# Ultrafast Relaxation of Electrons Probed by Surface Plasmons at a Thin Silver Film

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We present a novel subpicosecond optical transient-reflection method, which employs the surface-plasmon resonance of a thin silver film as a very sensitive probe to study small transients of the effective electron and lattice temperatures. By measuring under surface-plasmon resonant and nonresonant conditions, we can discriminate between lattice and electron heating. We find a change of the lattice and electron temperatures of, respectively, $\Delta T_l = 0.10(5)$ K and $\Delta T_e = 30$–$90$ K for an intensity of 180 W cm$^{-2}$ and an electron-phonon energy relaxation time of 670(70) fs.

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The initial relaxation dynamics of excited electrons in metals reveals fundamental information about the electron-phonon coupling and the electron-electron coupling.[1] These relaxation processes govern transport properties like electrical and thermal conductivity and depend on the same interactions that play an essential role in, e.g., superconductivity. Modern pulsed-laser techniques enable time-resolved studies of these relaxation mechanisms. The electron plasma is optically excited by an intense laser pulse that creates an electron gas which is out of equilibrium with the lattice. In recent years a variety of optical techniques have been developed to study the relaxation dynamics of the heated electron gas. We mention transient photoemission,[2] optical transmission,[3] and reflection[4,5] experiments with femtosecond time resolution and heat transport[6] and reflection[7,8] measurements with picosecond resolution. It was demonstrated that the electron gas is more than 600 K out of equilibrium with the lattice when high-power pulsed lasers are used.[2-4] At these extreme conditions the relaxation dynamics strongly depends on the electron temperature, resulting in a nonexponential decay. The typical relaxation time to bring the heated electron gas into equilibrium with the lattice is in the (sub)picosecond range. All the previously mentioned subpicosecond thermomodulation experiments were performed on the noble metals copper and gold, because the presence of an electronic transition frequency ($d$ band to Fermi level) near the laser frequency was needed to monitor the electronic heating by the absorption properties of the transition.

In this Letter we present a novel method, which employs the surface-plasmon (SP) resonance of a thin silver film as a very sensitive probe to small transients in the electron temperature. Other experiments like studies of adsorbates of metal films and nonlinear optical surface effects[9] have already shown that SP's can be used as a powerful spectroscopic tool to enhance the sensitivity to small changes of the dielectric constant of a metal film. We will show that the thermomodulation of the absorption edge at $\approx 4$ eV in silver appears as a dispersive modulation around the laser frequency (photon energy = 2.0 eV). We observed for the employed low-power pulsed laser system an instantaneous electron-temperature rise of $\Delta T_e = 30$–$90$ K, after which it decayed exponentially with a time constant of 670(70) fs.

We heat and probe the electrons of a thin silver film by the excitation of a surface plasmon (SP). A SP is a transverse coupled excitation of the electron gas and electromagnetic field and can easily be optically excited with the method of Kretschmann,[10] based on attenuated total reflection (ATR). We reflect a $p$-polarized laser beam internally from the hypotenuse face of a fused-silica prism which is coated by a thin silver film (see Fig. 1). At a critical angle of incidence, $\Phi_{SP}$, the parallel momentum of the light inside the fused silica matches the momentum of the SP's and practically all the light is converted into SP's at the silver-air interface. The curve of the reflectivity $R(\Phi)$ versus the angle of incidence $\Phi$ shows a sharp dip at the plasmon angle ($\Phi_{SP}$). The position, depth, and width ($\Delta\Phi_{SP}$) depend strongly on the

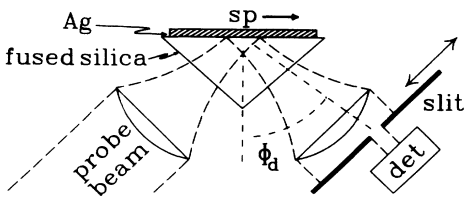


FIG. 1. Kretschmann geometry for the optical excitation of surface plasmons. The laser beam strikes the silver film at the fused-silica–silver interface. Surface plasmons are excited at the silver-air interface. A movable slit selects a portion of the reflected probe beam at the angle of detection $\Phi_d$. The pump beam is not shown.

