MICROSTRUCTURAL CHANGES IN GOLD NANOPARTICLES UPON PULSED LASER IRRADIATION. Lisa Eurenius(1), Yury Alaverdyan(1), Dinko Chakarov(1), Mikael Käll(1), Bengt Kasemo(1), Eva Olsson(1). (1) Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden.
Email: lisa.eurenius@fy.chalmers.se

Metallic nanoparticles interact with light by excitation of localized surface plasmons (LSPs). These plasmons have resonance energies that depend on the size and shape of the particle as well as on the properties of the surrounding medium [1, 2]. Irradiation with laser light at the particle plasmon resonance can be used for controlled modification of the particle distribution [3] as the resonant light stimulate either thermal- or photo emission of atoms from particles with certain sizes and shapes [4]. Together with diffusion of atoms on the substrate surface, this can result in changes in the particle shape and size distribution. This opens possibilities for fabrication and manipulation of optically active nanostructures. Within this work, we investigate the influence of laser light on supported gold particle distributions. The Au nanoparticles are prepared by Volmer-Weber growth, i.e. deposition of atoms and subsequent surface diffusion and nucleation. The particles are grown by electron beam evaporation onto substrates of fused silica and Si_3N_4 TEM windows, fabricated in-house [5]. The substrates are transferred to a vacuum system, where they are irradiated with the focused light from a Nd:YAG pulsed laser. The laser is equipped with an optical parametric oscillator (OPO), enabling tuning of the laser wavelength and thereby irradiation at the plasmon resonance frequency. The spectral response of the particles before and after irradiation is studied by optical dark field scattering microscopy (DF). The particle shape and size distributions are determined by analysis of images obtained by transmission electron microscopy (TEM) in combination with low vacuum scanning electron microscopy (LV-SEM) and atomic force microscopy (AFM). Changes in size, shape and crystallinity are studied as a function of laser wavelength, intensity and number of pulses. The as-grown Au particles are non-homogeneous in size as well as in shape before irradiation with pulsed laser light (see Fig. 1). The effect induced by the laser light depends on the fluence and wavelength of the laser. At low fluences, resonant particle plasmon excitation is expected to be the main mechanism for particle modification while at higher fluences, also thermal effects become important. Pulsed laser irradiation at fluences of about 0.3 J/cm^2 alter the shape and size distributions significantly (see Fig. 1). For these fluences, the number density of particles is reduced to approximately half of the initial value. Particles with originally non-regular shapes are seen to be faceted after irradiation and the ratio of major to minor particle axes has decreased, so that the particles appear more circular. An estimation of the amount of material present before and after irradiation indicates that the particles are nearly spherical after irradiation, given that no significant desorption has occurred. For lower fluences, the changes are less significant. The number density of particles is only slightly smaller than before irradiation and the particle axial ratio is less affected than in the case of higher fluences. Some faceting can be seen, but the effect is less pronounced. Optical DF measurements of the scattering efficiencies of non-irradiated and irradiated particle distributions show that the plasmon resonance of irradiated particles is blue-shifted. This indicates shrinking of the long axis, which agrees well with the results obtained using TEM. A probable process for the changes seen for these fluences is melting or partial melting, depending on the laser fluence. It has previously been reported that partial melting below the melting temperature for bulk material can cause reshaping and/or structural transitions in gold nanoparticles [6, 7].

