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Laser-induced manipulation of the size and shape of small metal particles: Towards monodisperse clusters on surfaces

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Abstract. A novel experimental technique is presented for post growth narrowing of the size distribution of metal nanoparticles on dielectric substrates. In order to demonstrate the potential of the method, oblate Ag clusters with mean radii of $\langle R \rangle = 6$ nm and broad size distributions were prepared under ultrahigh vacuum conditions on quartz substrates. Narrowing of the width of their size distribution was accomplished by irradiation with short laser pulses. The laser light excites plasmons in the particles, the frequency of which depends on the size and shape of the clusters. By choosing the light frequency such that only the smallest and the largest particles selectively absorb light, evaporate atoms and shrink in size, the size distribution was narrowed by 40%. A scenario for producing monodisperse particles is discussed.

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1 Introduction

There is a remarkable trend of current research to prepare and characterize nanoparticles on surfaces. These systems of reduced dimensions do not only bridge the gap between atomic and solid state physics but are also attractive for potential technological applications (see e.g. [1–6]). One of the key issues in this field is the generation of nanoparticles with well defined size and narrow size distribution. In principle two approaches are possible. First, size selected clusters can be produced in the gas phase by methods like gas aggregation or ion sputtering followed by mass separation and soft landing on a substrate. Though this technique has been applied successfully it is restricted to clusters containing at most about 20 atoms [1–4]. Furthermore, only a tiny fraction of the material initially dispersed into clusters is finally deposited on the substrate surface. A second possibility is to produce clusters on a substrate, for example by Volmer–Weber growth, and subsequently apply a technique to narrow the resulting broad size distribution.

This paper presents new experimental results which demostrate that the size distribution of small metal particles can be manipulated in a well defined way by irradiation with pulsed laser light. In particular, a considerable narrowing of a given distribution on a surface can be achieved. This becomes feasible by laser induced evaporation of atoms from the surface of the particles, a process which can be controlled such that only clusters in a certain size interval of the distribution shrink selectively. The method can be applied with little technical effort and is not restricted to small clusters.

2 Principle of size manipulation

First, atoms of a thermal atomic beam are deposited on a dielectric substrate surface. They are adsorbed only weakly and form clusters by surface diffusion and nucleation (Volmer–Weber growth). It is well-known from electron and scanning probe microscopy that particles generated along these lines have a broad size distribution the width of which is about 30 to 50% of the mean cluster radius [4, 7]. Therefore, as the second step, the given distribution is narrowed by irradiating the clusters with pulsed laser light. For a fixed wavelength the absorption cross section depends on particle radius [8]. Therefore, the frequency of the incident laser radiation can be chosen such that only particles in a certain size interval of the distribution absorb light efficiently. The absorbed photon energy is rapidly converted into heat, the temperature rises and the heated clusters evaporate atoms from their surfaces [9–13]. As a consequence, they selectively shrink and the size distribution alters. It actually narrows if the frequency of the laser radiation is chosen such that only particles larger or smaller than the average radius $\langle R \rangle$ interact.

The process automatically comes to an end as soon as the evaporating clusters have decreased so much that they are shifted out of the particular size intervall and, consequently, do not absorb the light any longer. The narrowing process has not only been demonstrated here experimentally but also modelled theoretically and, in contrast to non-thermal bond breaking [12], offers the advantage of rapid processing.

The variation of the size distribution has been monitored by recording the optical extinction spectra of the clusters before and after laser treatment.

