Laser manipulation of the size and shape of supported metal nanoparticles

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ABSTRACT

Laser manipulation of the size and shape of metal nanoparticles generated by self-assembly of atoms on dielectric substrates is discussed. Techniques are presented that allow one to prepare nanoparticles with a narrow size distribution and with well-defined shape by using laser irradiation after and during particle growth. Optical spectroscopy of supported nanoparticles is demonstrated to be a very versatile tool for characterizing the particles in addition to direct imaging by scanning probe microscopy. We also show that laser manipulation of the size or shape of nanoparticles can be used to determine the homogeneous linewidth of surface plasmon excitation and thus examine the ultrafast decay time of this collective electron oscillation in nanoparticles. Prospects for future experiments in this field and applications of monodisperse nanoparticles are outlined.

Keywords: Nanostructures, nanoparticles, laser ablation, silver, surface plasmon, size manipulation, dephasing time, ultrafast electron dynamics

1. INTRODUCTION

This paper gives an overview of recent experiments carried out with the objective of fabricating metal nanoparticles of well-defined size and shape[1-3]. Such systems of reduced dimensions possess physical and chemical properties that usually differ considerably from those of the corresponding bulk material of macroscopic dimensions, and, most importantly, depend upon their size and shape[4]. An example that has recently attracted much interest is the catalytic activity of gold nanoparticles[5,6]. While a macroscopic piece of Au is chemically inert, gold dispersed into small particles supported on titaniumoxide has been found to catalytically promote the oxidation of carbonmonoxide

$$CO + ½\ O_2 \rightarrow CO_2 \ ,$$

a reaction, however, that only takes place if the size of the nanoparticles lies within a narrow interval centered around about 3 nm. Therefore, most profitable use of the catalytic enhancement is made only if such particles of well-defined size and with a narrow distribution can be produced. More generally speaking, assembly of nanoparticles of precisely controlled size and shape on substrate surfaces or in encapsulating matrices opens the door to fabricate tailor-made materials with novel optical, structural, chemical and other functional properties[5-10].Besides this essential issue of applied research, truly monodisperse nanoparticles make it possible to explore the transition from atomic and molecular physics to the characteristics of bulk matter, a highly interesting issue in basic research. Both fields, i.e. investigation and understanding of the properties as well as technical exploitation of nanoparticles, are intimately connected to the availability of advanced techniques to produce, manipulate and characterize nanoparticles in such a way that the genuine identity of each single entity is preserved while precisely controlling the dimensions. Unfortunately, however, development of methods to prepare nanoparticles of well-defined size with narrow distributions as well as controlled shape is very difficult and has been one of the most longstanding problems in nanostructure science[11-14]. Before we come to an overview of such methods developed recently in our laboratory, preparation of nanoparticles on substrate surfaces by classical Volmer-Weber growth and characterization, in particular by using their optical properties, will be described briefly.

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2. GENERATION AND CHARACTERIZATION OF NANOPARTICLES

Supported nanoparticles are often made by the deposition of atoms from a thermal atomic beam on dielectric substrate materials[15-17]. Initially, the atoms are adsorbed only weakly and migrate over the surface. If, however, an atom meets a surface defect or an already existing nanoparticle, the binding energy is strongly increased and the atom is bound tightly. This gives rise to the growth of small particles where the surface defects serve as nucleation centers, a process known as Volmer-Weber growth in thin film epitaxy[16]. Owing to the statistical distribution of the defects, each of them is surrounded by a "capture area" of *different* size in which the impinging atoms contribute to nucleation and growth of each particle. As a consequence, the generated nanoparticles have a broad size distribution; its width usually amounts to as much as 30 to 50 % of the mean particle size[1,15-17]. Therefore, while Volmer-Weber growth allows one to generate supported nanoparticles in a very simple way, the broad distribution of sizes constitutes a serious drawback and prevents use of such particles as grown for a great variety of applications.

