Laser-based method for fabricating monodisperse metallic nanoparticles

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An experimental method is presented for fabrication of almost monodisperse metal nanoparticles on substrate surfaces. It relies on substantial narrowing of broad size distributions through irradiation with short laser pulses by exploiting the size dependent optical absorption coefficient of the metal particles. Successive irradiation by applying two laser wavelengths completely removes the smallest clusters of the distribution and causes a size reduction of the largest particles. Finally, only clusters with diameters in a very narrow size interval remain on the surface. By using this method, Ag clusters with mean diameters of \(\langle d \rangle = 10 \text{ nm} \) and size distributions with standard deviations of \(\Delta d/\langle d \rangle = 0.13 \) have been prepared. © 1999 American Institute of Physics.

The properties of metal nanoparticles are unique functions of their size and shape and differ considerably from those of the corresponding bulk material. Unfortunately, however, the size dependent characteristics are often obscured, since fabrication of small particles usually results in a mixture of different diameters.\(^1\)–\(^4\) This does not only make it difficult to correlate certain properties to well-defined particle sizes but also prevents extensive use in future technological applications like, for example, novel catalysts with optimized selectivity,\(^2\)–\(^5\) thin film technology,\(^7\)–\(^8\) or magnetic disk drives.\(^9\)–\(^10\) Therefore, the preparation of nanoparticles of well-defined size on support materials has long been a key issue of cluster science, e.g., Refs. 3, 4 and 6–8. In the past, such systems have been synthesized, for example, by generating charged clusters in the gas phase through methods like gas aggregation or ion sputtering followed by mass separation and soft landing on the substrate. The main drawback of this method, however, is its restriction to small clusters with at most 20 atoms.\(^11\)–\(^12\) Very large particles, on the other hand, can be created with high size uniformity using lithographic techniques, methods which are, however, restricted to structures larger than about 20 nm.\(^6\)–\(^13\)

Here, we present an experimental technique for the fabrication of metallic nanoparticles of predetermined size and with very high size uniformity. The method can be applied with little technical effort, allows one to generate a large amount of particles in parallel, is not restricted to certain size ranges, and results in almost monodisperse particles, i.e., distributions with standard deviations of about 10%. The principle is as follows: Metal clusters are prepared by deposition of atoms and subsequent surface diffusion and nucleation on the substrate surface, i.e., Volmer–Weber growth. The initial widths of their size distributions are about 40% of the mean particle diameter. Therefore, as the next step, the given distribution is narrowed by irradiating the clusters with pulsed laser light. Since the absorption cross section depends on the particle size,\(^1\) 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. During decay of the electronic excitation the absorbed photon energy is rapidly converted into heat. The heated clusters evaporate atoms from their surfaces and selectively shrink in size.\(^14\)–\(^17\)

As a consequence, the distribution alters. To accomplish the size manipulation the overall \(R^3\) dependence of the optical absorption cross section can be exploited or, more efficiently, the well-known surface plasmon resonance which is redshifted as a function of particle radius in the size regime considered in the present work. As will be explained in more detail below, the distribution narrows dramatically if two appropriately chosen laser wavelengths \(\lambda_1\) and \(\lambda_2\) are applied: Irradiation with \(\lambda_1\) causes removal of the smallest particles and firing of laser pulses with \(\lambda_2\) results in shrinking of the particles larger than the mean size, a process which automatically comes to an end if the clusters have shifted out of resonance and do not interact with the laser light anymore.

