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Femtosecond investigation of electron thermalization in gold

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Electron-electron and electron-phonon thermalization processes are investigated in gold films using a high-sensitivity multiple-wavelength femtosecond pump-probe technique. A nonequilibrium electron distribution is excited by free-carrier absorption of an infrared femtosecond pulse and its relaxation dynamics followed by measuring the transient reflectivity and transmissivity with a visible probe pulse. Measurements performed in a thin gold film in the very low perturbation limit ($\Delta T_e \sim 20$ K) yield evidence for the existence of a non-Fermi electron distribution with an electron thermalization time of ~ 500 fs and an electron-lattice interaction time of 1 ps. The apparent thermalization dynamics of the electron gas is much faster in optically thick samples and is shown to be dominated by transport effects.

Studies of the interactions of free carriers between themselves and with their environment constitute one of the major problems of solid-state physics. With the advance of femtosecond lasers, time-resolved techniques have emerged as a powerful tool for the investigation of transient nonequilibrium electron effects in semiconductors and metals. Metals are particularly interesting because they have a very high electron density and electronic effects can be predicted using relatively simple models.[1,2] The possibility of creating and probing transient nonequilibrium electron populations in metals with ultrashort laser pulses has been demonstrated by several different groups[3–6] and applied to various metallic systems.[7–9] In these experiments the electron gas relaxation dynamics has been followed by probing the transient changes of the optical properties of the sample. Because of the large electron population, electron-electron interactions were assumed to be fast enough to instantaneously thermalize the electron gas, although some slight deviations from the expected thermalization behavior were observed.[5,7] On the basis of this hypothesis important information on electron-phonon interaction in metals and metallic superconductors[2,7] and on hot-electron transport in thin metallic films[8] were obtained.

Recent investigations using transient photoemission have demonstrated the existence of non-Fermi electron distributions with thermalization times as long as 600 fs. These results were observed in gold films in the high excitation limit (~ 400 K electron temperature changes).[10,11] Taking advantage of the surface plasmon-polariton resonance, similar conclusions were indirectly drawn at lower excitation by analyzing the temperature dependence of the optically measured electron-phonon interaction time in gold and silver.[12] These results are in sharp contrast with the basic hypothesis used in transient thermomodulation experiments and additional investigations are clearly needed to analyze the role of the slow electron thermalization in this measurement technique.

We have investigated the effect of the noninstantaneous electron-electron interaction on the optical response of a metal film by performing transient reflectivity and transmissivity measurements in the very low perturbation regime. In contrast to most of the previous experiments, we use a multiple wavelength femtosecond pump-probe technique. An infrared pulse perturbs the electron gas and the changes in the optical properties of the metal are probed with a visible. This technique uses widely separated pump and probe wavelengths and thus permits a more definitive measurement of electron dynamics by separating the effects of pump-induced transitions from those monitored by the probe. This separation is essential to avoid any influence of the *d*-band electrons on the measured rise time. In addition, by proper tuning of the probe wavelength, the transient electron distribution can be monitored very close to the Fermi surface where the optical property changes are maximum. This renders the measurement very sensitive and permits weak perturbations of the electron distribution [peak electron temperature changes (ΔT_e) of the order of a few degrees Kelvin]. In these conditions, the system response is linear and the measured changes in reflectivity and transmissivity can be directly related to the electron distribution. This is in contrast to previous transient reflectivity and transmissivity experiments probing electron far from the Fermi surface and thus necessitating large perturbation of the electron gas.

Experiments were performed on gold films because the band structure is relatively well known[13] and band to band transition can be easily probed by a frequency-doubled Ti:Al_2O_3 femtosecond laser. The high-stability, high repetition rate and tunability of the Ti:Al_2O_3 laser is particularly suited to our low pump fluence measurements. A related multiple wavelength femtosecond technique using an amplified CPM dye laser has been used to investigate the transient reflectivity of optically thick gold film.[5] However because of the low repetition rate (8 kHz) and lower stability of the laser system, measurements were performed only for very large perturbations

of the electron gas ($\Delta T_e \sim 1000$ K) and with a visible pump pulse (2.0 eV) permitting perturbation of the probed transition (around 2.4 eV in gold).