3 Experimental setup and procedure

The experimental arrangement consists of an ultrahigh-vacuum (UHV) system with a base pressure of $p = 4 \times 10^{-10}$ mbar, the sample, a Xenon arc lamp combined with a monochromator for measuring the extinction spectra, an electron beam evaporator for generation of Ag atoms, a UHV atomic force microscope and a Nd:YAG laser for manipulation of the size distributions. The Ag particles were prepared on quartz surfaces by deposition of atoms and subsequent surface diffusion and nucleation. Their number density was measured by atomic force microscopy to be $10^{11}\,\mathrm{cm}^{-2}$, for the coverages considered here. The mean particle radius was determined from the known silver coverage and the number density. The clusters resemble oblate ellipsoids, the axial ratio of which decreases as a function of their size [14]. In view of the aspherical shape of the particles the mean radii quoted in this paper refer to spheres with the same volume. In order to characterize them, the optical extinction spectra were measured with the p-polarized light of a Xe arc lamp combined with a monochromator. The angle of incidence was 45° with respect to the substrate surface normal and the photon energies ranged from 1.2 to 5 eV. The spectra are dominated by two peaks which arise from excitation of surface plasmons in the direction of the long ((1,1)-mode) and short ((1,0)-mode) axis of the ellipsoidal particles, Fig. 1. Their energetic positions reflect the mean size and shape of the clusters. The width of the resonances is determined by homogeneous line broadening arising from the finite decay time of the plasmon, eventually, further increased due to the interaction with the substrate ($\tau \sim 10$ fs, $\Delta E \sim 0.15$ eV [16–18]) and an inhomogeneous contribution due to the dependence of the plasmon frequency on the particle size [6, 8, 15]. Because of the broad size distribution associated with Volmer-Weber growth inhomogeneous broadenening is predominant. Therefore, changes of the width of the resonances directly reflect modifications of the particle size distribution [19].

For laser treatment the clusters were irradiated with the light of a Nd:YAG-laser at $\lambda = 532$ and 355 nm with a pulse duration of 7 ns and a repetition rate of 10 Hz. The fluence was set to 100 and 150 $\mathrm{mJ/cm}^2$, respectively, and the number of applied laser pulses ranged from 100 to 10^4. The angle of incidence was 45° with respect to the substrate surface normal.

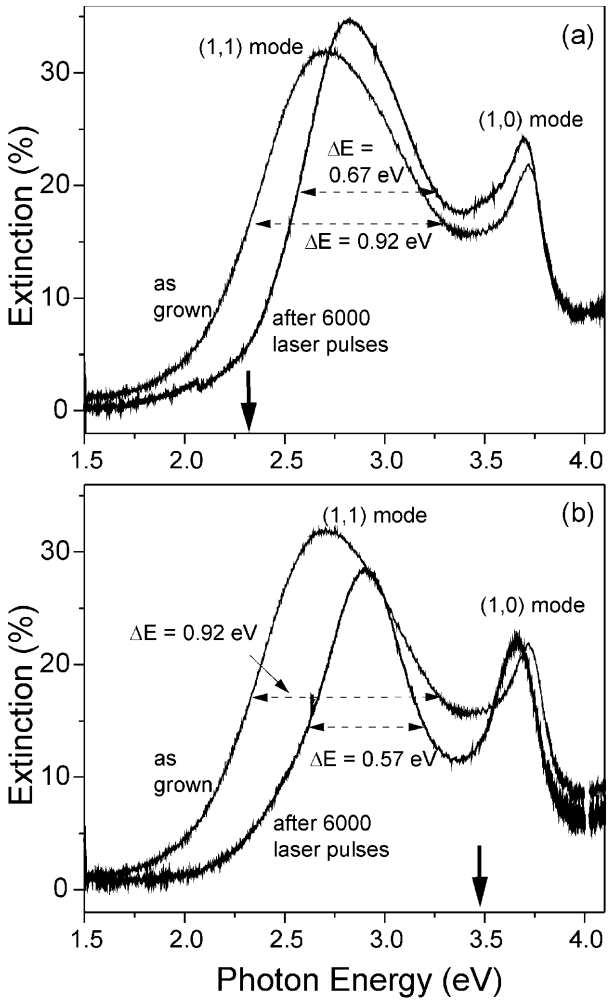

Fig. 1. Optical extinction spectra of Ag particles with a mean radius of $\langle R \rangle = 6$ nm on quartz substrates as grown and after 6000 laser pulses of $\lambda = 532$ (a) and 355 nm (b). The fluence was set to $\phi = 100$ and 150 $\mathrm{mJ/cm}^2$, respectively. The arrows indicate the energetic positions of the photon energy of the laser light with respect to the resonance position of the (1,1) mode for (a) $\lambda = 532$ and (b) 355 nm.