Nanoparticles made by the deposition of atoms on dielectric substrates must be characterized with regard to their size and shape before being used for further experiments. This can be done in a variety of ways, preferentially by techniques that can be applied *in situ*. In our work, the samples were first investigated by scanning force microscopy usually applied in non-contact mode[1,3,17]. From the recorded images the number density of the generated nanoparticles could be determined. The number of deposited metal atoms being known from measurements of the flux of the atomic beam with a quartz crystal microbalance, the average size <r>, i.e. the mean number of atoms per nanocluster, was extracted. <r> only constitutes an overall measure of the dimensions since the particles are not necessarily spherical but often resemble oblate rotational ellipsoids. The shape, however, cannot be determined by atomic force microscopy since the dimensions in the direction of the surface plane appear too large because of the finite radius of curvature of the probe tip. Therefore, characterization by alternate methods becomes necessary and is accomplished in our experiments by optical spectroscopy[1,3,4,17]. For this purpose, the optical transmission spectra were measured with p-polarized light. They are dominated by the resonances of surface plasmon-polariton excitation, a collective oscillation of the conduction electrons. If the nanoparticles are aspherical, two such resonances appear that are denoted as (1,1)- and (1,0)-mode and can be understood as oscillations of the electrons in the direction of the substrate plane and the surface normal, respectively[4]. Often, the nanoparticles can be treated as oblate spheroids with two main axes *a* and *b* aligned in the direction of the surface normal and the surface plane, respectively, thus making *a/b* a useful measure of the shape. Since the distance of the resonance frequencies of the two plasmon modes increases if *a/b* drops off, comparison of the experimental spectra with theoretical spectra computed by the quasi-static approximation allowed us to extract the axial ratio and thus characterize the shape of the nanoparticles. It turns out that particles prepared by Volmer-Weber growth are almost spherical at small sizes before they turn into rotational ellipsoids, the axial ratio decreasing during further growth[3,17]. This can be understood by coalescence of particles. Furthermore, the ellipsoidal shape represents a very long-lived metastable state that turns into a truncated sphere representing thermal equilibrium only if the samples are heated. At room temperature, however, diffusion of atoms on the surface of the generated nanoparticles is so slow that the shape changes, if at all, only on a timescale of years. As a result, there is a correlation between the mean size and the shape of such nanoparticles, and the broad size distribution mentioned above is inevitably accompanied by a distribution of axial ratios. In our experiments Ag nanoparticles on quartz substrates were studied. The mean particle sizes <r> and axial ratios *a/b* typically ranged from below 1 nm to about 10 nm and from unity to values as low as about 0.1, respectively.

3. SIZE MANIPULATION OF METAL NANOPARTICLES

The idea of our experiments to produce nanoparticles of well-defined size is to exploit the conceptual simplicity of Volmer-Weber growth and subsequently narrow the resulting broad size distribution. For this purpose, the dependence of the center frequencies of the surface plasmon resonances on the size and shape of the nanoparticles is used. First, nanoaprticles are prepared by Volmer-Weber growth as described above. The resulting size distribution leads to inhomogeneous broadening of the absorption profile. Therefore, in a second step, the metal nanoparticles as grown are irradiated with laser light the frequency of which is chosen such that only the largest particles of the distribution absorb the impinging photons selectively. The plasmon decays rapidly on a timescale of only few femtoseconds, the absorbed photon energy is finally converted into heat by electron-phonon coupling, and the temperature of the nanoparticles rises[18,19]. If the increase is sufficiently high, atoms evaporate from the surface of the particles that thus shrink in size. Simultaneously, the absorption profile

shifts because of the dependence of the resonance frequency on the size and/or shape of the particles, and the nanoparticles gradually move out of resonance. Therefore, the evaporation process automatically comes to an end, and nanoparticles originally larger than the mean size finally take the desired dimensions. Subsequently, as a further step, the nanoparticles are exposed to laser light of a second frequency that is only absorbed by the smallest particles of the distribution. Again, atoms are thermally released and the nanoparticle size decreases. As a result, the excited particles disappear completely after only few laser pulses since the vapor pressure grows exponentially as the particle size drops off. Finally, an ensemble of metal nanoparticles is left over on the substrate surface that exhibits a size distribution substantially narrower than the particles as grown. At present, we have produced size distributions as narrow as about 10 % of the mean particle size[1]. This, in fact, compares quite favorably to other methods such as deposition of size-selected cluster ions from the gas phase[11] (15 to 20 %) or lithographic methods[14] (about 20 %), techniques that are limited, however, to either very small or rather large particles. In contrast, the method presented here is applicable to nanoparticles almost independent of size as long as there is a monotonous dependence of the position of the plasmon frequency on the particle dimensions. Moreover, there are several ways to narrow the obtained width of the size distributions even further. One can, for example, shine in light for laser treatment of the nanoparticles and narrow the distribution as explained above. Subsequently, the two applied laser frequencies can be tuned closer to the center of the surface plasmon resonance, the size-selective evaporation procedure being repeated. Such two- or even multi-step step treatment should produce nanoparticles with size distributions as narrow as few percent. Even more elegantly, a laser system can be used which allows continuous tuning of the applied frequencies towards the center of the plasmon resonance during tailoring of the particle size. In such experiments, the particles do not shift out of resonance and the laser photons are used most efficiently.

