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Ultrashort Surface-Plasmon and Phonon Dynamics

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We have studied the excitation and decay of surface plasmons at a silver-air interface using a time-resolved optical technique. Monitoring the surface-plasmon propagation enabled us to measure the dephasing of surface plasmons via their mean free path and a momentum lifetime of 48 fs (13 μm) was found. After a very rapid plasmon decay the energy is transferred into a strain wave and an increase in the temperature of the silver film. We have observed the acoustic phonons, associated with the strain, bouncing up and down the silver film and the heat diffusion on a picosecond time scale.

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Surface plasmons (SP) are very important elementary excitations of metal-dielectric interfaces. Kretschmann[1] demonstrated the technique of attenuated total reflection (ATR) as one of the ways to excite these surface plasmons optically. He demonstrated that the reflectivity of a thin metal layer (e.g., silver) evaporated on a transparent and optically dense substrate (e.g., glass) as measured by a light source coming from the glass side depends strongly on the angle of incidence. In the neighborhood of the so-called "plasmon angle," the reflectivity of the glass-metal-air system can display a sharp minimum. The reflectivity can even vanish at the plasmon angle for optimum thickness of the film. This decrease in reflectivity is called ATR and is a result of surface-plasmon generation. The electromagnetic field penetrates into the metal and excites "leaky" SP at the metal-air interface.

We have applied modern optical pump-probe techniques to study ATR resolved in time as well as position for the first time. The extreme sensitivity of our detection system[2] made it possible to observe the femtosecond decay of the SP. These measurements will be presented in the first part of this Letter. As the SP decay their energy is converted into heat and strain of the lattice. Both can be observed beautifully in the time-resolved pump-probe experiment that forms the second part of this Letter.

We study a 45-nm film of silver evaporated on a prism of BK7 glass at room temperature. Two synchronously pumped mode-locked dye lasers are tuned at slightly different frequencies and each one produces a synchronized train of pulses with a typical FWHM of 5 ps at a repetition rate of 82 MHz (12.2 ns). The two beams are almost collinear and they both reach the silver film from the glass side at approximately the plasmon angle ($\Theta = 43°$ in our case). The experimental geometry is sketched in the inset in Fig. 1. The yellow pump beam creates SP propagating along the silver film at almost the speed of light. The energy dumped by the decaying "yellow" SP changes the dielectric constant of silver temporally. After a variable delay the red probe pulse measures the, slightly changed, reflectivity of the glass-silver-air system in the same ATR configuration (Fig. 1). Naturally the red probe beam also creates SP but, as the yellow pump beam is modulated and the red probe beam is detected synchronously, heating due to the creation of "red" SP goes on undetected. Notice that we have three basic experimental variables: the angle of incidence of both beams, the spatial overlap between their foci, and the time delay between the pump and the probe pulse.

Under typical experimental conditions we focus two laser beams of 15-mW average power each on the film. After a few picoseconds the temperature of the film is independent of the direction normal to the interface. The calculated rise in temperature, corresponding to the energy dumped by one laser pulse, is about 1 K. The resulting gain or loss in the intensity of the reflected probe

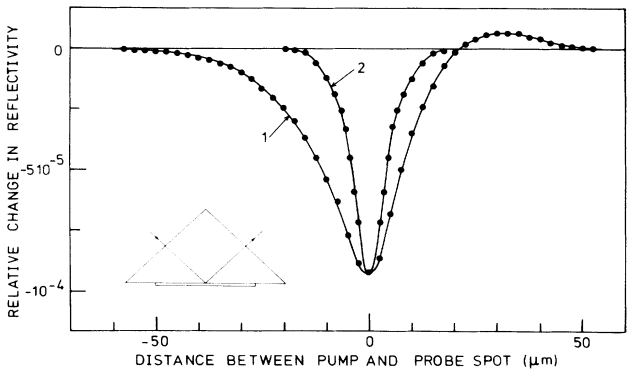

FIG. 1. Inset: Interaction region shown schematically. Two (almost) collinear beams, drawn here on top of each other, are focused through glass onto a 45-nm silver film. We measure changes in the reflectivity of the red probe pulse resulting from SP creation and decay by the yellow pump pulse. Main figure: This change shown as a function of position of both focused spots with respect to each other for a probe pulse arriving a few tens of picoseconds after the pump. Curve 1 displays the change in reflectivity for a displacement in the direction of propagation of the SP, whereas curve 2 shows the same effect for a perpendicular displacement.

beam is typically 10^{-4}–10^{-5}. The difference in color of the probe and the pump beams made the separation at the detection stage easy and a special double-modulation technique[2] at 8.8 MHz allows us to reach almost the quantum noise limit and detect changes in the reflectivity of 10^{-7} (RC time=0.4 s).

