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Thermoreflectance dependence on Fermi surface electron number density perturbations

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The effects of an optical excitation on the thermoreflectance spectra of a solid are studied. A photonic excitation with sufficient energy will cause a perturbation in the electron number density around the Fermi surface. As the number density changes, so do the plasma frequency and carrier scattering rates, creating a change in the thermoreflectance response. Not accounting for the appropriate electron number density around the Fermi level after an optical excitation leads to an underestimate of electron scattering rates. © *2010 American Institute of Physics*.
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Thermomodulation spectroscopy is a powerful, noncontact technique that contains a wealth of information regarding the electronic properties of materials.[1] The thermoreflectance signal of a material—defined as the change in reflectance of a material from a change in temperature divided by the reflectance at the initial temperature ($\Delta R/R$)—contains valuable information regarding electronic transitions and band structure.[2–7] Furthermore, the temporal decay of the thermoreflectance spectra is related to various electronic scattering mechanisms, and in metal systems, this transient thermoreflectance (TTR) is related to the thermal properties and has been used to measure electronic relaxation into a Fermi distribution,[8,9] rates of electron-phonon heat transfer,[10–16] and thermal conduction.[17–23] TTR is particularly useful for studying these processes in nanosystems since it is noncontact and, if the nanosystems are coated with a thin metal, the relatively small radiation absorption depth [$\mathcal{O}(10$ nm)] allows for nanoscale resolution. However, interpretation of TTR data is difficult due to various electronic scattering processes around the Fermi surface, especially after large electronic temperature perturbations.[24–26]

TTR data are obtained in a pump-probe experimental configuration in which the thermoreflectance signal obtained by the probe after pump excitation is highly dependent on the pump perturbation. For example, in short pulse TTR experiments, large pump powers can cause the thermoreflectance signal to become highly nonlinear.[24,25] Not only do electronic scattering events change with temperature, but changes in electronic populations can also drastically affect electron scattering rates.[27,28] Previous studies only consider the temperature effects on thermoreflectance signals,[24,25,29] making these models inapplicable in some TTR experiments that utilize different pump and probe wavelengths.[15,30–33] The goal of this letter is to investigate the dependency of the thermoreflectance signal on electronic population density to elucidate the scattering mechanisms contributing to TTR analysis after the pump excites a sample at a given wavelength that changes the electronic number density in the probe band being interrogated. Since the probe is monitored during TTR experiments, the thermoreflectance model must accurately depict the available transitions that the probe will induce in the post-pump-excited sample. In this work, discussions are limited to scenarios where the probe pulse will interrogate the sample by only inducing intraband transitions and electron system temperatures that will not excite any "thermal" interband transitions via Fermi smearing.[34] Example calculations are shown for Au for probe pulse energies of 1.55 eV, but this model is applicable to any free electron metal or semiconductor with any probe pulse energy.

The calculation of the thermoreflectance signal from a probe pulse interrogating the sample via intraband transitions is discussed in detail elsewhere.[24] In short, the thermoreflectance signal is defined as $\Delta R/R=[R(T_{\text{excited}})-R(T_0)]/R(T_0)$, where T_{excited} is the temperature after the pump excitation and T_0 is the initial temperature before the pump excitation. The temperature dependency of the reflectance is described by the dielectric function predicted by Drude model,[1] given by

$$\varepsilon = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\tau)}, \tag{1}$$

where ε_∞ is the high limit dielectric constant, ω_p is the plasma frequency, ω is the probe frequency (wavelength at which the thermoreflectance signal if being interrogated), and τ is the electron scattering time. The reflectivity at various temperatures is calculated by considering that $\tilde{n}=\sqrt{\varepsilon}$, where $\tilde{n}$ is the complex index of refraction.

Although the only temperature dependency in Eq. (1) lies in the electron scattering time (assuming no population change due to temperature, i.e., Fermi smearing), the dielectric function has a complex relationship on electron number density. First off, the plasma frequency is directly related to the electron number density around the Fermi surface through

$$\omega_p^2 = \frac{4\pi n e^2}{m}, \tag{2}$$

where n is the electron number density, e is the fundamental charge, and m is the free electron rest mass. Second, the optical response is related to both the electron-electron and electron-phonon scattering times, which are both related to the conduction band number density. The total electron scattering time is estimated by

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$$\tau^{-1} = A_{ee}T_e^2 + B_{ep}T_p, \tag{3}$$

where A_{ee} is the electron-electron scattering coefficient, T_e is the electron system temperature, B_{ep} is the electron-phonon scattering coefficient, and T_p is the phonon system temperature. The number density dependence of B_{ep} can be deduced straightforwardly from Kaganov *et al.*'s original theory of electron phonon coupling[34,35] as $B_{ep}=6G/(\pi^2 m v^2 n)$ where G is the electron-phonon coupling factor describing the rate of heat flow between the electrons and phonons, and v is the speed of sound. The electron-phonon coupling factor can be evaluated from the electron-phonon scattering matrix and the second moment of the phonon spectrum;[34] using this approach, G is dependent on changes in electron number density induced by some photonic excitation.[28] Once the B_{ep} is evaluated, A_{ee} is determined by recognizing that $A_{ee} \propto T_F^{-2}$ and $B_{ep} \propto T_F^{-1}$, where T_F is the Fermi temperature, and therefore $A_{ee} \approx B_{ep}/T_F$.

