Femtosecond Relaxation of Localized Plasma Excitations in Ag Islands

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We report the first direct measurement of the relaxation of plasma oscillations in a solid. Via the second-harmonic autocorrelation of femtosecond laser pulses, the lifetimes of localized plasma oscillations in silver island films were investigated. Decay times of 40 ± 7 fs were obtained, which indicate that single-particle scattering is mainly responsible for the energy relaxation of the plasma oscillations.

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Considerable interest has been directed to the fundamental understanding of the behavior of plasma oscillations in solids [1]. In the literature, lifetimes and damping mechanisms of surface plasmons (SP) have been examined theoretically [2–7] and experimentally [8–12]. Studies of nonlocalized long-range plasma oscillations have been carried out in the infrared region to determine the mean free path, with typical values for the propagation length of long-range, photonlike SP in the mm range [12]. Reflection measurements in the visible using attenuated total reflection (ATR) methods or grating couplers were often limited by the spectral resolution of the experimental detection system [13]. Recently van Exter and Lagendijk [8] were successful in measuring the short-range SP propagation in the prism configuration with a picosecond pump-and-probe technique via heat distribution, giving a value of 48 fs. Lifetimes of localized SP in small systems (metal islands) of fermions [9,10] have been derived from optical absorption spectroscopy. However, the nonuniformity of the particle sizes gives rise to an inhomogeneous broadening of the absorption. Indeed the full width at half maximum (FWHM) varies between 0.1 and 1 eV depending on the size of the particles [10,11]. Quantum-mechanical and semiclassical theoretical calculations predict lifetimes which differ strongly from each other [2–6]. To the authors' knowledge, until now, *no direct* observation of the decay of SPs has been reported.

In this Letter we report the first time-resolved measurement of the relaxation (damping) of plasma oscillations in Ag. The experiments were performed using Ag island films in order to prevent the influence of propagation effects. A reference second-harmonic (SH) correlation signal of femtosecond pulses was first generated with a potassium dihydrogen phosphate (KDP) crystal, in which the second-harmonic generation (SHG) occurs quasi-instantaneously. In the experiment the KDP crystal was replaced by an Ag island film sample. The broadening of the second-harmonic autocorrelation signal on the island film in comparison to the autocorrelation of KDP is caused by the excitation of electron plasma oscillations with finite lifetimes τ_{SP}. We obtain a value of $\tau_{SP} = 40 \pm 7$ fs for the exponential decay of the oscillation energy.

The optical properties of metal island films differ essentially from that of the corresponding bulk metal as they show a strong and broad absorption band in the visible [2–6] caused by the resonances of the collective electron plasma oscillations. Assuming the shape of islands as oblate rotational ellipsoids the frequency-dependent complex polarizability $\alpha(\omega)$ of a single island is given by [14] $\alpha(\omega) = V[\varepsilon_{\mathrm{met}}(\omega) - \varepsilon_m]/\{\varepsilon_m + [\varepsilon_{\mathrm{met}}(\omega) - \varepsilon_m]L\}$. V is the volume of the particle and ε_m is the dielectric function of the surrounding medium. L is the "depolarization factor" dependent on the geometry of the ellipsoid and $\varepsilon_{\mathrm{met}}(\omega)$ is the complex dielectric function of Ag. As a result of the laser wavelength of 610 nm, only a narrow range of the inhomogeneous particle size distribution is excited resonantly (diameter ≈ 12 nm [14]). The absorption cross section $C_{\mathrm{abs}}(\omega)$ of a single island is, according to [14],

$$C_{\mathrm{abs}}(\omega) = k\,\mathrm{Im}\{\alpha(\omega)\} = \frac{\omega}{c} V \frac{\mathrm{Im}[\varepsilon_{\mathrm{met}}(\omega)]\varepsilon_m}{\{\varepsilon_m + L(\mathrm{Re}[\varepsilon_{\mathrm{met}}(\omega)] - \varepsilon_m)\}^2 + \{\mathrm{Im}[\varepsilon_{\mathrm{met}}(\omega)]\}^2 L^2} \quad (1)$$

with k the light's wave vector.