Earlier studies on the propagation of SP were performed with only one laser beam.[3,4] In these experiments the profile of the reflected beam is compared with the incoming profile making it possible to derive the mean free path of the SP, but only when it is relatively long. To comply with the restriction of a long lifetime these measurements had to be done on very photonlike SP, like infrared SP or long-range surface plasmons. We introduce a pump-probe technique that does not have this restriction and that enabled us to observe short-lived SP.

Propagation effects will lead to a plasmon density that is spatially different from the spot profile of the incoming laser beam. Conservation of momentum along the film (phase matching) restricts the propagation of the SP to one direction. One thus expects the heat distribution along the film, resulting from the decay of SP, to have an exponential tail. Experimentally we observe the spatial distribution of heat by moving the red probe spot with respect to the yellow pump spot over the film meanwhile monitoring the signal strength. The time delay between the pump and the probe as well as the angle of incidence is kept fixed in this experiment.

We expect the mean free path (l) of optical SP to be small. Both laser beams thus had to be focused very tightly to see effects of the propagation of SP. With effectively a 15-mm lens the spot profile of each focus is an ellipse with a short axis of about 6 μm and a 1.4 times larger long axis. Because of strong focusing the opening angle (numerical aperture) of the laser beams is larger than the angular width of the ATR curve. This smears out the ATR curve and decreases the signal strength.

In Fig. 1 the change in reflectivity is pictured as a function of the spatial overlap between the two lasers in the direction parallel as well as perpendicular (as a check on the spot size) to the wave vector. The measurements show a striking appearance of both negative signals (decrease in reflection) and positive signals, features which reproduced satisfactorily. A perfect exponential tail (more than two decades) is observed when the spot of the probe beam lies upstream with respect to the spot of the pump beam. This is at the other side as we had expected it to be! When the spot of the pump beam was situated downstream of the probe spot no exponential spatial decay could be detected in the small positive signal. The decay length related to the exponential tail is 12.8(7) μm.

To explain the appearance of an increase as well as a decrease in the reflectivity of the probe beam due to heating and induced strain one has to notice that the red probe beam creates SP as well. In Refs. 3 and 4 the reflection of a Gaussian-shaped laser beam from a glass-metal-air system, at an angle of incidence close to the plasmon angle, is calculated rigorously. Part of the light incident on the interface is directly reflected (mirror reflection). The rest excites SP at the silver-air boundary. When the angle of incidence of the laser differs from the plasmon angle the SP are excited off resonance and they accumulate a phase difference with respect to the phase of the laser when they move along the interface. As a result there will be a phase difference between light emitted by the radiatively decaying SP and the direct mirror reflection. To summarize, reflectance is a nonlocal quantity and any change in the reflectivity of the red probe beam results from a change in the balance between SP generation at one place and radiative decay at another.

From the last paragraph it is clear how the reflectivity of the red probe beam can be influenced even when the probe spot lies upstream with respect to the pump. In this situation the red SP are created in a cool region and, after a propagation of a few micrometers, decay in a hotter region (thermal gradients along the film of almost 10^6 K/m), being slightly different through a different ϵ_{Ag}. This influences the radiative decay of the red SP and consequently the reflectivity. Although a detailed geometrical description is beyond the scope of this Letter the idea of a balance explains the induced increase as well as the decrease of the reflectivity. As we have only observed an exponential decay when the probe lies upstream of the pump we conclude that the radiative decay is apparently much more easily influenced by heating than the SP excitation process.

The exponential "heat" tail of 12.8(7) μm in Fig. 1 signifies the decay of the light intensity associated with the SP. As the SP density is proportional to the intensity, the mean free path of the SP is just l=12.8(7) μm. From the theoretical dispersion relation of the SP we know their group velocity to be 0.89c and so the measured mean free path reflects a momentum lifetime of 48(3) fs. We use the word momentum lifetime because elastic as well as inelastic processes can scatter SP to other directions (momentum states). One can associate these two contributions with pure dephasing and energy decay, respectively. The dephasing time is usually defined as the decay time of the amplitude of the exitation (96 fs) and is consequently twice the value associated with the intensity. It is rewarding to see that one can obtain this tremendous time resolution simply by observing the effect of a change in the relative position of the pump and probe spots.

