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Spectral hole burning in absorption profiles of metal nanoparticles prepared by laser assisted growth

Towards the systematic investigation of the size dependent decay time of surface plasmon excitation

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Abstract. We have combined two novel methods, *i.e.* persistent spectral hole burning and laser assisted growth, to measure the decay time T_2 of surface plasmon excitation in metal nanoparticles of different size at constant well defined shape. The measured values of T_2 amount to 6 ± 0.4 fs and are independent of size for diameters ranging from 8 to 25 nm.

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1 Introduction

The dynamics of electronic excitations in metal nanoparticles has attracted a lot of attention in recent years, see *e.g.* [1–7]. Such investigations are of fundamental importance in order to study, for example, the influence of the reduced dimension of the aggregates, *i.e.* the confinement of the charge motion by a boundary, on the relaxation mechanisms. An essential issue of the ultrafast electron dynamics is the time scale on which collective excitations, *i.e.* surface plasmon (SP) resonances, loose their phase coherence and decay into single particle excitations. Although SPs have been studied already since long [8], no systematic investigations of the dephasing time T_2 are available at present. Nevertheless, measurement of the decay time as a function of particle size and surrounding material is highly desirable to elucidate the mechanisms responsible for the plasmon decay, *i.e.* to clarify the role of relaxation processes like Landau fragmentation, electron-electron scattering, electron surface scattering or chemical interface damping. In addition, knowledge of the decay time is interesting from the viewpoint of a variety of applications, since SP excitation leads to a strong enhancement of the electric field near the nanoparticles, the enhancement factor f being directly proportional to T_2. This field enhancement is exploited, *e.g.*, in surface enhanced Raman scattering [9] and is currently discussed for applications like all-optical switching devices [10], improved biophysical sensors [11] or optical tweezers [12]. Detailed understanding of the dependence of the dephasing time on the size and shape of the metal particles would allow one to optimize f.

In contrast to the pronounced scientific and applied interest, systematic investigations of $T_2 = 2\hbar/\Gamma_{\mathrm{hom}}$, Γ_{hom} being the homogeneous line width of the resonance, are not available yet, the main reason being that the particles under study usually have broad size and shape distributions. As the SP frequency depends on both parameters, this introduces inhomogeneous line broadening of the plasmon peaks measured in the optical absorption spectra of such samples [8,13,14]. Since the magnitude of inhomogeneous broadening is not known quantitatively, the homogeneous width and the decay time cannot be extracted. The same effect also prevents determination of T_2 by time resolved experiments using femtosecond laser pulses and second harmonic generation [15,16]. In such experiments, inhomogeneous line broadening leads to a narrowing of the recorded autocorrelation traces. In principle, the problem can be overcome either by fabricating very narrow size and shape distributions using lithographic techniques [7,16] or by optical spectroscopy of single nanoparticles with scanning nearfield microscopy [17]. Both approaches are, however, limited to date to very large aggregates with diameters above about 40 nm.

Recently, we have shown that persistent spectral hole burning in inhomogeneously broadened plasmon profiles of metal nanoparticle ensembles can be used to measure the homogeneous width and thus determine T_2 [18]. Main advantage of this technique is that it is not restricted to certain particle sizes, does not require special size and shape distributions and is compatible with ultrahigh vacuum

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conditions, *i.e.* allows one to control and systematically vary the chemical environment. By applying spectral hole burning to oblate Ag particles, *i.e.* silver spheroids with a short axis a perpendicular and a long axis b parallel to the supporting substrate surface (the shape is characterized by the axial ratio a/b and the size by the diameter d, *i.e.* the diameter of a sphere with the same volume as the actual particles), we have shown that the homogeneous line width and thus the decay time are influenced by the reduced dimension of clusters, the shortest axis being below 5 nm [18]. Moreover, the decay time has been found to depend strongly on the particle shape. With increasing axial ratio a/b, T_2 decreases from 4.8 (clusters with $a/b = 0.18$) to 3.5 fs (clusters with $a/b = 0.25$). This shape dependence is brought about by two effects. First, the SP shifts to higher photon energies the more and more the nanoparticles approach the shape of a sphere [8,19]. Secondly, with increasing plasmon frequency, the influence of the d-electrons of silver on plasmon excitation grows [8]. The shape dependence has strong consequences for investigations with the objective of systematically studying T_2 as a function of particle size: one has to make sure that the shape is kept constant during preparation, although the size can be varied over a diameter range as wide as possible. The main problem is that most fabrication techniques do not allow to precisely control the particle shape irrespective of the size.

