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Femtosecond decay-time measurement of electron-plasma oscillation in nanolithographically designed silver particles

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Abstract. The decay time of the electron-plasma oscillation in silver nanoparticles is measured at a nanoparticle film consisting of regularly arranged, identically shaped and identically oriented particles. By design of a noncentrosymmetric particle shape, SHG in transmission at normal incidence of t he fundamental beam is obtained. Therefore the autocorrelation function of the optical near field oscillation of the particle, excited by two temporally overlapping fs laser pulses separated by a defined delay time, could be measured. A decay time of 10 ± 1 fs was extracted. This result shows that the damping of the electron-plasma oscillation in nanometric particles is approximately a factor of 2 larger than expected from the value of the imaginary part of the bulk metal dielectric function when consideration of the radiation damping in the particles is included.

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In metal nanoparticles a resonance of the collective electron-plasma oscillation (localized surface plasmon) is possible in the visible part of the spectrum, whereby the resonance frequency is mainly determined by the real part, ε', of the dielectric function of the metal and by the shape of the particle [1]. The reason for this structural resonance, which is not possible in extended bulk metal, is the spatial confinement of the electron-plasma (dielectric confinement): when the quasi-free metal electrons are shifted by the irradiated light field, repulsion forces build up by surface charging, causing resonance behavior.

The electron-plasma resonance in metal nanoparticles leads to two important physical effects: (i) spectral selective absorption and (ii) remarkable enhancement of the light-field strength close to the surface of the particle (local field enhancement). Both effects are highly relevant for linear and nonlinear optics. Such metal particles can be applied as spectrally selective light absorbers and as local field enhancers; the latter property is particularly important for nonlinear optical materials. For existing technologies, such as microoptics, optical information processing and optical data storage, as well as for optical sensorics, two-dimensional arrangements of metal nanoparticles are of special interest. Single particles can be applied as spectrally selective light-field concentrators in future nanooptics.

Two-dimensional metal nanoparticle arrangements (metal nanoparticle films) represent an optical thin-film system, with properties widely tunable by the structural parameters, and can be fabricated comparatively simply with existing technologies [2,3]. The homogeneous width of the absorption band and the local field enhancement factor are determined by the damping of the electron-plasma oscillation. For a film consisting of a large number of individual metal particles a direct experimental determination of the electron-plasma oscillation damping is possible only by direct measurement of the oscillation decay time [4] and not by deduction from the absorption bandwidth. This is because it cannot be excluded that an inhomogenous broadening of the absorption linewidth is also present as a result of a distribution of resonance frequencies caused by a distribution in particle shape. The dominating damping mechanism is the electric conductivity of the used metal (electron mobility) at optical frequencies, characterized by the imaginary part, ε'', of the dielectric function of the metal.

In this paper we present new measurements of the electron-plasma oscillation decay time at lithographically designed silver nanoparticles on a transparent substrate. Silver was choosen because the high mobility of its conduction electrons means it has the lowest ε'' in the visible of all noble metals. As the result of a suitable value of ε', the resonance frequency of silver nanoparticles is in the visible. Silver is chemically fairly stable and can be easily evaporated. These two features are important for the realization and handling of nanoparticle films. From measurements at extended plasmons in Ag layers excited in an ATR geometry, a decay time of 48 fs was estimated [5]. This value suggests that the decay-time for Ag particles is also in the femtosecond regime, which is experimentally accessible only by ultrashort laser methods.

Figure 1 shows the experimental setup used. It is similar to the standard geometry used for measurement of ultrashort pulse duration. The central part is a Michelson interferometer. At its output, two equal-intensity pulses, delayed by an adjustable time τ, are collinearly focussed onto the sample. Interferometric accuracy for the two overlapping beams is necessary in order to ensure perfect collinearity, which allows us to obtain the correct decay time from the measured