Ag islands on indium tin oxide (ITO) with a thickness of 200 nm on silicate glass substrates were prepared by low-rate evaporation (0.05 nm/s) and annealing (140 °C, 2 min) in an argon atmosphere. The typical diameter of the Ag islands is 20 nm, as determined by transmission electron microscopy of carbon replicas. Curve *a* in Fig. 1 shows the measured absorption spectrum of a 4-nm-thick Ag island film on ITO-glass substrate; curves *b–e* show the absorption

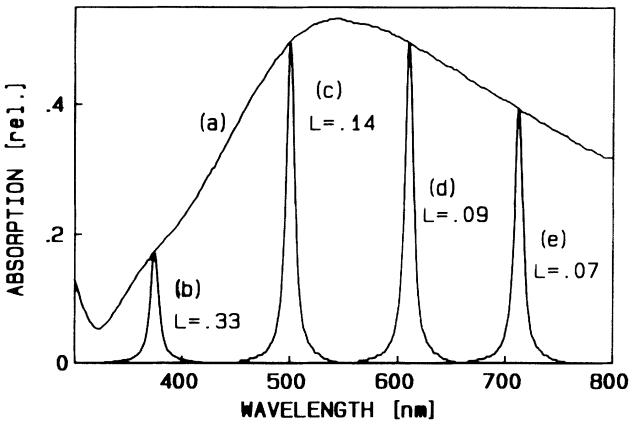

FIG. 1. Absorption spectrum of a 4-nm mass thickness Ag island film (curve *a*) and the (normalized) calculated spectra [Eq. (1)] of single Ag particles with different depolarization factors L (curves *b*–*e*), which are considerably smaller than the bandwidth of the island film.

spectra of a single Ag particle according to Eq. (1) for varying depolarization factors L, using bulk optical constants [14]. The measured broad absorption spectra (curve *a*) reflects the inhomogeneous size distribution of the particles.

Nonlinear effects, e.g., second-harmonic generation and Raman scattering, are dramatically enhanced by the excitation of surface-plasmon resonances [15–18]. This results from the strong electric-field enhancement due to the high induced depolarization field, reaching also a few angstroms into the metal. The total linear homogeneous polarization of the island particle in the presence of the incident laser field $\mathbf{E}_{\text{in}}(t,\omega)$ is given by

$$\mathbf{P}(t,\omega)=[\varepsilon_{\text{met}}(\omega)-\varepsilon_m][\mathbf{E}_{\text{in}}(t,\omega)+\mathbf{E}_{\text{dep}}(t,\omega)]$$
$$=[\varepsilon_{\text{met}}(\omega)-\varepsilon_m]\mathbf{E}_{\text{loc}}(t,\omega)\,,$$

where $\mathbf{E}_{\text{dep}}(t,\omega)$ is the plasma oscillation field. The field enhancement is expressed by $\mathbf{E}_{\text{dep}}(t,\omega)=f(\omega)\mathbf{E}_{\text{in}}(t,\omega)$, where the enhancement factor $f(\omega)$ can be written as

$$f(\omega)=\{1+[\varepsilon_{\text{met}}(\omega)-\varepsilon_m]L\}^{-1}$$
$$=\text{Im}[\alpha(\omega)]/V\,\text{Im}[\varepsilon_{\text{met}}(\omega)]$$

[19,20]. Using the parameters of our samples the theoretical enhancement factor is approximately 16. Thus, $\mathbf{E}_{\text{dep}}(t,\omega)$ is much larger than the laser field and the total electric field $\mathbf{E}_{\text{loc}}(t,\omega)$ can be well approximated by $\mathbf{E}_{\text{dep}}$ alone. Therefore the second-order polarization $\mathbf{P}^{(2)}(t,2\omega)$ can be considered to be proportional to $\chi^{(2)}_{\text{eff}}(2\omega):\mathbf{E}_{\text{dep}}(t,\omega)\mathbf{E}_{\text{dep}}(t,\omega)$, where the local effective second-order susceptibility $\chi^{(2)}_{\text{eff}}$ of the island-substrate system takes into account the processes concerning bulk and surface effects. The presence of the surface and the inhomogeneity of the surrounding medium breaks the inversion symmetry of silver [19], which allows the generation of the 2ω wave. The intensity of the second-harmonic wave is proportional to $|\mathbf{P}^{(2)}(t,2\omega)|^2 \propto |\mathbf{E}_{\text{dep}}(t,\omega)|^4$. *Because of the field enhancement the second-harmonic signal is generated mainly by the localized plasmons and is present for the duration of the plasma oscillation and not only for the duration of the light pulse. The second-harmonic wave, therefore, gives direct information on the duration of the plasma oscillation.*

