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ULTRAFAST ELECTRON-PHONON COUPLING AT THE METAL-DIELECTRIC INTERFACE

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ULTRAFAST ELECTRON-PHONON COUPLING AT THE METAL-DIELECTRIC INTERFACE

For the degree of Master of Science in Mechanical Engineering

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Date

ULTRAFAST ELECTRON-PHONON COUPLING AT THE METAL-DIELECTRIC
INTERFACE

A Thesis

Submitted to the Faculty

of

Purdue University

by

Qiaomu Yao

In Partial Fulfillment of the

Requirements for the Degree

of

Master of Science in Mechanical Engineering

December, 2015

Purdue University

West Lafayette, Indiana

For my parents, my sister, my girlfriend, and for all the people believe in love.

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TABLE OF CONTENTS

	Page
LIST OF TABLES.....	v
LIST OF FIGURES.....	vi
ABSTRACT.....	vii
CHAPTER 1. INTRODUCTION.....	1
1.1 Introduction to Past Related Research.....	1
1.2 Band Structure of Metals.....	3
1.3 Interaction of Ultrafast Laser and Metals.....	5
1.4 Objective and Organization of This Thesis.....	7
CHAPTER 2. EXPERIMENT SETUP AND TRIANSIENT REFLECTANCE MEASUREMENT.....	9
2.1 Pump and Probe Technique.....	9
2.2 Ultrafast Transient Reflectance Spectroscopy.....	11
2.3 Transient Reflectance Change and Dynamics of Energy Carriers.....	13
CHAPTER 3. TRANSIENT DYNAMICS OF CARRIERS BASED ON TEMPERATURE DEPENDENT MODEL.....	16
3.1 Two-Temperature Model on Metal-Dielectric Interface.....	16
3.2 Dielectric Constant and Drude-Lorentz Model.....	19
3.3 Non-Thermalized Electrons.....	27
CHAPTER 4. EXPERIMENTAL RESULTS AND ELECTRON-PHONON COUPLING ACROSS METAL-DIELECTRIC INTERFACE.....	30
4.1 Experiment Results on Thick Gold.....	30
4.2 Experiment Results on Thin Gold Film on Silicon.....	32
4.3 Electron-Phonon Coupling within Film and Across Metal-Dielectric Interface ...	35
CHAPTER 5. CONCLUSIONS AND FUTURE WORK.....	38
5.1 Summary and Conclusions.....	38
5.2 Future Work.....	39
LIST OF REFERENCES.....	41

LIST OF TABLES

Table	Page
Table 3.1. Summary of the parameters in the Drude - Lorentz model	24
Table 3.2. Fitting parameters for TTM and Drude-Lorentz model	26
Table 4.1. Thermal Resistance for different pump fluences at Au-Si sample with thickness 24 nm, 39 nm, 65 nm when measured with 490 nm probe and 800 nm pump.	33

LIST OF FIGURES

Figure	Page
Figure 1.1. Distribution of probability density for travelling waves on both negative and positive directions (Kittel, 2005).	5
Figure 1.2. Interband transition from d band to s/p band (dashed arrow) and intraband transition inside s/p band (solid arrow) in gold, where gold has an ITT of 2.47 eV. The electrons population in s/p band follows the Fermi-Dirac distribution.	6
Figure 2.1. Experiment Setup for Pump and Probe Ultrafast Laser.	10
Figure 2.2. Signal Processing for pump and probe technique to measure the reflectance variation with two photodiode detectors, chopper, pre-amplifier, function generator, and lock-in amplifier.	13
Figure 3.1. Calculated real part (3.1a) and imaginary part (3.1b) of dielectric constant ϵ_1 and ϵ_2 dependence on probe wavelength and temperature with Drude-Lorentz model. (3.1c) is the $\epsilon_1(T)$ real part of elevated temperature's difference with room temperature real part $\epsilon_1(T_0)$. (3.1d) is the $\epsilon_2(T)$ real part of elevated temperature's difference with room temperature real part $\epsilon_2(T_0)$	25
Figure 3.2. The reflectance change ΔR with electron temperature at different probe wavelength.	26
Figure 3.3. Electrons distribution change for nonthermalized electrons and thermalized electrons, the dashed line indicates the probe energy at 2.53 eV (490 nm) chosen for measurement where change from nonthermalized electrons is much less than that from thermalized electrons.	28
Figure 4.1. Experiment and fitting result of Au-Si with gold thickness at 1000 nm (4.1a) and 250 nm (4.1b) at pump fluences 33.0, 74.3, and 116 J/m ²	31
Figure 4.2. Experiment and fitting result of bulk Au with 490 nm probe and 800 nm pump at 33.0 J/m ²	32
Figure 4.3. Experiment and fitting result of 24 nm (5a), 39 nm (5b), 65 nm (5c) Au-Si with 490 nm probe and 800 nm pump at 33.0, 74.3, 116 J/m ²	34
Figure 4.4. Thermal resistance R_{es} and thermal conductance $h = 1/R_{es}$ between gold electron and silicon phonon at interface relationship with electron and phonon temperature $T_e + T_l$. And fit h with linear equation $2.051 \times 10^{-4} (T_e + T_l) + 0.1126 = h$	36

ABSTRACT

Yao, Qiaomu. M.S.M.E., Purdue University, December, 2015. Ultrafast Electron-Phonon Coupling at the Metal-Dielectric Interface. Major Professor: Xianfan Xu, School of Mechanical Engineering.

The pump-probe technique is an ultrafast spectroscopy method of detecting the dynamics of energy carriers such as electrons, phonons, and holes with transient thermal reflectance measurement. A laser beam is divided into a pump beam and probe beam with different wavelength or polarization and time delay. According to the transient reflectance result, this method could be applied to investigate the interaction between electron-phonon and electron-electron coupling with a high temporal resolution on the order of 10 femtoseconds.

Energy transfer of photo-excited electrons in a metal film to the dielectric substrate at the metal-dielectric interface is important for understanding the ultrafast heat transfer process across the two materials. Many researches have been conducted in finding this energy transfer process in different materials. In this thesis, by measuring the transient reflectance variation, the two-temperature model (TTM) is used to analyze the interface metal electron and dielectric substrate coupling. In order to relate temperature to the reflectance change, a temperature and wavelength dependent Drude-Lorentz model was developed which represents the temperature dependent dielectric constant and can be used to calculate reflectance variation. Ultrafast pump-and-probe interband transition

measurements on Au-Si samples were carried out, where the probe photon energy was chosen to be close to the interband transition threshold (ITT) of gold to minimize the influence of non-equilibrium or non-thermalized electrons on the optical response, and to increase the signal to noise ratio for reflectance change.

In the experiment, different pump fluences have been used to test the transient reflectance variation on Au-Si samples of different thicknesses. The pump wavelength is taken as 800 nm while the probe wavelength is taken as 490 nm. A thick gold of 1000 nm thickness has been used to determine the electron-phonon coupling strength represented by a constant G_0 , and thinner films have been tested by fitting the transient reflectance change with this G_0 and the electron-phonon thermal resistance across interface. Interface thermal conductance (inverse of thermal resistance) at different pump laser fluences was obtained, and was found to increase with the interface electron and phonon temperature.

For future work, with the model and measurement method implemented in this thesis, more gold film samples with more types of substrate, such as Au-Glass, Au-Quartz, can be tested to see the difference when the non-equilibrium electrons factor has been reduced. Also, more proper probe wavelengths which maximize the signal-noise ratio for different materials can be concluded from the Drude-Lorentz model. The contribution of non-thermalized electron compared with thermalized electron at different wavelength for other samples shall be investigated in the future.

CHAPTER 1. INTRODUCTION

Electron-phonon coupling in thin metal films and across metal-dielectric interfaces is one of the major topics in ultrafast heat transfer researches. As an ultrafast laser beam is focused onto a metal thin film, the photon energy will be absorbed first by free electrons, and it takes a few tens to hundreds of femtoseconds for electrons to reach electron thermal equilibrium. The electron-phonon energy coupling then heats up the lattice of the metal film. For thin metal films on substrate, there can be electron-phonon coupling across metal-dielectric interface as well, which then spread the energy into the substrate through heat diffusion.

