Time-Resolved Observation of Electron-Phonon Relaxation in Copper

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Amplified 150–300-fs laser pulses are applied to monitor the thermal modulation of the transmissivity of thin copper films. Nonequilibrium electron and lattice temperatures are observed. The process of electron-phonon energy transfer was time resolved and was observed to be 1–4 ps, increasing with the laser fluence.

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The phenomenon of inequality between electron and lattice temperatures in metals subjected to ultrafast heating (laser pulse width $\leq$ electron-phonon energy relaxation time) was postulated some time ago.[1] However, very few experimental observations of such inequality have been accomplished. Previously, the thermal modulation of the reflectivity of copper was used to observe nonequilibrium electron and lattice temperatures during picosecond ($\sim$5 ps FWHM) laser heating.[2,3] Although nonequilibrium heating was demonstrated in these experiments, the time resolution was insufficient to resolve electron-phonon relaxation. In addition, as a result of the low laser fluence, electrons were heated to only a few degrees above the lattice temperature. In another report, the phenomenon of thermally enhanced multiphoton photoemission in tungsten heated by amplified 75-fs laser pulses has provided evidence that electron-phonon relaxation is accomplished within a few hundred femtoseconds in tungsten.[4] By use of such a technique it is possible to determine the electron temperature experimentally and to resolve in time the electron-lattice energy transfer. However, experimental difficulties associated with space-charge effects, due to the very short time scales considered, hindered the determination of the electron temperature and the accurate resolution of the electron-phonon relaxation rate.

In this Letter we report results obtained using amplified 150–300-fs laser pulses to resolve in time the electron-phonon relaxation by monitoring of the laser-heating–induced modulation of the transmissivity of thin copper films. The time resolution was sufficient to resolve electron-phonon coupling in copper. In addition, the laser energy (up to 0.3 μJ per pulse) was sufficient to produce up to a few thousand degrees difference between electron and lattice temperatures. We expect that difficulties associated with hot-electron diffusion were minimal, which would not be the case for reflectivity experiments from a thick sample.

The pump-probe experiments were performed with use of a 1-kHz synchronously amplified, colliding-pulse mode-locked laser ($\lambda \simeq 620$ nm).[5] The excitation beam was divided into a pump and a probe beam. The fundamental was directly used to heat the sample. Time-resolved measurements of the transmissivity of the thin copper films were made at the fundamental ($\lambda \simeq 620$ nm) or by use of a 10-nm (FWHM) band from white light generated by focusing of the probe beam into an ethylene glycol cell. The pump and probe were collinearly incident normal to the copper film (polarized perpendicular to each other) and focused to $\sim$27- and $\sim$14-μm-diam spots, respectively. The probe was positioned near the center of the pump. The absolute value of the thermal modulation of the transmissivity was sensitive to the relative pump and probe positions. Thus, each experimental data set was obtained with no modifications in the alignment. The probe pulse intensity was attenuated such that it was less than $\frac{1}{30}$ th of the pump intensity. The relative intensities of the pump and probe beams were maintained constant and both the pump and the probe beam intensities were varied by attenuation of the excitation pulse. A portion of the probe beam was directed to a reference photodiode. Both the reference and signal probe pulses were digitized and recorded on a shot-to-shot basis. The reference was used for normalization of the signal and for selection of reference signals with relatively small fluctuations (typically 5% for the reported results).

The copper films were deposited on a 200-μm-thick glass slide by means of a conventional evaporation apparatus. The film thickness was determined by a crystal-thickness monitor with an estimated accuracy of better than $\pm$ 50 Å. The unirradiated parts of the film were typically exposed to air for several hours at room temperature, thus subjecting it to oxide formation. With reference to experimental data by Rhodin[6] on the rate of low-temperature oxidation of copper, it is estimated that an oxide layer $\leq$ 20 Å is formed on the film prior to laser irradiation.

