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Acoustic vibrations in nanosized gold-shell particles

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Abstract. We demonstrate and discuss acoustic vibrations in spherical shell particles. The particles consist of 38-nm-thick gold shells, sandwiched between an inner silica core of 456 nm in diameter and an outer silica shell of 10 nm in thickness. Employing standard and asynchronous optical sampling (ASOPS) ultrafast pump-probe experiments, we excite acoustic vibrations of the shells and detect the oscillations via modulations of the optical reflectivity. Two kinds of vibrations were excited and observed. One oscillation with 400 ps period corresponds to the prediction of Lamb theory for breathing modes of free thin gold shells. The other oscillation with 25ps-period corresponds to resonant longitudinal thickness vibrations of the gold shells. At later times, echoes appear corresponding to the travel time through the silica core.

1. Introduction

Recently, vibrations of nanosized metallic structures generated by absorption of ultra-short laser pulses have attracted much interest. The conduction electrons are excited and subsequently decay by electron-electron interactions in tens of femtoseconds [1].Hot electrons thermalize with the lattice typically in a few picoseconds. The thermal expansion caused by such rapid heating creates mechanical stress in the metal and results in the excitation of acoustic vibrations.

Acoustic vibrations of solid nanoparticles can be observed both in time-resolved measurements [2] and Raman scattering experiments [3], and strongly depend on the size of particles. In this paper, we demonstrate time-resolved coherent oscillations of submicron, nanometer-thick gold shells, sandwiched between an inner silica core of submicro diameter and a nanometers thick outer silica shell.

2. Acoustic vibration modes

The problem of mechanical vibrations in a sphere was analyzed by Lamb [4].The wave equation for elastic and isotropic media can be expressed [5] as

$$(c_l^2 - c_t^2)\nabla(\nabla \cdot \mathbf{u}) + c_t^2\nabla^2\mathbf{u} + \Omega^2\mathbf{u} = 0 \ , \tag{1}$$

where $\mathbf{u} \sim \exp(-i\Omega t)$ is the lattice displacement, and Ω the angular frequency. Further c_l and c_t are the longitudinal and transverse sound velocities, respectively. For a spherical symmetry of

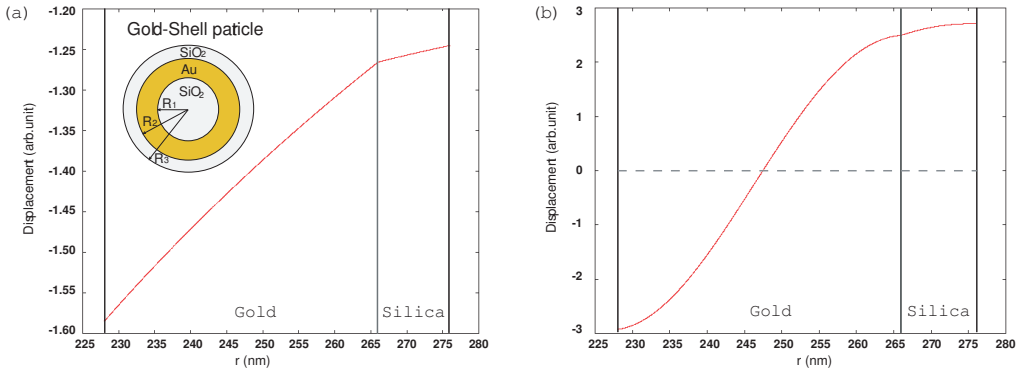

Figure 1. Calculated radial displacement along the double layers shells. (a) Lowest radial mode with a calculated eigenfrequency of 2.58 GHz. (b) The first higher harmonic mode with a calculated eigenfrequency of 41.1 GHz.

particles, the solution of Equation (1) is expressed in spherical coordinates (r, θ, φ). The radial displacements $\mathbf{u}$ has the form

$$u_r = \frac{\partial \Upsilon_{lm}(h_l r)}{\partial r} + \left\{ \frac{\partial^2 [r \Upsilon_{lm}(h_l r)]}{\partial^2 r} - r\nabla^2 \Upsilon_{lm}(h_l r) \right\}, \tag{2}$$

where $h_l = \Omega/c_l$, $h_t = \Omega/c_t$, and Υ_{lm} is the spherical distribution function,

$$\Upsilon_l m(kr) = \left(A_l \sqrt{\frac{\pi}{2kr}} J_{l+1/2}(kr) + B_l \sqrt{\frac{\pi}{2kr}} Y_{l+1/2}(kr) \right) \times P_{lm}(\cos\theta) e^{im\varphi - i\Omega t}. \tag{3}$$

Here A_l and B_l are constants to be determined from the boundary conditions, $J_n(kr)$ and $Y_n(kr)$ are the n-th order Bessel functions of the first and the second kind, respectively, $P_{lm}(\cos\theta)$ is the Legendre function with the angular numbers l and m. For the ground mode, $l = 0$, displacements are purely radial. Here we only consider the pure radial vibrational modes.

