Decay Times of Surface Plasmon Excitation in Metal Nanoparticles by Persistent Spectral Hole Burning

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We describe a new technique to determine the homogeneous linewidths of surface plasmon resonances of metal nanoparticles and thus measure the decay time of this collective electron excitation. The method is based on spectral hole burning and has been applied to supported oblate Ag particles with radii of 7.5 nm. From the experimental results and a theoretical model of hole burning the linewidth of 260 meV corresponding to a decay time of 4.8 fs was extracted. This value is shorter than expected for damping by bulk electron scattering. We conclude that additional damping mechanisms have been observed and reflect confinement of the electrons in nanoparticles with sizes below 10 nm.

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Surface plasmon (SP) excitation in small metal particles has found great interest in the past, in particular, since this collective oscillation of the conduction electrons can be stimulated with light and since its resonance frequency can be tuned over a wide spectral range by varying the size and shape of the clusters, by changing the dielectric surrounding, and choosing different metals. Even though numerous investigations on SPs have been reported [1], an essential issue has remained open. At present, no systematic investigation of the decay time T_2 and the decay mechanisms of SP excitation are available. Ideally, one would like to carry out such measurements as a function of the particle size and shape for different dielectric surroundings to clarify the role of damping mechanisms like electron-electron and electron-surface scattering. Furthermore, SP excitation is accompanied by a pronounced enhancement of the electric field near the particle surface, the enhancement factor f being proportional to T_2 [1,2]. This enhancement is used, e.g., in surface enhanced Raman scattering [3] and is currently discussed for applications like all-optical switching devices [4], improved biophysical sensors [5], and optical tweezers [6]. In short, measurement of T_2 is essential for basic science and for a great variety of applications.

At first glance, one might argue that T_2 can be extracted from the widths of the resonances. In practice, however, nanoparticles usually have a certain size and shape distribution which introduces inhomogeneous line broadening [7,8]. Its magnitude being unknown, the homogeneous width $\Gamma_{\text{hom}} = 2\hbar/T_2$ cannot be determined. Similarly, time-resolved experiments with femtosecond (fs) laser pulses based on optical second harmonic generation also suffer from inhomogeneous line broadening [7–9] which narrows the measured autocorrelation traces [7,8]. Thus, an unambiguous determination of T_2 could be achieved so far only in two cases. Aussenegg *et al.* used particles with narrow shape distributions to measure T_2 with fs laser pulses [8,10]. The samples, however, were made lithographically, limiting the experiments to large particles with sizes above about 50 nm. Another approach was applied by Klar *et al.* who measured the spectra of single particles by optical near field microscopy and could extract T_2 directly from the homogeneous width [2]. This technique also seems to be applicable only to relatively large aggregates because of the limited spatial resolution of optical near field microscopy and the limited signal-to-noise ratio.

In this Letter we present a new technique that allows us to measure Γ_{hom} of SP resonances and thus determine the decay time of this collective electron excitation. The method is based on persistent spectral hole burning in the inhomogeneously broadened absorption profiles of nanoparticles. It is not restricted to certain particle sizes, does not require special size and shape distributions, is compatible with ultrahigh vacuum conditions, i.e., offers control of the chemical surrounding, and is easy to apply. We have used the technique to extract SP decay times of silver nanoparticles with radii of 7.5 nm and studied the influence of the particle shape on T_2.

The idea of the method is as follows. First, nanoparticles with a broad size distribution are prepared on a transparent substrate by deposition of metal atoms with subsequent surface diffusion and nucleation. After measuring their optical absorption spectrum, the nanoparticles are irradiated with short laser pulses, the photon energy being located within the inhomogeneously broadened absorption profile and the spectral width of the light being negligibly small as compared to the homogeneous and inhomogeneous line broadening. The fluence of the light is chosen such that the temperature increase of the particles induced by rapid conversion of the absorbed energy into heat is sufficiently high to stimulate evaporation of atoms. As a result, the distribution changes and a hole is burned into the absorption profile. Finally, the optical spectrum is measured a second time and subtracted from the spectrum of the particles as grown to determine the width of the hole, i.e., Γ_{hom}.

