

# RELATION BETWEEN PLASMONS, VIBRATIONS AND MORPHOLOGY OF SELF-ALIGNED SILVER NANOCOLUMNS

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The optical response of metallic nanoparticles (NPs) is known to be dominated by an enhanced absorption at the surface plasmon resonance (SPR). More recently, an enhanced Raman response of metal NPs related to SPR-optical vibration interactions has also been identified. This has led to intensive research due to its high potential for the study of organic molecules. In the case of silver, the SPR is spectrally well separated from the absorption due to the interband transitions which allows the study of its dependence on NPs morphological features such as size, shape or their dispersions.

In this work a comparison between the optical and Raman response of spherical NPs organized in layers and nanocolumns (NCLs) oriented perpendicular to the substrate is presented. The aim of the work is to investigate the interaction between surface plasmons and confined acoustic vibrations as well as their dependence on the nano-objects morphology. The specimens consist in silver nano-objects embedded in an amorphous  $\text{Al}_2\text{O}_3$  host prepared by alternate pulsed laser deposition on silicon and glass substrates. The specimens contain layers (separated by 2 nm of  $\text{Al}_2\text{O}_3$ ) of spherical NPs with  $2 \pm 0.2$  nm or NCLs with average diameter of  $2.7 \pm 0.2$  nm and height of  $6.7 \pm 0.2$  nm (aspect ratio of 2.5). The latter are produced by reducing the distance between consecutive layers of NPs until each metal "layer" interacts with the previous one leading to the self-assembling of NPs. This results in NCLs oriented in the direction perpendicular of the substrate.

The non-spherical shape of the NCLs is evidenced in the optical absorption spectra through the presence of two absorption peaks corresponding to transverse and longitudinal SPRs, respectively at lower and higher wavelengths than that of the spherical NPs. Under resonant excitation of the spherical NPs surface plasmons, a confined spheroidal-like vibrational mode ( $l=2, m=0, \pm 1, \pm 2$ ) is observed in the low frequency Raman spectra. In the case of the NCLs, for resonant excitation of the longitudinal SPR, a shift (with respect to the NPs) of the confined acoustic vibration band is observed. This band is assigned to a spheroidal-like vibrational mode ( $l=2, m=\pm 2$ ) of the NCLs. The vibrations frequencies calculated for NCLs and NPs using molecular dynamics simulations agree well with the measured frequencies. Moreover, the elongated shape of the particles and their self-alignment along the direction perpendicular to the surface, allowed investigating the Raman selection rules which shed light on the plasmon-phonon interaction.