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Polarization dependence of the permanent deformation of silver nanoparticles in glass by ultrashort laser pulses

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Abstract. Glass containing spherical silver nanoparticles has been irradiated with single, intense, ultrashort laser pulses, with a wavelength corresponding to the surface plasmon resonance of the particles. After irradiation with linear polarization, dichroism is observed. Transmission electron microscopy studies reveal that these spectral changes are caused by deformation of the particles to anisotropic (in the TEM projection approximately ellipsoidal) shapes with an additional halo of small silver particles around the central one. The deformed particles are uniformly oriented with their longer axes perpendicular to the laser polarization. Using laser pulses with circular polarization, again a halo is formed around the particles, but the central particles remain spherical, and no dichroism was observed in the optical spectra.

PACS. 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes and nanocrystals – 81.40.Tv Optical and dielectric properties (related to treatment conditions)

1 Introduction

The properties of metal nanoparticles in various surroundings such as liquid or glass, and also of free clusters have been studied extensively during the last decades [1–6]. One of the main fields of interest is the dynamical behaviour of surface plasmon resonances (SPR) of the metal particles after high excitation with intense, ultrashort laser pulses [7–9].

Recently, we observed permanent spectral changes when irradiating intense femtosecond laser pulses on glasses containing spherical silver nanoparticles. In particular, using linear polarization, also dichroism could be produced. Both spectral analyses of the intensity dependence of the spectral changes and first electron microscopy studies suggested that the optical modifications are caused by changes of the form of the silver particles [10]. In addition, ultrafast single-color pump-probe experiments after SPR excitation revealed dynamical spectral changes on a time scale of 100 ps, which are assumed to be characteristic for these deformation processes [11].

In our previous investigations samples with a very steep gradient of particle sizes were used, which did not allow to find an unambiguous correlation between the orientation of individual particles and the laser polarization in the transmission electron micrographs. This kind of information was now obtained using a different kind of sample with a homogeneous distribution of particle sizes. The corresponding results are presented in this work.

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2 Experimental setup

The samples used for the experiments described here, consist of glass containing spherical silver nanoparticles with a mean radius of $\sim$ 12 nm, a size distribution of about $\pm 30\%$ and a volume fill factor of 10^{-4}. These samples are prepared from standard flat glasses of usual composition [12] by an ion exchange in a $AgNO_3$:$NaNO_3$ mixed melt. Subsequent heating to temperatures above the glass transition temperature T_g (600 °C), results in a chemical reduction of the silver ions, which then aggregate to spherical silver nanoparticles as shown in the top of Fig. 2.

These samples were irradiated with single laser pulses from an amplified, frequency-doubled titanium:sapphire-laser (wavelength 400 nm, pulse duration $\sim$ 150 fs, pulse intensity in the order of 10^{11} W/cm^2, linear or circular polarization). Optical extinction spectra were taken both in not irradiated and in irradiated areas of the sample with linearly polarized light, whose polarization was either parallel or perpendicular to the polarization of the laser pulse.

For structural characterization by electron microscopy, an array of single spots, 3×3 mm^2 in size, was produced on the samples, the spots (diameter 100 μm) being separated from each other by about 250 μm. Then the glass was thinned from the backside by mechanical polishing, dimple grinding and finally Ar ion beam etching until a small breakthrough was formed. During the final ion thinning step the samples were cooled to prevent any heating that could modify the laser-induced structural changes. The hole formed by the thinning procedure was of such a size

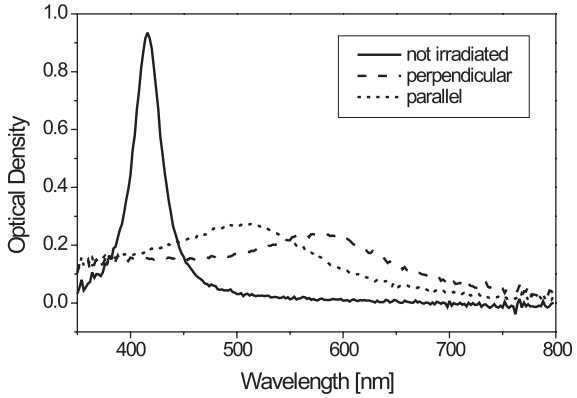

Fig. 1. Typical optical spectra of glass containing silver nanoparticle before (solid line) and after irradiation with a single, linearly polarized femtosecond laser pulse at 400 nm (dashed lines), where the measuring light was linearly polarized, once parallel with respect to the laser polarization, once perpendicular to it.