For particles prepared by deposition of atoms one has to distinguish between two different kinds of inhomogeneous broadening and hole burning. Very small clusters with

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sizes below about 1 nm resemble spheres which display a single plasmon resonance and the inhomogeneous line broadening is due to the size distribution [1,11]. Larger particles, however, are oblate and can be described as rotational ellipsoids with two main axes a and b (Fig. 1). The axial ratio a/b is a measure of the shape; the mean radius $\langle r \rangle$, i.e., the radius of a sphere with the same volume as the actual clusters, characterizes their size. a/b drops off as a function of radius [11]; i.e., there is a correlation between size and shape. For radii above about 1 nm the SP frequency is essentially size independent; it splits, however, into two modes, the distance of which depends on a/b. As a result, the inhomogeneous linewidth is determined exclusively by the shape distribution [8,11] and hole burning in this regime depletes the population of nanoparticles within a certain interval of axial ratios. In fact, there is a twofold change of the resonantly excited aggregates. First, since atoms are preferentially released from the edges and perimeters of the clusters [12,13], their long axis b shrinks predominantly making the clusters more spherical and increasing their SP frequency. Second, material being removed, the particle volume decreases and the amplitude of the SPs drops off.

Spectral hole burning is, of course, a well-known technique in atomic, molecular, and solid-state physics [14,15]. There is, however, an essential difference as compared to the application described here. In the present case, the "final" state, i.e., the size and shape of the particles after interaction with light, is close to the initial dimensions of the clusters as grown. The nanoparticles change size or shape only until they do not interact with the laser light anymore. As a result an adjacent peak accompanies the hole, making its profile asymmetrical.

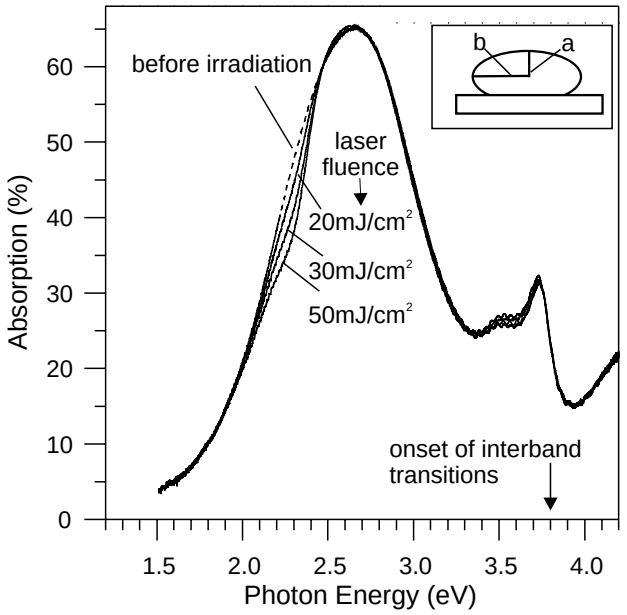

FIG. 1. Absorption spectra of Ag particles as grown (dashed line) and after laser irradiation with $\hbar\Omega_L = 2.30$ eV and different laser fluences (solid lines). Inset: Schematic illustration of oblate nanoparticles.

In our experiments, Ag nanoparticles were prepared under UHV conditions through deposition of Ag atoms on quartz substrates. The number density of the clusters was determined by *in situ* noncontact scanning force microscopy. The deposited Ag coverage being known from measurements with a quartz crystal microbalance, the mean radius of the particles could be extracted [11]. The oblate clusters exhibit Gaussian size distributions with a width of about 33% and a rather broad shape distribution [11,13]. The mean axial ratio a/b of the clusters was determined from the positions of the plasmon resonances that appear in the optical spectra [11]. They were measured before and after laser irradiation with p-polarized light. The angle of incidence was 45° with respect to the substrate surface normal. Figure 1 shows an absorption spectrum of particles with a mean radius of $\langle r \rangle = 7.5$ nm and a mean axial ratio of $\langle a/b \rangle = 0.25$. The spectrum is dominated by excitation of two plasmon modes located at 2.6 [$(1,1)$ mode] and 3.7 eV [$(1,0)$ mode]. Since the profile of the $(1,0)$ mode is strongly disturbed by interband transitions, only the $(1,1)$ mode was used for hole burning. Its width of 1.1 eV is mainly determined by inhomogeneous broadening due to the distribution of axial ratios.

