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# Laser modification of silver and gold nanoparticles in dielectric thin films

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Thin films of $SiO_2$ containing silver or gold nanoparticles were prepared by magnetron co-sputtering followed by thermal annealing. The concentration of metal in the films was determined by Rutherford backscattering. Laser treatment of the films was performed using the second or fourth harmonic of a Nd: YAG laser with a pulse length of 5 ns and frequency of 10 Hz. Laser fluences were below 125 mJ/cm$^2$. The changes induced in the films by the laser radiation were monitored by measuring the optical absorption. A marked difference in the effect of laser radiation on the nanoparticles in the case of Ag and Au was found. For silver, a laser induced fragmentation of the nanoparticles was observed and in the range of laser energies studied the final mean particle size scaled linearly with laser fluence without a major reduction of the amount of precipitated metal. In the case of gold, such a dependence on laser fluence could not be shown and in some cases the intensity of the surface plasmon resonance was greatly reduced. The mechanism of interaction of the laser light with the metal nanoparticles is discussed.

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## 1. Introduction

Noble metal nanoparticles have been much studied recently, because of their many potential applications in nanotechnology. Thin dielectric films containing such particles possess considerable third order optical non-linearity and could be used in non-linear waveguides and in all-optical switching. Recently it has been shown that noble metal nanoparticles have potential applications for enhancing the light coupling in silicon solar cells [1] and as plasmonic nanoheaters [2].

Laser radiation can cause changes in the size and shape of metal nanoparticles [3] depending on its wavelength, fluence, and pulse duration. It was demonstrated that silver nanoparticles formed in co-sputtered $SiO_2$ thin films can be fragmented with the second and fourth harmonic of a Nd: YAG laser at moderate fluences [4,5]. The mechanism of this phenomenon is not yet clarified in detail. In this paper, we report comparative results on laser fragmentation of Ag and Au nanoparticles. The differences in the effect of laser treatment on nanoparticles of the two different metals can give additional information on the fragmentation process.

## 2. Experimental

### 2.1. Deposition and treatment of the samples

Thin films of $SiO_2$ containing Ag or Au were deposited by magnetron co-sputtering in an Ar atmosphere. Chips of Ag or Au were placed on the $SiO_2$ target and the metal concentration in the film was varied by changing their number. The films were deposited on silica and Si substrates and their thickness was between 100 and 300 nm. The metal concentration in the films was determined by Rutherford backscattering (RBS). The concentrations used in these experiments were between 1 and 6 at. %. After deposition, the films were annealed in air at temperatures between 650 and 950 °C for 2.5 to 5 hours in order to form metal nanoparticles.

The metal nanoparticles were modified by laser irradiation with the 2$^{nd}$ (532 nm) and 4$^{th}$ (266 nm) harmonic of a New Wave Research Co. Nd: YAG laser with a pulse width of 5 ns at a repetition rate of 10 Hz. Laser fluences of 35 to 125 mJ/cm$^2$ per pulse were employed. The laser beam with diameter of 0.5 cm was scanned with a velocity of 8 μm/s on the surface, in such a manner that an area of 0.5 cm$^2$ was irradiated uniformly.

### 2.2. Information derived from the optical absorption spectra

The existence of Au or Ag nanoparticles was demonstrated by the appearance of the characteristic surface plasmon resonance (SPR) in the visible region. The optical transmission was measured at normal incidence using an Ocean Optics single beam fiberoptic spectrophotometer.

Au and Ag nanoparticles display a SPR band, the position and width of which depends on the nanoparticle size, shape and volume fraction. In previous studies [6] we have shown that for the case of Ag nanoparticles in $SiO_2$ thin films deposited in the way described above the Mie model in the dipole approximation, combined with a size dependent dielectric function for small metal nanoparticles, gives good fits to the spectra. As shown by Transmission Electron Microscopy (TEM) [5] the nanoparticles are spherical in shape, much smaller in size than the

wavelength of visible light and isolated from each other so that interaction between them can be ruled out. These conditions are a prerequisite for the application of the above model. In the case of Au nanoparticles in our samples, preliminary TEM results [7] show that they satisfy these conditions as well. By comparing the experimental SPR spectra with simulated curves based on the above mentioned model, an estimation of a mean nanoparticle radius (R) and a precipitated metal content in the corresponding sample can be derived.

