Influence of intraband transitions on the electron thermoreflectance response of metals

Andrew N. Smith\textsuperscript{a)\ ) and Pamela M. Norris

Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia 22901

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Ultrashort pulsed lasers have repeatedly been demonstrated as effective tools for the observation of transport properties on atomistic time and length scales. Transient thermoreflectance scans of a Au thin film taken using a 200 fs pulsed laser are compared to the parabolic two step model using both the assumption of a linear relationship between reflectance and temperature and using an intraband reflectance model. In this study, the incident photon energy was less than the interband transition energy, therefore the thermoreflectance response is primarily due to intraband transitions. The intraband transitions are influenced by the electron and lattice temperatures through the electron collisional frequency. © 2001 American Institute of Physics. [DOI: 10.1063/1.1351523]

During the ultrashort pulsed laser heating of metals the radiant energy is initially absorbed by the electrons.\textsuperscript{1} The subsequent rate of energy exchange between the electrons and lattice can be related to an electron–phonon coupling factor and the temperature difference between the two systems.\textsuperscript{2} The electron–phonon coupling factor is typically measured using a transient thermoreflectance technique with thin reflective films; however, a relationship between the change in reflectance of the sample surface and the electron and lattice temperatures is required.\textsuperscript{3–5} A number of studies have also been performed on metallic nanoparticles\textsuperscript{6,7} observing the transient changes in the absorbance. Whether probing thin films or nanoparticles, the importance of intraband transitions must be considered.

In this investigation we observe the thermoreflectance response of Au thin films at probe photon energies far below the interband transition energy. The Drude model is used to estimate the complex dielectric function;\textsuperscript{8} therefore the thermoreflectance response is primarily due to intraband transitions. The intraband transitions are influenced by the electron and lattice temperatures through the electron collisional frequency.

\begin{equation}
C_e(T_e) \frac{\partial T_e}{\partial t} = \frac{\partial}{\partial x} \left( k_e(T_e, T_l) \frac{\partial T_e}{\partial x} \right) - G[T_e - T_l] + S, \quad (1)
\end{equation}

\begin{equation}
C_l \frac{\partial T_l}{\partial t} = G[T_e - T_l]. \quad (2)
\end{equation}

The electron–phonon coupling factor $G$ and the lattice heat capacity $C_l$ are constant. The electron heat capacity is lin-

\begin{figure}[h]
\centering
\includegraphics[width=0.5\columnwidth]{figure1.png}
\caption{Femtosecond transient thermoreflectance response of a 23 nm Au film measured at various incident fluence values.}
\end{figure}

\textsuperscript{4}Electronic mail: ans8f@virginia.edu
early related to the electron temperature, \( C_e(T_e) = C'_e T_e \) where \( C'_e = 70 \text{ Jm}^{-3} \text{ K}^{-2} \) is the electron heat capacity constant for Au. The thermal conductivity is proportional to the ratio of the electron to lattice temperature, \( k_e(T_e, T_l) = k_{eq}(T_e/T_l) \), where \( k_{eq} = 317 \text{ Wm}^{-1} \text{ K}^{-1} \) was used for the equilibrium thermal conductivity.

The Drude model accounts for the contribution to the dielectric function of metals from the free electrons in the conduction band which are able to undergo intraband transitions. The electron collisional frequency \( \omega \), in the following expression makes the dielectric function complex, and is therefore responsible for absorption:

\[
\varepsilon = 1 - \frac{\omega_p^2}{\omega(\omega + i\omega)} ,
\]

where \( \omega \) is the frequency of the incident radiation and \( \omega_p \) is the plasma frequency. This expression for the dielectric function is only reasonable for photon energies below the first intraband transition, for higher photon energies interband absorption becomes dominant. At temperatures above the Debye temperature, the electron–phonon collisional frequency is proportional to the lattice temperature. Electron–electron collisions are significantly less frequent at room temperature and are generally proportional to the square of the electron temperature:

\[
\omega_e = \frac{1}{\tau} = A_{ee} T_e^2 + B_{ep} T_l ,
\]