Demonstration of our experimental technique for size manipulation was accompanied by theoretical modeling of the laser treatment of metal nanoparticles, the objective being not only to quantitatively understand and describe the method but also to optimize the process efficiently[3]. This is particularly important since a variety of parameters are involved ranging from the resonance frequency and the particle size over the frequency to the fluence to the laser light. In the theoretical description, the laser manipulation process was divided into four steps, i.e. calculation of the absorption spectra of the particles as grown, of the resulting temperature increase, the thermal evaporation rate of atoms accompanied by shrinking of the particles and, finally, computation of the resulting new size (and possibly shape) distribution. The most essential result of the model calculation is that all details of the process can be described and understood quantitatively; in short, excellent agreement between theory and experiment is obtained.

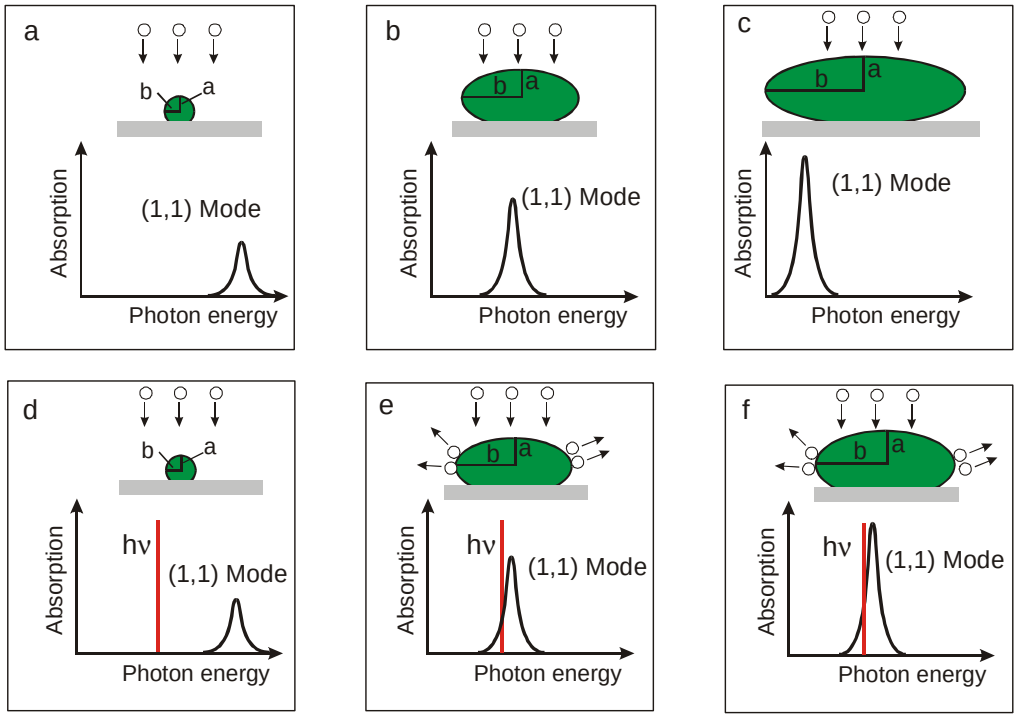

Figure 1: Schematic illustration of the laser-based method for fabricating metal nanoparticles with exactly predetermined shape. **a, b, c**: Preparation without laser light, **d, e, f**: Preparation with laser light

The method described here for tailoring the size of nanoparticles has an enormous potential for application to all those elements or compounds that exhibit sharp plasmon resonances like gold, silver, copper, tantalum, aluminum and alkali metal aggregates. Furthermore, the technique is expected to be useful for narrowing broad size distributions even if the particles do not show plasmon modes. Examples where this usually is the case are iron, nickel and platinum. For such metals, substrates with a high refractive index like TiO_2 or Ta_2O_3 can be chosen. Our calculations show that use of such substrate materials shifts the plasmon modes of the particles considerably to lower photon energies. This minimizes the influence of interband transitions that usually damp plasmon excitation. Also, the technique may be feasible for semiconductors like silicon, if special substrate materials are chosen and particle morphologies are realized that are accompanied by valence band plasmons in the visible or near ultraviolet spectral range.