dielectric constant. The SP travels along the surface with a group velocity close to the velocity of light ($v_g = 0.90c$) and gradually decays due to the finite conductivity of silver. The mean free path is estimated to be $l_{SP} = 40$ $\mu$m, which corresponds to a momentum lifetime of $t_{SP} = 140$ fs.[11] As the SP decays, it creates an electron-hole pair that rapidly distributes its energy in the Fermi sea via electron-electron collisions.

A hot electron gas cools by transferring its kinetic energy to phonons. In metals with a weak electron-phonon interaction such as silver and gold the time scale on which the electron energy relaxation to the phonon bath takes place is of the order of a picosecond.[1] The last step in the relaxation is the diffusion of heat out of the film into the substrate, which takes a time as long as 200 ps.[6,11] Electronic heat transport normal to the film, with a typical heat transport time of 50 fs, will have smoothed out any inhomogeneity by the end of the $\approx 150$-fs-long heating pulse.

The optical setup consists of a colliding-pulse mode-locked (CPM) dye laser delivering a continuous train of short pulses (repetition frequency 95 MHz) at a center wavelength of $\lambda = 620$ nm and an average output power of 20 mW. A pump-probe setup is used where the pump beam is doubly amplitude modulated by a chopper at 500 Hz and at high frequency of 8.8 MHz by an acousto-optic modulator (AOM1). The high-frequency double-modulation scheme enables a sensitive homodyne demodulation with a signal-to-noise performance close to the quantum limit.[12] Moreover, the high modulation frequency eliminates slow thermal effects. We used the deflected beam from AOM1 that is frequency shifted by 80 MHz. This enables us to suppress the spurious interference signal around zero delay time due to SP's that were excited by the pump beam and were scattered from surface roughness.

The probe beam runs through a second AOM crystal (AOM2) and passes a stepper-motor-driven delay line. We precompensate for the large group-velocity dispersion in AOM1 and AOM2 by slightly chirping the laser pulses with the dispersion-compensating prisms of the CPM laser. This yields a final pulse duration of $\tau_p = 150$ fs after compression by the AOM's. Both pump and probe beams are focused by a 50-mm focal-length lens on the fused-silica–silver interface. To be able to spatially separate them after reflection, the parallel beams are displaced a few millimeters with respect to the optical axis, in the direction perpendicular to the plane of incidence. After reflection, both beams show the characteristic beam profile of a circular spot, from which a band of light has been absorbed by SP. The pump beam is immediately blocked. The probe is recollimated and falls via a movable slit on the photodetector (see Fig. 1). The slit determines the angle of detection $\Phi_d$. At the focus, the doubly modulated pump beam has an intensity of 180 W cm$^{-2}$.

The sample is prepared by evaporating a 45-nm-thick silver film from a tungsten vessel at a pressure of $10^{-6}$ mbar onto the hypotenuse face of a right-angle fused-silica prism. After evaporation the thickness is deduced from the transmissivity of a thin glass microscope slide that was coated together with the prism. The dielectric constant of the silver $\epsilon_{Ag} = \epsilon_r + i\epsilon_i = -19 + 0.60i$ ($\pm 5\%$) at the laser wavelength was determined by measuring $R(\Phi)$ around the plasmon angle $\Phi_{SP}$ ($\approx 45°$).