For hole burning, the Ag particles were irradiated with the p-polarized light of an optical parametric oscillator pumped by the third harmonic of a Nd:YAG laser. The pulse duration was 5 ns and the repetition rate 10 Hz. Figure 1 displays absorption spectra of Ag nanoparticles measured after firing 100 pulses with a photon energy of $\hbar\Omega_L = 2.30$ eV and different fluences. A dip in the absorption profile and a slight increase of the optical absorption at about 2.55 eV are observed. The depth of the dip increases if the fluence rises.

Figure 2 displays the difference of spectra measured after and before laser irradiation with $\hbar\Omega_L = 2.30$ and 2.65 eV. In both cases, the dip exhibits an asymmetrical, non-Lorentzian line shape. The deviation from a Lorentzian that one would expect for purely homogeneous line broadening comes from two effects. First, there is an increase of absorption right next to the dip (see above). Second, the dip broadens as a function of laser fluence which is accompanied by a Gaussian: for increasing fluence the temperature rise of particles with neighboring axial ratios not fully in resonance with the laser light gains importance since more and more energy is absorbed in the wings of their plasmon profiles. We note in passing that fluence dependent broadening is also known from "classical" hole burning [15].

To extract Γ_{hom} from the dips, we have investigated the fluence dependence of the actual widths and modeled the hole burning process theoretically. Briefly, we consider an ensemble of supported metal particles with broad size and shape distributions. The plasmon frequency Ω of each (single) aggregate depends on the axial ratio a/b.

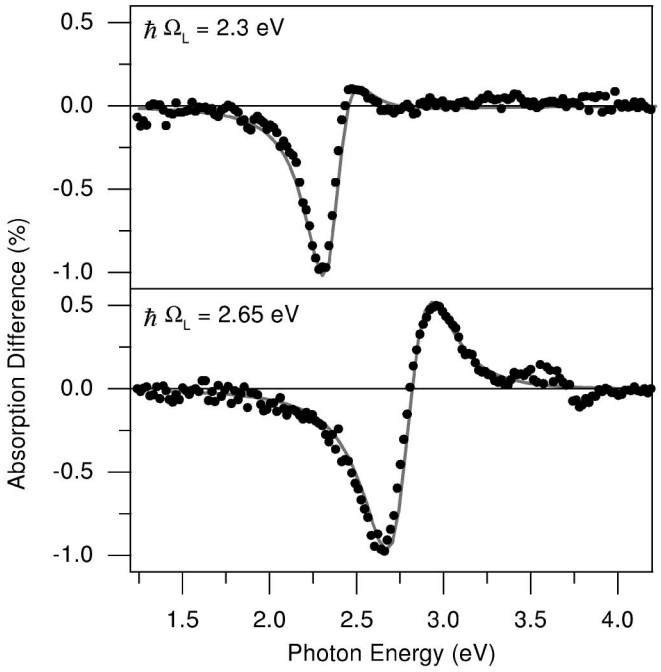

FIG. 2. Difference of absorption spectra measured after and before laser irradiation with $\hbar\Omega_{\mathrm{L}} = 2.30$ eV (top) and $\hbar\Omega_{\mathrm{L}} = 2.65$ eV (bottom). The laser fluence was set to $\Phi = 30$ mJ/cm^2 in both cases. Solid lines: fits to a theoretical model.

The absorption cross section $\sigma(\omega, \Omega)$ is described by a Lorentzian with amplitude $\sigma^0(V)$, resonance frequency $\Omega(a/b)$, and homogeneous width Γ_{hom}. V is the volume of the cluster. Γ_{hom} contains all possible damping mechanisms. Since the collective excitations of the s electrons in Ag are modified by polarization of the core electrons, Γ_{hom} depends on the plasmon frequency [1]. The absorption spectrum of the whole ensemble is given by $S_1(\omega) = \int f(\Omega)\sigma(\omega, \Omega)\, d\Omega$, $f(\Omega)$ being the inhomogeneous distribution of the plasmon frequencies due to the shape distribution of the particles.