4 Experimental results

In the present paper, Ag particles with a mean radius of $\langle R \rangle = 6$ nm will be considered as an example. In addition to spectra for particles as grown, Fig. 1 also displays extinction spectra measured after firing 6000 laser pulses of a wavelength of $\lambda = 532$ (Fig. 1a) and 355 nm (Fig. 1b).

We first note, that laser irradiation causes a considerable shift of the resonance position of the (1,1) mode to larger energy. Furthermore, a reduction of its width by 30% for $\lambda = 532$ nm and 40% for $\lambda = 355$ nm is found. Measurements, in which the width of the (1,1) mode has been determined as a function of the number of applied laser pulses have shown that it decreases drastically during the first 1000 pulses and changes only little upon further irradiation (not shown here). As indicated in Fig. 1, the used laser wavelengths of $\lambda = 532$ and 355 nm are located in the low and the large energy wing of the (1,1) mode, respectively.

Therefore, the magnitude of the peak shift, the reduction of the width and the shape of the resulting resonance peak differ considerably for both used laser frequencies (Fig. 1a and b).

The shift of the energetic positon of the (1,1) mode indicates that the mean particle size has decreased as a result of laser irradiation. The reduction of the width, on the other hand, reflects a pronounced narrowing of the size distribution of the particles.

5 Discussion and model calculation

In order to correlate the observed changes quantitatively to modifications of the size distribution, the laser stimulated manipulation process has been modelled theoretically. First, optical spectra were calculated for each particle size using the quasi static approximation [20]. In the second step, these spectra were multiplied by the relative frequency of each size and summed to result in the optical spectrum of the Ag particle ensemble. The frequency factor accounts for the size distribution of the particles which was determined from the AFM images and approximated by a Gaussian. The decrease of the axial ratio as a function of increasing particle size as evaluted from the optical spectra recorded for different mean diameters has also been included [21]. These calculations allow us to convert a given size distribution into its optical spectrum and, in particular, to correlate modifications of the distribution with changes of the spectrum. As the third step, the absorption cross section and the temperature rise of the clusters were computed as a function of size. To calculate the temperature rise induced by absorption of light, the heat diffusion equation of Ag clusters adsorbed on quartz substrates was solved [22]. Subsequently, the evaporation rate during each laser pulse was determined using the Arrhenius equation [23]. It is well known from earlier investigations that the atoms located at the edges or perimeters of oblate metal particles have particular low binding energy and evaporate preferentially [24, 25]. This was considered in the calculations in such a way that only the long axis of the particles was allowed to shrink. In contrast, the length of the short axis pointing into the direction of the surface normal remained constant. As the last step of the model calculation, the resulting changes of the size distribution and the optical spectra were determined. Further details of the model will be published elsewhere [26].

Examples for the laser wavelengths of $\lambda = 532$ and 355 nm and a mean particle radius of 6 nm will be described here. Figure 2a and 3a display the dependence of the absorption cross section and the evaporation rate on the particle size. For both wavelengths the absorption coefficient follows the plasmon resonance which is superimposed on the overall R^3-increase. The dependence of the desorption rate on cluster radius is much narrower than that of the absorption cross section because of the exponential dependence of the vapor pressure on temperature. This makes laser-induced changes of the size distribution highly size selective. Since the desorption rate peaks