In the present paper, an experimental procedure which makes possible the investigation of the decay time as a function of particle dimension while keeping the shape constant is described. It is based on the combination of spectral hole burning and laser manipulation of the growth process [20] of the metal nanoparticles. Before describing in detail the experimental procedure and presenting first results, the basic idea of hole burning in absorption profiles of metal particle ensembles is briefly recalled.

2 Basic idea of spectral hole burning

In the first step, nanoparticles with a broad size and shape distribution are prepared on a transparent substrate. Their optical spectrum is measured. Then, the samples are irradiated with nanosecond laser pulses, the photon energy being located within the inhomogeneously broadened plasmon profile whereby the spectral width of the light is negligibly small with respect to the homogeneous and inhomogeneous width of the SP modes. In the particles the absorbed optical energy is rapidly converted into heat. The laser fluence is chosen such that the temperature increase of the particles is sufficiently high to stimulate evaporation of atoms [21]. As a result, the distribution changes and a hole is burnt 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 homogeneous line width and T_2.

In our experiments, two different kinds of hole burning have to be distinguished. Very small clusters with diameters below about 1 nm resemble spheres which have a single plasmon resonance and the inhomogeneous line broadening is due to the size distribution of the aggregates [19]. Larger particles, however, are oblate with two main axes a and b, see above. From our earlier work we know that a/b drops off as a function of d, *i.e.* there is a correlation between size and shape [19,20]. For such particles the SP frequency is essentially size independent and splits into two modes, the frequencies of which depend on a/b. As a result, the inhomogeneous linewidth is determined mainly by the shape distribution and hole burning in this regime depletes the population of nanoparticles within a certain interval of axial ratios. This makes possible to selectively excite aggregates with different a/b by changing the photon energy and study T_2 as a function of cluster shape. In fact, there is a twofold change of the resonantly excited clusters [21]. First, since atoms are preferentially ejected from the edges and perimeters of the particles their long axis shrinks predominantly making the aggregates more spherical and increasing their SP frequency. Secondly, material being removed, the particle volume decreases and the amplitude of the SPs drops off.

3 Preparation of nanoparticles with well defined shape

In these experiments, Ag nanoparticles on sapphire are prepared under ultrahigh vacuum conditions by a recently developed technique [20]. Very briefly, the method relies on generation of particles through deposition of silver atoms and simultaneous irradiation of the samples by nanosecond laser pulses. Without laser irradiation this method yields clusters, the axial ratio of which decreases during growth, *i.e.* there is a correlation between size and shape, see above. By exploiting the shape dependence of the plasmon frequencies laser irradiation allows one to stabilize the axial ratio during the growth process through selective heating of aggregates that have taken a certain shape. Details can be found in reference [20]. The samples are characterized by in situ scanning force microscopy (SFM) operated in non-contact mode and by optical absorption spectroscopy. As we have shown earlier, the combination of both techniques allows one to determine the mean radius and shape of the particles as well as their number density and size distribution [19]. For hole burning the samples are irradiated by the p-polarized light of an optical parametric oscillator pumped by the third harmonic of a Nd:YAG laser. The pulse duration is 5 ns and the repetition rate 10 Hz.