4. SHAPING METAL NANOPARTICLES

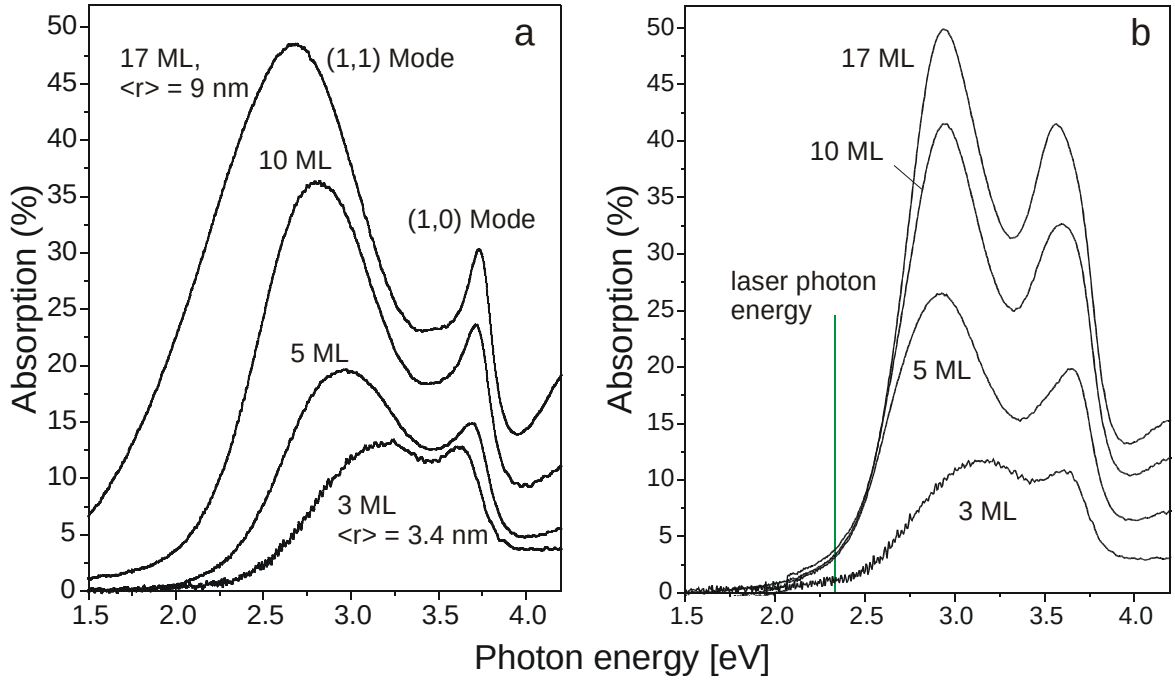

Figure 2: : Optical absorption spectra of Ag particles prepared by deposition of atoms on quartz substrates **a** without and **b** with laser irradiation during growth. The amount of deposited silver is given in equivalent monolayers (ML). The photon energy of the laser light was set to 2.33 eV (λ = 532 nm) and the fluence to 400 mJ/cm^2. The spectra were recorded using the p-polarized light of a Xe-arc lamp at an angle of incidence of 45°. For laser irradiation the light of a Nd:YAG laser with a pulse duration of 7 ns was used.

In addition to the size, the shape of supported nanoparticles often also influences their properties markedly. Examples are the optical spectra, the catalytic activity or the dielectric constant of composite materials, characteristics that can be exploited in optical filters, integrated optical polarizers, all-optical ultrafast switches, miniature planar capacitors or novel catalytic converters with improved selectivity and enhancement of the reaction rate, to mention only few examples[4-7,17]. Undoubtedly, anisotropic nano-particles of well-defined shape are urgently needed. We have seen above, however, that the size distribution of nanoparticles made by Volmer-Weber growth is accompanied by a distribution of shapes. In addition to the size manipulation described above, we have therefore developed a technique to prevent the undesired correlation between the size and the shape of the particles, and precisely and independently control both parameters[2]. For this purpose, laser light was used again. However, in contrast to post-growth tailoring of the size, the nanoparticles were exposed to laser radiation for shaping *during* atom deposition and nucleation. The idea of this method is as follows. As mentioned above, the undisturbed nanoparticles flatten with increasing size. Simultaneously, the (1,1)-plasmon resonance shifts to lower photon energy, Figure 1 (a, b, c). As a consequence, the photon energy hν of the incident laser light can be chosen such that only