Femtosecond thermomodulation transmissivity and reflectivity measurements in metals are performed by perturbing the electron population with a short pump pulse. If the energy of the pump photons is much smaller than the transition from the d band to the Fermi surface (2.4 eV in gold), excitation occurs only through free carrier absorption without any perturbation of the d band. A broad non-Fermi distribution extending up to the pump photon energy above the Fermi level is thus created. Energy is redistributed among the electrons through electron-electron interactions, producing a hot Fermi distribution with temperature T_e. This first step of the nonequilibrium population evolution is of central interest here. After thermalization (and partly during it if it is slow enough[12]), the electron gas loses its energy and equilibrates with the lattice through electron-phonon interaction. The dynamics of nonequilibrium electron and lattice temperatures associated with this second step has been extensively studied and the electron-phonon interaction parameters have been measured.[2,7] As soon as the electron temperature is established and assuming that the electron-electron and phonon-phonon interactions are fast enough to maintain a local equilibrium for both of the populations, the evolution of the system can be modeled by a set of coupled differential equations:[1,2]

$$C_e(T_e)\partial T_e/\partial t = \nabla(\kappa \nabla T_e) - G(T_e - T_l) + H(z,t) , \quad (1a)$$

$$C_l \partial T_l/\partial t = -G(T_l - T_e) , \quad (1b)$$

where C_e and C_l are the electronic and lattice heat capacities [$C_e(T_e) \ll C_l$ for the investigated temperatures], κ is the thermal conductivity, and G is the electron-phonon coupling constant. Heating of the electron population is accounted for by the source term $H(z,t)$. For optically thin samples at the pump wavelength, diffusion effects can be neglected since the initial excitation is almost homogeneous over the thickness of the sample and homogenizes on a time scale shorter than the pulse duration.[8] For large changes in electron temperature, the dependence of C_e on T_e has to be explicitly taken into account [$C_e = \gamma T_e$ where $\gamma = 66$ J m^{-3} K^{-2} (Ref. 13)] resulting in nonlinear temperature dynamics.[7,14] Interpretation of the measurements is much simpler if only small temperature changes are induced, $\Delta T_e \ll T_0$, where T_0 is the initial sample temperature (~ 300 K in our experiment). C_e is then approximately constant and the electron temperature decays exponentially with a characteristic time $\tau_e = 1/[G(1/C_e + 1/C_l)]$.

The heating of the electron population produces a modification of the electron distribution close to the Fermi energy, changing the interband absorption spectrum and consequently the dielectric constant of the sample. These changes are maximum close to the energy of the transition from the top of the d band to the Fermi level.[15,16] For small ΔT_e the changes in the electronic occupation number can be linearized and the changes in the real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric constant are directly proportional to ΔT_e. The time-dependent modifications of the dielectric function can be monitored by measuring the transient reflectivity ($\Delta R/R$) and transmissivity ($\Delta T/T$) of the sample which are linear combinations of $\Delta\epsilon_1$ and $\Delta\epsilon_2$.[17] If small perturbations are induced, $\Delta R/R$ and $\Delta T/T$ give information on the temperature dynamics of the system and are expected to decay exponentially with the time constant τ_e.