4 Experimental results

Figure 1 shows absorption spectra of silver particles on sapphire prepared by using a laser photon energy of 2.33 eV and a fluence of 160 mJ/cm^2 during growth. The spectra have been measured with the p-polarized light of a Xe-arc lamp combined with a monochromator and are dominated by $(1,1)$ and $(1,0)$ plasmon modes corresponding to the excitation of the collective resonances in the

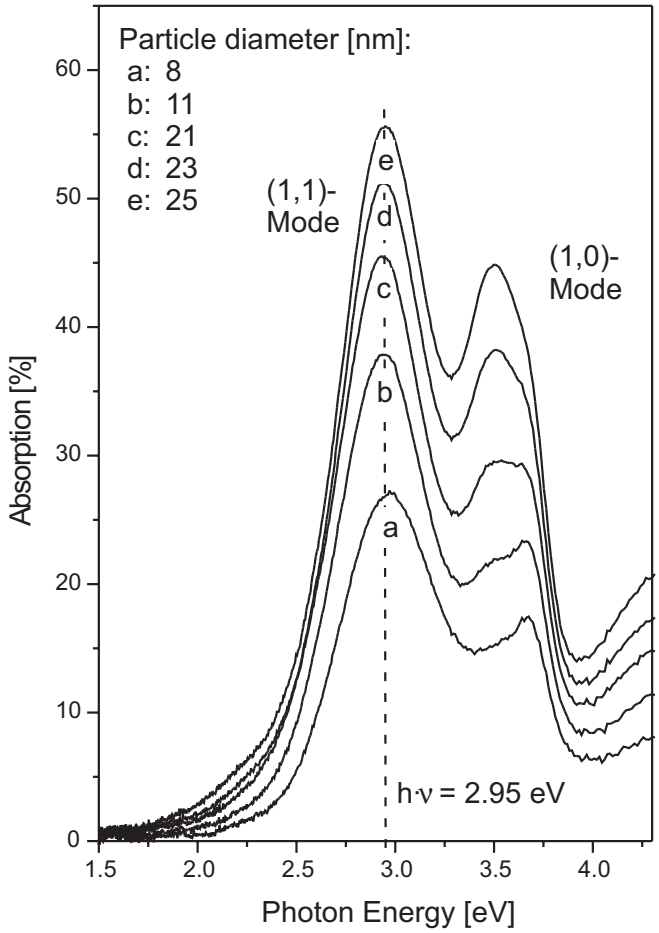

Fig. 1. Absorption spectra of silver nanoparticles with different diameters indicated in the figure. The particles have been prepared by laser assisted growth on sapphire substrates, for details see text. For measurement of the optical spectra the samples were irradiated with the p-polarized light of a Xe-arc lamp combined with a monochromator under an angle of incidence of 45° with respect to the substrate surface normal.