In this chapter, we give a brief review on the past related research that has been done on electron-phonon coupling within film or across interface with the pump-probe technique. A discussion on the metal band structure and dynamics of energy carriers has been shown to help to understand the physical background of this thesis. The gold band structure has been introduced in detail, including the physics of band gap in metal, and how the ultrafast laser would interact the energy carriers in metal.

1.1 Introduction to Past Related Research

Many researches have been carried out to quantify electron-phonon coupling, characterized by a coupling constant G , particularly in gold (Elsayed-Ali, *et al.*, 1991, Qiu, *et al.*, 1993, Wellershoff, *et al.*, 1999 and Chowdhury, *et al.*, 2003). Holfield, *et al.*

(2000) found G is independent of the electron temperature with 10 nm - 100 nm gold sample and independent of the film thickness within 20% uncertainty when the film is pumped with 400 nm wavelength and probed around gold ITT. Other investigations considered the electron-phonon coupling factor G as film thickness and/or pump fluence dependent, and fitted the value of G to the measured thermal reflectance variation (Hohlfeld, et al., 2000, Elsayed-Ali, et al., 1991, and Fann, et al., 1992). During the electron relaxation process, the excited electrons relax to the Fermi-Dirac distribution mainly through electron-electron collisions and electron-phonon scattering (Kittel, 2005). This thermalization process of excited electrons can influence the optical response, which can be manifested by varying the probe wavelength. Sun et al. (1994) found that the optical response is largely influenced by the non-thermalized electrons when probing with wavelengths other than the inter-band transition (ITT) energy (2.47 eV for gold), but the non-thermalized electrons contributed much less to the optical response at energy close to ITT. Guo and Xu (2014) confirmed the probe wavelength-dependent optical responses in gold. They used a probe of 490 nm wavelength (2.53 eV), slightly above the ITT of gold, and found the electron-phonon coupling G in gold to be $1.5 \times 10^{16} \text{ W}/(\text{m}^3\text{K})$, which is less than values reported in other works using other wavelengths. A more recent study showed the electron-phonon coupling factor G increased with the electron temperature, and was less influenced by non-thermalized electrons with higher pump fluence (up to $10.7 \text{ J}/\text{m}^2$) because of the higher rate of electron-electron scattering (Giri, et al., 2015). Energy coupling between electrons and phonons across interface has also been studied, and a linear relation between electron-phonon interfacial thermal

conductance and electron temperature has been found in Au films using both 800 nm as pump and probe beams (Hopkins, *et al.*, 2009).

This thesis investigates the interface electron-phonon coupling across gold/silicon interface. Electron and lattice temperatures in gold together with the lattice temperature in silicon are modeled to account for the electron-phonon coupling in gold and electron-phonon coupling across the interface. The optical response is computed using a modified temperature-dependent Drude-Lorentz model. The probe photon energy is chosen as 2.53 eV to minimize the effect of non-thermalized electrons on the optical response. The temperature-dependent electron-phonon coupling factor G is first analyzed from the experimental data on bulk gold. The temperature-dependent interface conductance or resistance is then obtained from the experimental data on gold thin films.

1.2 Band Structure of Metals

The band structure helps to understand the distinction between metals, semiconductors, and insulators, the relation of conduction electrons in the metal to the valence electrons of free atoms. Electrons in crystals are arranged in energy bands and separated by band gaps which results from the interaction of conduction electrons and applied electric field. This section is mainly based on Solid State Physics text book by Kittel (2005).

The free electrons wavefunctions can be described as follows:

$$\psi_{\vec{k}}(\vec{r}) = \exp(i\vec{k} \cdot \vec{r}) \quad (1.1)$$

Where $\vec{k}$ represents the wavevector and $\vec{r}$ is the spatial coordinate distance. This equation represents the running wave carrying momentum $p = \hbar k$. This model describes the band

electrons are treated as perturbed only by the ion cores periodically and can be used to explain almost all the questions of electrons behaviors. Bragg reflection will happen when $\bar{k}$ matches the following condition:

$$\left(\bar{k} + \bar{G}\right)^2 = \bar{k}^2 \quad (1.2)$$

Where G vector is the reciprocal lattice vector equals to $2\pi/a$, and this condition will be satisfied when $k = \pm 0.5G = \pm n\pi/a$, where n is an integer. In the 1-D circumstance, in the first Brillouin zone, the travelling wave at $\pm\pi/a$ will be Brag-reflected at these boundaries into inverse direction, so the time-independent state of wavefunction is represented by standing waves with positive and negative directions:

$$\psi(+) = \exp(i\pi x/a) + \exp(-i\pi x/a) = 2\cos(\pi x/a) \quad (1.3a)$$

$$\psi(-) = \exp(i\pi x/a) - \exp(-i\pi x/a) = 2i\sin(\pi x/a) \quad (1.3b)$$

The negative and positive signs are the directions of travelling waves, and these equations explain well about the origin of band gap. The probability of standing wave can be described with equations:

$$\rho(+) = |\psi(+)|^2 \propto \cos^2(\pi x/a) \quad (1.4a)$$

$$\rho(-) = |\psi(-)|^2 \propto \sin^2(\pi x/a) \quad (1.4b)$$

Where $\rho(+)$ and $\rho(-)$ is the distribution of probability density for travelling waves and is plotted in Fig. 1.1. Since the ions core is positive and attracts negative electrons, the positive wavefunction $\psi(+)$ concentrated near the cores of particles would decrease the potential energy in comparison with average potential energy seen by travelling waves and vice versa for negative wavefunction $\psi(-)$ which is concentrated in between two

cores. Because of this difference on energy potential near the brilliouiin zone boundary area, band gap has been formed in this case.

Figure 1.1. Distribution of probability density for travelling waves on both negative and positive directions (Kittel, 2005).

The difference of metals from insulators is the difference of electrons states of band structures. If the valence electrons has filled exact one or more bands and no more free electrons are left in any band, the crystal would be an insulator. For an insulator, a filled band is separated by an energy gap from the next higher band and no electrons can be excited to higher states. For metals, there are one or more states that is half filled with electrons and this is called conduction band which has free electrons that plays an important role for the energy transfer when excited with laser pulse. The band with all filled electrons is called valence band. The band gap is described as the energy difference between the lowest point of conduction band and highest point of valence band. If the minimum point of conduction band and maximum point of valence band have the same wave vector, this band gap is named as direct band gap, otherwise it is called indirect band gap. Indirect band gap transition would require the absorption or emission of phonons.

1.3 Interaction of Ultrafast Laser and Metals

Ultrafast laser would provide a high power density on the sample surface in a very short time and the electron temperature would largely increase by absorption of photons,

and electron-electron and electron-phonon coupling process can be measured with the reflectance change of laser beam. Gold has been widely used as the metal film sample in the studies of ultrafast spectroscopy and nanoscale heat transfer analysis. Gold has a typical band structure as a noble metal, its free electrons would absorb some of the photons from the laser beam and reflect the rest for reflectance measurement (no transmission is considered in this thesis). Due to the electrons occupancy variation, d-s/p band excitation will slightly affect the absorption of light and the reflectance. As photons are absorbed by free electrons of both *d* band and *s/p* band, electrons would become thermalized in a few hundreds of femtoseconds and reach into the Fermi-Dirac distribution:

$$f(E, T) = \frac{1}{e^{(E-E_F)/kT} + 1} \quad (1.5)$$

Where E denotes the energy, E_F is Fermi energy of gold, k is Boltzmann's constant, and T is absolute electron temperature.

Figure 1.2. Interband transition from d band to s/p band (dashed arrow) and intraband transition inside s/p band (solid arrow) in gold, where gold has an ITT of 2.47 eV. The electrons population in s/p band follows the Fermi-Dirac distribution.