The temperature rise of a cluster with resonance frequency Ω induced by the laser radiation with frequency Ω_{L} and fluence F is $T(\Omega) = CF\sigma(\Omega_{\mathrm{L}})$. C is a constant determined by the thermal properties of the substrate. The atom evaporation rate and the resulting variations of the volume and axial ratio of the clusters are proportional to $\exp[-E_a/k_B T(\Omega)]$, where E_a is the activation energy for evaporation and k_B is the Boltzmann constant. For small modifications of the volume and shape the same exponential dependence holds for the changes of $\sigma^0(V)$ and $\Omega(a/b)$, denoted as $\delta\sigma^0$ and $\delta\Omega$. Substituting $T(\Omega)$ in the exponential one finds that the dependences of $\delta\sigma^0$ and $\delta\Omega$ on the plasmon frequency Ω are given by Gaussians centered at the laser frequency Ω_{L}. Their width

$$\Delta_L \propto \sqrt{\frac{k_B C \sigma^0}{E_a}\, F} \tag{1}$$

specifies to which extent the optical spectra of particles not fully in resonance are modified, i.e., Δ_L describes the fluence dependent broadening of the dip.

Assuming a Gaussian with width Δ_0 for $f(\Omega)$, the modified inhomogeneous distribution and the changes of the plasmon resonance of the whole ensemble can be calculated to first order in $\delta\sigma^0$ and $\delta\Omega$. We obtain

$$\delta S(\omega) = -A\,\frac{(\gamma/2)^2}{(\omega - \Omega_{\mathrm{L}})^2 + (\gamma/2)^2} + B\,\frac{(\omega - \Omega_{\mathrm{L}})(\gamma/2)^2}{[(\omega - \Omega_{\mathrm{L}})^2 + (\gamma/2)^2]^2}, \tag{2}$$

where γ is given by

$$\gamma = \Gamma_{\mathrm{hom}}\left(1 + \frac{3}{4}\,\frac{\Delta_L^2}{\Gamma_{\mathrm{hom}}^2}\right). \tag{3}$$

The first term of (2) describes the spectral changes induced by the overall shrinking of the resonantly excited nanoparticles; the second term represents the changes stimulated by the increase of a/b. A and B reflect the relative importance of both processes; γ is the width of the dip and includes the homogeneous width as well as the fluence dependent broadening. We finally mention that (2) is valid if Γ_{hom} and Δ_L are both much smaller than the inhomogeneous width Δ_0, a condition fulfilled in our experiments.

Equation (2) was used to fit our experimental data, Fig. 2, with A, B, and γ serving as fitting parameters. For $\Phi = 30$ mJ/cm^2 the fits reproduce the experiments almost perfectly if $\gamma = 285$ and 390 meV are chosen for $\hbar\Omega_{\mathrm{L}} = 2.30$ and 2.65 eV, respectively. Similar fits were obtained for all fluences and both photon energies. Figure 3 shows that the extracted values of γ increase linearly with fluence. This is exactly as predicted by the model, (1) and (3). Based on this linear dependence, Γ_{hom} could be determined by extrapolation to zero laser fluence. For $\hbar\Omega_{\mathrm{L}} = 2.30$ eV, a width of 260 ± 10 meV

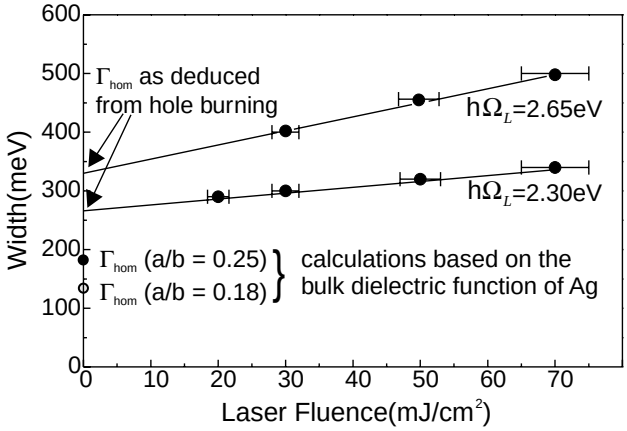

FIG. 3. Width of the dip as a function of the laser fluence used for hole burning (the error bars of the widths are within the data points of the graphs). The solid lines represent the extrapolation of the linear dependence to zero fluence from which Γ_{hom} of the SP was extracted. For comparison, the figure shows results of calculations based on the bulk dielectric function.

was found. This corresponds to $T_2 = 4.8 \pm 0.2$ fs. For $\hbar\Omega_L = 2.65$ eV, the width is 330 ± 10 meV corresponding to $T_2 = 3.8 \pm 0.2$ fs [16].

