Femtosecond Studies of Nonequilibrium Electronic Processes in Metals

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High-intensity femtosecond laser pulses are used to induce nonequilibrium electron heating in gold metal. The thermal relaxation of the electronic distribution is studied through pump and continuum probe measurements of transient reflectivity. Measurements are performed for different heating-pulse fluences and probe-photon energies. The observed reflectivity line shape demonstrates the generation of nonequilibrium electron temperatures which cool to the lattice on a 2–3-ps time scale.

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The possibility of generating transient nonequilibrium electron temperatures in metals was predicted theoretically over a decade ago.[1] Previous attempts to generate and measure nonequilibrium electron temperatures by use of picosecond laser pulses and thermally assisted multiphoton photoemission did not show evidence for nonequilibrium electron heating.[2,3] The first evidence for this phenomenon was obtained by use of picosecond thermomodulation techniques; however, the time resolution was insufficient to permit a measurement of the electron-cooling time.[4,5] Subsequent extension of photoemission studies into the femtosecond regime allowed a measurement of electron cooling but was restricted to high temperatures and suffered from space-charge effects.[6] Recently, femtosecond thermomodulation transmissivity[7] and reflectivity[8] measurements provided the first opportunity to investigate nonequilibrium electron temperatures and cooling dynamics. Because metals exhibit small changes in optical properties, these investigations have only recently been made possible through the development of new high-repetition-rate femtosecond sources which provide high-sensitivity detection with femtosecond time resolution.[9-11]

In this paper we present an investigation of nonequilibrium electron heating and temperature dynamics in gold using femtosecond transient thermoreflectivity measurements. This research represents the first extension of thermoreflectance spectroscopy in metals into the femtosecond regime. Electron heating is induced by high-intensity 65-fs laser pulses and the evolution of the reflectivity line shape is measured on a femtosecond time scale with use of a continuum probe. Cooling times of 2–3 ps for the electron distribution are observed and the temperature dynamics is investigated.

In the consideration of nonequilibrium electron heating, the metal may be modeled as two coupled thermal systems composed of the electrons and the crystal lattice. An incident ultrashort laser pulse imparts energy to the conduction electrons which thermalize rapidly via electron-electron scattering. Energy is then transferred to the lattice through electron-phonon scattering. If the incident-pulse duration is sufficiently short compared to the electron-phonon energy-transfer time, then a nonequilibrium electron-lattice temperature difference will exist. Since the electronic heat capacity is much less than the lattice heat capacity, it is possible to produce transient electron temperatures far in excess of the lattice temperature. Furthermore, the dynamics of this process is nonlinear since the electronic specific heat is temperature dependent.

The time evolution of the electron and lattice temperatures T_e and T_i may be modeled by a set of coupled nonlinear differential equations,[1]

$$C_e \partial T_e/\partial t = K\nabla^2 T_e - g(T_e - T_i) + A(r,t), \quad (1)$$

$$C_i \partial T_i/\partial t = g(T_e - T_i), \quad (2)$$

where C_e and C_i are the electronic and lattice heat capacities, and K is the thermal conductivity. Heating due to the incident optical pulse is accounted for by the source term $A(r,t)$ and electron diffusion is accounted for by the diffusion term $K\nabla^2 T_e$. The electron and lattice temperatures are coupled through the electron-phonon coupling constant g which is independent of temperature.[12] Since the electronic heat capacity depends linearly on the electron temperature ($C_e = \gamma T_e$), the effect of an increased electronic temperature is an increased thermal-relaxation time. Furthermore, hot electrons have a much larger thermal diffusivity (K/C_e) than in the case of equilibrium thermal transport (K/C_i).

Nonequilibrium electron heating may be observed experimentally through transient-reflectivity measurements. This approach is an extension of traditional thermomodulation spectroscopy in which small thermal perturbations are induced in a sample and the resulting reflectivity change is detected.[13-16] A variety of effects

may contribute to the reflectivity signal, including smearing of the electronic occupancy near the Fermi level, Fermi-level shifting, lattice expansion, and the electron-phonon interaction.