Once the number density dependence of A_{ee}, B_{ep}, and ω_p are determined, the thermoreflectance spectra can be calculated from the dielectric function. For Au, v is 1990 m s^{-1},[36] T_F is 64 200 K,[37] and n is be calculated based on the band structure and the energy of the photonic excitation.[28] For example calculations, pump pulse energies of 1.55, 3.1, and 4.65 eV are assumed; these energies are chosen since they represent the fundamental, frequency doubled, and frequency tripled outputs of a Ti:Sapphire laser cavity that is commonly used in thermoreflectance experiments. The number of empty states in the conduction band for which there is sufficient photon energy to excite subconduction band electrons (thereby changing the conduction band number density) is estimated by

$$n_{available} = \int_{-\infty}^{\infty} D_C(\varepsilon)\{1 - f[\varepsilon, \mu(T_e), T_e]\}(1 - H\{\varepsilon - [\mu(T_e) - (\varepsilon_{ITT} - h\nu)]\})d\varepsilon, \tag{4}$$

where $H[\cdots]$ is the Heaviside function, $D_C(\varepsilon)$ is the conduction band density of states, $\mu(T_e)$ is the Fermi–Dirac distribution function with $f[\varepsilon, \mu(T_e), T_e]$ being the electron energy and ε being the chemical potential, ε_{ITT} is the interband transition threshold energy, which, in a metal, represents the minimum energy separation from the conduction band to the first underlying d-band,[30] or, in a semiconductor corresponds to the band gap, and $h\nu$ corresponds to the energy of the pump photons. The conduction band density of states is estimated by $D_C=3n_C\varepsilon^{1/2}/(2\varepsilon_F^{3/2})$, where the Fermi energy of Au is 5.53 eV (Ref. 38) and n_C is the nonperturbed electron number density in the conduction band, which for Au is 5.9×10^{28} m^{-3}. The total number density in the conduction band (to be used in thermoreflectance calculations) n, is therefore given by $n_C=n_C+n_{excited}$, where $n_{excited}$ is the number of electrons excited from the d-band to the conduction band from incident photons, which is a function of the number of photons absorbed by the material. If there are enough photons absorbed by the metal to excite all the electrons in the d-band up to available states in the conduction band, then $n_{excited}=n_{available}$, where $n_{available}$ is defined by Eq. (4), and therefore $n_C=n_C+n_{available}$. For this condition to be true, then $n_{available} \leq n_{photons}$, where $n_{photons}$ is the number of photons per unit volume in the absorbed laser pulse. The number of photons per volume can be estimated as $n_{photons}=A/(h\nu\delta)$, where

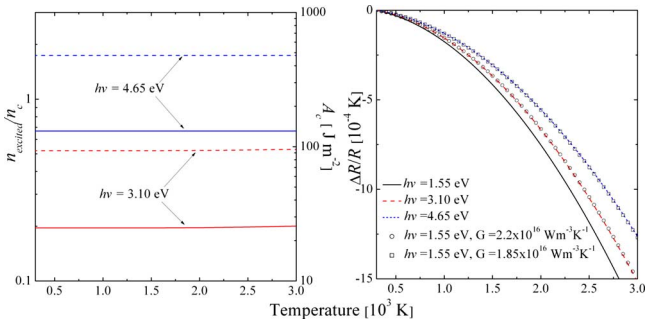

FIG. 1. (Color online) (a) $n_{excited}=n_{available}$ (solid lines) calculated with Eq. (4) as a function of temperature for two of the three different photonic excitations considered, along with A_c for three different pump excitation energies (dashed lines). Note that the 1.55 eV excitation is not shown since the number of carriers excited from the d-band to the conduction band from the 1.55 eV pulse is negligible, and reaches only 0.2% of n_C at 3000 K. (b) Thermoreflectance response as a function of temperature. The difference in the thermoreflectance responses are more apparent at higher temperatures, and are attributed to the change in the conduction band number density induced by the pump-probe excitation. Also shown in this figure are thermoreflectance calculations assuming no conduction band number density perturbation but iterating G until ΔR gives a best fit with the 3.10 (open circles) and 4.65 eV (open squares) thermoreflectance calculations. If a 3.10 eV pump excitation is absorbed (giving rise to $G=2.9\times10^{16}$ W m^{-3} K^{-1} due to population increase), and the increase in conduction band number density is not taken into account, the thermoreflectance spectra will incorrectly appear to reflect Au having an electron-phonon coupling factor of 2.2×10^{16} W m^{-3} K^{-1}, a value that is nearly 25% too low. Similarly, for a 4.65 eV pump excitation, not accounting for the change in conduction band number density will result in an electron-phonon coupling factor that is 36% too low.