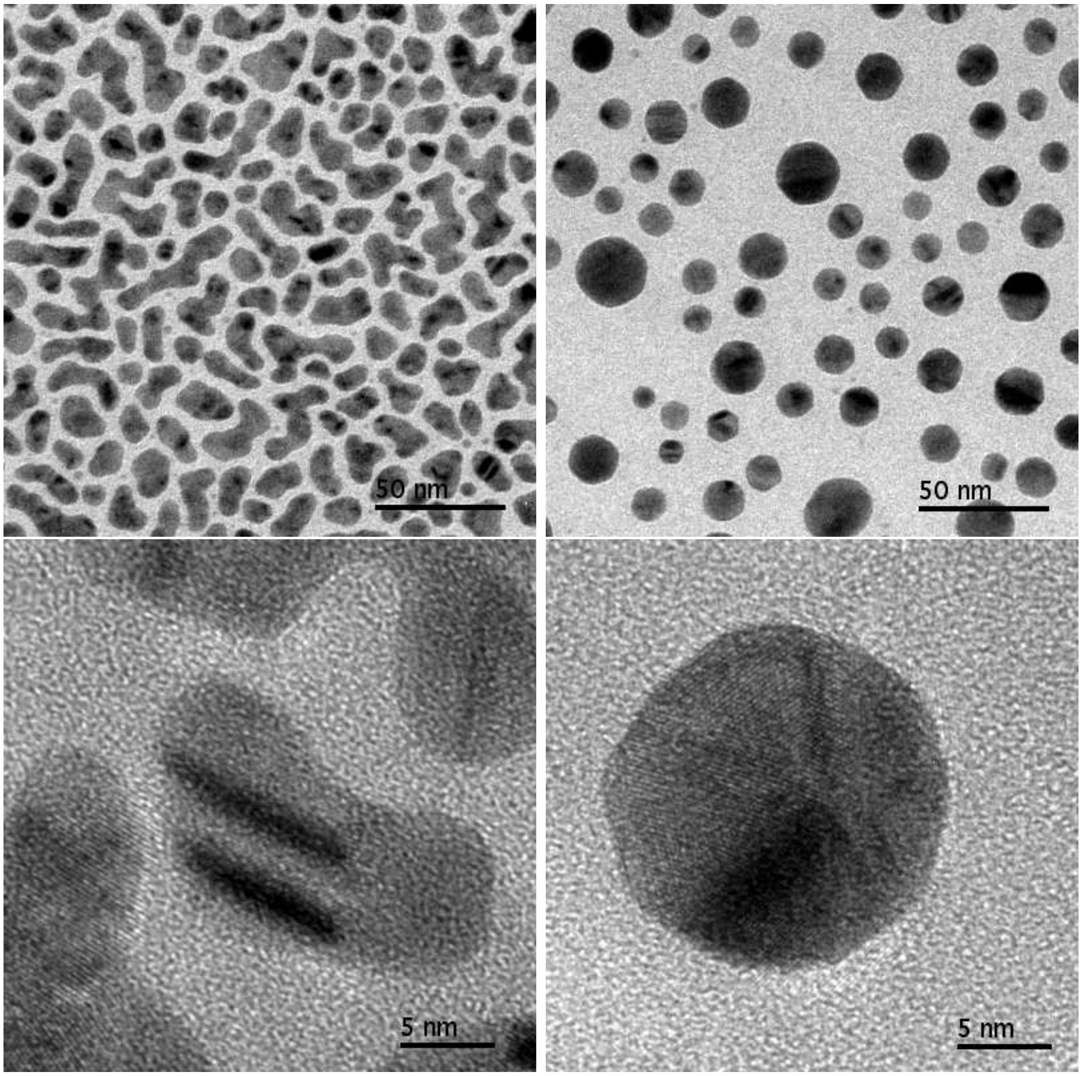

Figure 1: TEM micrographs of as-grown Au particles (left) and Au particles irradiated with three pulses at 532 nm (right) and a fluence of about 0.3 J/cm^2. The amount of Au evaporated equals a uniform layer of 3 nm, as measured with a quartz crystal microbalance (QCM).

References

[1] Zayats, A. & Smolyaninov, I. *Journal of Optics A* **5**, 16–50 (2003).

[2] Kelly, K., Coronado, E., Zhao, L. & Schatz, G. *Journal of Physical Chemistry B* **107**, 668–677 (2003).

[3] Bosbach, J., Martin, D., Stietz, F., Wenzel, T. & Trager, F. *Applied Physics Letters* **74**, 2605–2607 (1999).

[4] Stietz, F. *Applied Physics A* **72**, 381–394 (2001).

[5] Grant, A., Hu, Q.-H. & Kasemo, B. *Nanotechnology* **15**, 1175–1181 (2004).

[6] Koga, K., Ikeshoji, T. & Sugawara, K. *Physical Review Letters* **92**, 115507 (2004).

[7] Inasawa, S., Sugiyama, M. & Yamaguchi, Y. *Journal of Physical Chemistry B* **109**, 3104–3111 (2005).