particles that have reached a certain axial ratio *a/b* absorb the light efficiently, Figure 1 (d, e, f). The deposited energy is rapidly converted into heat[18,19], and, provided the slope of the absorption profile and the laser line is large enough to induce a sufficiently high temperature rise, evaporation of atoms is stimulated. Since these atoms preferentially come off from the edges and perimeters of the particles, i.e. the large axis *b* is affected almost exclusively by the laser treatment, the axial ratio tends to increase. As a result, the shape of the generated nanoparticles is stabilized and remains unchanged although the mean size grows during deposition of further atoms. The method has several advantages. First, it is simple to apply. Second, it is even self-regulating since the slope of the absorption profile automatically locks to the position of the used laser frequency. Third, choice of the laser frequency automatically determines the axial ratio of the generated particles. Thus, tuning the laser to different output frequencies, nanoclusters of different, predetermined shapes can be made in a simple way. Verification of constant shape of the nanoparticles generated under laser irradiation can most profitably be accomplished by exploiting the optical properties, i.e. by measuring the absorption spectra. In fact, the positions of the (1,0)- and the (1,1)-mode remain constant during particle growth thus indicating a constant, well-defined shape irrespective of size, Figure 2.

5. APPLICATION OF NANOPARTICLE MANIPULATION WITH LASER LIGHT: INVESTIGATION OF ULTRAFAST ELECTRON DYNAMICS

The techniques presented above to modify size and shape distributions of metal nanoparticles are not only of high value for the preparation of such ensembles with well-defined dimensions but can also be used profitably to study their properties. Even ultrafast electron dynamics on the femtosecond time scale can be investigated as will be explained below. The principle of these experiments is to use laser radiation with a bandwidth much narrower than the inhomogeneously broadened absorption profile of the particles and the homogeneous linewidth to deplete the population in a certain interval of particle sizes and/or shapes by thermal evaporation. This is quite similar to the well-known technique of classical hole-burning, for example into inhomogeneously broadened Doppler profiles of atomic or molecular transitions, an essential difference being, however, that a peak appears here right next to the generated dip. This is because the nanoparticles excited selectively by the chosen light frequency shrink in size but do not disappear completely from the substrate surface. In fact, they only shift out of resonance and enhance the population at slightly larger photon energies, thus creating an asymmetric dip. Comparison of a certain size dependent parameter of the nanoparticles, for example the chemical reactivity, measured before and after hole burning then allows one to determine its value exclusively for particles located within the narrow bandwidth of the generated dip. Signal-to-noise ratio permitting, such experiments make possible size-selective investigations of nanoparticles without the necessity of preparing monodisperse ensembles. The