## 3. Results

Fig. 1 exhibits the transformation of the SPR spectrum of a $SiO_2$ thin film containing 1.5 at. % Au and Au nanoparticles with R = 5 nm after laser treatment with the two laser lines - 532 nm and 266 nm, using the same fluence of 75 mJ/cm$^2$. It can be seen that there is a marked difference in the effect of the two laser lines. While the result of the 532 nm treatment is almost negligible, that of the 266 nm treatment with the same fluence is considerable – the mean radius of the particles becomes at least two times smaller and the amount of precipitated metal is somewhat reduced. The position of the laser lines is marked in the figure. As can be seen from the graphs, the absorption of the samples at the wavelengths of the two laser lines used for treatment is very similar.

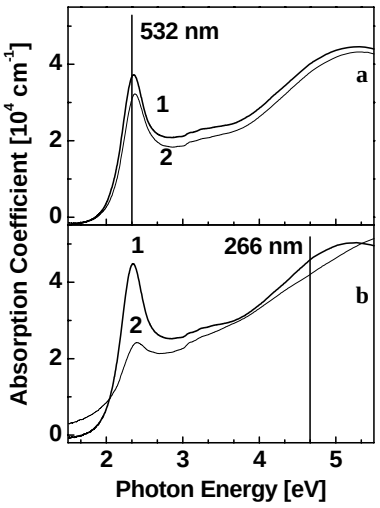


*Fig. 1. SPR spectra of Au nanoparticles in $SiO_2$ before (curves 1) and after (curves 2) laser treatment with 75 mJ/cm$^2$ at a) 532 nm and b) 266 nm.*

Fig. 2 shows the absorption spectrum before and after laser treatment (75 mJ/cm$^2$ of the 266 nm line) of Ag nanoparticles with an initial mean radius of about 5 nm in a $SiO_2$ thin film containing 5.9 at. % Ag. The analysis of the spectra using the Mie theory as described above shows that there is no reduction of the precipitated metal content while fragmentation of the nanoparticles has occurred and the radius is about 4 times smaller than the initial one.

Fig. 3 summarizes the results of several laser treatment experiments. The upper panel shows the decrease of the precipitated metal content in the samples, estimated from the ratio of the integrals of the SPR peaks before and after the laser treatment as a function of the laser fluence for Au nanoparticles (at 266 nm and 532 nm) and for Ag nanoparticles (at 266 nm). In the lower panel, the ratio between the sizes of the nanoparticles before and after laser treatment is shown. The initial mean radius of the nanoparticles for all experiments was about R = 5 nm.

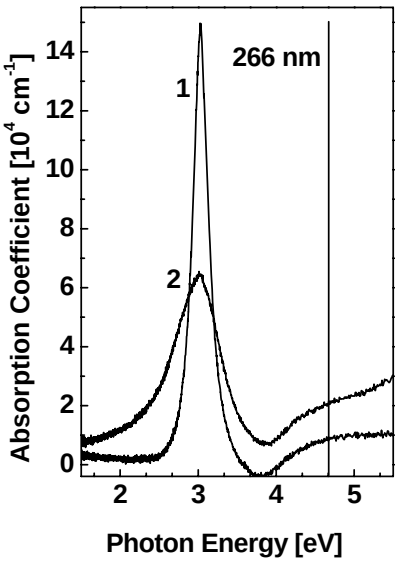


*Fig. 2. SPR spectra of Ag nanoparticles in $SiO_2$ before (curve 1) and after (curve 2) laser treatment at 266 nm with 75 mJ/cm.*

Several observations can be made:

1. The optically derived mean radius reduction is much stronger in the case of Ag than in the case of Au, and for Ag it clearly depends on laser fluence. For Au, a much narrower range of fluences was applied (45 – 75 mJ/cm$^2$) as below 45 mJ/cm$^2$ no effect was observed and above 75 mJ/cm$^2$ it was very likely for the films to be partially destroyed.

2. In the case of Au, the particle size and precipitated metal reduction is stronger as a result of irradiation at 266 nm compared to the effect of the 532 nm irradiation.

3. For Ag, there is no decrease of precipitated metal content in the interval of fluences used (35 – 125 mJ/cm$^2$).

## 4. Discussion

The first thing that is noticeable from the laser treatment experiments on Au nanoparticles in $SiO_2$ is the strong wavelength dependence of the effect of the laser exposure, given the fact that the absorption of the films at the two wavelengths is very similar. Even if the difference in absorption is taken into account, the treatment with the 266 nm line leads to a more significant nanoparticle fragmentation and a noticeable decrease in the precipitated

metal content (which is most probably due to the dissolution of some particles under laser radiation), while the application of the 532 nm line has hardly any effect.

