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Femtosecond thermoreflectivity and thermotransmissivity of polycrystalline and single-crystalline gold films

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A femtosecond laser is used to generate and probe hot electrons in polycrystalline and single-crystalline thin gold films. Transient thermoreflectivity and thermotransmissivity measurements are performed. The hot-electron energy-loss lifetime is shown to be 1–3 ps and increases with laser fluence. For film thicknesses comparable to the optical skin depth, the lifetime for polycrystalline films is slightly shorter than that for single-crystalline films. For thicker films, hot-electron transport competes with energy loss. Electron transport appears to be slower in the polycrystalline films.

If a metal is excited by a laser pulse with a duration less than or comparable to the hot-electron energy-loss lifetime (τ_e), a transient inequality between the effective electron and lattice tempertures (T_e and T_l) occurs.[1] In metals τ_e can vary greatly. At low lattice temperatures, the coupling of the electrons to the phonons is weak. This results in a 1-ms lifetime[2] for Cu at 25 mK. At higher temperatures, τ_e is significantly reduced and near liquid-nitrogen temperatures can be as short as a few picoseconds.[3] This has made the observation of nonequilibrium heating, in this region, inaccessible except through ultrafast lasers. Early femtosecond thermomodulation of metals temporally resolved the decay of the hot-electron population by energy loss in geometrically confined copper films[4] (with thicknesses comparable to the laser skin depth) and by a combination of energy loss and electron transport in thicker gold films.[5,6] Subsequently, surface-plasmon resonance in thin silver films has been shown to provide a very sensitive probe of nonequilibrium heating.[7] A systematic study of electron-phonon coupling in different thin metal films was recently conducted.[8] Although results for τ_e showed agreement with theory,[9] there remains unresolved the role of lattice imperfections on hot-electron energy loss and transport. An approach to measuring electron-phonon coupling in metals based on a comparison of the experimental damage threshold for different laser pulse widths with a heat-transport model was previously proposed.[10] However, some concerns regarding its implementation were subsequently commented on.[11]

Heating-induced modulation of the optical properties of metals can result from many effects. Of particular importance to transient thermomodulation studies is the change in the occupancy of electronic states near the Fermi level.[12] The energy difference from the top of the d band to the Fermi level in Au is ~2.4 eV.[13] However, thermomodulation measurements[13] and relativistic band calculations[14] for Au have shown the existence of an absorption tail extending as low as 1.7 eV.

We now report observation of femtosecond time-resolved thermoreflectivity ($\Delta R/R$) and thermotransmissivity ($\Delta T/T$) for thin (100–800 Å) polycrystalline (PCF) and single-crystalline (SCF) Au films. Reflectivity and transmissivity are complimentary in the sense that reflectivity probes a depth comparable to the skin depth of the laser in Au (~150 Å) whereas transmissivity probes across the film. Moreover, for a uniformly heated film, the combined transient reflectivity and transmissivity along with the known thickness of the film is sufficient to determine transient changes in the real and imaginary parts of the dielectric constant (ϵ_1 and ϵ_2, respectively).[15]

The Au films are fabricated by evaporation. The film thickness is determined by a crystal thickness monitor with an estimated absolute accuracy better than ±50 Å. Polycrystalline Au films are evaporated on a glass slide. Examination of films evaporated on an electron microscope grid adjacent to the glass slide reveals a wide distribution of grain sizes with an average of a few hundred angstroms. Single-crystalline thin Au films are fabricated by epitaxial growth on a $\lesssim$20-Å Ag layer grown on a heated NaCl crystal. The film is floated on distilled water, washed in sulfuric acid to remove the Ag and any Au-Ag alloy, then washed in distilled water. Finally, the film is caught on a glass slide. Electron diffraction obtained from these films shows a single-crystal pattern in the (100) orientation. These films are known to possess high dislocation densities (10^{10}–10^{11} cm^{-2}) and twins.[16] Experiments are performed using a 76-MHz femtosecond dye laser [~150 fs FWHM (full widths at half maximum), with a wavelength $\lambda=615$ nm, maximum pulse energy ~0.6 nJ]. A pump-probe setup is used with both beams at near normal incidence (focal spot on the sample 4±1 μm). The probe energy is fixed whereas the pump energy is varied. The pump-to-probe energy ratio is always >17. The pump beam is mechanically chopped and the thermomodulation signal is detected using lock-in amplification tuned to the chopping frequency.