The experiments were carried out at room temperature using a balanced colliding-pulse mode-locked (CPM) dye laser ($\lambda=610$ nm, FWHM variable from 80 to 200 fs, average output power 20 mW, repetition rate 100 MHz, focus diameter ≈ 5 μm). The laser beam was divided into two identical beams (see the inset of Fig. 2). After temporal delay τ of one pulse in steps of 8.3 fs, the pulses were recombined and focused collinearly onto the surface of the sample using a microscope objective. The excitation angle was 45° in order to optimize the nonlinear polarization. Both beams were polarized parallel to the incident plane (*p* polarized) to obtain a more efficient excitation of longitudinal plasma oscillations. The reflected wave passed a UG11 filter to separate out the fundamental wave before entering the single $\frac{1}{4}$-m spectrometer with a slit width of 2 mm. The detector was a cooled photomultiplier with a GaAs photocathode. Using a polarization filter in the reflected beam the polarization of the 2ω wave was determined to be *p* polarized, too.

In Fig. 2 a typical autocorrelation signal of Ag islands (solid curve) obtained by second-harmonic generation as a function of the delay time between two laser beams is plotted. The dashed line shows the autocorrelation of KDP. The width of the correlation signal of Ag particle films is considerably broader than the width of the autocorrelation from KDP. Measurements for various pulse widths of the CPM laser are shown in Fig. 3, where the

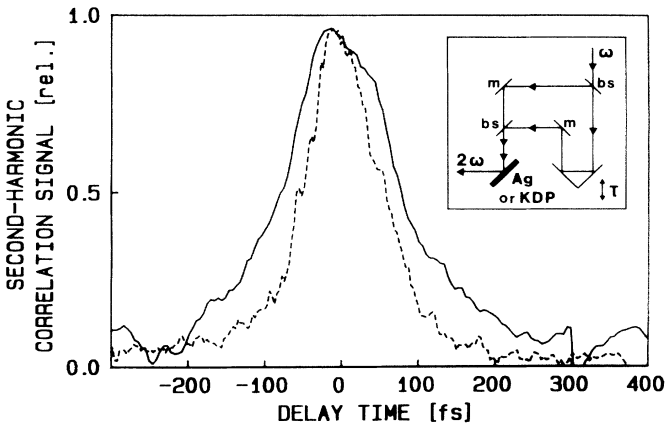

FIG. 2. Second-harmonic correlation signal of the laser pulses on an Ag island film (solid line) and on KDP (dashed line). Inset: A schematic of the experimental setup (m, mirror; bs, beam splitter).

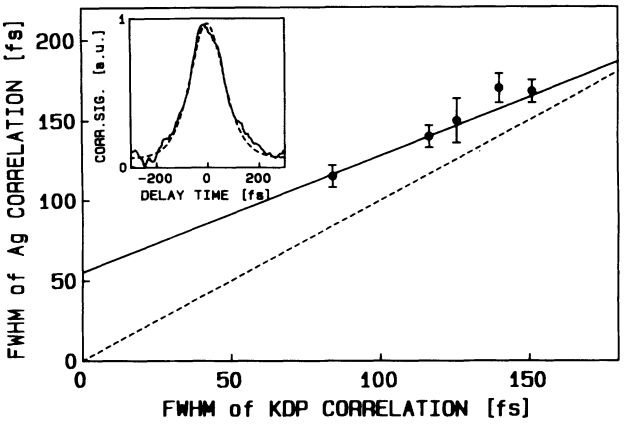

FIG. 3. FWHM of the autocorrelation signal measured on Ag islands vs FWHM of the autocorrelation signal of KDP. The solid line shows the calculated FWHM of Ag islands ($\tau_{SP}=40$ fs) in comparison to the measured FWHM of KDP autocorrelation. The dashed line displays a 1:1 relation. Inset: Experimental correlation of silver (solid line) in comparison with the calculated curve (dashed line) [using Eq. (2) and the lifetime τ_{SP} of 40 fs].