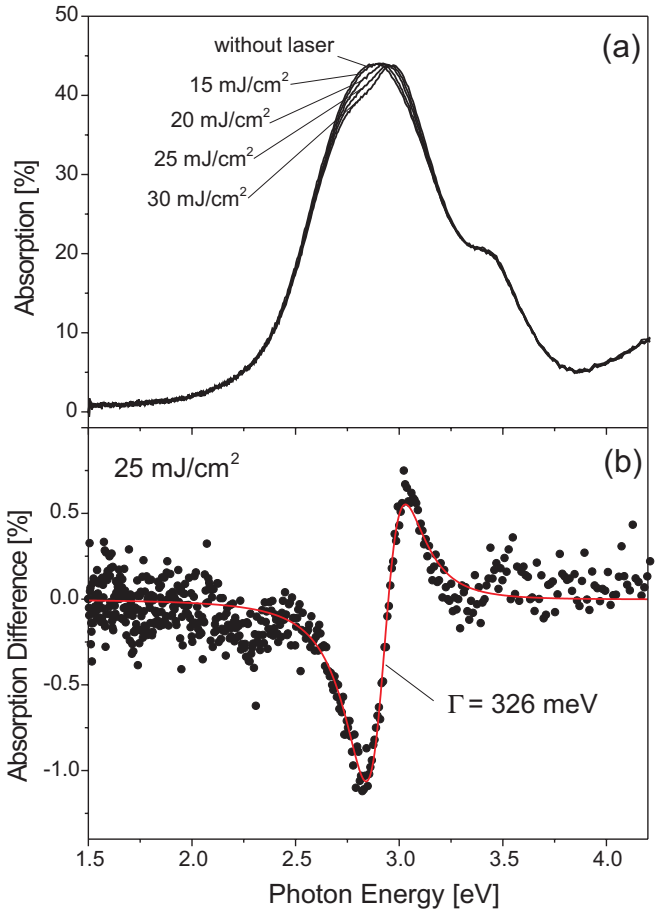

Fig. 2. (a) Optical spectra (measured with s-polarized light) before and after laser irradiation with $\hbar\Omega = 2.95\,\mathrm{eV}$ and different fluences. The small maximum in the high energy wing of the (1,1) mode is not due to electromagnetic coupling between the particles, its physical meaning will be discussed elsewhere [22] (b) Difference of absorption after and before laser irradiation with a fluence of $25\,\mathrm{mJ/cm^2}$. The solid line is the result of a theoretical model, for details of the computations see [18].

direction of the long and short axes of the clusters, respectively. The amplitude of both modes increases, if the size of the particles measured by scanning force microscopy rises, Figure 1. The plasmon frequencies, however, remain unchanged for particle diameters between $\langle d \rangle = 8$ and 25 nm. This shows that the axial ratio of the particles remains constant although their size rises. By comparing the measured peak positions with frequencies calculated using the quasi static approximation, an axial ratio of 0.5 has been extracted.

Figure 2a displays absorption spectra of particles with $\langle d \rangle = 11$ nm recorded before and after laser irradiation with a photon energy of 2.95 eV and different fluences. In contrast to the results of Figure 1, which have been recorded using p-polarized light, s-polarized radiation is used in these measurements in order to simplify the determination of the homogeneous line width and thus only the (1,1) mode appears. A spectral dip at the position of the laser line and a slight increase of absorption at higher photon energies is observed. As can be seen from Figure 2b which displays the difference of spectra measured after and before irradiation with a fluence of 25 $\mathrm{mJ/cm^2}$, the dip exhibits an asymmetrical, non-Lorentzian line shape. The deviation from a Lorentzian that is, in principle, expected for purely homogeneous broadening of the dip is due to two effects [18,21]. First, there is an increase of absorption right next to the dip which induces the asymmetry. It is because the nanoparticles change size and shape only until they do not interact with the laser light anymore but do not disappear and cause increased absorption right next to the dip. Secondly, for a certain laser fluence, there may be a contribution to the width of the dip brought about by particles that have neighboring axial ratios, *i.e.* of clusters with plasmon modes not fully in resonance with the laser light. For increasing fluence the temperature rise of such clusters gains importance since more and more

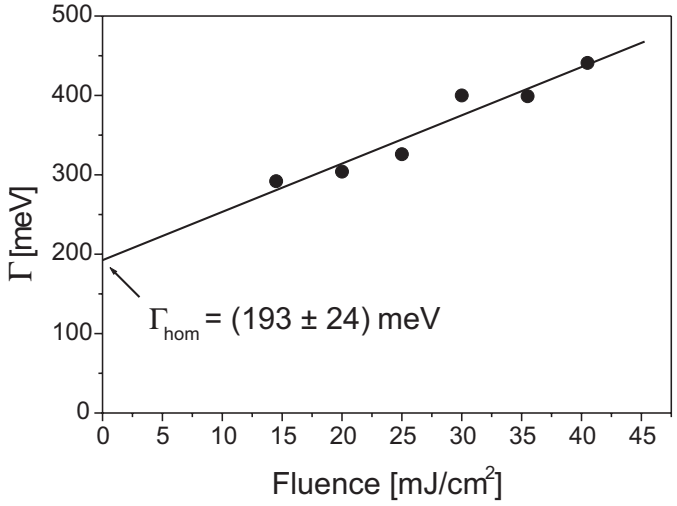

Fig. 3. Width of the spectral dip Γ as a function of the laser fluence used for hole burning. The linear dependence allows to extract the homogeneous line width of $\Gamma_{\rm hom} = 193 \pm 24$ meV.