In noble metals, differential reflectivity measurements can be used to monitor interband electronic transitions from the d bands to conduction-band energies near the Fermi level.[4,5,13-16] In gold, the transition threshold $(E_F - E_d)$ is 2.38 eV. For photon energies near this interband transition, the dominant contribution to the thermoreflectance signal is Fermi smearing resulting from electron heating.[13-16] This smearing is characterized by increased electronic occupancy above the Fermi energy and decreased occupancy below the Fermi energy.

A simple model for understanding experimental measurements of electron heating may be constructed by the consideration of interband transitions from flat d bands to states about the Fermi level.[14] For large electron-temperature changes, the smearing of the electron distribution is given by

$$\Delta\rho = \rho(\hbar\omega, T_1) - \rho(\hbar\omega, T_0), \quad (3)$$

where we use the Fermi distribution,

$$\rho(\hbar\omega, T) = \{1 + \exp([\hbar\omega - (E_F - E_d)]/kT)\}^{-1}, \quad (4)$$

to model the electronic occupancy near the Fermi energy. E_F is the Fermi energy and E_d the d-band energy. Figure 1 shows the smearing of this occupancy in gold for various electron temperatures. The line shape displays an inflection point about the Fermi energy indicating increased occupancy at higher energies and decreased occupancy at lower energies. As the temperature T_1 is decreased, the line shape narrows and the peaks shift slightly toward the Fermi energy. At high temperatures, the smearing of the occupancy begins to saturate. In contrast, for small temperature changes the change in occupancy may be approximated by the derivative of the Fermi function.[14]

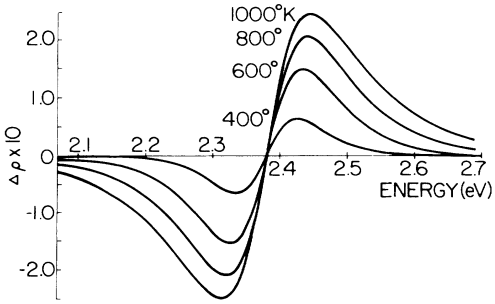

FIG. 1. Calculated change in electronic occupancy about the Fermi energy for various electron temperatures. $\rho(T)$ is the Fermi function and $\Delta\rho = \rho(T_1) - \rho(T_0)$ where T_1 is the temperature of the electronic distribution and $T_0 = 300$ K.

The change in electron occupancy may be investigated by our measuring differential changes in reflectivity $\Delta R/R$ for energies near the d-band Fermi-level transition. For small changes in optical constants, the differential reflectivity is linear in $\Delta\epsilon_1$ and $\Delta\epsilon_2$:

$$\frac{\Delta R}{R} = \frac{1}{R}\left[\frac{\partial R}{\partial \epsilon_1}\Delta\epsilon_1 + \frac{\partial R}{\partial \epsilon_2}\Delta\epsilon_2\right]. \quad (5)$$

Changes in the electron occupancy produce changes in interband absorption which are directly proportional to the change in the imaginary component of the dielectric constant, $\Delta\epsilon_2$. The corresponding change in $\Delta\epsilon_1$ can be determined by Kramers-Kronig analysis.

A more detailed modeling of electron-occupancy change $\Delta\rho$ must account for the curvature of the d bands and density of states about the Fermi level. This analysis has been performed in detail in previous thermomodulation studies.[16] Intuitively, the effect of increasing electron temperature will enhance and deplete increased interband absorption for photon energies above and below the d-band to Fermi-level transition, respectively. This in turn will produce a "derivativelike" differential reflectivity $(\Delta R/R)$ line shape with a width determined by the electron temperature.

In our investigation we utilize a femtosecond pump and continuum probe technique to perform time-resolved measurements of transient reflectivity changes in 1000-Å gold films on sapphire. Nonequilibrium electron temperatures are produced by laser pulses of 65-fs duration at a wavelength of 630 nm (2.0 eV). These pulses are generated by a balanced colliding-pulse mode-locked dye laser[9] and amplified at 8-kHz rate with a copper-vapor laser amplifier.[10] Continuum pulses are generated by focusing of the amplified pulses in an ethylene glycol jet[11] and are used to probe the sample reflectivity in the wavelength range of 580–450 nm. Pump and probe beams are focused to ~ 20 μm diam on the sample at near-normal incident angle. The probe pulses are delayed with respect to the pump pulses by a computer-controlled delay stage with 0.1-μm step size.