We will now discuss our experimental results. Figure 2(a) shows a typical measurement of the time-resolved change of the reflectivity under SP-resonance conditions at room temperature. We observe a rapid increase of the reflectivity $-\Delta R$ on a time scale of the pulse duration to a maximum ("peak") value, followed by an exponential decay to a constant level with a time constant of $\tau_E = 670(70)$ fs. The final ("plateau") level is significantly

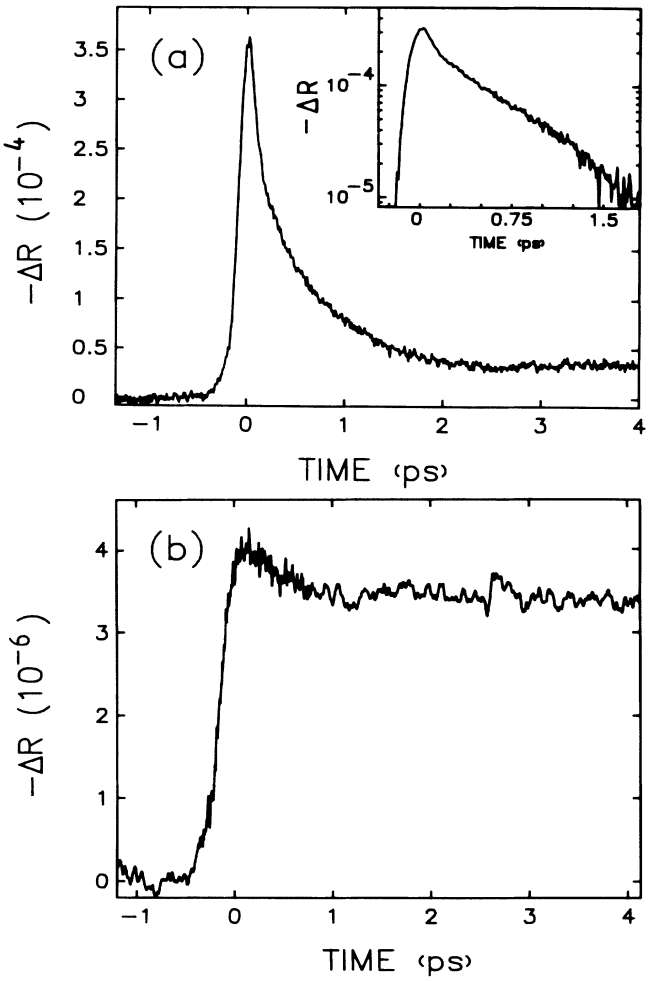


FIG. 2. Measured change of the reflectivity $\Delta R$ as a function of time delay between pump and probe pulses: (a) Surface plasmons (SP) are used to excite and probe the silver film. Inset: Part of the same curve, plotted logarithmically. (b) Only the pump pulse excites SP. The probe beam is now $s$ polarized and orthogonal to the pump beam and does not excite surface plasmons.

higher than the initial level and is constant on a picosecond time scale. No numerical filtering was performed. Some scattered pump light was allowed to interface with the probe beam in order to determine the zero delay time ($t=0\pm 50$ fs). Figure 2(b) shows the average of ten successive scans when we probe nonresonantly. In this experiment the probe is orthogonally ($s$) polarized to the pump beam and does not excite SP's. The change of $\epsilon_{Ag}$ is observed via a change of the ordinary reflectivity of the $s$-polarized light. We observe again a rapid increase, but now the peak level around zero delay time is much smaller and comparable with the plateau level. The results of an extensive analysis of a large series of SP-resonant scans on four different samples are depicted in Fig. 3(a). It shows the peak level (close to zero delay time) and the plateau level (at a few picoseconds delay time) of the change in reflectivity $\Delta R$ versus the detection angle $\Phi_d$, relative to the plasmon angle $\Phi_{SP}$. Evidently, the sign of the peak level reverses as $\Phi_d$ passes the plasmon angle.