where \( A_{ee} \) and \( B_{ep} \) are constant coefficients. The dielectric function, Eq. (3), can then be used to calculate the index of refraction, \( \tilde{n} = n + ik = \sqrt{\varepsilon} \). The changes in reflectance as a function of the electron and lattice temperatures can be calculated using the expressions for an absorbing thin film on a nonabsorbing substrate. However, knowledge of the scattering coefficients \( B_{ep} \) and \( A_{ee} \) from Eq. (4) is required. The electron–phonon scattering constant is estimated from the room temperature thermal and electrical resistivity. The value of \( B_{ep} = 1.45 \times 10^{11} \text{ s}^{-1} \text{ K}^{-1} \) was used in the model and held constant. The electron–electron scattering constant is estimated from low temperature measurements, where the \( T^2 \) dependence is significant in the thermal and electrical resistivity, \( A_{ee} = 1.7 \times 10^7 \text{ s}^{-1} \text{ K}^{-2} \).}

When the electrons and lattice are in thermal equilibrium, electron–phonon collisions dominate at room temperature. Therefore, a linear relationship is valid for the lattice response expected for our experimental conditions. The peak electron temperature change for the highest fluence, 3.6 Jm\(^{-2}\), is predicted to be \( \sim 350 \text{ K} \). The absorption was measured to be \( A = 0.06 \) at the pump angle of incidence where \( \theta_{inc} = 30^\circ \). Since the electrons initially absorb the energy and quickly reach thermal equilibrium, the electron temperature is \( \sim 650 \text{ K} \), while the lattice remains at the initial temperature 300 K. Figure 2 shows the predicted change in reflectance for changes in the electron temperature while the lattice remains at the ambient temperature. This relationship is not linear because the electron–electron collisional frequency is proportional to the square of the electron temperature. It is important to recognize that the reflectance response is affected by changes in both the electron and lattice temperatures, therefore both systems must be considered in order to explain the entire experimental response.

In order to determine the electron–phonon coupling factor \( G \) the thermal model must be compared to the experimental data. Traditionally, the reflectance is assumed to be linearly related to the electron and lattice temperatures for small perturbations in temperature: \( \Delta R/R = a \Delta T_e + b \Delta T_l \). Since the coefficients \( a \) and \( b \) are unknown, the thermal model is scaled to the experimental results at two points, the peak of the fast transient where the electron temperature change is

**FIG. 2. Change in reflectance according to the Drude model for the change in the electron temperature while the lattice remains at the initial temperature, \( T_e > T_o = T_l \).**

**FIG. 3. Comparison of the transient thermoreflectance response for a 23 nm Au film, and the PTS model using a linear relationship between changes in reflectance and temperature.**

**FIG. 4. Comparison of the transient thermoreflectance response for a 23 nm Au film, and the PTS model using an intraband transition model for predicted changes in reflectance with temperature.**
dominant and the end of the scan where the electrons and phonons have thermalized. The only free parameter in the thermal model is $G$, and its value is determined using a least squares fitting routine. The results are shown in Fig. 3. The model clearly does not decay rapidly enough in the early portion of the scan and decays too quickly in the latter part of the scan. This discrepancy increases with increasing fluence. Also, the measured values of $G$ change with fluence indicating a failure in either the model or the comparison of the model to the data.

A nonlinear relationship between the change in reflectance and the electron temperature was demonstrated in Fig. 2 when intraband transitions were considered. The thermal model was again compared to the reflectance response using the intraband model. A single scaling coefficient was then used to match the data to the model near the end of the scan when the contribution is primarily from the lattice. This is equivalent to using a single linear coefficient for the lattice response. The value for $A_{ee}$ was adjusted to match the model to the peak of the fast transient. The value of $A_{ee}$ estimated in this manner was $1.4 \times 10^7$ s$^{-1}$ K$^{-2}$, which is consistent with published values.\textsuperscript{15}

The electron–phonon coupling factor was again determined using a least squares fitting routine and the results are shown in Fig. 4. Within the experimental error, the results are independent of fluence. Therefore, using the intraband reflectance model resulted in a significant improvement in the comparison between the thermal model and the experimental results. This investigation has shown that electron–electron scattering is responsible for the large initial electron thermoreflectance response when the probe photon wavelength is less than the interband transition energy and that intraband transitions must be considered when interpreting the results of a transient thermoreflectance experiment.

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\textsuperscript{14} F. Abeles, in \textit{Advanced Optical Techniques}, edited by A. C. S. Van Heel (Wiley, New York, 1967), Chap. 5, pp. 144–188.