In order to demonstrate that this method can indeed be used for producing particles with a very high size uniformity, Ag clusters were grown under ultrahigh vacuum conditions on quartz substrates as explained above. The surface and cluster morphology was characterized in situ with scanning force microscopy (SFM) and optical spectroscopy. The generated particles resemble oblate ellipsoids, the axial ratio of which decreases as a function of average size. Deposition of \(1.1 \times 10^{10}\) atoms/cm\(^2\), for example, leads to Ag particles with a number density of \(2.0 \times 10^{11}\) cm\(^{-2}\), [Fig. 1(a)]. The SFM images give a mean cluster height (measured in the direction of the substrate surface normal) of \(\langle h \rangle = 4 \text{ nm}\) and an average diameter (measured in the direction parallel to the surface) of \(\langle d_{\text{SFM}} \rangle = 30 \text{ nm}\). A careful analysis of the SFM images and the optical spectra obtained for different cluster sizes shows that the particle height is reproduced correctly; the diameter is overestimated due to the finite radius of the SFM tip (\(r \approx 12 \text{ nm}\)). However, the actual mean diameter \(\langle d \rangle\) of the clusters could be derived from the Ag coverage measured by a quartz crystal microbalance and the known cluster density to be \(\langle d \rangle = 12 \text{ nm}\).\(^18\) The distribution has been determined from the SFM images and resembles a Gaussian with a rather large width of \(\sigma^p = \sigma(\langle d \rangle) = 0.40\), Fig. 1(b). \(\sigma\) is the standard deviation of all particle diameters. The size distributions presented in this letter are based on the evaluation of several hundred clusters in many images similar to the ones displayed in Fig. 1.

After imaging, the particles were irradiated with light...
Fig. 1. SFM image (a) and size distribution (b) of Ag particles formed by deposition of 1.1 × 10^16 Ag atoms per cm². The substrate temperature during growth was 300 K. The solid line represents a fit to a Gaussian size distribution with a mean cluster size of ⟨d⟩ = 12 nm. SFM image (c) and size distribution (d) of the Ag particles after irradiation with 6000 laser pulses of λ = 355 nm and 6000 laser pulses of λ = 532 nm. The fluence was set to φ = 150 and 300 mJ/cm², respectively, and the angle of incidence was 45° with respect to the substrate surface normal. The solid line represents the size distribution calculated theoretically.

The drastic narrowing of the size distribution is also reflected in the optical spectra of the Ag particles, Fig. 2. They were measured at an angle of incidence of 45° with respect to the substrate surface normal with the p-polarized light of a Xe arc lamp combined with a monochromator and are dominated by two maxima which arise from the excitation of surface plasmon polaritons in the direction of the long [(1,1) mode] and short [(1,0) mode] axis of the particles. Their energetic positions reflect the mean size and shape of the clusters. The width is determined by homogeneous broadening arising from the finite decay time of the plasmon and an inhomogeneous contribution due to the above mentioned dependence of the plasmon frequency on the particle diameter. For particles as grown, the (1,1) mode has a rather large width of ΔE = 0.92 eV. After laser irradiation with λ = 355 and 532 nm, i.e., for the particles of Fig. 1(c), the resonance position is shifted to higher energy. This is consistent with recent investigations of laser-induced manipulation of optical properties of metal nanoparticles and is caused by the reduction of the mean size of the silver particles which is also reflected in the SFM images of Fig. 1. Due to the drastic decrease of the width of the size distribution, the shift is accompanied by a pronounced reduction of inhomogeneous broadening of the (1,1) mode. Its width converges to the homogenous linewidth of the plasmon resonance and now amounts to as little as ΔE = 0.35 eV.

The size manipulation has also been modeled theoretically with the objective of quantitative understanding and efficient optimization of the narrowing process. For this purpose, the absorption coefficient, the temperature rise, and the evaporation rate have been calculated as a function of cluster size. For computation of the absorption coefficient electrodynamical theory (quasistatic approximation) was used. The temperature rise was determined by solving the heat diffusion equation and the resulting evaporation rate during each laser pulse was calculated using the Arrhenius equation. Details of the model calculations will be published elsewhere. It is well known from earlier investigations that atoms located at the edges or perimeters of the oblate metal particles have particularly low binding energies and evaporate preferentially. This was taken into account by only allowing the long axis of the particles to shrink. In contrast, the length of the short axis was assumed to remain constant. As the next step of the calculations, the resulting changes of the initial size distribution [solid line of Fig. 1(b)] were determined. An example of the results of the modeling is shown in Fig. 3. For the cluster sizes studied here, the absorption coefficient follows the plasmon resonance and peaks at about d = 14 nm, if light of λ = 532 nm is used.
FIG. 3. Calculated absorption cross section and evaporation rate of Ag particles on quartz substrates as a function of diameter. The laser wavelength was set to (a), $\lambda = 532$ nm and (b), $\lambda = 355$ nm.