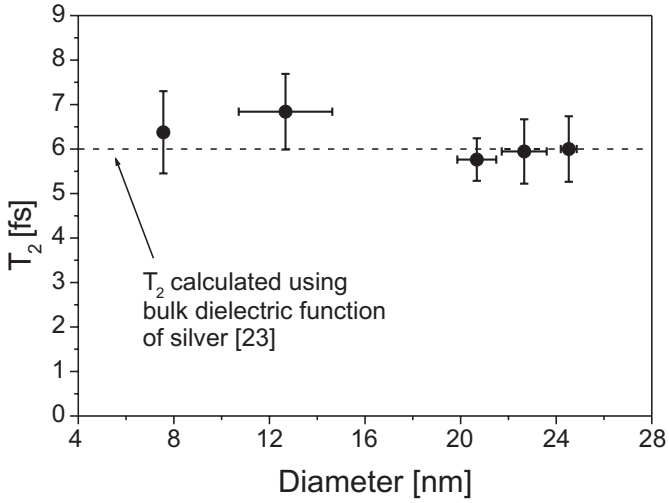

Fig. 4. Dependence of the dephasing time T_2 on the particle size in the diameter range between 8 and 25 nm.

energy is absorbed in the wings of their plasmon profiles thus broadening the dip.

The homogeneous line width can be extracted by investigating the fluence dependence of the burnt holes and by modeling the spectral changes of the absorption profiles theoretically. Details of the model have been described in reference [18]. Here, we only mention that the computations reproduce the spectral changes perfectly, see Figure 2b, and predict that the width of the dip depends linearly on the applied laser fluence. Based on this linear dependence, Figure 3, $\Gamma_{\rm hom}$ can be determined by extrapolation to zero laser fluence. This results in the homogeneous line width of $\Gamma_{\rm hom} = 193 \pm 24$ meV corresponding to the decay time $T_2 = 6.8 \pm 0.9$ fs.

In Figure 4, results obtained for particle diameters between $\langle d \rangle = 8$ and 25 nm are summarized and the dephasing times are plotted as a function of the cluster size. Within the error bars no systematic dependence of the dephasing time on the particle size is found in the investigated size range.

5 Discussion and conclusions

The results presented in section 4 demonstrate that the combination of laser assisted growth of metal nanoparticles and persistent spectral hole burning based on laser manipulation of their size and shape can be used to measure the homogeneous line width and thus determine the decay time of surface plasmon excitation as a function of nanoparticle size for a given well defined axial ratio. Two problems that made such experiments very difficult in the past have been overcome. First, laser irradiation during growth makes it possible to avoid the correlation between the particle size and shape. Thus, both parameters can be controlled independently. Secondly, spectral hole burning can be used to overcome inhomogeneous line broadening and its unfavorable influence on the measurement of T_2.

In order to demonstrate the potential of the method and test its versatility and precision, we have applied it to relatively large particles with diameters between 8 and 25 nm (*i.e.* the shortest dimension, axis a perpendicular to the substrate surface, is above 5 nm) where a strong influence of the cluster dimensions on the decay time is not expected and thus size independent values of T_2 and $\Gamma_{\rm hom}$ are found, Figure 4. Moreover, the actual values of around $T_2 = 6$ fs are almost identical to those measured by photon emission spectroscopy of individual Ag particles on Al_2O_3 with diameters between 6 and 12 nm [14] and to decay times extracted from calculations based on the silver bulk dielectric function as published by Palik *et al.* [23]. This indicates that for such large aggregates the relevant relaxation mechanisms are already included in the bulk dielectric function. In contrast, in our earlier experiments for silver clusters on quartz [18] and similar diameters, much smaller decay times have been found. This shows that the substrate material, *i.e.* sapphire in the present work and in the experiments of Freund *et al.* [14] and quartz in our earlier investigations, strongly influences the plasmon decay. In future experiments the combination of both methods, *i.e.* hole burning and laser assisted particle growth, will be applied to particles smaller than $\langle d \rangle = 5$ nm where strong size dependent effects are expected.

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