Time-resolved $\Delta T/T$ of a 200-Å single-crystalline Au film is shown in Fig. 1. The initial sharp rise in the thermomodulation is due to the heating of the electrons by the laser pulse while the lattice remains very close to its initial temperature. Hot electrons thermalize mostly through electron-electron (*e-e*) scattering and transfer their energy to the lattice through electron-phonon (*e*-ph) scattering. These scattering mechanisms are periodically interrupted by scattering of the electrons at imperfections (*e-i*). Finally, the slow decay of the thermomodulation signal reflects the enhanced *e*-ph scattering as the phonons slowly equilibrate to the thermal bath of the substrate. The temporal evolution of the transient reflectivity and transmissivity is found, to a first-order approximation, to be exponential for all laser fluences. Both $\Delta T/T$ and $\Delta R/R$ are negative. The maximum $\Delta T/T$ and $\Delta R/R$ are directly proportional to the laser fluence and for $\Delta T/T$ it is almost independent of film thickness for 200–800 Å ($\Delta T/T \sim 4\times10^{-3}$ for a heating fluence of 4 mJ/cm^2). On the contrary, for the same fluence of 4 mJ/cm^2, the maximum $\Delta R/R$ decreases from $\sim 4\times10^{-3}$ for the 200-Å films to $\sim 1\times10^{-3}$ for the 800-Å films. For the 200-Å films, laser heating is expected to be uniform since the film thickness is comparable to the skin depth and since electron transport can rapidly smooth the electron effective temperature profile across the film. Under these assumptions, transient changes in the real and imaginary parts of the dielectric constant (ϵ_1 and ϵ_2, respectively) can be related to $\Delta T/T$ and $\Delta R/R$ if the thickness of the film and the index of refraction of the transparent substrate are known. Results of this analysis show that ϵ_2 undergoes a significantly larger perturbation than ϵ_1 (peak $\Delta\epsilon_2/\epsilon_2$ is about two orders of magnitude larger than peak $\Delta\epsilon_1/\epsilon_1$). Moreover, the shape of $\Delta\epsilon_2/\epsilon_2$ seems to follow closely that of $\Delta R/R$ and $\Delta T/T$. Details of this analysis will be presented elsewhere.

If we assume that electron-electron (Coulombic) scattering and phonon-phonon (anharmonic) scattering maintain the electron and the phonon subsystems in pseudoequilibrium at separate temperatures T_e and T_l, then the usual expressions for the temporal evolution of T_e and T_l are[1]

$$C_e(T_e)\frac{\partial T_e}{\partial t}=\nabla\cdot(\kappa\nabla T_e)-G(T_e-T_l)+P_0(r,t) \tag{1}$$

and

$$C_l\frac{\partial T_l}{\partial t}=G(T_e-T_l)\ . \tag{2}$$

In Eqs. (1) and (2) the electronic heat capacity $C_e(T_e)$ is assumed proportional to T_e, C_l is the lattice heat capacity, κ is the electronic thermal conductivity, G is the *e*-ph coupling parameter (assumed constant), and $P_0(r,t)$ represents the laser energy deposited into the film. The assumption of pseudoequilibrium could be violated over a part of the duration, or even the entire transient time. In this case T_e and T_l become "effective" temperatures. At this stage, the effect of point and line imperfections in both the PCF and in the SCF as well as the effect of grain boundaries in the PCF are not explicitly included in Eqs. (1) and (2) except as they affect G. Moreover, for films of thickness of the order of (or less than) the photon skin depth, the term for electron diffusion can be deleted in Eq. (1). We choose to analyze, in these terms, the experimental results for the 200-Å films. For thicker films, hot-electron transport cannot be neglected. Moreover, the diffusion term in Eq. (1) might have to be modified to account for possible ballistic transport of hot electrons.[6] Also, modifications to these simple expressions may be needed if electron-imperfection scattering must be explicitly included. If we assume that the film is heated uniformly, a solution of Eqs. (1) and (2) indicates that initially, T_e is increased $\gtrsim 1000$ K for a heating laser fluence of 4 mJ/cm^2 whereas the maximum increase in $T_l \sim 40$ K.[17]

We next consider the experimentally obtained transient decay time and the theoretical hot-electron relaxation time, τ_e. In the experimental measurements we define the decay time as the duration of $\Delta T/T$ and of $\Delta R/R$ as measured at $1/e$ of the peak value less that at the slowly decaying tail. For the theoretical model we define the transient decay time as the duration at $1/e$ of the difference between peak T_e and its final equilibrium value with the lattice. These definitions are made here mainly to facilitate a comparison of the results for single-crystalline versus polycrystalline films. No direct correspondence between the hot-electron relaxation time obtained by solving Eqs. (1) and (2) and the fast transient thermomodulation signal is implied. Our measurements, however, indicate that the decay of the thermomodulation is, to a first-order approximation, exponential and there does appear to be a qualitative correspondence between the transient decay time and τ_e. In Fig. 2 the experimental measurements of the transient decay time are displayed for various values of the pump laser fluence[18] along with the theoretical curves for τ_e for different values of G.[17] These results show that (i) the dependence of $\Delta T/T$ and that of $\Delta R/R$ on time is the same, (ii) the decay rate in PCF is faster than that of SCF, (iii) its