By applying the boundary condition at the interfaces for radial displacements u_r and radial components of the stress tensor [6]

$$\sigma_{rr} = \rho \Big[c_l^2 \frac{\partial u}{\partial r} + (c_l^2 - 2c_t^2) \frac{2u}{r} \Big], \tag{4}$$

the eigenfrequencies and normalized displacements can be numerically calculated.

Since the thermal expansion coefficient of gold is much larger than silica, the contact between gold and inner core is bound to be weak when the gold-shell is heated. Therefore we simplify the boundary conditions as a two-layer free shell, i.e. the gold-shell has a free inner boundary and a good connection with outer silica shell, that in turn has a free boundary at the particle surface. In the calculations, we used the longitudinal and transverse sound velocities for gold of $c_l = 3240$ m/s and $c_t = 1200$ m/s, respectively, and for silica $c_l = 5970$ m/s and $c_t = 3760$ m/s, respectively [8]. The particles have a 228-nm radius silica core, a 38-nm thickness gold shell, and a 10-nm thickness outer silica shell [7].

Figure 1. shows the calculated normalized displacements corresponding to the first two eigenfrequencies. The calculated eigenfrequency of the free double-layer shells is 2.58 GHz, which has 388 ps in period. This is the breathing mode in Lamb's theory [4]. The first higher harmonic of the radial vibration is 41.1GHz, which has 24.3 ps period. We notice that in Figure 1(b) one zero point appears and the displacement of the inner and outer boundary have different directions so that this mode corresponds to a thickness vibration.

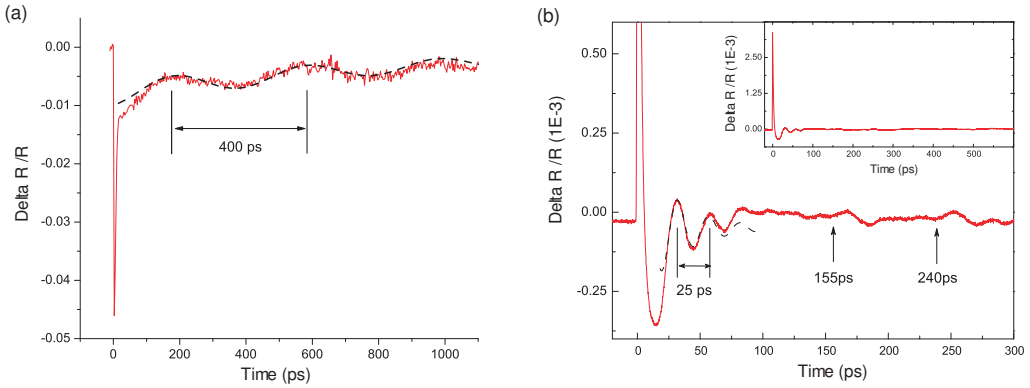

Figure 2. Transient reflectivity of a gold-shell photonic crystal following a pump pulse. Solid lines are experimental results, dashed lines are fitting curves. (a) is measured by the 1 kHz setup, probe wavelength is 670 nm, pump fluency 10 mJ/cm^2 laser pulse at 800 nm. (b) is measured by ASOPS, probe wavelength is 750 nm, pump fluency 0.01 mJ/cm^2 laser pulse at 820 nm. Inset is an expanded time scale of the measurement.

3. Setups and experiments

The gold-shell particles were fabricated by a multistep reaction [7]. First spherical silica particles were grown in a stepwise seeded Stöber growth process. Then gold nanoclusters of 1-2 nm in diameter were attached to the silica spheres and were put in a solution. This results in reductive growth and coalescence of the deposited gold nanoclusters and the formation of a closed thin gold shell. Finally capping the colloidal particles with an outer silica layer was achieved. A size dispersion of $< 5\%$ was deduced. The sample was carefully dried on a silicon wafer to produce a close-packed multi-layer array of particles.