The energy decay can be separated into a radiative process, SP emitted into the glass in the form of photons, and a nonradiative process, a multiphonon decay process. For our film thickness both energy-decay processes are of

equal importance. Comparing the measured mean free path with the value of 0.6 for the imaginary part of ϵ_{Ag} given in the literature[5] we have reason to believe that elastic scattering, due to impurities and roughness, does also contribute in our experiment though not dominantly. Studies on an older and already slightly "eroded" film resulted in a mean free path of l=9.3(6) μm. This indicates an increase in the scattering of SP as the film grows old.

The previous spatially resolved data were obtained for a probe pulse arriving about a hundred picoseconds after the pump pulse. It is also very interesting to observe the change in reflectivity as a function of *time* for fixed angle and exact overlap between the laser foci. As we have a time resolution of 5 ps there is no possibility to observe the decay of the SP directly in the time domain, but we can look at their decay products. For these measurements we used a weaker lens (127 mm) as there is no need for high spatial resolution.

If we perform time-resolved runs for different angles the existence of two time scales is immediately clear. The angle of incidence influences the sensitivity strongly, but the main features of the decay are insensitive to the exact alignment of the beams. In Fig. 2 we have pictured a typical time-resolved measurement. The long-time decay (nanoseconds) of the reflectivity results from the diffusion of heat along the silver film and, more importantly, the diffusion into the glass substrate. In Fig. 3 we present a measurement, concentrating on the short-time decay, that clearly shows an intriguing oscillation in the reflectivity. We will explain these small and fast (24 ps) oscillations in terms of acoustic phonons bouncing up and down the film. Similar oscillations have been recently observed by Thomsen and co-workers[6,7] in the absorption of a-As_2Te_3.

The electric field associated with the surface plasmons has a penetration depth in the silver of only 12 nm, and so most of the energy is released in a thin upper layer at the silver-air interface. The deposited energy first of all gives rise to an increase in the temperature but also creates an expansion of the lattice, part of it being stationary and part of it in the form of a "strain wave" traveling at the speed of sound perpendicular to the surface.[7] From a microscopic point of view acoustic phonons are generated by multiphonon decay in the 12-nm thin upper layer and initially all directions of propagation are present. The phase relation between the "coherent" phonons (created at the same instant!) causes them to interfere destructively in all directions except perpendicular to the film. This gives rise to a strain wave in the macroscopic picture.

For an infinitely short laser pulse the wavelengths of the acoustic phonons will reflect the penetration depth of the light. For a laser pulse of finite duration the width of the phonon packet is spread. The phonons generated by the front of the light pulse already move through the lattice while the back still generates new ones. As this width approaches the thickness of the silver film the phonon packet becomes more or less a broad modulation of the expansion of the lattice that bounces up and down the film, the most important wavelength present being twice the thickness of the film.

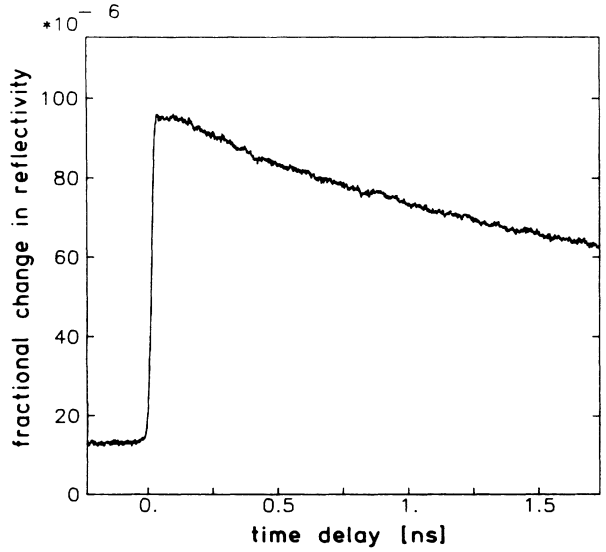

FIG. 2. The change in reflectivity of the probe beam as a function of the time delay between the pump and the probe beam. The nanosecond decay is a result of heat diffusion, primarily into the glass.