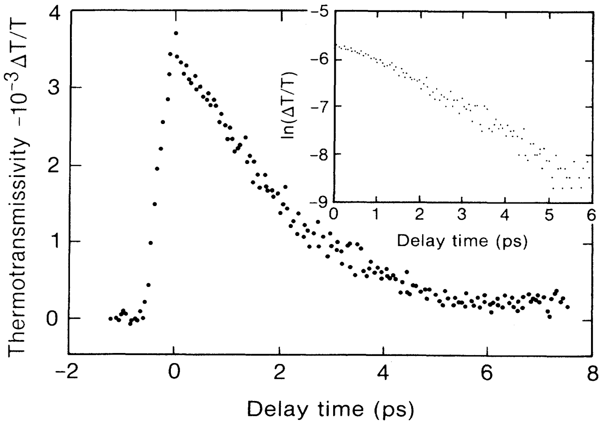

FIG. 1. Temporal evolution of the transient thermotransmissivity ($\Delta T/T$) of a 200-Å-thick single-crystalline gold film. Heating laser fluence is 4.1 mJ/cm^2. Inset shows the logarithm of $\Delta T/T$.

dependence on laser fluence essentially follows the model, (iv) $G = 4\times10^{16}$ W/m^3 K overlaps with the transient decay time obtained experimentally in 200-Å PCF, and (v) G for SCF is somewhat smaller than that for PCF. An increased decay time is also observed for the epitaxially grown 100-Å Au films when compared to the 100-Å Au polycrystalline films. The value of G deduced from Fig. 2 should be interpreted in view of several uncertainties. These include the pump laser fluence, which depends on the laser focal spot (4 ± 1 μm) and, as noted above, in relating a thermomodulation signal to hot-electron decay. Moreover, previously it has been shown[5] that the relaxation rate observed by thermomodulation is dependent on the probe wavelength due to the narrowing of the electronic distribution as the electrons thermalize with the lattice.

We next consider the various possibilities for the observed difference in τ_e in polycrystalline versus single-crystalline films. Variations in the optical properties of the PCF and SCF could cause variation in the energy absorbed from the laser. To check this point, we have compared the maximum $\Delta T/T$ for the PCF and SCF. Three independent measurements were made for four laser fluences ranging from 0.7 to 4 mJ/cm^2. The maximum $\Delta T/T$ for the PCF and for the SCF showed better than 5% agreement (the maximum $\Delta T/T$ was slightly higher for the PCF). This precludes the possibility that the difference in τ_e in Fig. 2 is due to differences in the energy absorbed. In addition, errors in relative film thicknesses are too small to explain this difference. Also, when fabricating the 200-Å SCF films, the Ag layer was only ~10 Å. Thus, alloying and subsequent removal of Au could not have reduced the film thickness by much more than 10 Å. Moreover, the possibility that the removal from the substrate of the SCF introduces changes in film properties that affects electron dynamics can be ruled out since transient thermomodulation of PCF deposited on a NaCl crystal at room temperature and removed using the same techniques, are in agreement with those directly deposited on a glass slide. This leads to the conclusion that the shorter transient decay time observed for the PCF, relative to that for SCF, is due to faster hot-electron energy loss promoted by increased lattice imperfections.

Electron-imperfection scattering (*e-i*) can modify *e-e* and *e*-ph coupling.[19] Enhanced electron-acoustic phonon coupling in the presence of imperfections has been postulated to result from the partial removal of constraints on (crystal) momentum conservation as the result of the randomization of the electron wave vector by *e-i* scattering.[20] If we assume that the concentration of point and line defects are the same in the PCF and SCF, then the observed difference should lie in the grain boundaries. Moreover, the scattering strength of electrons is thought to be significantly stronger at grain boundaries than at point and line imperfections and at stacking faults.[21] On the other hand, for the 200-Å films, the average grain size is comparable to the film thickness and it becomes difficult to separate the role of grain boundaries from that of surfaces. Studies of the resistivity suggest that the surface roughness of polycrystalline Au films causes diffuse scattering of electrons whereas the atomically smooth surface of single-crystalline Au films cause specular reflection of the electrons.[22] Theoretically, electron collisions with surfaces distort their distribution in a manner that could depend on surface roughness.[23]

We next consider transient thermomodulation experiments on films of thickness greater than the skin depth. As an illustration, we display in Fig. 3 the results from an 800-Å film.[24] In this case, an initial thermal gradient exists between hot-electron concentration within the skin depth and that in the rest of the (unexcited) film. As time progresses, energy stored within the skin depth region is lost through transport of some of the electrons into the unexcited region of the film. Thus, one would expect that the transient decay rate of $\Delta R/R$ be faster than observed in 200-Å films. Comparison of the results in Figs. 2 and 3