The reflectance signal from the sample and a reference signal from the continuum are simultaneously filtered by a tunable monochromator with ~ 3-nm resolution and are detected by photomultiplier tubes. The pump beam is chopped to provide for lock-in amplification of the signal. This allows suppression of probe fluctuations by the combination of lock-in amplification with real-time differential detection. Transient-reflectivity measurements are performed as a function of time delay at various probe-photon energies by time averaging of the signal over several scans.

Figure 2 shows transient-reflectivity measurements at 2.59 eV probe-photon energy with pump fluences of 4 and 0.4 mJ/cm^2. We observe an increase in reflectivity, $\Delta R/R > 0$, consistent with enhanced electronic occupancy above the Fermi energy and relaxation times of ~ 3

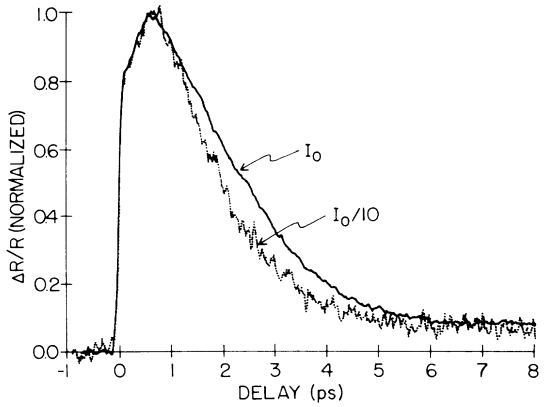

FIG. 2. Transient-reflectivity measurements vs time delay from the heating pulse. The probe energy is 2.59 eV and the incident fluences are 4 and 0.4 mJ/cm^2.

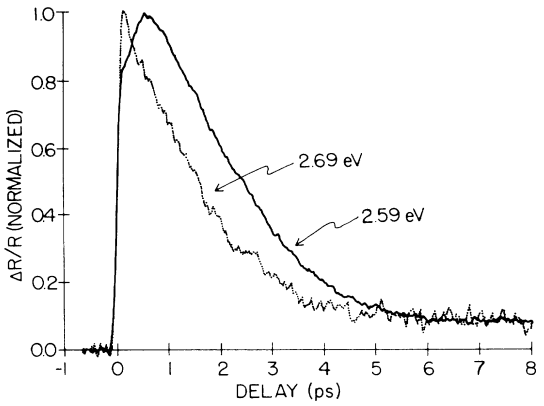

FIG. 3. Transient-reflectivity measurements vs time delay from the heating pulse. The probe photon energies are 2.59 and 2.69 eV and the incident fluence is 4 mJ/cm^2.

and ~ 2 ps, respectively. At the higher pump fluence the peak change in reflectivity is $\Delta R/R \sim 10^{-2}$ and the estimated electron temperature is ~ 1000 K. The estimated temperature is based on comparison of the transient-reflectivity relaxation times to numerical solutions of the nonlinear heat equations[1,3-8] as well as comparison of the peak change in reflectivity to previous thermomodulation studies.[4,5,13-16] The change in lattice temperature is several tens of degrees. At the lower pump fluence the peak change in reflectivity is $\Delta R/R \sim 10^{-3}$. The long-time component of the reflectivity signal results from residual lattice heating which cools in several tens of picoseconds via diffusion.

The increased relaxation times of the reflectivity transient at higher pump fluence are consistent with the temperature dependence of the electronic specific heat. Higher pump fluence results in greater electron temperatures and a corresponding increase in the electronic specific heat, implying longer thermal-relaxation times. Furthermore, at higher temperatures the change in electronic occupancy $\Delta\rho$ begins to saturate (see Fig. 1), and produces a transient-reflectivity relaxation time which is longer than the electron-cooling time.