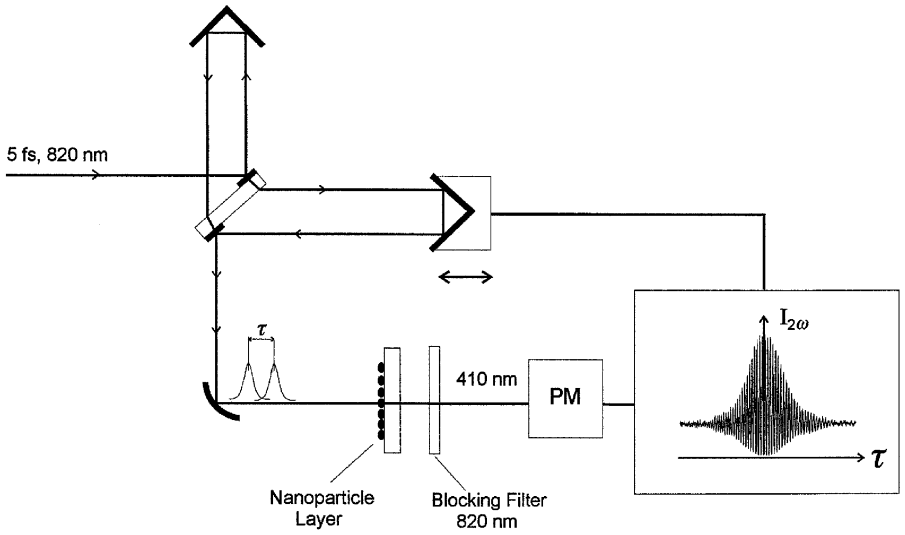

Fig. 1. Experimental set up for measuring the autocorrelation function of the electron-plasma oscillation near field in two-dimensional metal nanoparticle arrangements and the autocorrelation function of the laser pulse (when the sample is substituted by a 30 μm thick BBO crystal)

autocorrelation function without beam-overlap errors. If the metal particles posses an optical second-order nonlinearity ($\chi_{(2)} \neq 0$) which is due only to the movement of conduction electrons (electron-plasma oscillation), measuring the resulting SH intensity $I_{2\omega}(\tau)$ as a function of the delay time gives the autocorrelation function of the electron-plasma oscillation near the field E_{loc}. The autocorrelation function is [6]

$$I_{2\omega}(\tau) = \frac{1}{2t_{\mathrm{i}}} \int_{-t_{\mathrm{i}}}^{+t_{\mathrm{i}}} \left| \left| E_{\mathrm{loc}}(t) + E_{\mathrm{loc}}(t-\tau) \right|^2 \right|^2 \mathrm{d}t, \qquad (1)$$

where E_{toc} is the local field (near-field at the particle surface) originating from the electron-plasma oscillation and t_{i} the integration time of the photodetector.

In principle, at every metal surface a nonvanishing second-order nonlinearity is obtained as a result of symmetry breaking. As in our case the wavelength dependence of the SH intensity corresponds to the shape of the resonance curve (off-resonance we obtain 1/20 of the SH intensity at resonance), we deduce that the obtained SH originates from only the movement of the plasma electrons (driven by the laser field) and not from the laser field itself. Thus the above-requested condition is fulfilled.

With a centrosymmetric particle shape, however, the nonlinear surface polarization at any surface element is compensated by the nonlinear polarization at the corresponding element at the inverted position of the particle surface, and thus the total second-order nonlinearity of a particle equals zero. In order to obtain metal nanoparticles with nonvanishing $\chi_{(2)}$ tensor components for fundamental irradiation vertical to the surface plane, specially designed low-symmetry particles in regular arrangement and equal orientation were fabricated by an electron-beam lithography technique, described in [3]. Figure 2 shows the SEM picture of a section through the particle arrangement. The size of these shape designed particles is approximately 200 nm.The highest SH signal is obtained for light polarization parallel to the mirror plane of the particle (see Fig. 2). With respect to this polarization direction,

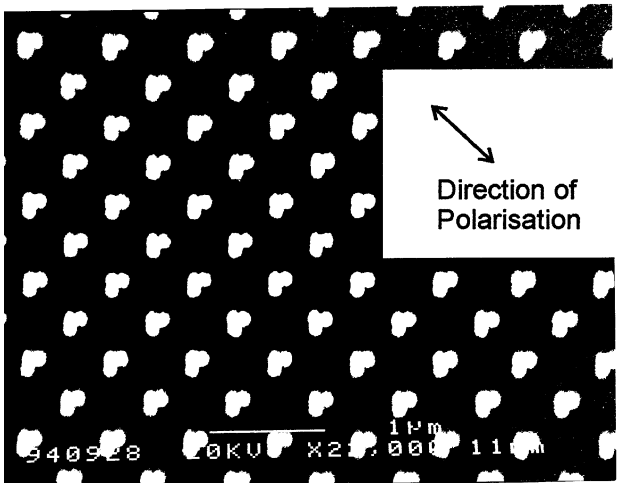

Fig. 2. Scanning electron microscope (SEM) pictures of a section through the used low-symmetry silver nanoparticles

the particles show different field strengths at opposite positions at their surface. The induced nonlinear polarizations are also strongly different and thus do not compensate completely when integrated over the whole particle circumference. (Note that SH polarizations have opposite signs for opposite positions at the particle surface.) In our case the particles are off-resonance for the SH frequency, so the obtained SH signal is proportional to the squared local field intensity at the particle and thus corresponds to the electron plasma-oscillation.