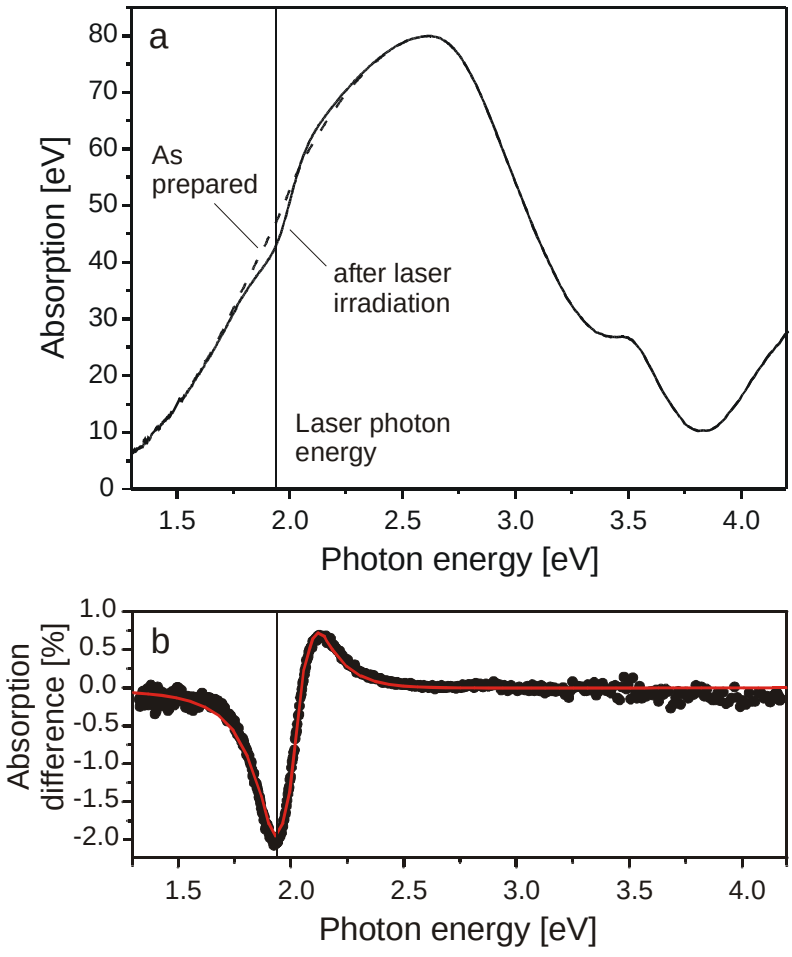

Figure 3: a Optical absorption spectra of Ag-nanoparticles with a radius of <r> = 10 nm before and after irradiation with 300 laser pulses from a BBO-OPO pumped by a Nd:YAG laser. The laser photon energy was set to 1.95 eV and the laser fluence to 10 mJ/cm^2. The pulses had a length of 5 ns. **b** Difference spectrum, filled circles: experimental data, solid line: fit to the theoretical model with a width of Γ = 291 meV. All measurements were performed at T = 300 K.

main differences as compared to tailoring the size and shape of nanoparticles as outlined above, is that the laser frequency is not necessarily chosen to interact only with the largest and smallest particles of the distribution and that the population in the selected interval is diminished only to create a detectable hole but not depleted completely. Therefore, the fluence can be kept at a low value, and nanoparticles of the desired dimensions interact with the light selectively.

As an example, we will present experiments in which the homogeneous linewidths of surface plasmon resonances have been measured[20,3]. The uncertainity relation then allows us to calculate the dephasing time of this collective excitation, i.e. examine ultrafast electron dynamics. The motivation of these studies is as follows. While surface plasmon excitation in small metal particles has found great interest in the past and numerous studies have been reported[4,21-24], an essential issue has remained open: at present, no systematic investigation of the decay time T_2 and the decay mechanisms of surface plasmons are available. Ideally, one would like to measure T_2 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[4,25]. Also, plasmon excitation is accompanied by a considerable enhancement of the electric field near the particle surface, the enhancement factor f being proportional to T_2^4. This enhancement is exploited e.g. in surface enhanced Raman scattering and is discussed for applications like all-optical switching devices or improved biophysical sensors[4,7,9]. Therefore, determination of T_2 is essential for fundamental science and for a variety of applications. At this point, persistent spectral hole burning in inhomogeneously broadened plasmon profiles of metal nanoparticles comes into play to measure the homogeneous width and thus determine T_2. Advantages of this technique are that it is not restricted to certain particle sizes, does not require special size and shape distributions and is compatible with ultrahigh vacuum conditions, i.e. allows one to control and systematically vary the chemical environment.