Our studies are performed using a Ti:Al_2O_3 laser (Coherent Mira 900) which is configured to generate femtosecond pulses in the wavelength range 1.06 μm–880 nm. At 1 μm wavelength which was used for our measurements, the average energy is 600 mW with a pulse duration of 140 fs and a repetition rate of 76 MHz. Measurements were performed using a standard pump-probe geometry. About half of the laser beam is directed through a variable delay stage and used as the pump. The remaining part is focused into a 100-μm-thick BBO crystal to generate a probe pulse at the second harmonic 530–440 nm (2.34–2.82 eV). At 500 nm, the average power is 70 μW with a duration of 210 fs as measured at the position of the sample by cross correlation with the fundamental beam in a BBO crystal. Since only a weak probe is necessary, no attempt has been made to improve the conversion efficiency ($\sim 5 \times 10^{-4}$). The infrared and blue beams are focused onto the sample using a 10× microscope objective with measured focal spot diameter of 11 and 8 μm, respectively. The pump beam is chopped and the signal is detected using a lock-in amplifier. Most of the experiments were performed in a polycrystalline gold sample whose thickness (200 Å) is comparable to the gold skin depth at 1 μm [~ 125 Å (Ref. 18)] so that diffusion of hot electrons can be neglected.

The maximum $\Delta R/R$ has been measured to be around 2.6 eV in a 1000-Å gold sample.[5] This maximum is slightly shifted in a 200-Å film because of the sample thickness dependence of the linear coefficient linking $\Delta R/R$ with $\Delta\epsilon_1$ and $\Delta\epsilon_2$. Using the tunability of the Ti:Al_2O_3 laser and taking into account the weak dispersion of free electron absorption, the maximum changes in $\Delta R/R$ and $\Delta T/T$ have been measured to occur at, respectively, 2.5 and 2.35 eV. The wavelength of the laser has thus been set at 1 μm (i.e., a probe energy of 2.48 eV) in order to get the highest sensitivity to the behavior of the nonequilibrium population.

The measured $\Delta R/R$ and $\Delta T/T$ are shown in Fig. 1 for a pump fluence of 14 μJ/cm^2. The absorption of the sample has been measured to be 5% in agreement with an estimation based on the known optical constant of the bulk[18] and the calculated reflectivity and transmission of a thin film.[17] Assuming that all the absorbed energy is stored into the electron gas, the peak change of the electron temperature is estimated to be about 15 K. Measurements performed at low power (fluence between 2.5 and 200 μJ/cm^2, corresponding to maximum $\Delta T_e \sim 3$–200 K) show the same dynamics.

The transient response is characterized by a rise time much longer than the cross correlation of the input pulses, followed by an exponential decay in agreement with the temporal evolution of the electronic temperature predicted by (1) in the low perturbation regime. The decay time constant $\tau_e = 1$ ps favorably compares with pre-

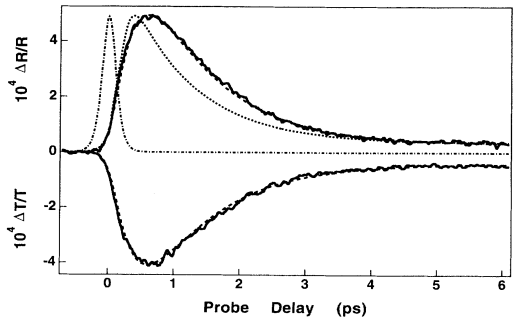

FIG. 1. Transient reflectivity ($\Delta R/R$) and transmissivity ($\Delta T/T$) measured in a 200-Å gold film. The laser fluence is 14 $\mu J/cm^2$. The dashed lines are the fits calculated assuming a delayed electron gas thermalization [response function (3)] while the dotted line corresponds to an instantaneous thermalization [response function (2)]. Cross correlation between pump and probe pulse is shown with a dotted-dashed line.

vious determination based on an extraction procedure[14] and results in an electron-phonon interaction constant G in agreement with previous determinations. Assuming an instantaneous thermalization of the electron gas, the system is fully described by the electronic and lattice temperature whose temporal evolutions are given by (1) where the heating source $H(t)$ is identified with the pump pulse intensity. For a weak perturbation of the electron gas in an optically thin sample, the response function of the system is thus of the form

$$S(t)=u(t)[\exp(-t/\tau_e)+\alpha]\ , \qquad (2)$$

where $u(t)$ is the step function. The exponential decay τ_e describes the cooling of the Fermi electron distribution to the lattice temperature. The small residual contribution α accounts for the increase of the final electron-phonon temperature from the initial temperature. This component decays on a hundred picosecond time scale through transverse heat diffusion[19] and coupling with the substrate.[20] To account for the finite duration of the pulses, the response function has been convolved with the measured pump-probe correlation, giving the dotted lines in Fig. 1 which clearly cannot reproduce the experimental data (with $\tau_e=1$ ps). Better agreement cannot be obtained by modification of the time constant τ_e. This suggests that the maximum signal is delayed.