As a light source for the fs experiments we used an Ar+-laser-pumped Kerr-lens mode-locked Ti-Sapphire laser with chirped resonator mirrors for group velocity dispersion (GVD) compensation [7]. This laser supplied band-width-limited pulses at a repetition rate of $80 \times 10^{-6}\,\mathrm{s}^{-1}$. The pulse energy was 0.4 nJ at a pulse duration of 15 fs. The pulse duration was determined by the same measuring geometry as

shown in Fig. 1 but with substitution of the sample by a 30 μm thin BBO crystal.

As the plasma-oscillation resonance of the particles depends on the particle shape, the particle height was 'tuned' in order to shift the resonance frequency for the previously defined polarization direction (parallel to the particles' mirror plane) to the laser wavelength of 820 nm. The sample area covered by the nanoparticles had a size of 150 μm $\times$ 150 μm. The focussed beam at the sample surface (spot size 30 μm) had an average intensity of 4.6×10^3 W/cm^2 (corresponding to a peak intensity of 3.8×10^9 W/cm^2), which gave a sufficiently high signal-to-noise ratio of the SHG signal at 1 s integration time, without any thermal damage of the sample. To check this, the particle morphology was investigated by SEM prior and after laser exposure of the particles. At the intensities used in our experiments, no morphological change could be observed.

Figure 3 shows the measured autocorrelation function of the electron-plasma oscillation driven by the sech^2-shaped, 15 fs laser pulse (Fig. 3a), and the autocorrelation function of the driving laser pulse (Fig. 3b). By comparison of this measured autocorrelation function with simulated curves, the decay time of the electron-plasma oscillation in the investigated silver nanoparticle arrangement was determined as 10 ± 1 fs by means of a least squares method. In the simulation, a harmonic oscillator with variable decay time (damping) was driven by the field of a sech^2-shaped, 15 fs laser pulse. This harmonic model is evident, as in our situation the very weak nonlinearity of the electron-plasma oscillation is negligible for the energetic mechanisms of damping. The validity of this model simulation was further corroborated by the fact that in the case of an appropriate decay time the simulated autocorrelation function fits well the experimental one for all τ values. To demonstrate the fit quality, the upper envelope of the calculated autocorrelation function for the three different decay times 7, 10, 13 fs are plotted in Fig. 3a.

Figure 4 shows the measured absorption spectrum of the particle film (for the fundamental polarization direction) together with a homogenously broadened absorption curve, determined from the lifetime measurement. The half-width of the latter is approximately 37 nm and a factor of 2 smaller than the absorption spectrum's half-width measured by a microscope spectrophotometer. From this it can be deduced that although we have used the lithographic method for particle shape design, we have a considerable inhomogenous broadening of the absorption spectrum, propably caused by a distribution in the particle resonance frequencies as a result of a distribution in particle shape (aspect ratios). On the other hand, this result shows, that the effective damping of the plasma oscillation in silver nanoparticle films is remarkably larger than the l7 fs (corresponding to a homogenous absorption line-width of 22 nm) resulting from a model calculation that takes the bulk dielectric function [8] into account and considers radiation damping [9]. This can be explained by a chemically modified surface of the silver nanoparticles, which leads to an essentially increased value of ε'' at λ = 820 nm compared with bulk silver by so-called chemical interface damping [10], which was not considered in the model calculation.

The decay time obtained from the experiments reported in this paper is remarkably shorter than that reported for previous experiments [4]. These very first measurements

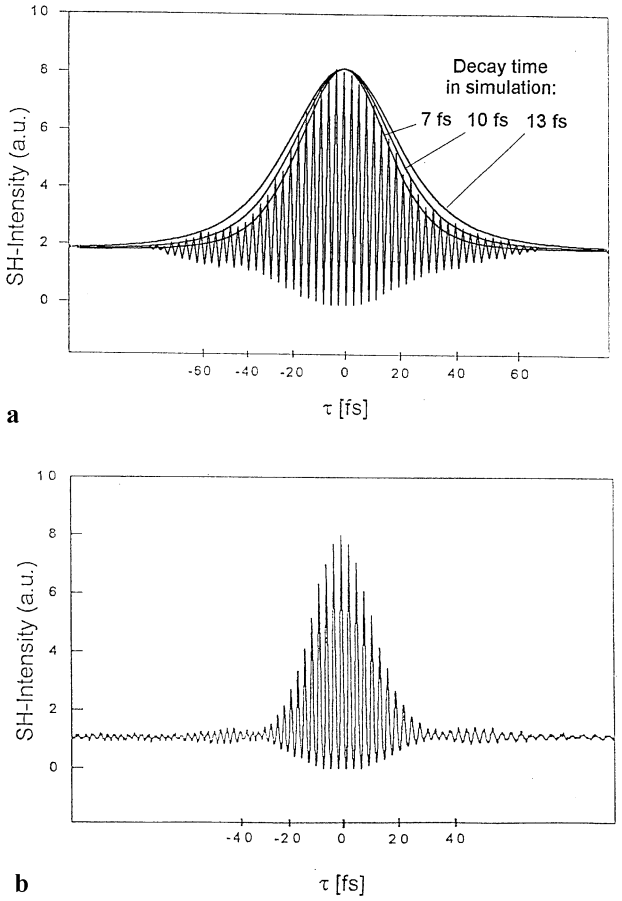

Fig. 3. Measured autocorrelation function of the electron-plasma oscillation and the upper envelope of the model autocorrelation function for the three different decay times 7, 10, 13 fs (**a**). Measured autocorrelation function of the driving laser pulse (**b**)