The experimentally observed time-resolved transmissivity of a 200 $\pm$ 50-Å copper film at $\lambda \simeq 620$ nm during laser heating ($\sim$300 fs FWHM) for a variable pump-probe fluence is shown in Fig. 1. The initial response of the transmissivity appears to be integration of the heating pulse. The rise time of the initial transient was shorter for $\sim$150-fs (FWHM) heating pulses, consistent with the above-mentioned observation. The decay of the

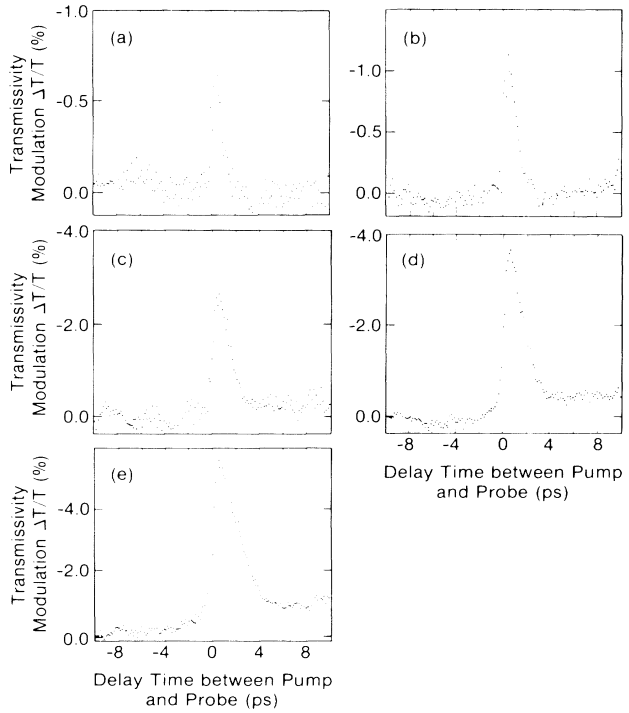

FIG. 1. Time-resolved transmissivity of ~200-Å Cu film at $\lambda \cong 620$ nm during laser heating (~300 fs FWHM) for different laser-pulse energies: (a) 8, (b) 15, (c) 30, (d) 44, and (e) 65 nJ. The heating laser was focused to ~27 μm; the probe laser to ~14 μm and positioned near the center of the heating-laser spot.

fast transient was found to be 1–4 ps, increasing with the heating-pulse fluence. This effect is due to larger differences between electron and lattice temperatures for higher fluences; thus, more electron-phonon collisions are required for thermalization. A much slower decay of the lattice temperature (mainly due to diffusion) was observed following the initial fast transient. Possible effects due to modulation of the optical properties of the substrate during laser heating were checked by the performance of the experiment with an uncoated glass slide. For conditions used in Fig. 1 and for our resolution limit, no modulation of the transmissivity of the substrate was observed.

As shown in Fig. 1, the amplitude of the thermal modulation of the transmissivity of the copper film is directly proportional to the laser fluence. For conditions shown in Fig. 1, sample transmissivity before and after laser heating was unchanged. For higher laser fluences, the amplitude of the thermal modulation was not linear with the laser fluence (amplitude saturation was observed). In addition, the film transmissivity was enhanced by a few percent during laser heating and reached an equilibrium value in a few minutes, indicating the possibility of fast oxidation during laser heating.

The heating-induced modulation of the optical properties of metals can result from many effects including thermal expansion, broadening and shifting of the Fermi level, and electron-phonon interaction.[7] The technique of thermomodulation of the optical properties of metals (with only a few degrees modulation in temperature) is a well-developed technique to study the band structure of metals.[8] More recently, transient thermoreflectance studies of copper have opened the possibility of separating (in time) the electronic and lattice contributions to the thermomodulation spectra of metals.[2,3] The thermomodulation spectrum of copper is well studied, and its structure is relatively well understood.[7] A clear feature of this structure is the sharp derivative peak at about 2.15 eV corresponding to an electronic transition from the top of the d band to empty conduction-band (p-band) states near the Fermi level. This structure was previously attributed to the smearing of the Fermi distribution.[7] Indeed, the observed fast transient in Fig. 1 is thought to be mainly due to Fermi-distribution smearing. The relatively small amount of modulation persisting after the fast transient is attributed to lattice effects which are caused by enhanced electron-phonon collisions and, to a lesser extent, by the thermal-expansion effects.