that its edge passes through at least one region irradiated by the laser pulses as well as a region where no irradiation occurred. Using successively higher magnification, the orientation of the TEM micrographs could be determined with respect to, *e.g.*, the macroscopic edge of the sample, thus also with respect to the laser polarization. However, due to the kind of preparation, the position of an individual picture can not be correlated to a distinct irradiation intensity. Transmission electron microscopy (TEM) was done by means of a JEM 100C operating at 100 kV. For structural characterization down to the atomic scale by high resolution electron microscopy (HREM) a JEM 4000EX operating at 400 kV was used.

3 Results

3.1 Irradiation with linearly polarized laser pulses

The glass samples containing silver nanoparticles show a characteristic optical extinction band as rendered in Fig. 1, with its maximum at 415 nm and a full bandwidth at half height (FWHH) of 34 nm. This band is caused by the surface plasmon resonance (SPR) of the silver particles (for details see *e.g.* [1]). After irradiation of the sample with a single laser pulse, the sample shows distinct permanent colour changes, which depend strongly on the local intensity evoked by the intensity profile of the laser pulse. These spectral changes have, for the case of polydisperse samples, been described in detail elsewhere [10].

A typical set of spectra from nearly the center of the laser spot is shown in Fig. 1. In contrast to the spectrum of the sample before irradiation, now anisotropic (dichroitic) behaviour can be seen, *i.e.* a dependence of the spectrum on the polarization of the analyzing light. Both bands show a significant shift of their respective band maximum to longer wavelengths with respect to the spectrum of the not irradiated area, accompanied by a strong broadening

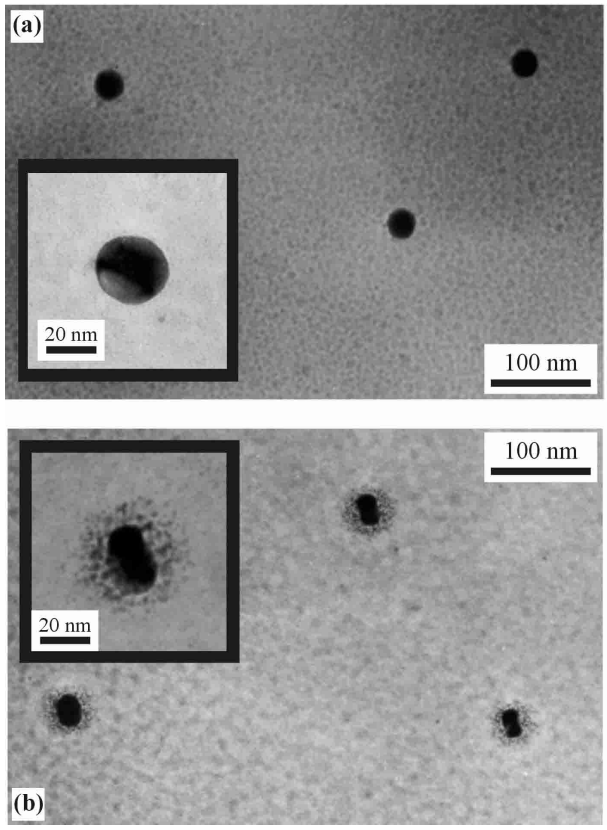

Fig. 2. TEM micrographs of silver particles in glass before (a) and after (b) irradiation with a single, linearly polarized femtosecond laser pulse at 400 nm.

of the band and a decrease of the peak extinction. Measuring the spectrum with light polarized parallel to the polarization of the femtosecond pulse, the band maximum is found at 510 nm (dotted line in Fig. 1), while for perpendicular polarization the band maximum is located at 575 nm (dashed curve). Both lines have a spectral width of more than 200 nm FWHH.