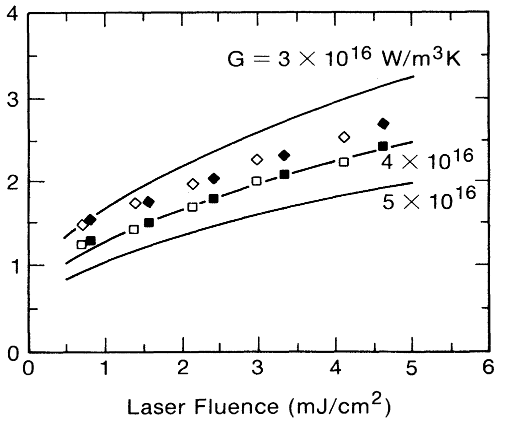

FIG. 2. Decay time of the fast transient in thermoreflectivity (solid symbols) and thermotransmissivity (open symbols) of 200-Å single-crystalline (diamonds) and polycrystalline (squares) gold films as a function of heating laser fluence. Solid lines represent τ_e obtained from Eqs. (1) and (2).

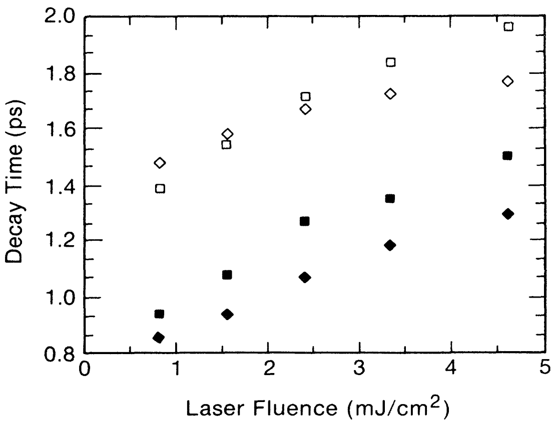

FIG. 3. Decay time of the fast transient in thermoreflectivity (solid symbols) and thermotransmissivity (open symbols) of 800-Å single-crystalline (diamonds) and polycrystalline (squares) gold films as a function of heating laser fluence.

indeed verifies this assumption. Results for $\Delta T/T$ show that it is affected less by the increased film thickness as expected since transmissivity probes across the film. In contrast to the 200-Å films, in the 800-Å films the decay time of the fast transient in $\Delta R/R$ is observed to be slower for PCF as compared to the SCF. This result is consistent with the conclusion that grain boundaries impede electron transport. An interesting sign reversal is observed in the difference between the decay time of the fast transient in $\Delta T/T$ for PCF and SCF as a function of laser fluence. This was also observed for 400-Å films. At this stage we can only offer the following qualitative explanation. We notice that $\Delta T/T$ is less affected by electron transport than $\Delta R/R$ and that hot-electron transport competes with energy relaxation. For low laser fluences, where diffusion is less important, the increased τ_e for the PCF results in a faster decay as observed for the 200-Å films. At the higher fluences, diffusion becomes more important. This affects the spatial distribution of hot electrons across the film causing it to be less uniform for the PCF than for the SCF due to lower κ. Since τ_e increases with the effective T_e, we would expect a slower transient decay time for the PCF. A quantitative analysis of electron transport would require a more extended treatment than permitted by the diffusion term in Eq. (1). Among the factors which need to be considered are the possible role of ballistic hot-electron transport,[8] the dependence of electron transport on T_e and T_l, and the nature of *e-i* scattering. Furthermore, difficulties arise through the presence of transient electromagnetic fields in the film as a result of hot-electron transport out of the skin depth region.

In conclusion, we have demonstrated that femtosecond thermoreflectivity and thermotransmissivity of polycrystalline and single-crystalline thin Au films indicate that the loss of energy of an initially hot-electron distribution is somewhat faster in PCF as compared to SCF, and that hot-electron transport is slower in PCF.

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[17] Equations (1) and (2) were solved for $C_e(T_e)=66T_e$ J/m^3 K, $C_l=2.4\times 10^6$ J/m^3 K, a Gaussian heating laser pulse (150 fs FWHM), an experimentally determined absorption of 5%, the resultant excitation is assumed to be deposited uniformly across the thickness of the film, and neglecting thermal conduction.

[18] Each datum is an average of six to eight different measurements conducted using three sets of PCF and SCF. The standard deviation in each decay time measurement is less than 10% of the average value.

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[24] Figure 3 is an average of four to six different measurements conducted on one set of films. The standard deviation in each decay time measurement is less than 12% of the average value.