FWHM of the correlation signals from Ag islands in comparison to the FWHM of the autocorrelations from KDP are shown. Again the FWHM of the Ag correlation signal is always broader than the KDP autocorrelation signal.

The evaluation of the measured results is based on the following model. We describe the process of the resonant plasmon excitation as a damped harmonic oscillator driven by the external laser field. Since the frequency of the 2ω wave is higher than the plasma frequency of silver we are not dealing with a 2ω plasmon but with the source of a free light wave at 2ω, which is emitted as long as the fundamental localized SP with frequency ω is excited. The excitation is collinear; therefore the intensity of the SH sum field, given by the fourth power of $\mathbf{E}_{loc}(t,\omega)$, is measured. Since in the experiment we average over the interference fringes, the measured signal corresponds to [21]

$$G^{(2)}(\tau,\tau_{SP}) \propto \int_{-\infty}^{\infty} I_{dep}(t,\omega) I_{dep}(t+\tau,\omega)dt\,, \qquad (2)$$

which is equal to the intensity autocorrelation of $I_{dep}(t,\omega)=|\mathbf{E}_{dep}(t,\omega))|^2$. To find the time dependence of $\mathbf{E}_{dep}(t,\omega)$, we describe the plasma oscillations by a damped-harmonic-oscillator model driven by $|\mathbf{E}_{in}(t,\omega)| \propto \mathrm{sech}^2(1.76t/\Delta)$, with Δ being the FWHM of the laser pulse. The corresponding one-dimensional equation of motion for $\mathbf{P}(\omega,t)=Ne\mathbf{x}(\omega,t)$ is solved numerically. With $I_{dep}(t,\omega)$ being proportional to $\int|P(t,\omega)|^2 dA$, where the integration is executed over the laser focus, we can fit our experimental correlation curves using Eq. (2). *The lifetime of the plasma oscillation τ_{SP} is the only parameter used to fit the experimental data.*

The inset of Fig. 3 shows an experimental Ag correlation curve (solid) in comparison to the calculated one (dashed). The best agreement is obtained for a value of $\tau_{SP}=40$ fs, using one single exponent; the contribution of an eventual different second exponent is less than 10%. The measured autocorrelation is found to be independent of the laser intensity (and also pulse width), which confirms that the relaxation is dominated by physical processes which are—within our experimental range—independent of the degree of excitation. The solid line of Fig. 3 shows the theoretically calculated FWHM for Ag islands ($\tau_{SP}=40$ fs) in comparison to the KDP autocorrelation. The error bars indicate the reproducibility of the experiment. From the whole set of experiments we obtain a value for the lifetime of the plasma excitation of 40 ± 7 fs, independent of the laser pulse width. This result agrees well with the relaxation time of propagating SP indirectly measured by van Exter and Lagendijk [8]. In comparison with the half-width of absorption measurements [10,11] giving ΔE between 0.1 and 1 eV (τ_{SP} between 18 and 1.8 fs), our result gives much more precise information. The theoretical lifetimes determined by [2–6] vary for the considered range of our particle size (radius $R=6$ nm) between $[0.38v_F/R]^{-1}=12$ fs to $[(4/\pi)v_F/R]^{-1}=3.3$ fs, where v_F is the Fermi velocity 1.4×10^6 m/s. However, good agreement is achieved by calculating the homogeneous linewidth in Eq. (1) [14] using the bulk values for $\varepsilon_{met}(\omega)$ of Ag [22].

In order to understand the physical processes leading to the relaxation time of the plasma oscillation in small Ag particles, we compare the value τ_{SP} with the momentum relaxation time of single electrons in bulk Ag, $\tau_m=37.5$ fs [23]. From this close agreement we conclude that the scattering of electrons as single particles is mainly responsible for the damping of the collective electron excitations. The contribution of radiation damping can be neglected, since the radiation decay time according to [24] is calculated to be 450 fs for the particle size of 12 nm, where resonance occurs. Carrier heating, as investigated by Groeneveld, Sprik, and Lagendijk [25], is negligible in our experiments due to the slightly lower excitation intensity and, even more important, a lower absorption cross section than in the experiments of [25]. In addition, we have performed the same experiments on different substrates, e.g., GaAs, giving the same result of 40 ± 7 fs, which confirms that the decay is due to intrinsic scattering mechanisms.