The nanoscopic situation in the sample before and after laser irradiation is shown in the TEM micrographs of Fig. 2: Fig. 2(a) shows a region of the original sample that contains spherical particles of crystalline silver with a radius of 15 ± 1 nm. These particles are separated from each other by a typical average distance of ten particle diameters and can therefore clearly be regarded as non-interacting with each other.

After laser irradiation, the particles exhibit modified forms (Fig. 2(b)): In the inset a single particle can be seen which shows an elongated, in the 2-dimensional projection of the TEM recording, nearly elliptical form. The size of the long axis of about 30 nm corresponds to the size of the particles before irradiation. The overview picture shows that all particles undergo similar deformations, with their long axes being approximately parallel to each other. The linear polarization of the laser was found to be perpendicular to this uniform direction of the long axes of the particles.

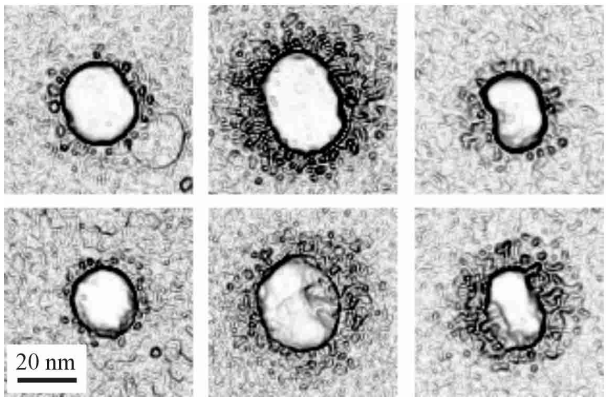

Fig. 3. TEM pictures of silver particles in glass after irradiation with a single, linearly polarized femtosecond laser pulse at 400 nm, numerically differentiated to enhance contrast. The bottom right picture corresponds to the inset of Fig. 2(b).

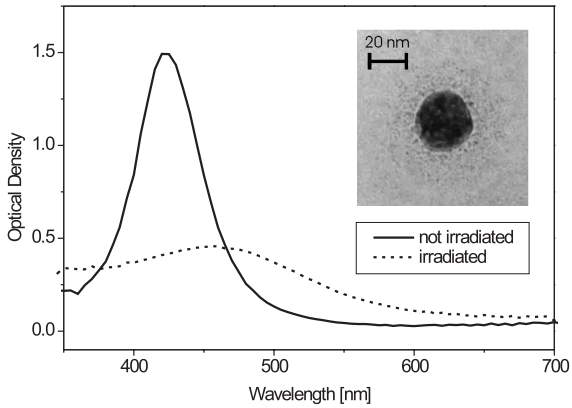

Fig. 4. Optical spectra of silver particles in glass before and after irradiation with a single, circularly polarized femtosecond laser pulse at 400 nm. Inset: TEM picture after irradiation.

In addition to these deformed central particles, a round halo of small silver particles can be seen around the large particles. HREM experiments (not shown here) yielded that these small particles also consist of crystalline silver and have diameters of 2-4 nm, with a next neighbour distance between the small particles and to the central particle of less than three diameters in any case. Accordingly, interactions between these small halo particles (and probably also with the core particle) have to be regarded in the interpretation of the optical spectra. In contrast to the elongated form of the central particles, the outer border of the halo region was found to be nearly spherical in all cases.

Fig. 3 shows pictures of additional particles from this sample, which were numerically differentiated to enhance the edges for better visibility. The relative orientation of all individual pictures in Fig. 3 is the same, and also coincides with that of Fig. 2. These pictures show that not all particles have an elongated shape after laser irradiation, but if they do show an aspherical form, the axes of the longest extension are all nearly parallel to each other and perpendicular to the laser polarization. Obviously the halo can have quite different diameters, but in each case its outline looks more spherical than reflecting the shape of the central particle. Please note that the shown micrographs were taken at different places within the sample, which might refer to different positions within the intensity profile of the laser pulse, and thus most probably have been irradiated with different intensities.