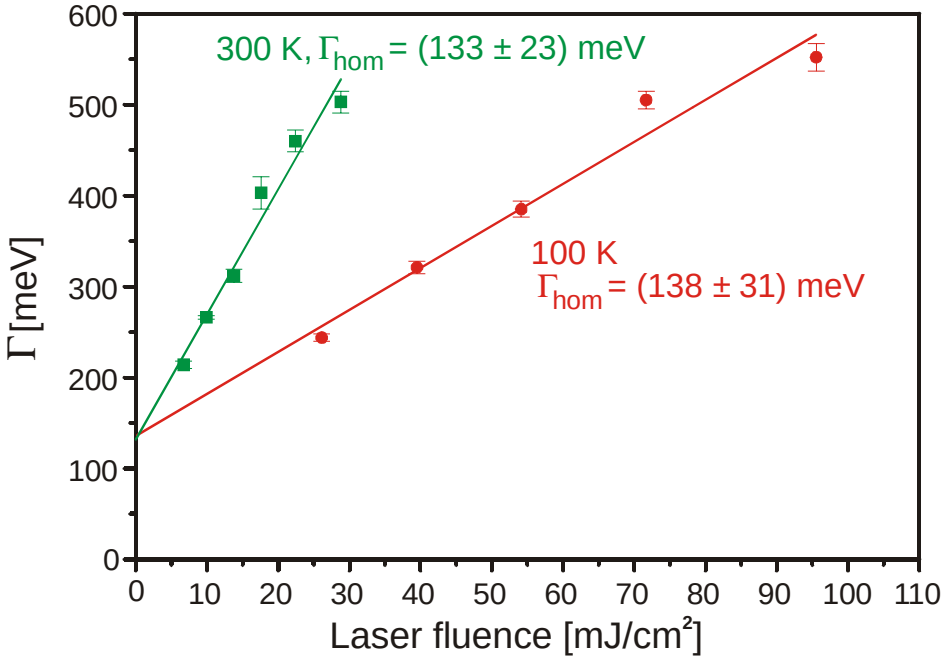

Figure 4: : Γ_{hom} of the surface plasmon in Ag-nanoparticles with a radius of <r> = 10 nm determined at two different substrate temperatures. The laser photon energy was set to 1.95 eV.

The dip burned into the population by the laser light can be probed readily by subtracting the optical absorption spectra measured after and before hole burning. An example is shown in Figure 3. The asymmetric shape with a peak adjacent to the dip can clearly be seen. The homogeneous linewidth has been extracted by investigating the fluence dependence of the burned holes and by modeling the spectral changes of the absorption profiles theoretically. Details of the model have been described elsewhere[20]. The most essential result of the model is an analytical expression for the shape of the hole and the prediction that its width depends linearly on the applied laser fluence. In fact, the dip broadens since the temperature rise of particles with neighbouring axial ratios not fully in resonance with the light gains importance as the laser fluence rises and more and more energy is absorbed in the wings of their plasmon profiles. We find indeed that the computations reproduce the spectral changes perfectly, Figure 3, and that the width of the dip depends linearly on the applied laser fluence. The

slope of the obtained straight line can even be different depending on the temperature of the substrate, Figure 4. This reflects the dependence of the thermal conductivity of the substrate material on temperature. The light-induced temperature rise of the nanoparticles and the thermal evaporation rate therefore vary as a function of the initial substrate temperature which gives rise to different slopes of the extrapolation line. This effect is another verification of the usefulness of the technique and the validity of the model description: we do not only obtain a straight line for each chosen substrate temperature, but also the same value for the true homogeneous linewidth by extrapolating to zero laser fluence. We finally find that the homogeneous width Γ_{hom} is on the order of several hundred meV and the decay times T_2 range from about 3 to 10 fs. At present, experiments are under way to measure the size dependence of T_2 using particles of constant axial ratio.

By applying spectral hole burning to oblate Ag particles, we have also shown recently that the reduced dimension of clusters influences the homogeneous line width and thus the decay time, the shortest axis being below 5 nm. 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 for clusters with $a/b = 0.18$ to 3.8 fs for clusters with $a/b = 0.25$. Two effects bring about this shape dependence. First, the plasmon shifts to higher photon energies the more the nanoparticles approach the shape of a sphere. Secondly, with increasing plasmon frequency, the influence of the d-electrons of silver on plasmon excitation grows. 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. This can be achieved by the method described above to stabilize the axial ratio of the nanoparticles.