The slow rise of the measured signal demonstrates that the perturbation of the electronic distribution close to the Fermi level is noninstantaneous, indicating a delayed thermalization of the electron gas and thus the presence of a long-living non-Fermi perturbation. In order to quantitatively characterize the electron transient behavior, following the model of Fann *et al.*[11] we have divided the electron distribution into a high-density Fermi distribution and a low-density non-Fermi distribution whose energy is transferred to the thermalized electrons by electron-electron collision. Probing close to the Fermi surface, our measurements are essentially sensitive to the thermal part of the electronic distribution. Identifying the heating term $H(t)$ in (1) with the decaying non-Fermi distribution, the system response function takes the form

$$S(t)=u(t)\{[1-\exp(-t/\tau_R)]\exp(-t/\tau_e)+\alpha\}\ . \qquad (3)$$

The first term introduced a delayed rise time of the signal with a time constant τ_R which describes the buildup of the Fermi distribution temperature through energy transfer from the nonthermal distribution by electron-electron interactions. Convolution of the response function with the measured pump-probe correlation gives the dashed lines in Fig. 1 which perfectly reproduce the experimental data with $\tau_R=500$ fs and $\tau_e=1$ ps. Note that the same time constants are used to fit the transmissivity and reflectivity data.

Our estimated electron thermalization time τ_R is comparable to the previous estimations,[10,11] making consistent the transient thermomodulation and photoemission measurements. Because of the very high electron density of metals, very fast electron-electron interactions might be expected. However, the interaction efficiency is considerably reduced by phase space filling which blocks most of the energetically possible interaction channels and by screening which considerably reduces the efficiency of the Coulombic interaction. In fact, using the Fermi-liquid theory, thermalization time of few hundred femtoseconds can be estimated close to the Fermi energy.[10,12] This inhibition of the electron-electron scattering in degenerated system has also been observed in modulation-doped quantum-well semiconductors.[21]

Measurements were repeated for high laser fluence up to 3 mJ/cm^2 (i.e., peak temperature changes up to 1300 K). Over the investigated range, the maximum amplitude $\Delta R/R$ varies almost linearly with the pump power. As the fluence increases over 200 $\mu J/cm^2$, modifications of the measured dynamics are observed, both in reflectivity and transmission measurements (Fig. 2). The decay of the signal is longer and nonexponential suggesting that the approximations used to linearize the response of the system are no longer valid and a more complicated description is needed. In particular the fitting procedure based on (2) can no longer be used to extract the temperature rise time. Qualitative comparison of the observed rise time (taking into account the slower decay) suggests a decrease in the thermalization time in agreement with very recent photoemission investigations[11] as expected because of the larger smearing of the Fermi distribution.

We have also tested the influence of the noninstantaneous electron thermalization on transient thermomodulation measurements in optically thick samples where diffusion of the non-Fermi electrons[8] takes place concurrently with thermalization. Here the excited electrons diffuse rapidly out of the skin depth region and produce a fast decay of the heating source (in typically less than 200 fs for a 1200-Å sample[8]). Consequently electrons in the probed zone (of the order of the skin depth for the probe pulse) quickly reach their peak temperature and the temperature change is much lower than that observed in a thin sample. This is illustrated in Fig. 3 which shows the measured $\Delta R/R$ in a 200- and a 1200-Å gold film for the same pump energy (fluence 200 $\mu J/cm^2$). The signals have been normalized and the actual $\Delta R/R$ is about 10 times smaller in the thick sample than in the thin one. Due to the additional fast decay of the nonthermal distri-