The left two pictures show particles with nearly spherical shape and a halo consisting of only one layer of small particles. The two middle pictures show ellipsoidal particles with a halo that has a diameter that is almost twice the size of the long axis of the central particle (top: particle 30 nm, halo 50 nm, bottom: particle 35 nm, halo 57 nm). The two pictures on the right show that an elongated form does not have to be ellipsoidal (in the TEM projection): In the top picture a dented ellipsoid can be seen, while the particle in the bottom one shows quite an irregular contour. Still, in both cases the outline of the halo is approximately spherical.

3.2 Irradiation with circularly polarized laser pulses

To verify that the linear polarization of the laser is indeed responsible for the orientation of the elongated particles, an identical experiment was carried out with circularly polarized laser pulses, *i.e.* irradiation without any directional preference. Here also, optical spectra and TEM pictures were taken (see Fig. 4). Other than with linear polarization, no dependence of the spectral changes on the polarization of the analyzing light was found, *i.e.* the spectra after laser irradiation are completely isotropic. But similar to the case of linear polarization, the spectrum after irradiation shows a distinct red-shift and broadening (maximum at 460 nm, bandwidth $\sim$ 180 nm FWHH).

This isotropic behaviour is reflected in the TEM pictures of this sample. One example is shown in the inset of Fig. 4: In no case could any anisotropic deformation be found, while many particles exist with a halo of varying diameter.

4 Discussion

Two different effects of laser irradiation have been found analyzing the TEM recordings: First, the formation of the halo and, second, the deformation of the central particle. The halo has been found not to reflect the shape of the core particle, but to exhibit a more or less spherical outline independent of the form of the central particle. Halo formation has been found upon irradiation both with linearly and with circularly polarized light. Accordingly the desorption of small particles forming the halo is obviously a feature which does only depend on sufficiently high intensity and, most probably, on the short duration of the laser pulses. As can be seen from the spectral analysis after irradiation with circularly polarized light, the formation of a halo in itself results in spectra, whose maxima

are at longer wavelengths than that of the original band. As the formation of a halo with laser pulses has so far not been described in literature, no theoretical calculations for the SPR band of a central particle with a halo of smaller particles are available to our knowledge. Instead the known case of homogeneously distributed interacting particles can only be taken for comparison, where the interaction of particles was found to lead to a red-shift of the SPR [13]. As the particles in the halo are near enough to each other to be considered as interacting, a similar effect might be involved in the observation of a red-shift of the SPR band due to halo formation.

When using linearly polarized laser pulses, in addition to the formation of the halo deformation occurs in the central particle. The originally spherical particles now show an elongated shape, where the longer axis is perpendicular to the laser polarization. As this effect does not occur after irradiation with circularly polarized light, this must be a particular feature of the linear polarization. Accordingly only here the irradiated area shows dichroism, where the spectrum taken with the polarization parallel to the longer axis has its maximum at the greatest wavelength. A similar splitting of the extinction bands has been calculated theoretically for spheroids of comparable size, but without halo [14]. But in contrast to the results shown here, the band corresponding to the short axis is blue-shifted in that case. This contradiction can be explained by the existence of the halo, which has already been discussed to be responsible for a red-shift of the SPR. It should however be considered that the presented TEM micrographs only give a 2-dimensional projection of the particle shapes on a plane perpendicular to the laser beam. No information about the third dimension can be derived from our results. So the observation of an elliptical projection could as well refer to a more disk-like particle shape with the disk axis lying in the plane of the TEM recording. Further experiments will be necessary to yield this information. But as the optical spectra are qualitatively characterized by the same projection of the particle shape, it can be stated that the presented results give a good qualitative agreement between the form changes of the particle induced by ultrashort laser pulses, and the corresponding optical extinction spectra. Still, details about the mechanism for the formation of the halo and the particle deformation have not been found so far, but can be expected from further work in this field, *e.g.* ultrafast time resolved experiments using a broadband continuum for probing, which are already being performed in our laboratory.

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