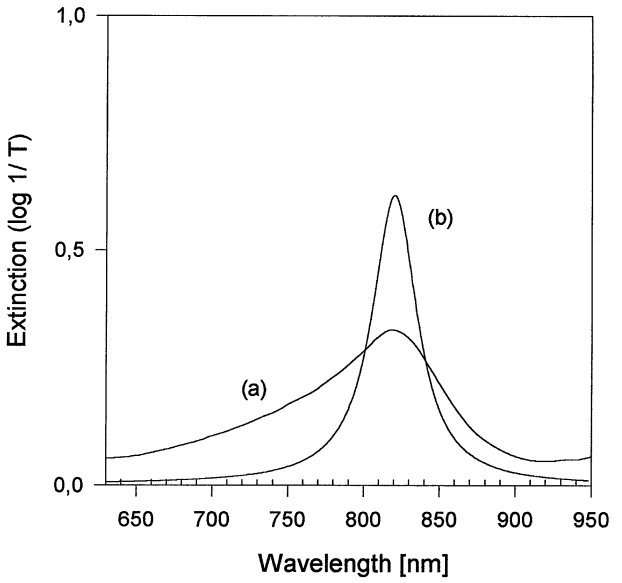

Fig. 4. Measured extinction curve $\log l/T$ (T = transmission) of the investigated silver nanoparticle film for the used polarization direction (**a**) and the extinction curve modeled for damping data derived from the measured decay time (**b**)

were performed at naturally grown nanoparticle films ('island films') consisting of randomly distributed, differently sized and shaped dropletlike particles with an average size of 20 nm. However, the pulse overlap in these experiments was not interferometrically collinear, which could also contribute to the difference in results.

In conclusion, we have measured by a femtosecond laser technique the decay time of the light-field-driven collective electron-plasma oscillation (local surface plasmon) of nanometric silver particles in a regular two-dimensional arrangement. With a special sample preparation technique the resonance frequency of the particles could be adjusted via the particle aspect ratio to the wavelength of the Ti-Sapphire laser used. By design of low-symmetry-shaped, parallel-oriented particles a high second-order optical nonlinearity, necessary for measurement of the autocorrelation function of the near-field oscillation, could be obtained, and thus the decay time could be determined with improved accuracy. The obtained decay time of 10 fs for the present experiments shows that the electron-plasma oscillation in the investigated silver nanoparticles is more damped than expected from model calculations using dielectric function data for bulk silver from the literature [8]. As a consequence a smaller field enhancement factor compared with the so-far-reported [11] value must be assumed. The reason for this increased damping may be chemical interface damping [10].

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References

1. U. Kreibig and M. Vollmer: Optical Properties of Metal Clusters, Springer Series in Material Sciences, 25, Springer, Berlin (1995)
2. W. Gotschy, K. Vonmetz, A. Leitner, F.R. Aussenegg: Opt. Lett. **21**, 1099 (1996)
3. W. Gotschy, K. Vonmetz, A. Leitner, F.R. Aussenegg: Appl. Phys. B **63**, 381 (1996)
4. D. Steinmüller-Nethl, R. Höpfl, E. Gornik, A. Leitner, F.R. Aussenegg: Phys. Rev. Lett. **68**, 389 (1992)
5. M. van Exter and A. Langendijk: Phys. Rev. Lett. **60**, 49 (1988)
6. J.-C.M. Diels, J.J. Fontaine, I.C. McMichael, F. Simoni: App. Opt. **24**, 1270 (1985)
7. A. Stingl, Ch. Spielmann, F. Krausz, R. Szipöcs Opt. Lett. **19**, 204 (1994)
8. P.B. Johnson and R.W. Christy: Phys. Rev. **B 6**, 4370 (1972)
9. A. Wokaun, J.P. Gordon, P.F. Liao: Phys. Rev. Lett. **48**, 957 (1982)
10. H. Hövel, S. Fritz, A. Hilger, U. Kreibig, M. Vollmer: Phys. Rev. **B 48**, 18178 (1993)
11. R.I. Chang, T.E. Furtak (eds.): Surface Enhanced Raman Scattering (Plenum, New York 1982)