In conclusion we have shown the first direct observation of energy relaxation of surface plasma oscillations in small metal particles. The experiments were performed by comparing the autocorrelation of femtosecond laser pulses in nonabsorbing KDP with the autocorrelation of Ag islands using the nonlinearity of the surface-plasmon polarization. We obtain a decay time of 40 ± 7 fs independent of laser pulse widths. Since this method leads to a direct determination of lifetimes of surface plasmons further investigations for nonlocalized SP are feasible,

too. Taking into account the propagation of the nonlocalized SP's, the time-delayed laser beam must be displaced in space. In addition, information on coherence, phase relaxation, and interaction of surface plasmons with each other can be obtained from similar experiments.

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[1] For a review, see e.g., *Surface Polaritons*, edited by V. M. Agranovich and D. L. Mills (North-Holland, Amsterdam, 1982).
[2] A. Kawabata and R. Kubo, J. Phys. Soc. Jpn. **21**, 1765 (1966).
[3] U. Kreibig and C. v. Fragstein, Z. Phys. **224**, 307 (1969).
[4] A. A. Lushnikov and A. J. Simonov, Z. Phys. **270**, 17 (1974).
[5] L. Genzel, T. P. Martin, and U. Kreibig, Z. Phys. B **21**, 339 (1975).
[6] D. B. Thoai and W. Ekhardt, Solid State Commun. **41**, 687 (1982).
[7] D. Sarid, Phys. Rev. Lett. **47**, 1927 (1981).
[8] M. van Exter and A. Lagendijk, Phys. Rev. Lett. **60**, 49 (1988).
[9] R. H. Doremus, J. Chem. Phys. **40**, 2389 (1964).
[10] H. Abe, W. Schulze, and B. Tesche, Chem. Phys. **47**, 95 (1979).
[11] M. A. Smithard, Solid State Commun. **13**, 153 (1973).
[12] W. P. Chen, G. Ritchie, and E. Burstein, Phys. Rev. Lett. **37**, 993 (1976).
[13] H. Raether, in *Surface Plasmons on Smooth and Rough Surfaces and on Gratings*, edited by G. Höhler and E. A. Niekisch (Springer-Verlag, Berlin, 1988), Vol. III, and references therein.
[14] *Absorption and Scattering of Light by Small Particles*, edited by C. G. Bohren and D. R. Huffman (Wiley, New York, 1983).
[15] *Surface Enhanced Raman Scattering*, edited by R. K. Chang and T. E. Furtak (Plenum, New York, 1982).
[16] A. Wokaun, in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich, D. Turnbull, and F. Seitz (Academic, New York, 1984), Vol. 38.
[17] C. K. Chen, A. R. B. de Castro, and Y. R. Shen, Phys. Rev. Lett. **46**, 145 (1981).
[18] L. Li, Y. Liu, G. Yu, W. Wang, and Z. Zhang, Phys. Rev. B **39**, 8728 (1989).
[19] A. Leitner, Mol. Phys. **70**, 197 (1990).
[20] P. W. Barber, R. K. Chang, and H. Massoudi, Phys. Rev. Lett. **50**, 997 (1983).
[21] J.-C. M. Diels, J. J. Fontaine, I. C. McMichael, and F. Simoni, Appl. Opt. **24**, 1270 (1985).
[22] P. B. Johnson and R. W. Christy, Phys. Rev. B **6**, 4370 (1972).
[23] H. Ehrenreich and H. R. Phillip, Phys. Rev. **128**, 1622 (1962).
[24] J. Crowell and R. H. Ritchie, Phys. Rev. **172**, 436 (1968).
[25] R. H. M. Groeneveld, R. Sprik, and A. Lagendijk, Phys. Rev. Lett. **64**, 784 (1990).