A is the absorbed fluence and δ is the optical penetration depth at $h\nu$. In the case that $n_{photons}$ is less than $n_{available}$, then only $n_{photons}/n_{available}$ of the empty states in the conduction band will be filled by electrons undergoing interband transitions.

If $n_{available} \leq n_{photons}$, then the absorbed laser fluence must be greater than the critical fluence, which is defined as $A_c=h\nu\delta n_{available}$. Figure 1(a) shows $n_{excited}=n_{available}$ [Eq. (4)] as a function of temperature for two of the three different photonic excitations considered, along with A_c for two of the three different pump excitation energies, $h\nu$=3.10, and 4.65 eV (note that the 1.55 eV excitation is not shown since the number of carriers excited from the d-band to the conduction band from the 1.55 eV pulse is negligible, and reaches only 0.2% of n_C at 3000 K). The optical penetration depth, δ, is calculated by $\delta=\lambda/(4\pi n_2)$, where n_2 is the extinction coefficient, or the imaginary part of the complex index of refraction. The extinction coefficient in Au at 1.55, 3.1, and 4.65 eV is 5.125, 1.956, and 1.803, respectively,[39] leading to an optical penetration depth at these energies of 12.4, 16.2, and 18.0 nm, respectively. The available states filled by the absorbed laser pulse are relatively constant over the temperature range of interest since in Au, d-band thermal excitations do not occur for temperatures less than ~3500 K.

Using the excited number density shown in Fig. 1(a), the thermoreflectance response as a function of temperature is calculated and shown in Fig. 1(b). The increased number density in the conduction band caused by the laser pulse will cause a change in the chemical potential and subsequent change in G. Once the chemical potential is determined for the different conduction band number density perturbations,[28,34] the electron-phonon coupling factor is calculated by[40]

$$G(T_e) = \pi\hbar k_B \lambda \langle \omega^2 \rangle \int_{-\infty}^{\infty} \frac{[D_T(\varepsilon)]^2}{D_T(\varepsilon_F)} \left\{ -\frac{\partial f[\varepsilon, \mu(T_e), T_e]}{\partial \varepsilon} \right\} d\varepsilon, \quad (5)$$

where $\hbar$ is the reduced Planck's constant, k_B is the Boltzmann constant, λ is the dimensionless electron-phonon mass enhancement parameter[41] and $\langle \omega^2 \rangle$ is the second moment of the phonon spectrum.[42] For Au, $\lambda\langle\omega^2\rangle = 23\ \text{meV}^2/\hbar^2$.[13] $D_T(\varepsilon)$ is density of states of all the electron bands modified by the excitation. For Au, $D_T(\varepsilon) = D_C(\varepsilon) + D_D(\varepsilon)$ where $D_D(\varepsilon)$ is the $5d$ (Ref. 10) band density of states, The density of states of the $5d$ (Ref. 10) band in Au can be approximated by a square function with a width of 5.28 eV and the high energy edge of the square function 2.4 eV below the Fermi energy giving rise to the interband transition threshold energy in Au,[43,44] so that $D_D(\varepsilon) = n_D[-H(\varepsilon - 3.13) + H(\varepsilon + 2.15)]/5.28$, where $n_D = 5.9 \times 10^{29}\ \text{m}^{-3}$. Note the calculation of temperature dependent thermophysical properties using this approximate band structure has shown close agreement with calculations of thermophysical properties using exact *ab initio* calculations for electronic band structure.[45] G is determined for the 1.55, 3.1, and 4.65 eV excitations as 2.5×10^{16}, 2.9×10^{16}, and $4.0 \times 10^{16}\ \text{W m}^{-3}\ \text{K}^{-1}$, respectively.

As seen in Fig. 1(b), the difference in the thermoreflectance responses are more apparent at higher temperatures, and are attributed to the change in the conduction band number density induced by the pump-probe excitation. The 1.55 eV excitation assumes no perturbation in conduction band number density. Also shown in this figure are thermoreflectance calculations assuming no conduction band number density perturbation (1.55 eV) but iterating G until ΔR gives a best fit with the 3.10 and 4.65 eV thermoreflectance calculations; this gives a quantitative estimate of the error generated if the conduction band number density perturbation is not taken into account. If a 3.10 eV pump excitation is absorbed (giving rise to $G = 2.9 \times 10^{16}\ \text{W m}^{-3}\ \text{K}^{-1}$ due to population increase), and the increase in conduction band number density is not taken into account, the thermoreflectance spectra will incorrectly appear to reflect Au having an electron-phonon coupling factor of $2.2 \times 10^{16}\ \text{W m}^{-3}\ \text{K}^{-1}$, a value that is nearly 25% too low. Similarly, for a 4.65 eV pump excitation, no accounting for the change in conduction band number density will result in an electron-phonon coupling factor that is 36% too low.

In conclusion, the dependency of the thermoreflectance response of a solid on the electronic population is studied. As the number density around the Fermi surface changes, so do the plasma frequency and carrier scattering rates, creating a change in the thermoreflectance response. Example calculations are given for Au, and not accounting for the appropriate electron number density around the Fermi level leads to an underestimate of electron scattering rates and the electron-phonon coupling factor.

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