Discussing our results, we first note that in very large nanoparticles the decay of SP excitation occurs on a time scale of about 10 fs [2,8,10]; T_2 in gold clusters with diameters of around 200 nm is 12 fs, and for 40 nm a value of 8 fs was found. In both cases, the measured values could be reproduced by calculations based on the bulk dielectric function of gold. This indicates that bulk electron scattering is the dominant damping mechanism and surface scattering (not included in the computations) does not play a role in these very large particles.

In contrast, the dephasing times of 3.8 and 4.8 fs extracted here for silver nanoparticles with a radius of 7.5 nm are by as much as a factor of 2 smaller than one would expect from the bulk dielectric function of silver (Fig. 3). We conclude that additional damping mechanisms, in particular, surface scattering, come into play in this size regime. This is supported by two arguments. First, it is known from our earlier work that clusters which interact resonantly with the two used energies of 2.65 and 2.30 eV have axial ratios of $a/b = 0.25$ and 0.18 and radii of 7.6 and 7.4 nm, respectively [11,12]; i.e., axis a of the aggregates is less than 5 nm. In this size range, surface scattering is predicted to be quite essential [1,17]. Second, the interface between the clusters and the substrate opens additional decay channels not included in the bulk dielectric function. From theoretical work it is known that SiO_2 can lead to an electronic resonance state a few eV above the Fermi energy of small silver particles [18,19]. As a result, the decay of the SP is accelerated.

T_2 obtained for particles with $a/b = 0.18$ is about 20% larger as compared to T_2 measured for $a/b = 0.25$. We suggest that this is due to the spectral dependence of the bulk dielectric function $\varepsilon_{\mathrm{bulk}}(\omega)$ of silver and the different SP energetic positions for both shapes [the particle sizes are almost identical, (see above)]. To support this argument, we have calculated the widths of SPs in Ag particles with $r = 7.5$ nm and axial ratios of $a/b = 0.18$ and 0.25 using the quasistatic approximation and $\varepsilon_{\mathrm{bulk}}(\omega)$ [20], i.e., neglecting surface damping. T_2 computed for $a/b = 0.25$ is by about 22% smaller as compared to T_2 for $a/b = 0.18$ (Fig. 3). This agrees with the difference observed in our experiments and reflects the dependence of Γ_{hom} on $\varepsilon_2(\omega)$ as well as on $d\varepsilon_1/d\omega$ and $d\varepsilon_2/d\omega$ [1].

In summary, we have demonstrated for the first time that persistent spectral hole burning can be used to determine the homogeneous linewidth and thus the decay time of SPs in metal nanoparticles. For this purpose, hole burning by selective absorption of laser light by clusters with a certain shape was exploited. For Ag particles with radii of 7.5 nm the homogeneous width was determined to be 260 meV which corresponds to $T_2 = 4.8$ fs. This value is shorter than expected for damping by bulk electron scattering, and we conclude that additional mechanisms, in particular, surface scattering, come into play if the electrons are confined in nanoparticles with sizes below 10 nm. In addition, an influence of the shape of the particles on the homogeneous width was found and explained by the dielectric properties of silver and the increase of the SP frequency for more spherical particles. Since the technique presented here is not limited to certain particle size ranges, it holds great promise for investigating SPs as a function of particle radius, an essential step towards a detailed understanding of the importance of the different decay mechanisms. In addition, further information on the width and the decay time of SP excitation is highly desirably to optimize the local field enhancement at the particle surface in a systematic way by generation of aggregates with optimum axial ratio and by precise control of the chemical surrounding including choice of the substrate material.

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