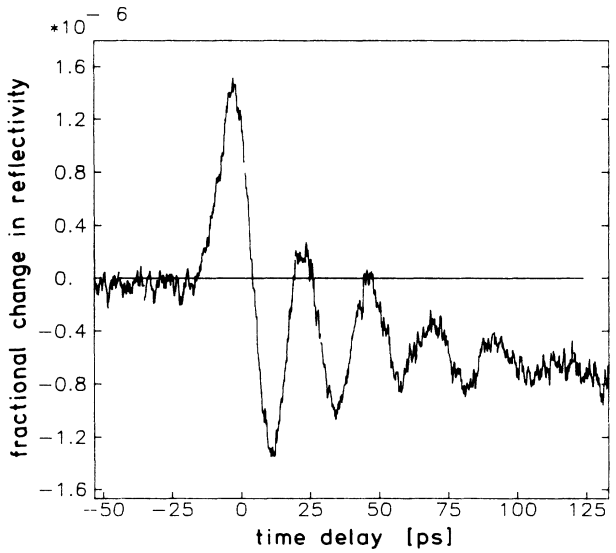

FIG. 3. A measurement showing in detail the short-time decay of the reflectivity. The wiggles are due to acoustic phonons running up and down the silver film. They have an oscillation period of 23.8(3) ps. The decrease in amplitude is almost completely due to the 52% acoustic reflection at the glass-silver interface.

The experimental run of Fig. 3 was fitted by an exponentially decaying sinusoidal curve, as our light pulses are relatively long. From the fit the oscillation period could be determined with 1% accuracy to be 23.8(3) ps. Using the 45-nm thickness of the film we calculate a longitudinal speed of sound of $v=3.78(5)$ km/s. The tiny difference with the sound velocity in bulk silver ($v=3.65$ km/s) should probably be explained by the inaccuracy in the thickness measurement as indicated by a quartz oscillator during the evaporation process. The decay of the acoustic signal is almost completely due to transmission of phonons into the glass. At the silver-glass boundary the macroscopic acoustic reflection coefficient, as calculated from the acoustic impedances of both materials, is 52%. Our measurements agree with this reflection coefficient [measured (50 ± 5)%] and losses due to other scattering processes must therefore be weak. From our data we conclude that the lifetime of 42-GHz (24 ps) phonons in Ag is much more than 100 ps.

When the relatively weak oscillations due to the acoustic phonons have decayed we are left with the general rise in temperature of the film that decreases on a nanosecond time scale as a result of the diffusion of the excess heat into the glass substrate and along the silver film (see Fig. 2). Although the heat-diffusion constant of silver is almost 1000 times larger than that of BK7 glass, the larger surface and larger thermal gradient perpendicular to the film make the heat diffusion into the glass dominant. This can also be concluded from the observed quasi one-dimensional behavior of the heat diffusion; the nanosecond decay is almost insensitive to the size of the focused laser spots. From the long-time changes in reflectivity we thus derive a heat-diffusion constant $D=5.2(5)\times10^{-7}$ m^2s^{-1} for BK7 glass being in good agreement with the value given by the manufacturer.

When the angle of incidence differed much from the plasmon angle we measured a different (usually longer) long-time decay of the temperature. For certain angles, however, a faster decay (twice as fast) than the one we normally measured could be observed. We attribute this fast diffusion to the existence of a peaked structure in the temperature profile of the silver film, enhancing the influence of heat diffusion along the film. When SP are excited off resonance the SP created upstream will interfere with the ones created downstream.[3,4] In this way a complicated temperature distribution can be generated, in spite of the smooth intensity profile of the focused laser spots.

Observation of changes in the reflectivity of the glass-metal-air system from the glass side is just one way of observing the SP generation and subsequent decays. We have also observed changes in the reflectivity of a probe laser coming from the air side. Naturally the pump beam is still coming from the glass side, because this is the best way to excite the SP. Although this method is about 5 times less sensitive than the one described in the bulk of this article, we were able to see the long-time diffusion of heat as well as the 24-ps oscillation of the acoustic phonons even in this setup.

We have introduced a new sensitive method to probe ultrafast surface dynamics. One can envisage many extensions and exciting applications of this contactless pump-probe technique. We only mention the feasibility of studying electron-phonon dynamics.

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