Due to the variation of electron occupancy as temperature changes, both the d band and s/p band excitation will affect the absorption of light and cause the change in reflectivity. Fig. 1.2 shows the band structure of gold and Fermi-Dirac distribution near the Fermi energy, which can be used to explain the impact of the change of the Fermi-Dirac distribution on the reflectance. As the temperature increases, the DOS occupation of electrons with energy above the Fermi energy increases and the DOS occupation of electrons with energy below the Fermi energy decreases. For probe photon energy larger than ITT (as indicated with dashed arrow in Fig. 1.2), this change in electron distribution will decrease the photon absorption for electron transitions from the d band to unfilled energy states above the Fermi energy and thus increase the reflection. On the other hand for probe photon energy less than ITT the absorption decreases and the reflection increases. These trends were experimentally observed (Hohlfield, et al., 2000).

1.4 Objective and Organization of This Thesis

In this thesis, pump and probe techniques are applied to measure the Au-Si samples using 490 nm probe and 800 nm pump, and different pump fluences. A TTM model has been used to get the temperature of electrons and phonons, and Drude Lorentz model is implemented to relate reflectance change with electron and phonon temperature. Chapter 2 introduces the ultrafast spectroscopy laser system and builds the relation of signal processing for transfer the chopped light signal into digital signal. Then it describes the basics of analyzing the reflectance variations with pre-amplifier, lock-In amplifier and function generator. Finally it explains the dynamics of energy carriers in the metal and how energy is transferred within metal film and across interface. Chapter 3 describes the basic model for calculating the electron temperature, phonon temperature, electron-

phonon coupling constant, metal-dielectric interface thermal resistance and interface heat conductance. In this chapter, TTM and Drude-Lorentz model have been combined together to fit the measured reflectance change, and non-thermalized electrons have been emphasized which can take an important role in the initial time of heating and introduce a significant difference on fitting parameters of our calculation, several methods has been applied to reduce its impact. Chapter 4 describes the experiment results on Au-Si samples, the experiment is tested on bulk gold and thin gold films on silicon substrate with multiple fluences and a similar form of thermal conductance model has been introduced to compare the result with past work, the consistency of results have been discussed and further work has been recommended.

CHAPTER 2. EXPERIMENT SETUP AND TRIANSIENT REFLECTANCE MEASUREMENT

The pump-probe method has been frequently used in the ultrafast spectroscopy in the field of heat transfer analysis of energy carriers. Many related research has been done with this method. Transient reflectance measurement is one of the way of measurement by recording the reflectance variation of samples in order to know physical reaction that happens inside the material. In this chapter, the experiment setup and measurement methods are introduced, and the basic three steps about the photon interaction of electron, and electron scattering with phonon have been discussed.

2.1 Pump and Probe Technique

Many results show that the energy transfer process within homogenous metals between electrons and phonons is within femtosecond or picosecond time duration. During this process, electrons are heated by the photons from the laser beam in a very short time, and transmit the energy to phonons in a few picoseconds.

High-speed temperature measurement technique is needed in this case. Many high temporal resolution temperature measurement systems, such as those for measuring superheating, femtosecond evaporation, and laser annealing, are determined by the speed of detectors. Since the response time of detectors is limited to the scale of nanosecond to picosecond, the pump and probe measurement technique plays a critical role in achieving high resolution.

In the pump and probe measurements, the laser beam is divided into two pulses by a beam splitter. Pump pulse has intense light and is with higher energy which is used for heating up the sample. Probe pulse is less intense (roughly 10% of main beam) and has a variable delay time against pump pulse which is controlled by a highly accurate delay stage. By repeating scanning the delay stage, the probe pulse detects the reflectance change of the samples at every delay time on the scale of femtosecond and a transient process is pictured statistically. On the other hand, the pump and probe pulses have been designed to travel through the same distance in order to make sure the same pulse separated by the beam splitter will join together when they hit on the sample.

Figure 2.1. Experiment Setup for Pump and Probe Ultrafast Laser.

As Fig. 2.1 shows, pump and probe are separated with a beam splitter, pump beam is chopped with a chopper which is reading a 500 Hz TTL signal from a function generator. This chopper cuts the pump with 500 Hz frequency and chopper will transit this real time frequency into lock-in amplifier. A stage is used to accurately control the

time delay between pump and probe, and dichroic mirror (reflect probe and pass pump) helps join pump beam and probe beam together. After dichroic mirror, both of the beams shall be collinear and are focused on the sample and reflected probe back to detector 1 after pump being filtered with filters and dichroic mirror. Meanwhile, some part of the probe beam has been splitted with dichroic mirror as a reference signal, in order to increase the signal-noise ratio. The photodiode in both of the detectors generate two electronic signal and join together before been resolved at lock-in amplifier. While the pump and probe has been focused at the same point on the sample and every pulse of pump and probe reaches to the sample at the same time, a signal represents the reflectance variation at the time delay defined by stage can be read from lock-in amplifier.

The ultrafast spectroscopy schemes used in this thesis has a Ti-Sapphire femtosecond laser beam centered at 800 nm with pulse width 100 femtoseconds and repetition rate of 5000 Hz. The pump pulse is fixed at 800 nm wavelength, and the probe pulse is tunable from 490 nm to 600 nm. The delay time between pump and probe is within 10 picoseconds. In this thesis, the probe wavelength is chosen as 490 nm in order to reduce the impact of non-thermalized electrons, and in Chapter 3, it will be discussed in detail.

2.2 Ultrafast Transient Reflectance Spectroscopy

The laser repetition rate is 5000 Hz, which means there are 5000 pulses every second, and every pulse is around 100 femtoseconds which is much shorter than the rise and fall time of the photodiode resolution (10 femtoseconds), the signal processing modulation is necessary for the measurement.

For every repetition time, the heating process takes 100 femtoseconds and follows a long period of non-heating process. It is obvious to assume that two heating process is independent and so it is with the reflectivity and temperature variation on the sample. The pump pulse is modulated by a mechanical chopper with 500 Hz frequency. During the open time of chopper, the probe beam after reflection will show the data with sample being heated, on the other hand, if the chopper is closed, the probe beam will read the data without thermalization process. The signal from the probe can be accessed within the response time of photodiode and after passing through the band-filter the AC signal turns into a sinusoidal function. The amplitude of this function is the reflectance change.

In order to increase the signal to noise ratio, two photodiode detectors are used for pump pulse and probe pulse separately. One of the photodiode detector measures the signal after the reflection on a heated sample, and the other detector is balanced and fixed when the sample is not heated. Those two values read by two photodiodes contain the frequency of the chopper. The signal processing is shown in Fig. 2.2, if the time difference between pump and probe is Δt , the detector will see a signal with $R_0 + \Delta R(\Delta t)$ because of the thermalization process caused by pump heating. Since the frequency of chopper is 500 Hz which is 10 times less than frequency of the laser, there are ten pulses that probed onto the sample would be measured by one of the detectors during the open time of chopper which has recorded the reflectance data of the sample surface, and during the chopper's close time this information is inaccessible. A preamplifier will be used to further amplify those signal values and filter out some noise with band pass filter. A lock-in amplifier will analyze the sinusoid signals and resolve the chopper frequency to read

out the ideal data. After scanning the delay stage for multiple times, the reflectivity response can be plotted and laser heating process can be accessed.

Figure 2.2. Signal Processing for pump and probe technique to measure the reflectance variation with two photodiode detectors, chopper, pre-amplifier, function generator, and lock-in amplifier.

2.3 Transient Reflectance Change and Dynamics of Energy Carriers

In the measurements, the pump photon energy is focused onto the sample in a very small time period and it will provide a high power density to excite the electrons. Due to the photon absorption of free electrons, the reflectance of probe pulse photons would change because of the thermal process and electrons excitations on the sample

surface. Although the reflectance change may vary with different pump-probe wavelength, different materials, different fluences and thicknesses, it is intuitively clear that high electron temperature would cause electron-electron scattering, and electron-phonon coupling in a few picoseconds, and diffusively transfer into deep part of the sample.