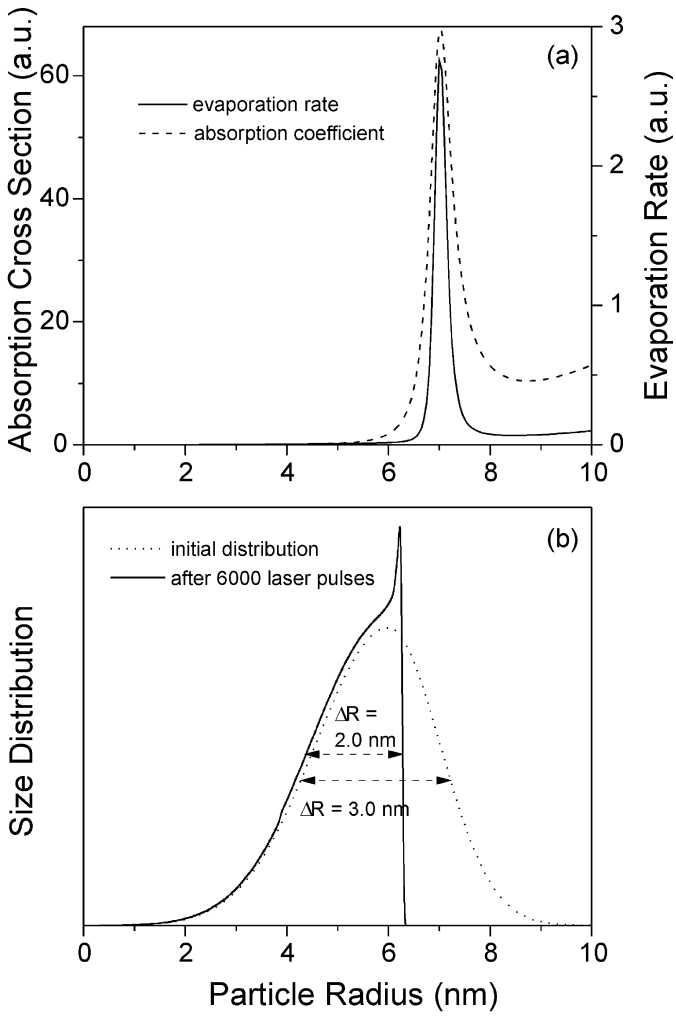

Fig. 2. (a) Calculated absorption coefficient and resulting evaporation rate as a function of the size of Ag particles. The laser wavelength was set to $\lambda = 532$ nm and the fluence to $\phi = 100\,\mathrm{mJ/cm^2}$. (b) Size distribution of Ag particles with an initial radius of $\langle R \rangle = 6$ nm and an initial width of 3.0 nm prior to and after firing 6000 laser pulses. The wavelength was $\lambda = 532$ nm and the fluence $\phi = 100\,\mathrm{mJ/cm^2}$.

at about $R = 7.0$ nm for $\lambda = 532$ nm only particles with radii above $R = 6.5$ nm experience a temperature rise sufficiently large for evaporation and shrink in size. This is reflected in the change of the size distribution illustrated in Fig. 2b. The number of particles with $R > 6.5$ nm has decreased drastically and the distribution narrows from $\Delta R = 3.0$ to 2.0 nm, i.e. by 33%. Furthermore, it is shifted slightly to smaller radii. The reduced width of the size distribution is reflected in the calculated extinction spectra as a decrease of the width of the (1,1) mode. Figure 4 a shows such spectra calculated by using the original and modified size distribution of Fig. 2b.