For conditions used in the present work where the laser pulse width was shorter than the electron-phonon relaxation time, the time evolution of the electron and lattice temperatures can be described by two coupled nonlinear differential equations[1]:

$$C_e(T_e)\frac{\partial T_e}{\partial t} = \kappa \Delta^2 T_e - G(T_e - T_l) + P_0(r,t), \quad (1)$$

and

$$C_l\, \partial T_l/\partial t = G(T_e - T_l). \quad (2)$$

The electronic heat capacity, $C_e(T_e)$, is proportional to the electron temperature [$C_e(T_e) = 96.6 T_e$ J/m^3·K].[9] The first term on the right-hand side of Eq. (1) represents thermal-conductivity losses. As a result of the thin-film geometry used in our work, thermal conductivity is thought to have a negligible contribution at the time scales of interest (few picoseconds after the laser-heating pulse) and can be ignored. The second term in Eq. (1) represents electron-phonon coupling. The coefficient of heat transfer between the electrons and the lattice,[10] G, is assumed to be constant for our experimental conditions and is obtained by a comparison of the experimental data with the model. The third term in Eq. (1) represents the laser-heating source. Measurements showed that at $\lambda = 620$ nm, 5% of the normally incident radiation is absorbed in the copper film at room temperature. Small deviations in this value due to laser heating are ignored in the present model. In the present calculations, the lattice heat capacity, C_l, had a value of 3.5×10^6 J/m^3·K.[9]

Equations (1) and (2) were solved numerically. Time evolution of the electron and the lattice temperatures for different values of electron-phonon coupling constant, G,

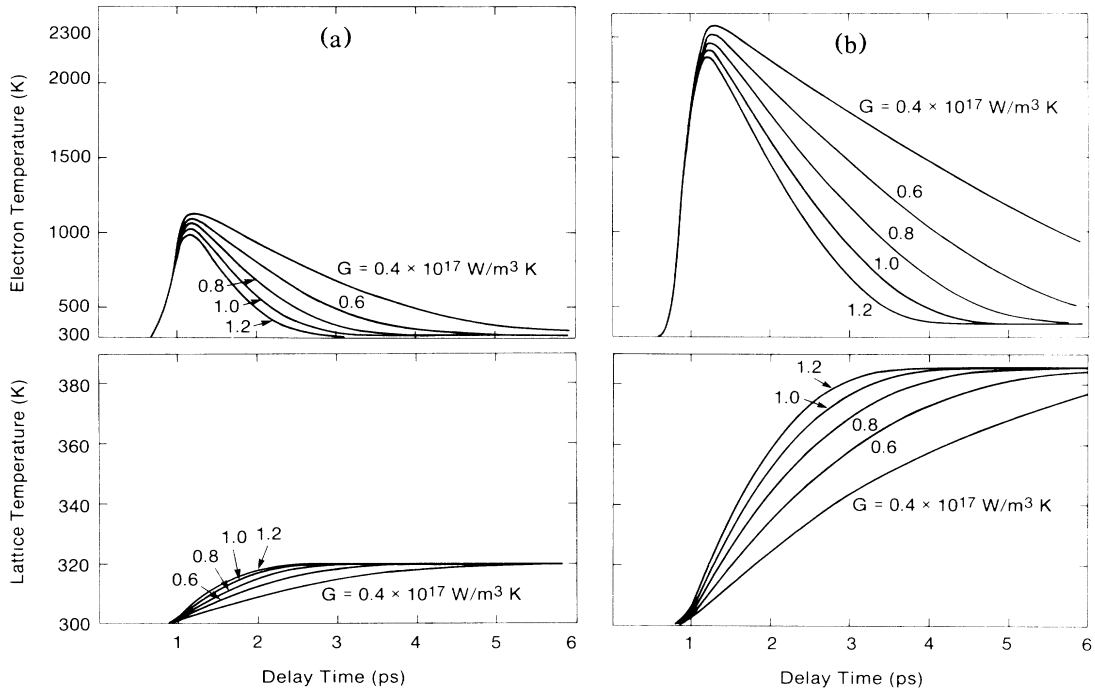

FIG. 2. Numerical modeling of the time evolution of electron and lattice temperatures for the experimental conditions in Figs. 1(b) and 1(e) [laser-pulse energy is (a) 15 nJ and (b) 65 nJ, with its peak at time =1 ps]. Simulations were conducted for different values of the coefficient of heat transfer between the electrons and the lattice, G.

