with a long pass filter (Semrock LP01-780RU-25) followed in series by a band pass filter (Semrock FF01-786/22-25). This tandem arrangement effectively red shifts the spectrally broad laser source as the combination allows the transmission of wavelengths between only 795 and 803 nm. The probe beam, meanwhile, is also shaped albeit in this case with a 3 nm wide laser line filter centered at 785 nm. As such, the pump and probe, while not distinguished in polarization, are distinct in their spectral character.

Like in the other arrangements described, the pump beam is modulated as it approaches the surface. Unlike the other arrangements, it passes through two 50/50 beam splitters implemented to: first, recombine pump and probe before impinging on the sample and second to direct the TTR signal to the photodiode. In this arrangement, the intensity of the pump beam is reduced by a factor of 4 before reaching the sample. However, as the overall laser power supplied by the Tsunami is greater than that currently employed, even with this reduction the amount of pump energy is expected to be sufficient enough to perturb the system.

The probe beam, after passing through the variable delay stage and laser line filter, interacts with a 45° dichroic beam splitter that is highly reflective for the 785 nm laser line even as it is highly transmissive for red/Stokes shifted light. Consequently, the beam splitter is used as a mirror to direct the probe to the sample even as it allows the resulting Stokes shifted Raman signal to be transmitted, and hence collected, via the fiber optic couplers directly behind it. Polarization of this collected Raman light may then be controlled using a half-wave plate placed before the spectrometer and notch filter. Noteworthy is the fact that the 50/50 beam splitter utilized to recombine the pump and probe reduces the intensity of both the incident and scattered radiation. As such, this arrangement will reduce the intensity of the Raman signal by ~ 4 in comparison to the arrangement described in Figure 17. Similarly, as the TTR signal is collected using an additional 50/50 BS in comparison to the arrangement of Figure 17, its signal strength will be reduced by ~ 4 as well. To alleviate this reduction in signal intensity while maintaining the ability to separate and recombine the beams, the use of D-shaped mirrors in place of the 50/50 beam splitters will be investigated as well.

5. CONCLUSIONS AND SUMMARY

The development of reliable high power, high performing, microsystems for satellite and weapon systems requires identification of the critical energy pathways governing thermal dissipation in the materials making up these components. To ascertain these dissipation mechanisms, tools must be implemented that can probe each of the relevant energy carriers, that is both electrons and phonons, at time scales relevant to their transport and interaction. In response, this late start project was an initial effort to develop a capability to simultaneously perform transient thermoreflectance (electrons) and Raman spectroscopy (phonons) at sub-picosecond timescales with the long term goal of developing a tool that is uniquely suited to probe and decipher the cascade of energy through a material. As a first step then, the project's goals centered not on the analysis of these thermal processes but rather on the acquisition of sub-picosecond TTR and Raman signals.

TTR signals have been acquired in a robust, rigorous, and repeatable fashion on a time scale of ~ 100 fs using a co-linear pump probe arrangement for a variety of materials including silicon. The employed optical arrangement is currently being utilized to measure and quantify such parameters as thermal conductivity, thermal boundary conductance, and the electron-phonon coupling factor. Acquisition of an ultrafast Raman signal was only demonstrated in an unrepeatable fashion using with this set up, however, due in large part to the spectral broadening inherent in the use of a 90 fs laser pulse. Analysis of this difficulty bounded, for the first time, the capability of performing ultrafast Raman at decreasing time scales. From this analysis, it was concluded that Raman signals may only be resolved when they are spectrally separated from the laser line by at least 3 times that of the bandwidth limited pulse. Therefore, future efforts focused on the acquisition of simultaneous Raman and TTR signals will utilize 150 fs pulses in order to balance the requirements of temporal and spectral resolving power.

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