3(a)]. The corresponding rate of evaporated atoms is even more size selective than the optical absorption because of the exponential increase of the vapor pressure with temperature. Obviously, only particles with diameters above about $d = 13$ nm experience a temperature rise sufficiently large for evaporation of atoms and shrink in size. If a wavelength of $\lambda = 355$ nm is used in the calculations, particles with sizes between $d = 5$ and $9$ nm are depleted preferentially because of resonant plasmon excitation, [Fig. 3(b)]. Due to the increase of the vapor pressure as a function of decreasing particle diameter ($p \propto \exp(1/d)$) they are completely removed at the fluences used in our experiments.

Combination of the two wavelengths of $\lambda = 532$ and 355 nm in subsequent manipulation steps has also been treated theoretically. In fact, the theoretical size distribution [solid line in Fig. 1(d)] agrees almost perfectly with the measured distribution and also reproduces the value of the standard deviation of $\sigma^* = 0.13$. It should be pointed out here, that this value compares quite favorably to results obtained by deposition of size selected metal cluster ions ($\sigma^* < 0.3$),\(^{11}\) lithographically designed nanoparticles\(^{25}\) or nanostructure arrays grown on specially prepared substrates ($\sigma^* < 0.2$).\(^{26}\) Moreover, size distributions of metal particles with standard deviations below $\sigma^* = 0.20$ have not been reported previously for the size range considered here, i.e. for metal particles with diameters of around $d = 10$ nm.

In conclusion, our experiments illustrate the feasibility of controlled fabrication of monodisperse metallic nanoclusters on substrate surfaces through laser-stimulated narrowing of broad size distributions. The applied method relies on the size dependence of the absorption coefficient of metal nanoparticles. It can be applied to a wide range of desired cluster sizes as long as the frequencies of the optical absorption lines shift monotonously as a function of size. The gradient of this red or blue shift and the difference $\Delta \lambda$ of the used laser wavelengths determine the remaining width of the size distributions. Even if the plasmon resonance of the particles, however, is located far away from available laser photon energies or the clusters do not develop sharp plasmon resonances the overall $d^3$ increase of the optical absorption coefficient can be exploited to narrow the distributions. The ability to fabricate monodisperse metal nanoparticles of desired size opens up the possibility to examine the chemical and physical properties of clusters in future experiments and correlate them to well defined sizes. In addition, the particles can also be covered with a protective layer and taken out of the vacuum system in order to exploit them in technological applications including, for example, linear and nonlinear optical devices.

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18 This value agrees very well with that calculated from the SFM images by taking into account the overestimation caused by the radius of curvature of the SFM tip. From $2(2r_{eq}-h)^{3/2} = d_{SFM}^3$ a diameter of $d = 11.5$ nm is determined whereby $h$ denotes the measured height of the particles and $d_{SFM}$ their diameter as determined with SFM. Taking this overestimation into account, the particles of Fig. 1 are well separated from each other.
20 C. F. Bohren and D. R. Huffman, Absorption and Scattering of Light by Small Particles (Wiley, New York, 1983).
22 The heat is transported from the particles into the substrate and propagates there according to the heat diffusion equation. As a consequence, the temperature of the substrate surface increases. As a result, individual atoms that might reabsorb on the substrate evaporate and can not assemble to form metallic bridges between the clusters.