The change in the reflectivity can be explained by a change in the dielectric constant of the silver film. From the calculated first derivatives of the reflectivity $R$ with respect to $\epsilon_r$ and $\epsilon_i$ [Fig. 3(b)], we conclude that the peak level [Fig. 3(a)] is the result of an increase in the real part of $\epsilon_{Ag}$. In addition, the nonresonant probe scheme is 20 times less sensitive to a change in $\epsilon_r$ than to a change in $\epsilon_i$ (the Fresnel formulas yield $dR/d\epsilon_r = -1.1\times 10^{-3}$ and $dR/d\epsilon_i = -2.2\times 10^{-2}$); in the SP-resonant probe scheme $dR/d\epsilon_r$ is comparable to $dR/d\epsilon_i$ (at the extremes, $dR/d\epsilon_r = \pm 0.4$ and $dR/d\epsilon_i = -0.5$). We estimate the actual maximum response $dR/d\epsilon_r$ and $dR/d\epsilon_i$ to be 2(1) times smaller than calculated in Fig. 3(b) due to nonuniform heating of the film over the focus spot. The observed increase of $\epsilon_r$ is $1.5(8)\times 10^{-3}$.

The dielectric constant of silver ($\epsilon_{Ag}$) is the sum of a contribution of the core electrons and ions ($\epsilon_c$) and of a free-electron part:[13] $\epsilon_{Ag}=\epsilon_c-\omega_p^2/(\omega^2+i\omega\Gamma)$, where $\Gamma$ is the Drude collision frequency, which is largely determined by the electron-phonon relaxation time, and $\omega_p \equiv (ne^2/\epsilon_0 m)^{1/2}$ is the bulk plasma frequency, which depends on the conduction-electron density $n$, the effective optical mass $m$, and the vacuum permittivity $\epsilon_0$. The time for the lattice to respond to a temperature rise of the electrons is of the order of picoseconds. On the shorter time scale we are observing, the lattice remains rigid and the density $n$ is a constant. The collision frequency is largely dependent on the phonon density, and will not change either. Screening effects that introduce a temperature-dependent plasma frequency[14] are negligible at long wavelengths. Hence, the free-electron part of $\epsilon_{Ag}$ does not contribute to any significant temperature dependence on a short time scale. Instead, there is a large effect of the filled $d$ and empty $s$ bands as will be discussed in the next paragraph.