If a wavelength of $\lambda = 355$ nm is applied, the number of particles with sizes between $R = 2$ and 4.5 nm and $R > 7$ nm has decreased, Fig. 3. Consequently, the size distribution narrows by even 40%. Again, this is reflected in the optical spectra as a significant decrease of the width of

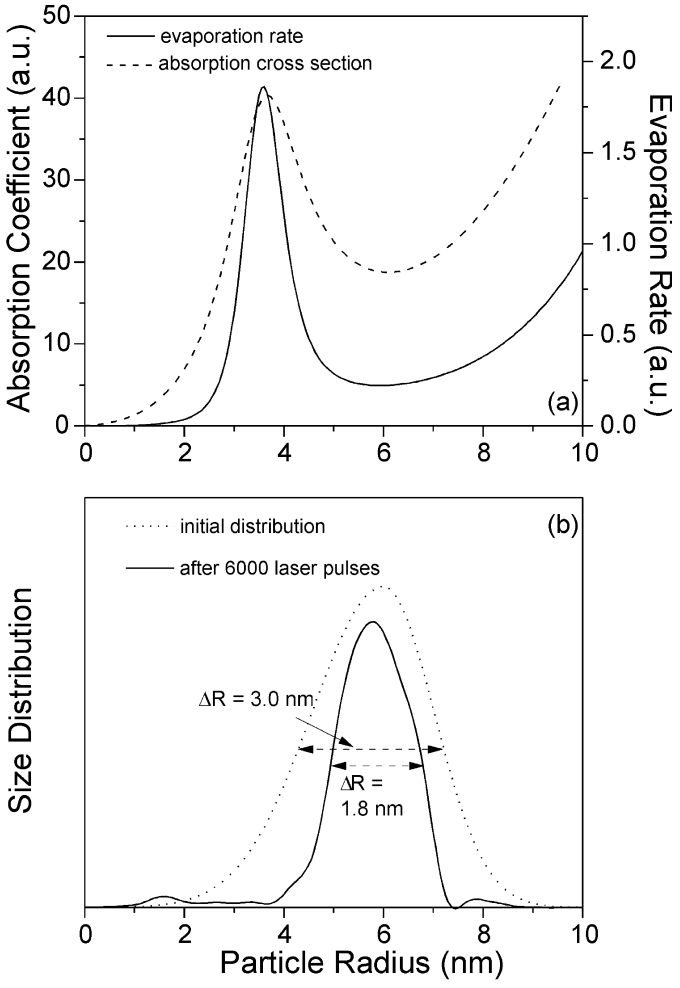

Fig. 3. (a) Calculated absorption coefficient and resulting evaporation rate as a function of the size of Ag particles. The laser wavelength was set to $\lambda = 355$ nm and the fluence to $\phi = 150\,\mathrm{mJ/cm^2}$. (b) Size distribution of Ag particles with an initial radius of $\langle R \rangle = 6$ nm and an initial width of 3.0 nm prior to and after firing 6000 laser pulses. The wavelength was $\lambda = 355$ nm and the fluence $\phi = 150\,\mathrm{mJ/cm^2}$.