There are mainly three steps for the electrons to absorb photon energy and interact with each other. Initially, photons will be absorbed by free electrons near Fermi levels at the sample surface, and these electrons would be excited into higher energy levels. At this time, ballistic transportation would happen where electrons would diffusively transported into deeper part of this sample at velocities close to Fermi velocities (10^6 m/s for gold). In the meanwhile, these excited electrons do not follow the Fermi-Dirac distribution, and can't be defined with a temperature, which are called non-thermalized electrons. Non-thermalized electrons would collide and exchange energy with free electrons and phonons in the first few hundred femtoseconds and finally reach the Fermi-Dirac distribution. The second step starts almost when the thermalization process is finished where hot electrons carry the energy and start to interact with cold lattice by electron-phonon scattering. At the same time, because of the high gradient of temperature, the heat is transferred into deeper part of the sample but with a lower speed (less than 10^4 m/s for gold) than ballistic motion. If the gold sample has a thin thickness, as temperature of electrons and lattice increases at the interface, the electron-phonon coupling between metal electrons/phonons and dielectric phonons stand out to have a large impact on the thermal transportation process. The electron-phonon scattering within the sample and across the interface in this step can be well defined with two-temperature model and this thesis will discuss it later.

The third step starts when electron and lattice temperatures have reached equilibrium, since phonon has larger heat capacity than electrons, the equilibrium temperature is roughly one to two orders smaller than the maximum electron temperature and the diffusion of energy becomes weak because of the low temperature gradient.

CHAPTER 3. TRANSIENT DYNAMICS OF CARRIERS BASED ON TEMPERATURE DEPENDENT MODEL

The two-temperature model is the most widely used method for the temperature profiling inside the metal. Almost all the related research analyzes the reflectance or transmission data based on this model, however, the original two-temperature model has some drawbacks which cannot describe the non-thermalized electron contribution to the transient reflectance change. In this chapter, the reflectance change is deduced from the dielectric constant, a detailed Drude-Lorentz model has been implemented to bridge the dielectric constant with electron and phonon temperature which proves to be able to maximize the signal to noise ratio.

3.1 Two-Temperature Model on Metal-Dielectric Interface

To quantify the temperature relation of electron and phonon on time and space, TTM (two-temperature model) is most used model developed by Anisimov, *et al.* (1974) which can be used to simulate the surface electron temperature with a term represents the electron-phonon coupling strength:

$$C_e \frac{\partial T_e}{\partial t} = k_e \frac{\partial^2 T_e}{\partial x^2} - G(T_e - T_p) + S \quad (3.1a)$$

$$C_p \frac{\partial T_p}{\partial t} = k_p \frac{\partial^2 T_p}{\partial x^2} - G(T_e - T_p) \quad (3.1b)$$

The subscripts e , p , and s stand for electrons, phonons and substrate, respectively. C_e and C_p are the respective heat capacities of electrons and lattice and k_e , k_p denote the thermal

conductivity of electrons and phonons. G is the coupling factor between electrons and phonons. In order to analyze the interface heat transfer, an extra equation has been added for the substrate to calculate the substrate lattice temperature.

$$C_s \frac{\partial T_s}{\partial t} = k_s \frac{\partial^2 T_s}{\partial x^2} \quad (3.2)$$

C_s is the heat capacity of substrate, and k_s is the thermal conductivity of substrate. On the interface, these three equations above can be written with the following relation:

$$-k_e \frac{\partial T_e}{\partial x} \Big|_{x=L} = \frac{T_e - T_s}{R_{es}} \Big|_{x=L} \quad (3.3a)$$

$$-k_p \frac{\partial T_p}{\partial x} \Big|_{x=L} = \frac{T_p - T_s}{R_{ps}} \Big|_{x=L} \quad (3.3b)$$

$$-k_s \frac{\partial T_s}{\partial x} \Big|_{x=L} = \frac{T_e - T_s}{R_{es}} \Big|_{x=L} + \frac{T_p - T_s}{R_{ps}} \Big|_{x=L} \quad (3.3c)$$

R is the thermal resistance between interfaces, L is the thickness of thin film on the substrate, the thermal resistance R has been used to calculate the heat flux across the interface including the scattering of metal electrons with dielectric substrate lattice, metal phonons with dielectric substrate lattice, since dielectric doesn't have free electrons so there is no electron-electron coupling.

The laser source term is given by considering the electron ballistic motion, time width of laser pulse, and laser fluence, which can be written in the following form:

$$S = 0.94 \frac{1-R}{(\delta + \delta_b) \left(1 - e^{-d/(\delta + \delta_b)}\right)} \cdot \frac{J}{t_p} \exp \left[\frac{x}{\delta + \delta_b} - 2.77 \left(\frac{t}{t_p} \right)^2 \right] \quad (3.4)$$

This equation represents a temporal Gaussian pulse with the consideration of the ballistic motion of electrons and thermal absorption in the x-direction. t_p is the FWHM (Full width at half maximum) of the laser pulse, R is the reflectivity of gold film, d denotes the thickness of sample, δ_b is the ballistic range of electrons, J is the fluence of laser beam, and δ is the absorption depth.

The electron heat capacity is taken to be proportional to the electron temperature:

$$C(T_e) = B_e \cdot T_e \quad (3.5)$$

Where B_e is the linear parameter for the relation between electron heat capacity and electron temperature. Also the electron thermal conductivity k_e can be taken to be propositional to electron temperature when the temperature is much smaller than Fermi temperature of material. The gold Fermi temperature is 6.42×10^4 K, so in this study, electron capacity can be expressed in this equation when the temperature gets close to Fermi temperature (Anisimov, et al., 1997):

$$k_e = \chi \frac{(\vartheta_e^2 + 0.16)^{1.25} (\vartheta_e^2 + 0.44) \cdot \vartheta_e}{\sqrt{\vartheta_e^2 + 0.092 (\vartheta_e^2 + \eta \cdot \vartheta_1)}} \quad (3.6)$$

Where $\vartheta_e = k_b T_e / \varepsilon_F$ and $\vartheta_1 = k_b T_1 / \varepsilon_F$ and $\chi = 353$, $\eta = 0.16$.

However, there is still some limitation on TTM (Fann *et al.*, 1992). From the comparison between measured electron distribution functions and those predicted from equilibrium thermodynamics, the electrons matches the TTM predictions well after several hundreds of femtosecond, but electrons temperature is not predictable before this time. This non-thermalization reaction of electrons has a wavelength dependence property which we will discuss in the later chapters.

With TTM, we can simulate the electron and phonon temperature inside of film and substrate with a value of coupling constant G , laser fluences, ballistic depth, pulse duration and thermal resistance. But the signal we are measuring is the reflectance change, simply getting to the surface temperature with TTM is not enough to explain the reflectance change. Some of the research has assumed the electron temperature variation has a linear relation with reflectance change (Norris, *et al.*, 2003) which can be written with:

$$\frac{\Delta R}{R} = AT_e + BT_p \quad (3.7)$$

Where A and B are the gradient of reflectance on electron temperature and on phonon temperature separately. A is determined by the peak of reflectance change and the slope of how fast it decreases, B is fitted with the lattice temperature several picosecond after the peak when the electron and phonon temperature have reached equilibrium. This relation is valid when both ΔT_e and $\Delta T_p < 150$ K and applies with most of the metals with high Sommerfeld constants which characterizing the strength of the electromagnetic interaction between elementary charged particles, but for low Sommerfeld constant metals such as noble metals, it won't work. In this case, a Drude Lorentz model has been used to bridge the relation between reflectance change and electron and phonon temperature.