Silver has two optical absorptions that are sensitive to

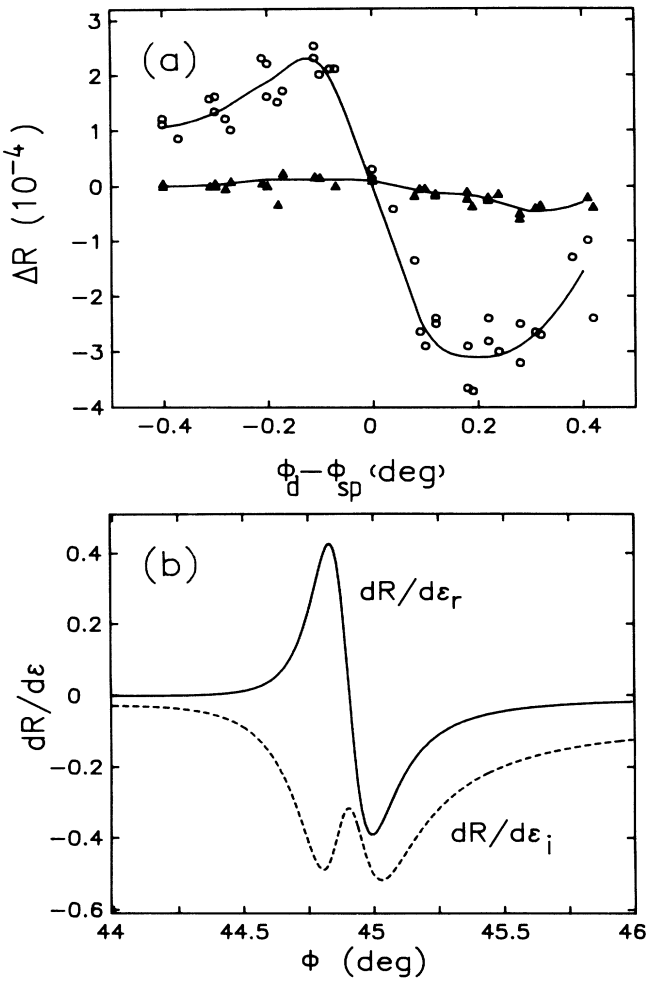


FIG. 3. (a) Measured change of reflectivity $\Delta R$ vs the angle of detection $\Phi_d$ relative to the angle at SP resonance $\Phi_{SP}$. The circles mark $\Delta R$ at its maximum around zero delay time (peak level); the triangles mark $\Delta R$ at a delay time $\approx 3$ ps (plateau level). The lines are a guide to the eye. (b) Calculated derivative of the reflectivity $R$ with respect to the real and imaginary parts of the dielectric constant of the silver of the film, vs the angle of incidence.

the energy distribution of the conduction ($p$-band) electrons around the Fermi level: the $d$-$p$ transition at 4.0 eV and the $p$-$s$ transition at 3.7 eV. These transitions give rise to a large imaginary part $\epsilon_i^c$ above 3.7 eV. Although $\epsilon_i^c$ vanishes below the transition frequency, the real part $\epsilon_r^c$ has a long tail that extends well into the lower-frequency region.

Based on the calculations by Rosei, Culp, and Weaver[13] of the variation of $\epsilon_i^c$ with temperature due to the shift of the Fermi level and smearing of the Fermi distribution, we estimate the response at 2.0 eV to be $d\epsilon_r^c/dT = 2.7\times 10^{-5}$ K$^{-1}$ and conclude that the electron gas was elevated to a temperature of only 30–90 K above the lattice temperature. Although the hot electron gas may not have been thermalized completely by the end of

the pump pulse, it can still be characterized by an effective temperature, close to the equilibrium temperature as is evident from the observed *exponential* decay of the electron temperature.

From the observed electron energy relaxation time $\tau_E = 670(70)$ fs we can estimate the electron-phonon coupling constant $g_{Ag}$ for the weakly heated electron gas in our thin silver films: $g_{Ag} = \gamma T_e/\tau_E = 3.5(3) \times 10^{16}$ $\mathrm{W\,m^{-3}K^{-1}s^{-1}}$, where $\gamma T_e$ is the electronic specific heat at temperature $T_e$ and $\gamma$ is a constant.[15] This value is close to the coupling constant of gold[4]

$$[g_{Au} = (2\text{-}3.5) \times 10^{16}\ \mathrm{W\,m^{-3}K^{-1}s^{-1}}]$$

as could be expected since the phonon-energy spectrum of silver is similar to the spectrum of gold.[16]

The plateau signal is due to the small temperature rise of the lattice after the electrons and the lattice are in thermal equilibrium again. The temperature rise amounts to $\Delta T_l = 0.10(5)$ K, as is calculated with the use of the temperature coefficients $d\epsilon_r/dT = 8.5 \times 10^{-4}\ \mathrm{K^{-1}}$ and $d\epsilon_i/dT = 1.5 \times 10^{-3}\ \mathrm{K^{-1}}$.[11] This is in good agreement with the dissipated energy of the pump laser and the observed plateau signal in the SP probing scheme.

We demonstrated that hot-electron relaxation in a thin metal film can be studied by exciting and probing surface plasmons. This technique is much more sensitive than direct reflection measurements and enables us to study the relaxation dynamics of a weakly heated electron gas. Combined with the usual nonresonant way of probing, we were able to distinguish between the heating of the electron gas and of the lattice. This method is in principle suitable to study other metal films with a well defined SP resonance ($|\epsilon_r| \ll \epsilon_i$), such as sodium, potassium, and gold, and is not restricted to wavelengths close to an electronic transition in the metal. The extremely low laser intensities and the moderate heating of the electron gas, which are already sufficient for the SP-resonance technique, provide good prospects to study relaxation dynamics and electron-phonon coupling in films at low temperatures.

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