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REFERENCES

1. J. Bosbach, D. Martin, F. Stietz, T. Wenzel, F. Träger, “Laser-based method for fabricating monodisperse metallic nanoparticles”, *Appl. Phys. Lett.* **74**, 2605-2607 (1999)
2. T. Wenzel, J. Bosbach, A. Goldmann, F. Stietz, F. Träger, “Shaping nanoparticles and their optical spectra with photons”, *Appl. Phys. B* **69**, 513-517 (1999)
3. F. Stietz, “Laser manipulation of the size and shape of supported nanoparticles”, *Appl. Phys. A* **72**, 381-394 (2001)
4. U. Kreibig, M. Vollmer, *Optical properties of metal clusters*, Springer Ser. Mat. Sci. 25, Springer, Berlin (1995)
5. M. Valden, X. Lai, D. W. Goodman, “Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties”, *Science* **281**, 1647-1650 (1998)
6. G. R. Bamwenda, S. Tsubota, T. Nakamura, M. Haruta, “The influence of the preparation methods on the catalytic activity of platinum and gold supported on TiO_2 for CO oxidation”, *Catal. Lett.* **44**, 83-87 (1997)
7. R.F. Haglund, Jr, L. Yang, R.H. Magruder III, J.E. Wittig, K. Becker, R.A. Zuhr, “Picosecond nonlinear optical response of a Cu:silica nanocluster composite”, *Opt. Lett.* **18**, 373-375 (1993)
8. L. Novotny, R.X. Bian, X.S. Xie, “Theory of nanometric optical tweezers”, *Phys. Rev. Lett.* **79**, 645 (1997)
9. S. Nie, S.R. Emory, “Probing single molecules and single nanoparticles by surface-enhanced Raman scattering”, *Science* **275**, 1102-1106 (1997)
10. J. R. Krenn, A. Dereux, J. C. Weeber, E. Bourillot, Y. Lacroute, J. P. Goudonnet, G. Schider, W. Gotschy, A. Leitner, F. R. Aussenegg, C. Girard, “Squeezing the optical near-field zone by plasmon coupling of metallic nanoparticles”, *Phys. Rev. Lett.* **82**, 2590-2593 (1999)
11. K. Bromann, C. Félix, H. Brune, W. Harbich, R. Monot, J. Buttet, K. Kern, “Controlled deposition of size-selected silver nanoclusters”, *Science* **274**, 956-958 (1996)
12. H. Brune, M. Giovannini, K. Bromann, K. Kern, “Self-organized growth of nanostructure arrays on strain-relief patterns”, *Nature* **394**, 451-453 (1998)
13. W. Gotschy, K. Vonmetz, K. Leitner, F. Aussenegg, “Thin films by regular patterns of metal nanoparticles: tailoring the optical properties by nanodesign”, *Appl. Phys. B* **63**, 381-384 (1996)

14. G. A. Somorjai, “New model catalysts (platinum nanoparticles) and new techniques (SFG and STM) for studies of reaction intermediates and surface restructuring at high pressure during catalytic reactions”, *Appl. Surf. Sci*. **121/122**, 1-19 (1997)
15. C. R. Henry, “Surface studies of supported model catalysts”, *Surf. Sci. Rep*. **31**, 231-325 (1998)
16. J. A. Venables, “Atomic processes in crystal growth”, *Surf. Sci.* **299/300**, 798-817 (1994)
17. T. Wenzel, J. Bosbach, F. Stietz, F. Träger, “In situ determination of the shape of supported silver clusters during growth”, *Surf. Sci*. **432**, 257-264 (1999)
18. J.Y. Bigot, J.C. Merle, O. Cregut, A. Daunois, “Electron dynamics in copper metallic nanoparticles probed with femtosecond optical pulses”, *Phys. Rev. Lett.* **75**, 4702-4705 (1995)
19. J.Y. Bigot, V. Halte, J.-C. Merle, A. Daunois, “Electron dynamics in metallic nanoparticles”, *Chem. Phys.* **251**, 181-203 (2000)
20. F. Stietz, J. Bosbach, T. Wenzel, T. Vartanyan, A. Goldmann, F. Träger, “Decay times of surface plasmon excitation in metal nanoparticles by persistent spectral hole burning”, *Phys. Rev. Lett.* **84**, 5644-5647 (2000)
21. T. Klar, M. Perner, S. Grosse, G. von Plessen, W. Sperkl, J. Feldmann, “Surface-plasmon resonances in single metallic nanoparticles”, *Phys. Rev. Lett.* **80**, 4249-4252 (1998)
22. C. Sönnichsen, S. Geier, N.E. Hecker, G. von Plessen, J. Feldmann, H. Ditlbacher, B. Lamprecht, J.R. Krenn, F.R. Aussenegg, V.Z-H. Chan, J.P. Spatz, M. Möller, “Spectroscopy of single metallic nanoparticles using total internal reflection microscopy”, *Appl. Phys. Lett*. **77**, 2949-2951 (2000)
23. B. Lamprecht, J.R. Krenn, A. Leitner, F.R. Aussenegg, “Resonant and off-resonant light-driven plasmons in metal nanoparticles studied by femtosecond-resolution third-harmonic generation”, *Phys. Rev. Lett.* **83**, 4421-4424 (2000)
24. B. Lamprecht, A. Leitner, F.R. Aussenegg, “SHG studies of plasmon dephasing in nanoparticles“, *Appl. Phys. B* **68**, 419–423 (1999)
25. B.N.J. Persson, “Polarizability of small spherical metal particles : influence of the matrix environment”, *Surf. Sci.* **281**, 153-162 (1993)