3.2 Dielectric Constant and Drude-Lorentz Model

Generally, the transient reflectance change of excited sample is due to the perturbation of metal band structure and electron occupancy. The direct influence of perturbation on the band structure and electron occupancy is the variation of imaginary

part of dielectric constant $\varepsilon = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ which determines the absorption of photons when the electron is excited into higher states. The refractive index $n + ik$ can be expressed in a form of dielectric constant (Pedrotti, *et al.*, 2007):

$$n = \sqrt{\frac{1}{2}|\varepsilon| + \varepsilon_1} \quad (3.8a)$$

$$k = \sqrt{\frac{1}{2}|\varepsilon| - \varepsilon_1} \quad (3.8b)$$

Where $|\varepsilon| = \sqrt{\varepsilon_1^2 + \varepsilon_2^2}$ and reflectance has a relation of n and k :

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (3.9)$$

And R can be written in a form of dielectric constant:

$$R = \frac{|\varepsilon| - \sqrt{2(\varepsilon_1 + |\varepsilon|)} + 1}{|\varepsilon| + \sqrt{2(\varepsilon_1 + |\varepsilon|)} + 1} \quad (3.10)$$

Dielectric constant is wavelength dependent and can be deduced once known either the real part of imaginary part with Kramers-Kronig dispersion (Wooten, 1972):

$$\varepsilon_1(\omega_0) = \frac{2}{\pi} P \int_0^\infty \frac{\omega \varepsilon_2(\omega) d\omega}{(\omega^2 - \omega_0^2)} + 1 \quad (3.11a)$$

$$\varepsilon_2(\omega_0) = -\frac{2\omega_0}{\pi} P \int_0^\infty \frac{[\varepsilon_1(\omega) - 1] d\omega}{(\omega^2 - \omega_0^2)} \quad (3.11b)$$

Where P is the principle value and ω_0 is the frequency where dielectric constant is measured. Basically the variation of imaginary part $\Delta\varepsilon_2$ can be simulated from the

reflectance change we have measured and $\Delta\epsilon_2$ can be calculated from the Equation (3.6), and this perturbation can be used to explain the electron occupation variations.

Since it is known that R has a relation with ϵ_1 and ϵ_2 . R can be expressed in a differential form of ϵ_1 and ϵ_2 to represent the relationship with dielectric constant:

$$\frac{\Delta R}{R} = \frac{1}{R} \left[\frac{\delta R}{\delta \epsilon_1} \Delta \epsilon_1 + \frac{\delta R}{\delta \epsilon_2} \Delta \epsilon_2 \right] \quad (3.12a)$$

$$\frac{1}{R} \frac{\delta R}{\delta \epsilon_1} = \frac{\sqrt{2} (\epsilon_1 + |\epsilon|)^{\frac{1}{2}}}{|\epsilon| \left[(\epsilon_1 - 1)^2 + \epsilon_2^2 \right]} (2\epsilon_1 - |\epsilon| - 1) \quad (3.12b)$$

$$\frac{1}{R} \frac{\delta R}{\delta \epsilon_2} = \frac{\sqrt{2} \epsilon_2 (\epsilon_1 + |\epsilon|)^{\frac{1}{2}}}{|\epsilon| \left(\epsilon_1 + |\epsilon|^2 \right)^{\frac{1}{2}} \left[(\epsilon_1 - 1)^2 + \epsilon_2^2 \right]} (2\epsilon_1 + |\epsilon| - 1) \quad (3.12c)$$

With Equation (3.10), the transient reflectance perturbation has been quantified with dielectric variations. In order to build the relationship with temperature and reflectance, the Drude model can be implemented with a temperature dependent modification to represent the dielectric constant with electron and phonon temperature.

The Drude model bridges the relation between electron temperature and phonon temperature to the dielectric function and then the index of refraction and reflectance change (Maier, 2007):

$$\epsilon = \epsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\Gamma_0)} \quad (3.13)$$

Where ω is the frequency of laser, ϵ_∞ is a constant taken to be 9.7, Γ_0 is the Drude damping term which stands for the scattering rate of free electrons, ω_p is the plasma

frequency (1.37×10^{16} rad/s in Au). The electron scattering rate, which is the inverse of electron relaxation time, can be represented to be proportional to T_p at high temperature (Kittel, 2005).

$$\Gamma_0 = A_{ee0}T_e^2 + B_{ep0}T_p \quad (3.14)$$

For the damping factor in the Drude model, the coefficient describing electron-electron scattering A_{ee0} is taken as $1.2 \times 10^7 \text{ s}^{-1}\text{K}^{-2}$ (Wang, *et al.*, 1994) which is obtained from the low temperature Fermi liquid theory (MacDonald, 1980). B_{ep0} is chosen as $3.6 \times 10^{11} \text{ s}^{-1}\text{K}^{-2}$ which is predicted by matching the experimental results of dielectric constant at room temperature.

Simply applying the Drude model can be only applied on intraband conditions with probe energy less than ITT, the dielectric constant cannot be well represented when the wavelength of probe gets close to ITT. However, there are some works with 800 nm probe to relate reflectance and electron-phonon temperature which has proved the correctness of this theory. Also, the interband transition could happen even with probe energy less than ITT (800 nm), where holes are formed at s/p band because of electrons excited to higher states so that d band electrons could be excited to these holes. So considering interband transition is vital in both their cases and in this thesis to give a good match with temperature dependent dielectric constant. The Drude model combined with Lorentz oscillators applies to interband transition of metal, and is implemented here to describe the relation between the electron temperature, the phonon temperature, and the probe wavelength with the temperature dependent dielectric function and resulting temperature dependent reflectivity.

The combined Drude – Lorentz model for gold considers two Lorentz oscillators at 330 nm and 470 nm to produce a close agreement with the dielectric constant at room temperature of gold (Etchegoin, *et al.*, 2006). This model is expressed as:

$$\varepsilon = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\Gamma_0)} + L_1(\omega) + L_2(\omega) \quad (3.15)$$

Where the first two terms are the contributions of the Drude Model. L_1 and L_2 are the Lorentz oscillators that describe the contribution of interband transitions. The two interband transition terms are expressed as (Etchegoin, *et al.*, 2006):

$$L_i(\omega) = D_i \left[e^{i\phi_i} (\omega_i - \omega - i\Gamma_i)^{\mu_i} + e^{-i\phi_i} (\omega_i + \omega + i\Gamma_i)^{\mu_i} \right] \quad (3.16)$$

D_i is the amplitude for the oscillator, ω_i is the energy gap, ϕ_i is the phase, μ_i is the order of pole, Γ_i is the damping factor, and this model with critical points (two points for gold) is proved to be consistent with Kramers-Kronig relation (Barchiesi, *et al.*, 2014).

The damping factor can be described as a result of electron-electron scattering and electron-phonon scattering and is expressed as (Kittel, 2005):

$$\Gamma_i = A_{eei} T_e^2 + B_{epi} T_p + Y_i \quad (3.17)$$

The subscripts i is 0, 1 or 2 for the Drude term and the two Lorentz oscillators terms, respectively. We also found that a temperature-independent term Y_i needs to be included in the expression for the Lorentzian oscillators, in order to fit the temperature-dependent dielectric function (Y_0 is taken to be 0). The electron-electron scattering rate of Lorentzian oscillators A_{ee1} , A_{ee2} are assumed to be the same as that in the Drude model A_{ee0} . B_{ep1} , B_{ep2} are determined using room temperature optical constants with Equation

(3.17). Y_1 , Y_2 are found to be 7.9×10^{14} rad/s and 1.9×10^{15} rad/s respectively. All the parameters are listed in Table 1:

Table 3.1. Summary of the parameters in the Drude - Lorentz model.