Experiments were performed in two different setups at room temperature. The first setup employs a 120-fs pulse extracted from an 800-nm amplified Ti-sapphire laser operating at 1 kHz. The pump pulses were focused onto a 300-μm spot at the sample surface with a fluence of 10mJ/cm^2 per pulse. The transient reflectivity was probed by a white light generated by a split-off beam from the same laser pulse and coupled into a piece of photonic crystal fiber. The beam was passed via an optical delay line and focused onto a 40-μm spot at the sample surface in the pump light area. The reflected light was dispersed by a grating and a bandwidth of 20-nm 'single color' light from the reflected probe was focused onto a photodiode. The signal from the photodiode was read out and intergrated by a digital voltmeter over 10 μs.

The second setup is a pump-probe scheme with low excitation fluence employing asynchronous optical sampling (ASOPS) [9]. The ASOPS is a technique relying on two mode-locked femotosecond lasers at repetition rates of 1 GHz, that enables ultrafast time-domain spectroscopy without a mechanical delay line. Two mode-locked Ti:sapphire lasers are frequency stabilized and running with repetition rate f_R. They are linked at a fixed difference repetition rate Δf_R=10 kHz, and served as pump and probe lasers, respectively. As a result their relative time delay is continuously ramped between zero and $1/\Delta f_R$, which gives a 1-ns temporal measurement window with femotosecond time resolution. This method allows us to detect changes of the reflectivity of 10^{-7} with only a minute of data acquisition time. The pump and probe beams have a 50-μm focus size spot on the sample surface.

Two experimental traces are shown in Figure 2. In Figure 2(a),we employ the 10 mJ/cm^2 pump pulses at 1kHz repetition rate, and find a vibrational period of 400 ps (2.5 GHz) . Since this figure compares favorably with the calculated period of 388 ps, we interpret the vibration

as the breathing Lamb mode of the shell particle. In Figure 2(b), a vibrational period of 25 ps was observed in ASOPS. Here we pump it with only 0.01 mJ/cm^2 at 1-GHz repetition rate. The measured frequency fits very well with the first higher harmonic of the pure radial vibrational period of 24.3 ps and corresponds to a thickness vibration of the shell.

4. Discussion and conclusion

The close-packed organization of particles gives a symmetric environment, which only permits symmetric vibrational modes such as breathing mode and thickness modes. We note that the vibrational modes are independent of probe wavelength, it is remarkable that two different types of vibrations of the gold-shell particle were measured in two experiments. In 1-kHz experiments, both modes should be excited. Presumably, the noise level is too high to detect the thickness mode. Indeed, in the more sensitive ASOPS experiments, the thickness mode is clearly detected. However, the 1-GHz repetition rate destructively interferes with the 2.5-GHz breathing mode, reducing the amplitude of excitation because the internal damping time of the breathing mode is in nanosecond range.

The damping of the vibrations can be discussed in terms of inhomogeneous variations of the particle size, which is expressed by $\tau_d = r_s T/\sqrt{2}\pi\sigma_r$. Here T is the vibrational period, r_s the particle radius, and σ_r the particle size dispersion. We know $\sigma_r/r_s = 0.05$ [7]. Assuming the particle to particle variation of shell thickness has a comparable value as the variation of particle size, we obtain 740 ps and 110 ps for the breathing and thickness vibrational modes, respectively. In the experimental data, by assuming exponential decay, the measured damping times are 600 ps and 33 ps, respectively. For the breathing mode, the internal damping time thus is in the nanosecond range. However, the measured damping time of thickness mode is much shorter because echoes return to the surface from inner core at 75 ps with opposite phase, which leads to destructive interference, and a suppressed echo. Those echoes reappear in Figure 2(b) at time 155 ps and 240 ps with 25-ps period. The time separation between them is about 95 ps, which corresponds to the transfer time of longitudinal acoustic waves through the particle core. Although the free double-layer shell model explains our results well, the echoes imply that the inner core is not completely free.

5. Conclusion

In conclusion, we have observed two types of vibrations of gold-shell particles, which are driven by rapid optically induced thermal expansion. The experimental results correspond to the lowest and first higher harmonic mode of the pure radial vibration of free double layer shells. From the calculated periods and displacements, they can be interpreted as a breathing mode and a thickness vibrational mode.

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