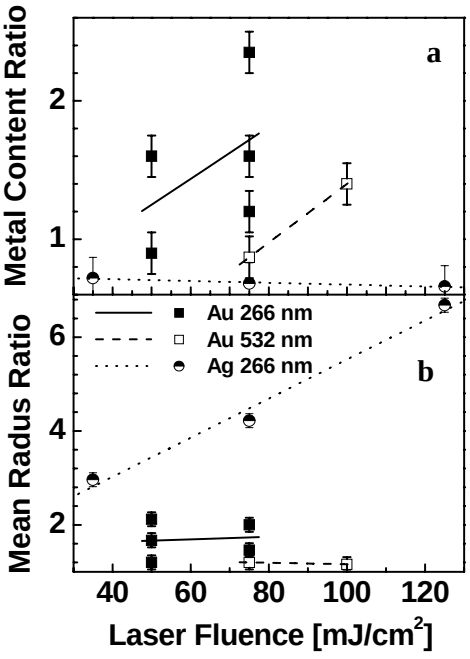


*Fig. 3. Ratio between the precipitated metal content (a) and nanoparticle sizes (b) before and after laser treatment as a function of laser fluence for Au and Ag nanoparticles of initial mean radius R=5 nm.*

One of the major differences between the two laser wavelengths used is their position in relation to the optical absorption spectrum of the Au nanoparticles. The 532 nm laser line is very near the SPR (Fig. 1a) while the 266 nm line is far away from it and in the region of the interband electronic transitions. As a consequence, there is a significant difference in the dependence of absorption at these wavelengths on the metal nanoparticle size. The absorption at 266 nm for a given precipitated metal content is largely size independent between R=1 nm and R= 10 nm, while the absorption at 532 nm decreases significantly with decreasing R as the SPR becomes broader and less intensive at its maximum. That is why the 532 nm line would act mainly on larger particles and the nanoparticle fragmentation itself would lead to a decrease in the absorption at 532 nm. The radiation at 266 nm would be absorbed by all sizes of particles, in proportion to their volume. That is probably one of the reasons for the stronger effect of the 266 nm laser treatment.

Using the approximation proposed in [8] for evaluating the heating of metal nanoparticles by laser radiation, it can be calculated that the intensity and pulse length of the laser radiation in our experiment are such that Au and Ag nanoparticles with R=5 nm are just heated but not melted or evaporated. In that case, fragmentation of a metal nanoparticle can take place due to excitation of its vibrational modes, leading to ejection of monomers or dimers [4] – a process called separation or dissociation of a nanoparticle, which has been observed for free particles or particles on a surface. Another possible mechanism of fragmentation is the ionization of the nanoparticle, leading to a surface charging which in turn causes it to disintegrate into smaller particles [9]. Separation or dissociation energies of metal nanoparticles are smaller than their ionization energies, and are reported to converge to the cohesive energy of the corresponding bulk metal [10] which is 3.79 eV for gold [11]. One 266 nm (4.66 eV) photon would be enough to supply that energy. Ionization of a gold nanoparticle would require at least two 266 nm photons and more than two 532 nm (2.33 eV) photons if we use the work function of bulk gold - 5.1 eV [11]. As processes requiring fewer photons are more probable than higher order ones, the 266 nm lines would be naturally more effective in gold particle dissociation and ionization.

In the case of Ag, one 266 nm photon is enough for the dissociation (2.94 eV [11]) and just enough for the ionization (4.3 eV [11]) of a silver nanoparticle. This could be a possible reason for the easier fragmentation of silver nanoparticles irradiated at 266 nm (Fig 2b).

If dissociation was the main mechanism for the fragmentation of Au and Ag nanopaticles irradiated at 266 nm we would not observe such a difference between the two types of metal nanoparticle, as one photon would be enough for dissociation in both cases. This is an argument that ionization could be an important process contributing significantly to metal nanoparticle laser assisted fragmentation in solid matrices.

## 5. Conclusion

We have performed experiments on the laser fragmentation on Au and Ag nanoparticles in two types of dielectric thin film. Two different laser lines were used. The higher effectiveness of the 266 nm line (as compared to 532 nm line) for laser fragmentation of Au nanoparticles is explained by the independence of the absorption at that wavelength on particle size (for a given metal volume fraction) and the lower number of photons required for particle ionization. Nanoparticle ionization could be a dominant mechanism, leading to metal nanoparticle fragmentation.

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