Parameter (units)	Value	Parameter (units)	Value
$A_{ee0}, A_{ee1}, A_{ee2}$ ($s^{-1}K^{-1}$)	1.2×10^7	Y_0 (rad/s)	0
B_{ep0} ($s^{-1}K^{-1}$)	3.6×10^{11}	Y_1 (rad/s)	7.9×10^{14}
B_{ep1} ($s^{-1}K^{-1}$)	7.8×10^{10}	Y_2 (rad/s)	1.9×10^{15}
B_{ep2} ($s^{-1}K^{-1}$)	1.9×10^{11}	D_1 (m^{-1})	2.0×10^6
ϕ_1, ϕ_2 (rad)	$-\pi/4$	D_2 (m^{-1})	4.1×10^6
Γ_0 (rad/s)	1.3×10^{16}	μ_1, μ_2 (rad)	-1
ε_∞	1.53	ω_1 (rad/s)	4.0×10^{15}
ω_p (rad/s)	1.37×10^{16}	ω_2 (rad/s)	5.7×10^{15}

The calculated dielectric constant ($\varepsilon = \varepsilon_1 + \varepsilon_2 i$) at room temperature matches with what is given in Etchegoin. *et al.* (2006), and this model also provides a temperature- and wavelength-dependent dielectric constant. At elevated temperatures (up to 553 K), ε_1 is nearly a constant and ε_2 shows a strong temperature dependence as shown in Fig. 3b, in the wavelength range from 100 nm to 1000 nm. Note that at wavelengths less than 490 nm, the imaginary part of dielectric constant ε_2 almost the same (Fig 3.1d). A closer examination of the difference between the dielectric constant at elevated temperature and room temperature shows that the change of the real part of dielectric constant ε_1 at 490 nm is more significant compared with those at other wavelengths (Fig. 3.1c).

Figure 3.1. Calculated real part (3.1a) and imaginary part (3.1b) of dielectric constant ϵ_1 and ϵ_2 dependence on probe wavelength and temperature with Drude-Lorentz model. (3.1c) is the $\epsilon_1(T)$ real part of elevated temperature's difference with room temperature real part $\epsilon_1(T_0)$. (3.1d) is the $\epsilon_2(T)$ real part of elevated temperature's difference with room temperature real part $\epsilon_2(T_0)$.

Equation (3.10) describes the transient reflectance can be calculated from dielectric constant and with Drude Lorentz model the dielectric constant can be measured with the electron and phonon temperature variations during ultrafast heating by comparing with the experimental data using TMM. Fig. 3.1 shows how temperature would change the dielectric constant, at higher probe wavelength, such as 800 nm, the term $\sqrt{2(\epsilon_1 + |\epsilon|)} + 1$ increases as temperature rises, the reflectance variation ΔR would decrease since the denominator becomes larger. So taking the probe wavelength at 490

nm also maximizes the reflectance variation ΔR with decreasing ε_I as temperature rises, and improves the signal to noise ratio in this way.

The reflectance change can be described with Drude-Lorentz model by calculating reflectance from dielectric constant, the wavelength dependent reflectance change with increasing electron temperature is shown in Figure (3.2) and it is obvious that when the electron temperature is lower than 1000 K, the 480 nm gives the strongest reflectance variation and it matches the result in Holfield, *et al.* (2000).

Figure 3.2. The reflectance change ΔR with electron temperature at different probe wavelength.

All the fitting properties and parameters applied in this thesis experiment has been conclude in the following table:

Table 3.2. Fitting parameters for TTM and Drude-Lorentz model.

B_e	$70 \text{ J}/(\text{m}^3 \text{K}^2)$	Y_0	$3.59 \times 10^{-4} \text{ rad}$
A_{ee0}	$1.2 \times 10^7 \text{ s}^{-1} \text{K}^{-2}$	C_p	$2.49 \times 10^6 \text{ J}/(\text{m}^3 \text{K})$
B_{ep0}	$3.6 \times 10^{11} \text{ s}^{-1} \text{K}^{-2}$	C_s	$1.66 \times 10^6 \text{ J}/(\text{m}^3 \text{K})$
J	$147 \text{ J}/\text{m}^2$	χ	$353.0 \text{ W}/(\text{mK})$
η	0.16	E_F	5.53 eV
t_p	450 fs	δ	16.28 nm
k_p	0.311 W/(mK)	δ_b	100 nm
k_s	148 W/(mK)	L	24, 39, 65, 250, 1000 nm

The electron-phonon coupling factor G is regarded as temperature dependent in this thesis. Its relation with A_{ee0} and B_{ep0} in the Drude model can be expressed as following (Chen, *et al.*, 2005):

$$G(T) = G_0 \left(\frac{A_{ee0}}{B_{ep0}} (T_e + T_l) + 1 \right) \quad (3.18)$$

Where G_0 is the room temperature electron-phonon coupling factor, with conditions: $A_{ee0} \ll B_{ep0}$, $T_e, T_l > T_D$ and $T_e < T_F$ where T_D is the Debye temperature and T_F is the Fermi temperature, the T_e and T_l in our measurement ranges from 300 K to 6000 K, T_D is 170 K, and T_F is 6.39×10^4 K for gold, which satisfies this condition.

3.3 Non-Thermalized Electrons

After photons hit on the sample surface, the electrons are excited into non-thermalized states where they do not follow the rule of Fermi-Dirac distribution and cannot be defined with a temperature. In this case, only part of the electrons have been excited, and the rest of the electrons would interact with the excited electrons in the following several hundred femtoseconds, this is called the non-thermalization process. This non-thermalized electrons have studied by a lot of work (Fann, *et al.*, 1992, Groeneveld, *et al.*, 1992, and Sun, *et al.*, 1994) This instantaneous variation of electron distribution have been discussed and quantified in the following equation:

$$\Delta f \propto f_0(E - E_p)[1 - f_0(E)] - f_0(E)[1 - f_0(E + E_p)] \quad (3.19)$$

Where f_0 is the Fermi-Dirac distribution described in Equation (1.5), E_p is the excitation photon energy. The amplitude of the population change is due to the pump fluence. In the first few tens of femtoseconds, the electrons would transport normal to the film and will smooth out inhomogeneity in the electron distribution leading to a homogenous non-

Fermi distribution. After this period, the electron-electron scattering will dominate and causes the temperature rise of cold electrons. Electrons would become thermalized in a few hundreds of femtoseconds leading to a hot Fermi distribution with current electron temperature larger than the initial electron temperature. Fig. 3.2 plots the normalized electron distribution variation vs probe photon energy difference by assuming all the nonthermalized energy distribution has been redistributed into thermalized energy without any loss to the lattice.

Figure 3.3. Electrons distribution change for nonthermalized electrons and thermalized electrons, the dashed line indicates the probe energy at 2.53 eV (490 nm) chosen for measurement where change from nonthermalized electrons is much less than that from thermalized electrons.

The thermalized electrons follow the Fermi distribution and can be calculated by comparing Equation (1.5) with Fermi energy. Notice that at probe energy close to the Fermi energy, the population of thermalized electrons is significantly larger than that of non-thermalized electrons, while with probe energy far from Fermi energy, the non-thermalized electrons would dominate. This process happens in the very initial time period where TTM cannot be used to predict the electron-phonon coupling G because it

assumes the electrons are fully thermalized. A time constant has been used to add into the pulse width in the source term of TTM to get rid of the influence non-thermalized electrons (Hopkins, *et al.*, 2011), however, this method only improves the fitting of rising edge. Guo and Xu(2014) has extended the scale of all the signal by 1.1 which assumes the non-thermalized electrons have taken some contribution to the reflectance perturbation but cannot be predicted by TTM, also the intraband transition of the 490 nm probe photon could lead to reduce the reflectance, but the drawback is the thermalized electron contribution is also being scaled which will lead to inaccuracy to the data analysis. In this work, probe wavelength is taken as 490 nm (2.53 eV) at which the nonthermalized electrons population is much less than the population of thermalized electrons on average. This has helped largely reduced the impact of thermalized electron contribution to the TTM prediction and has increased the accuracy for calculation. On the other hand, this probe wavelength has provided with a larger signal ($\Delta R/R$) than other wavelength according to the analysis in Section 3.2 and experiment result shown in the next Chapter. The larger absolute signal of reflectance change increases the contribution of thermalized electrons because at 490 nm it takes larger portion of population than non-thermalized electrons as shown in Fig 3.2. Also, the relative contribution from non-thermalized electrons is more obvious for thicker films since heat diffusion and ballistic transportation reduce the contribution from thermalized electrons, and this contribution is more obvious for thin film. That is the reason why past work has reached a reasonable result with thin film even at a probe energy far from the Fermi energy.