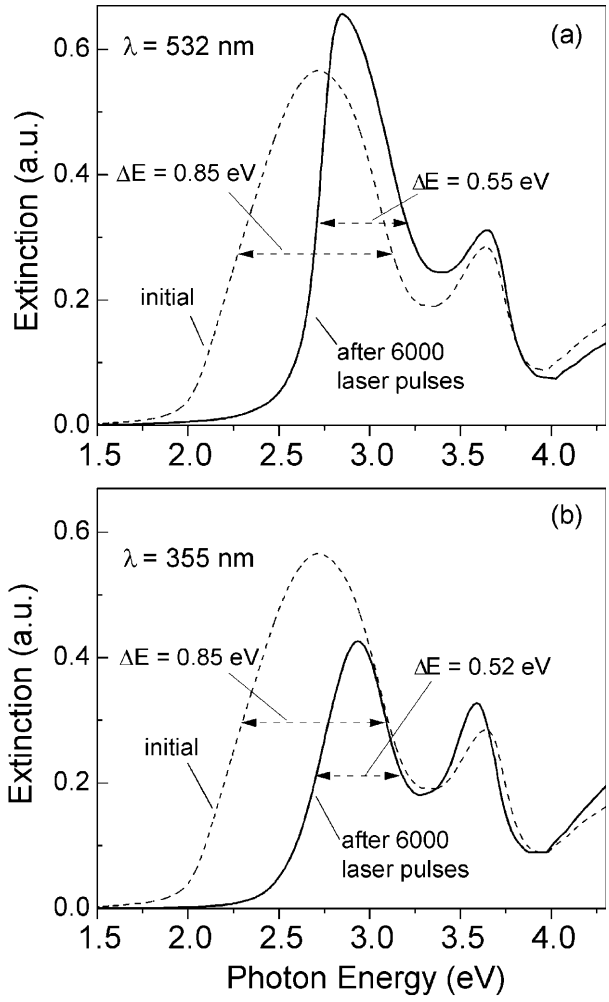

Fig. 4. Calculated optical extinction spectra of Ag particles with mean radius of $\langle R \rangle = 6$ nm and computed from the theoretical size distributions of Figs. 2b and 3b (before and after irradiation with 6000 pulses of $\lambda = 532$ (a) and 355 nm (b)).

the (1,1) mode by 39%. As can be seen in the experimental determined extinction spectra displayed in Fig. 1 and in the calculated changes of the size distribution shown in Fig. 2b and 3b, the narrowing of the distribution is even more pronounced if a wavelength of $\lambda = 355$ nm is used for manipulation. This can be understood as follows. For this wavelength particles with sizes between $R = 2.5$ and 4.5 nm are depleted because of resonant plasmon excitation. In addition, clusters with $R > 6$ nm shrink in size because of the overall R^3 dependence of the absorption cross section and, consequently, the number of particles with $R > 7$ nm is reduced drastically, Fig. 3b. As a result the size distribution is narrowed almost symmetrically. This is also reflected in the symmetric peak shape of the (1,1) mode after laser irradiation with $\lambda = 355$ nm, Fig. 1b. On the other hand, only the large radii tail of the distribution is depleted if a wavelengh of $\lambda = 532$ nm is applied resulting in the asymmetric peak shape of the (1,1) mode, Fig. 1a.

Comparison of the calculated spectra of Fig. 4 to the experimental data of Fig. 1 shows good agreement. The peak shifts and, in particular, the reductions of the width of the (1,1) mode are reproduced well for both used laser frequencies.

Obviously, measurement of the optical spectra provides an ideal tool to detect changes of the size distribution. In contrast, atomic force microscopy which was also applied to the samples suffers from the finite tip curvature of about $R = 15$ nm which prevents a precise quantitative determination of the changes of the size distribution.

In conclusion we have demonstrated that the size distribution of metal nanoparticles grown on dielectric substrates can be narrowed efficiently by irradiation with short laser pulses. The method relies on the dependence of the optical absorption cross section, in particluar of the plasmon resonance, on the particle size. By choosing the light frequencey such that only particles larger and smaller than the mean size selectively absorb light, evaporate atoms and shrink in size, the width of the size dis-

tribution of Ag clusters on quartz has been narrowed by about 40%. The narrowing is reflected in the optical spectra of the particles as a reduction of the width of the inhomogenously broadened (1,1) mode. Theoretical modelling reproduces all features well and predicts scenarios for optimal processing, i.e. for generating monodisperse particles. In particular multistep experiments using different laser wavelengths consecutively open the door for further narrowing of the size distribution. The model suggests that almost monodisperse clusters in the size range considered here can be prepared by irradiating them first with $\lambda = 532\,\mathrm{nm}$ to reduce the number of particles larger than the mean size and, subsequently, with $\lambda = 355\,\mathrm{nm}$ in order to deplete the low radii tail of the distribution. In such calculations the width of the plasmon resonance has almost converged to the homogeneous linewidth given by the lifetime of the plasmon. Experiments along these lines are in progress in our laboratory.

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