and for conditions used in Figs. 1(b) and 1(e) are shown in Figs. 2(a) and 2(b). The laser-heating pulse was assumed to be Gaussian with a FWHM =0.3 ps and peaking at 1 ps. Clearly, the electron-phonon relaxation time is strongly dependent on the value assigned to G and increases with a decrease in the electron-phonon coupling constant. In addition, the electron-phonon relaxation time was found to increase with the applied heating-laser fluence which is consistent with the experimentally observed results. Since the electron-phonon relaxation times considered in the analysis are larger than the laser-heating pulse width, the peak electron temperature had only a small dependence on the value of the electron-phonon coupling constant. Although the equilibrium electron and lattice temperatures predicted by the model were directly proportional to the heating-laser fluence, the peak electron temperature had nearly a square-root dependence on the laser fluence. Indeed, deviation from this square-root dependence is due to the fact that some electron-phonon energy transfer does take place during the laser-heating pulse. Thus, this deviation from square-root dependence is enhanced for larger values of G.

Comparison of the time-resolved thermomodulation-transmissivity measurements of the time required for the electrons and the lattice to reach equilibrium with that predicted by the model indicates that G has a value of $\sim 1\times 10^{17}$ W/m^3·K. For a pulse energy of 65 nJ (peak fluence $\simeq 3.8\times 10^{10}$ W/cm^2), the model predicts a peak electron temperature of 2200 K and an equilibrium electron-phonon temperature (ignoring conduction losses) of 385 K. Although this simple model seems to be consistent with the experimental observations, more accurate modeling can include the modulation of the deposited laser energy due to the thermal modulation of the optical properties of the film, in addition to accounting for the small dependence of G and C_l on tempera-

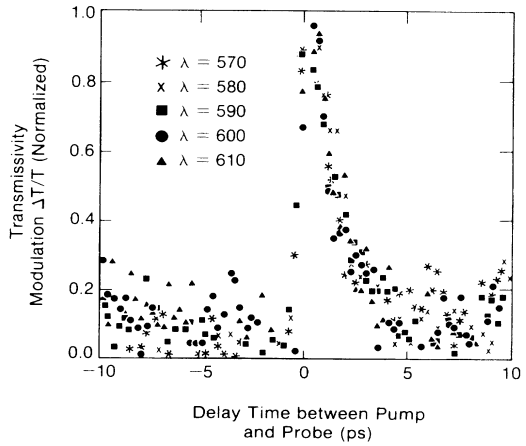

FIG. 3. Time-resolved transmissivity of 200-Å copper film for varied wavelengths of the probe.

ture.

Filtered white-light pulses in 10-nm steps from $\lambda = 560$ nm to 640 nm ($\lambda = 590$ nm corresponds to an electronic transition from the top of the *d* band to the Fermi level) were also used to probe the transmissivity modulation; results, shown in Fig. 3, display no dependence of the decay of the fast transient, attributed to electron-phonon relaxation, on probe wavelength. This observation is consistent with a thermalized hot-electron population.

In conclusion, we have used the thermal modulation of the transmissivity of thin copper films to measure the electron-phonon relaxation time in copper as a function of pump-laser fluence at $\lambda = 620$ nm and as a function of probe photon energy for $\lambda = 560$–640 nm. We have demonstrated nonequilibrium heating with up to a few thousand degrees difference between electron and lattice temperatures. Additional studies are needed to actually relate the modulation of the optical properties of metals with electron and lattice temperatures.

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