CHAPTER 4. EXPERIMENTAL RESULTS AND ELECTRON-PHONON COUPLING ACROSS METAL-DIELECTRIC INTERFACE

In this chapter, the experiment is carried out and the model that has been discussed in the last chapter is applied. The gold films were deposited on a silicon wafer using electron beam evaporation. CHA and Lesker evaporators at Birck Nanotechnology Center were used for the process. The substrates were cleaned using toluene, acetone, methanol, and isopropanol before the gold deposition. Thin gold films with thicknesses of 24 nm, 39 nm, 65 nm, and bulk gold ($> 1 \mu\text{m}$ thick gold film on silicon) are measured at different pump fluences. A bulk gold has been used to verify the electron-phonon coupling constant within metal, and thermal resistance has been fitted to match the data of thinner gold film. A linear trend of thermal conductance has been shown with electron and phonon temperature.

4.1 Experiment Results on Thick Gold

The experiment is carried on Au-Si sample with different thickness of gold (24 nm, 39 nm, 65 nm, 250 nm, 1000 nm) and different pump fluence (33.0 J/m^2 , 74.3 J/m^2 , 116 J/m^2). The fluence is chosen at a higher level to reduce the influence the non-thermal electron scattering. For the measurement of thick gold, non-thermalized electrons have taken larger portion of contribution to the transient reflectance perturbation as last Chapter discussed, so applying the probe wavelength at 490 nm is quite necessary in this step to guarantee the correctness. In this step, a very thick gold sample has been applied

to define the value of coupling constant G of electron-phonon interaction. Considering the G is a thickness independent factor, many other thickness dependent factor can be eliminated in this case, such as thermal resistance at interface, pump fluences, and so on.

In Fig. 4.1, a 250 nm gold and 1000 nm gold have been tested in order to distinguish the pump fluence dependence at large thickness gold sample. As we can notice in the result, the decreasing rate for both of the samples increases with increasing fluence and the decreasing rate with thinner thickness 250 nm is obviously larger than the 1000 nm thickness gold. In the 1000 nm gold sample where gold thickness might not be enough to ignore the diffusion in the film because of the high fluence applied in our experiment but is reasonable to prospect the property of bulk gold.

Figure 4.1. Experiment and fitting result of Au-Si with gold thickness at 1000 nm (4.1a) and 250 nm (4.1b) at pump fluences 33.0, 74.3, and 116 J/m².

In Fig. 4, the data of the bulk gold film is shown and is used to find the coupling factor G_0 . For these the pump fluences, as Fig. 4.1a shows, the coupling between electrons and phonons within gold film is almost fluence independent, and for 250 nm gold, there shows a fluence dependent trend in Fig 4.1b. This is reasonable for bulk gold, since the ballistic transport exists, electrons are transferred deep into the material, and the temperature change is lower than the thin film with the same fluence. It matches the

result of G in Equation (3.18) which would stay almost the same when the temperature change of bulk gold is small. It can be seen that the entire relaxation process of electrons match the model prediction, as shown in Fig. 4.2. The value of G_0 is determined to be $1.4 \times 10^{16} \text{ W}/(\text{m}^3\text{K})$, similar with the electron-phonon coupling parameter from (Guo and Xu, 2014) ($1.5 \times 10^{16} \text{ W}/(\text{m}^3\text{K})$). Maximum electron temperature T_e are calculated as 463 K, 620 K, 751 K separately for fluences at $33.0 \text{ J}/\text{m}^2$, $74.3 \text{ J}/\text{m}^2$, $116 \text{ J}/\text{m}^2$, while in their work, T_e are 368 K, 427 K, 481 K, and 528 K for fluences at $17.6 \text{ J}/\text{m}^2$, $35.2 \text{ J}/\text{m}^2$, $52.8 \text{ J}/\text{m}^2$, and $70.4 \text{ J}/\text{m}^2$. Temperature dependent G is $1.43 \times 10^{16} \text{ W}/(\text{m}^3\text{K})$ (similar for three fluences because of low temperature variation), however, the reflectance change in Guo and Xu (2014) is based on fitting with electron temperature T_e and doesn't consider the lattice temperature contribution.

Figure 4.2. Experiment and fitting result of bulk Au with 490 nm probe and 800 nm pump at $33.0 \text{ J}/\text{m}^2$.

4.2 Experiment Results on Thin Gold Film on Silicon

Fig. 4.3 is the pump-probe measurement data at 24 nm, 39 nm, and 65 nm, with pump fluence of 33.0 , 74.3 , and $116 \text{ J}/\text{m}^2$. G_0 is fixed as $1.4 \times 10^{16} \text{ W}/(\text{m}^3\text{K})$, R_{es} is taken as the fitting parameters of matching the decreasing slope, and phonon-phonon coupling at

interface is assumed to have no influence on interfacial heat transfer in the time domain in this paper (Guo, *et al.*, 2014). R_{es} is taken as the fitting parameters to match the experimental data. Phonon-phonon coupling at interface does not have influence on the measured data (Guo, *et al.*, 2012), and is taken as $1.0 \times 10^{-7} \text{ m}^2\text{K/W}$. It is seen from the figures that when the pump fluence increases, the decrease of reflectance is slower. This is because the electron heat capacity C_e increases as the electron temperature increases, which slows down the electron cooling. Comparing the results of different gold films at the same fluence, the thicker gold film has a faster reflectance decrease. This is because in a thick gold film, heat is transported deep into the film and the smaller electron heat capacity C_e caused by the lower temperature increases the relaxation rate.

Table 4.1. Thermal Resistance for different pump fluences at Au-Si sample with thickness 24 nm, 39 nm, 65 nm when measured with 490 nm probe and 800 nm pump.

Thickness (nm)	Pump Fluence (J/m^2)	Thermal Resistance ($\text{m}^2\text{K/W}$)
24	33.0	2.1×10^{-9}
24	74.3	1.6×10^{-9}
24	116	1.3×10^{-9}
39	33.0	3.7×10^{-9}
39	74.3	2.9×10^{-9}
39	116	3.0×10^{-9}
65	33.0	3.7×10^{-9}
65	74.3	4.5×10^{-9}
65	116	4.0×10^{-9}

Thermal resistances between electrons in gold and the silicon lattice R_{es} are found to be 2.1×10^{-9} , 1.6×10^{-9} , $1.3 \times 10^{-9} \text{ m}^2\text{K/W}$, for laser fluences of 33.0, 74.3, and 116 J/m^2 for the 24 nm film, which is seen slightly decrease with the increasing fluence. The resistance values are 3.7×10^{-9} , 2.9×10^{-9} , $3.0 \times 10^{-9} \text{ m}^2\text{K/W}$ for the 39 nm film, and 3.7×10^{-9}

⁹, 4.5×10^{-9} , 4.0×10^{-9} m²K/W for the 65 nm film for laser fluences of 33.0, 74.3, and 116 J/m².

The uncertainties in the data obtained above are largely determined by the temperature rise in the gold film. For example, the low temperature obtained with 33.0 J/m² on the 65 nm-thick film results in a large uncertainty in determining R_{es} . The coupling between interfaces is smaller when the temperature is lower, whereas the lower temperature also causes a lower reflectivity signal and a larger noise. The uncertainty of R_{es} for 33.0 J/cm², 65 nm thick film is roughly $\pm 13.5\%$ where R_{es} is $(3.7 \pm 0.5) \times 10^{-9}$ m²K/W, and for 116 J/cm², 24 nm film is reduced to $\pm 4.7\%$ where R_{es} is $(2.1 \pm 0.1) \times 10^{-9}$ m²K/W. All the uncertainties are represented as error bars in the next section.