Probing below the Fermi energy we observe a decrease in reflectivity, $\Delta R/R < 0$, and comparable relaxation times displaying the same dependence on pump fluence. The change in sign of the transient reflectivity about the Fermi energy is a characteristic signature of Fermi smearing as reported in previous thermomodulation studies.[13-16] This confirms that the reflectivity signal is produced by changes in electron temperature.

Figure 3 shows transient-reflectivity measurements with a pump fluence of 4 mJ/cm^2 at probe-photon energies near the largest change in electronic occupancy (2.59 eV) and in the tails of the distribution (2.69 eV). The decreased relaxation time of the reflectivity observed at 2.69 eV is consistent with the narrowing of the change in occupancy $\Delta\rho$ as the electrons cool. Complementary behavior is observed at probe-photon energies below the Fermi energy at 2.29 and 2.19 eV.

Figure 4 shows the measured transient reflectivity as a function of energy at various time delays. This is a compilation of reflectivity traces taken at fixed time delays with different probe-photon energies. The line shape has an inflection point near the d-band to Fermi-level transition energy and a derivativelike structure with minima and maxima above and below the transition energy, respectively. The line shape corresponds closely to results obtained in previous thermomodulation studies.[13-16] Furthermore, we observe changes of the reflectivity line shape as the probe pulse is delayed which indicate a cooling of the electronic distribution. At 200-fs delay, where the electron temperature is near the maximum, we observe the greatest smearing of the line shape. At longer delays, as the distribution cools, we observe a narrowing of the line shape and a shifting of the peaks toward the Fermi energy. The temporal evolution of the line shape is in qualitative agreement with our simple model based on changes in electronic occupancy $\Delta\rho$ and is consistent

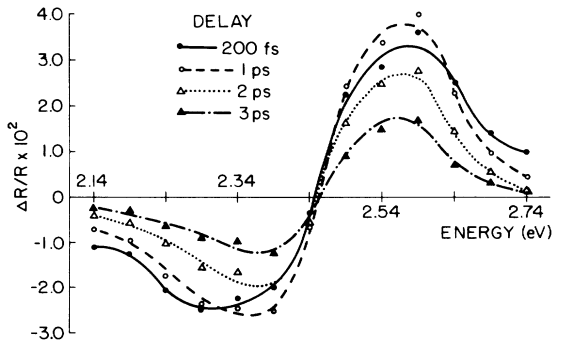

FIG. 4. Transient-reflectivity measurements as a function of probe-photon energy at various time delays from the heating pulse.

with previous thermomodulation studies performed as a function of temperature.[13-16] This demonstrates that the reflectivity signal results from changes in electron temperature and that the transient behavior corresponds to a cooling of the electrons to the lattice temperature.

An interesting feature observed in the data of Figs. 2-4 is the transient increase in $\Delta R/R$ for time delays of less than 1 ps. This is evident for probe-photon energies near peak changes in electronic occupancy above and below the Fermi energy. At present, the origin of this behavior is not completely understood. However, we believe that it is not a delayed heating process since the reflectivity line shape suggests a uniform cooling immediately following the pump pulse. It does not appear to be a saturation effect since it also occurs at lower pump fluences. This behavior may result from changes in refractive index which change the coupling of the optical probe field to the metal. More detailed continuum studies should yield a better understanding of this process.

In summary, nonequilibrium electron-heating dynamics in gold has been investigated by femtosecond pump and continuum probe techniques. Measurements of transient reflectivity demonstrate the generation of nonequilibrium electron temperatures which cool to the lattice on a time scale of 2-3 ps. The reflectivity line shape agrees closely with previous thermomodulation studies and exhibits a dynamic behavior demonstrating a cooling of the electron distribution. The observed cooling dynamics is consistent with the temperature dependence of the electronic heat capacity. Femtosecond thermomodulation is a potentially powerful technique since it allows a separation of electronic processes from phonon or lattice heating effects. Future extensions of these studies will allow the investigation of nonequilibrium electron and transport effects.

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