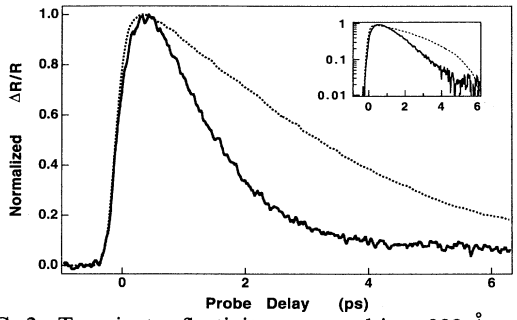

FIG. 2. Transient reflectivity measured in a 200-Å gold film for a pump fluence of 2.5 $\mu J/cm^2$ (full line) and 3 mJ/cm^2 (dotted line). Inset is a semilogarithmic plot with residual contribution α subtracted.

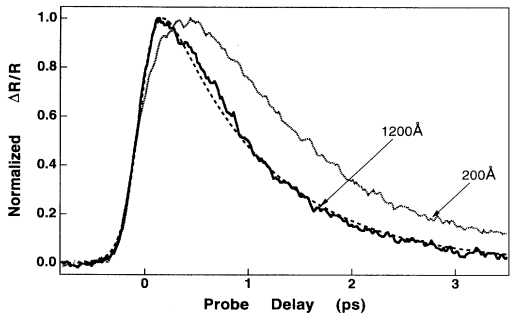

FIG. 3. Transient reflectivity measured in a 200- (dotted line) and a 1200-Å (full line) gold film. The dashed line is a fit to the 1200-Å data assuming an instantaneous electron thermalization.

bution by diffusion, the rise time is much faster in the thick sample and is limited by our temporal resolution. A good fit of the data can be obtained assuming an instantaneous electron thermalization and an exponential decay of the electron temperature with the same decay constant as the one measured in the 200-Å film (1 ps). This is expected since once carrier diffusion can be neglected in the thick sample (typically less than 200 fs) the electron temperature dynamics can be described by (1) with the same exponential decay.

In conclusion, the transient reflectivity and transmissivity of thin gold films were investigated using a high sensitivity multiple-wavelength pump-probe technique. The electron distribution was perturbed by free carrier absorption of an infrared femtosecond pulse and its relaxation dynamics probed by a visible pulse close to the *d* band to Fermi surface transition avoiding any spurious effect of the *d*-band electrons on the measured signal. The use of our improved thermomodulation technique permits measurements in the low perturbation limit (peak electron temperature change of a few degrees Kelvin). The results can be directly related to the temporal behavior of the free electron distribution greatly simplifying the interpretation of the measurements compared to previous investigations. In agreement with recent transient photoemission measurements, a delay in the electron gas thermalization was observed in optically thin films. Using a simple model, we have estimated a thermalization time of the order of 500 fs, independent of the laser fluence in the range 2.5–200 $\mu J/cm^2$ (i.e., estimated maximum peak changes in the electron temperature ranging from 3 to 200 K). The electron-lattice interaction time constant was measured to be 1 ps corresponding to an electron-phonon interaction constant in close agreement with previous transient thermoreflectance measurements.

In optically thick samples, diffusion of the non-Fermi electrons takes place concurrently with thermalization and results in a very fast apparent thermalization time of the electron gas. For the time resolution of our system, the initial nonthermal distribution decays almost instantaneously leading to an instantaneous rise time of the transient reflectivity. The electron-phonon coupling constant is identical to that measured in thin samples. The simplifying hypothesis of an instantaneous thermalization of the electron gas thus provides a correct description of the transient optical properties of optically thick film. These studies provide further evidence for a non-Fermi electron dynamics and characterize the influence of the initial thermalization dynamics of excited electrons on the transient optical properties of metal films.

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