Figure 4.3. Experiment and fitting result of 24 nm (5a), 39 nm (5b), 65 nm (5c) Au-Si with 490 nm probe and 800 nm pump at 33.0, 74.3, 116 J/m².

4.3 Electron-Phonon Coupling within Film and Across Metal-Dielectric Interface

The thermal resistance between metal phonons and substrate lattice at interfaces of gold and silicon has been testified to take no effect on transient reflectance variation (Guo, *et al.*, 2012). In this case, the gold electrons and substrate lattice coupling can be written into a similar form of temperature model of G in Equation (3.18):

$$h(T) = h_0 \left(C(T_e + T_l) + 1 \right) \quad (4.1)$$

Where $h(T) = 1/R_{es}$ is the thermal conductance between interfaces and is the inverse of thermal resistance between metal electrons and dielectric substrate phonons. C is the temperature dependence parameter. h and C can both be fit from the experiment result.

The temperature-dependent interface conductance obtained has the same trend to what was reported in (Hopkins, *et al.*, 2009), with the difference in the temperature coefficient $h_0 \times C$, $2.1 \times 10^5 \text{ W/(m}^2\text{K}^2)$ obtained in this work vs. $3.5 \times 10^5 \text{ W/(m}^2\text{K}^2)$, h_0 as $1.1 \times 10^8 \text{ W/(Km}^2)$ vs. $2.5 \times 10^7 \text{ W/(Km}^2)$, and C as $1.8 \times 10^{-3} \text{ K}^{-1}$ vs. $1.4 \times 10^{-2} \text{ K}^{-1}$. Therefore the results obtained in this work have a higher temperature thermal conductance and is less temperature-dependent. It is noted that 800 nm pump and probe beam were used in [9]. As discussed earlier, probing with energy near ITT significantly reduces the effect of non-thermalized electrons. Also, we determined electron-phonon coupling factor G_0 from bulk gold which was then used in the determination of thermal conductance at interface, instead of matching G and interface conductance together. We noted many related research obtained a higher value of G for electron-phonon coupling in gold and considering G as a temperature independent factor, for example, $2.9 \times 10^{16} \text{ W/(m}^3\text{K)}$ with an 800 nm probe in (Hostetler, *et al.*, 1999), $2.7 \times 10^{16} \text{ W/(m}^3\text{K)}$ with a 630 nm probe in

(Brorson, et al., 1990), $4.0 \times 10^{16} \text{W}/(\text{m}^3 \text{K})$ with a 615 nm probe in (Elsayed-Ali, et al., 1991), and $2.2 \times 10^{16} \text{W}/(\text{m}^3 \text{K})$ with a 785 nm probe in (Choi, et al., 2014). Because these probe wavelengths are farther from ITT, the states probed can be much affected by the non-thermalized electrons as shown in Fig. 3.2 and tend to disappear before the equilibrium between electrons and the lattice has been reached.

Figure 4.4. Thermal resistance R_{es} and thermal conductance $h = 1/R_{es}$ between gold electron and silicon phonon at interface relationship with electron and phonon temperature $T_e + T_l$. And fit h with linear equation $2.051 \times 10^{-4} (T_e + T_l) + 0.1126 = h$.

While the temperature dependence factor at interface is $C = 1.8 \times 10^{-3} \text{K}^{-1}$ the electron-phonon temperature coupling factor in Eq. 10 is A_{ee0}/B_{ep0} , it is not reasonable to compare the difference of temperature dependent strength of coupling between interface and gold film directly with these two terms. First of all, in our model, the temperature dependent term Γ_i has been distributed into one Drude term and two Lorentz oscillators where they all contribute to the temperature dependence of reflectance change, but A_{ee0} and B_{ep0} are calculated only with Drude term at room temperature. Second, the temperature defined in G in Equation (3.18) is transient, every timestamp G is calculated

with temporary electron and phonon temperature. However, the temperature plotted in Fig. 4.4 is maximum electron and lattice temperature at the interface, which obviously has larger gradient than the average gradient considering the transient temperature. So a more general temperature needs be defined instead of the maximum temperature of electrons and phonons in order to compare C and A_{ee0}/B_{ep0} .

CHAPTER 5. CONCLUSIONS AND FUTURE WORK

5.1 Summary and Conclusions

Heat transfer at the interface of nanoscale material is a major concern using ultrafast spectroscopy with the pump-probe technique, and ultrafast spectroscopy has been utilized to analyzing the dynamics of energy carriers with transient reflectance measurement.

Transient reflectance measurement is used on detecting the interface property on Au-Si sample in this thesis, in order to investigate the heat transfer at the interface between metal and dielectrics. The two-temperature model has shown to be a good model on the thermal conductance at the interface by considering minimizing the impact of non-equilibrium and non-thermal electrons. In most previous work, the probe energy chosen for detecting the transient reflectance change is far from ITT, which tends to be influenced by non-thermalized electrons during the first several hundred femtoseconds and overestimate both the electron-phonon coupling rate within the metal film and electron-phonon thermal conductance at the interface. The optical transient reflectance change is measured with 490 nm probe (near ITT of gold) and 800 nm pump to reduce the impact of non-thermalized electrons.

This work also introduces a temperature related Drude-Lorentz model for dielectric constant which bridges the electron and phonon temperature with transient reflectance

change. In this thesis, the real and imaginary part of dielectric constant has been expressed with a form of Drude-Lorentz term with temperature dependence, then, dielectric constant can be transferred into refractive index to match the transient reflectance change measured from ultrafast laser. The real part and imaginary part of dielectric constant are the minimum when we take the probe wavelength at around 490 nm above ITT, where the transient reflectance change has been maximize and increase the signal-noise ratio. On the other hand, the electron-phonon coupling rate G is fitted with the data of bulk gold. Since bulk gold is more sensitive to the non-thermalized electrons, 490 nm probe is also necessary in this case to reduce the non-thermal electrons influence on reflectance variation. This G is then used to find electron-phonon conductance h_{es} at thin film measurement, where h_{es} increases with temperature at a reasonable gradient which is larger than the past work whose result have been largely influenced by the non-thermalization process of electrons.

5.2 Future Work

The interaction of electrons and phonons between interface of gold and silicon has been investigated in this thesis, when considering minimizing the non-thermalized electrons contribution to the transient reflectance change. With this model and measurement method, more gold film sample with more types of substrate, such as Au-Glass, Au-Quartz, can be tested to see the difference when the non-equilibrium electrons factor has been reduced.

Also, more proper probe wavelengths which maximizes the signal-noise ratio for different film material can be chosen from the Drude-Lorentz model. With this model, it is easier to bridge the transient reflectance with the temperature, and select the best probe

wavelength in order to get the largest reflectance data. What's more, this model has considered both interband transition and intraband transition for probe pulse on a wide wavelength range, so more film materials can be simulated by selecting a wide range of probe wavelength with this method and TTM in order to carry out the pump-probe measurement.

On the other hand, the temperature dependent relation for thermal conductance across the interface has a different definition from the electron-phonon coupling G_0 dependence of temperature in Equation (3.18), although they both represent the coupling strength temperature gradient between electron and phonon. G_0 in this case is defined with transient temperature while the thermal conductance is related with the peak electron and phonon temperature on the whole time scale within the gold film. So a better mathematical model can be implemented to make the thermal conductance temperature dependence to be transient so that both of the two factors become comparable.

In addition, the dynamics of energy carriers of materials has important applications such as graphene, nanotubes and black phosphorene. Except the measurement with ultrafast spectroscopy, molecular dynamics and Monte Carlo simulations can be utilized to help to justify the assumption about dynamics of energy carriers during the transient reflectance measurement in this thesis.

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