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Surface Plasmon Mediated Interference Phenomena in Low-Q Silver Nanowire Cavities

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ABSTRACT

Optical excitation of surface plasmons in wet-chemically grown monocrystalline silver nanowires (~100 nm diameter and up to a few tens of micrometers length) is studied by broadband imaging spectroscopy. Surface plasmons excited by an incident light beam in the so-called Kretschmann–Raether configuration give optical interference phenomena in the spectral domain. These spectral oscillations are interpreted in terms of Fabry–Perot cavity modes for surface plasmons in silver nanowires and allow for a direct experimental determination of the surface plasmon group velocity and cavity losses.

In recent years the study of electromagnetic excitations at metal−dielectric interfaces, known as surface plasmons, has attracted a renewed significant interest. Surface plasmons (SPs) are electromagnetic excitations bound to and propagating along metal−dielectric interfaces accompanied by longitudinal fluctuations of surface charge density.[1] Since the discovery of the SP-assisted extraordinary high transmission through periodic arrays of subwavelength holes perforated in thin metal films,[2] SP excitation in metallic nanostructures remains in the focus of optical studies.[3,4] These studies can be very useful for a better understanding of electromagnetic interactions in metals but also of great importance for applications, especially in the rapidly developing fields of nanooptics and nanosensing.[5] Beyond the technological aspects, surface plasmons have been suggested for studies of fundamental quantum-optical phenomena using plasmonic nanocavities.[6,7]

One of the major characteristics of surface plasmons is related to their sub-wavelength confinement at metal surfaces and the ability to precisely tailor their propagation direction. Controlled propagation of surface plasmons has already been observed in lithographically produced thin metal stripes,[8,9] chains of metal nanoparticles,[10] and metal nanowires.[11−13]

In this work we report on the results of broadband optical spectroscopy on silver nanowires. We demonstrate that the analysis of surface plasmon mediated interference fringes by application of Fourier transform algorithms allows for a (i) precise determination of SP group velocity in silver nanowires over a broad spectral energy range between 1.2 and 2 eV, (ii) observation of multiple reflections of surface plasmons in such low-*Q* nanowire cavities, (iii) the possibility of identifying structural defects inside the nanowire. These results may be important for future design of nanoplasmonic devices and optimization toward higher quality factors in plasmonic nanocavities.

Silver nanowires with diameters of 100−500 nm and a few tens of micrometers in length were prepared by wet chemical synthesis. Briefly, platinum seeds ca. 5 nm in diameter were synthesized first by reducing $PtCl_2$ dissolved in ethylene glycol. Then, heterogeneous nucleation and growth of silver nanowires in the presence of polyvinylpyrrolidone as a surface modifier was achieved by adding dropwise silver nitrate to the ethylene glycol solution with Pt seeds at 160 °C. This procedure produced opaque gray−green colloidal solution containing silver nanowires and spherical nanoparticles that can be separated using size separation procedure. Silver nanowires were isolated from ethylene glycol solution, washed several times with propanol and redispersed in trichloroethylene or methanol. Once obtained, a droplet of silver nanowire dispersion was cast onto a standard 160 μm thick glass cover slide for optical microscopy and dried. The sample was then put onto a glass

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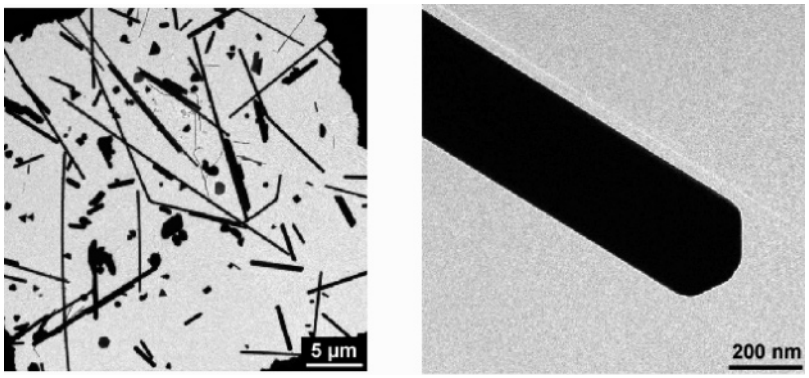

Figure 1. Transmission electron microscope images of silver nanowires used in the optical experiment. All wires are uniform in lateral cross section but differ in length. The high-resolution TEM image on the right side aims to demonstrate a very smooth nanowire surface and faceted tip.

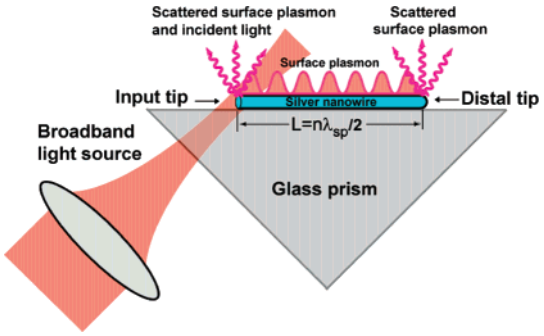

Figure 2. Scheme of the experiment. A beam of a spatially coherent white light source was tightly focused on the input tip of a single silver nanowire by a microscope objective. Alternatively, a nonfocused spatially incoherent beam from a halogen lamp was used to excite the whole nanowire. Light scattered/emitted from both tips of the nanowire was collected by a microscope objective (60X, NA = 0.85) and then spectrally dispersed with a grating monochromator and recorded with a liquid nitrogen cooled CCD.

prism with the index-matching silicon oil in between with the side covered with Ag nanowires exposed to air. Figure 1 represents TEM images of as-synthesized silver nanowires containing a fraction of other particles just before size separation. The silver nanowires are monocrystalline, 1-dimensional particles with well-faceted tips.

The scheme of the experimental setup is shown in Figure 2. Surface plasmons in silver nanowires were excited in the so-called Kretschmann−Raether configuration on a prism.[1] The light from a laser or a commercially available, spatially coherent white light source[14] was tightly focused through the prism on the nanowire tips by a long working distance microscope objective. The light scattered or emitted from the nanowire tips was collected by a microscope objective and focused either on the CCD camera or on the entrance slit of a monocromator coupled to a liquid nitrogen-cooled CCD camera. In this paper we mainly discuss the experimental data obtained when focusing the light on the input tip of the wire and collecting the scattering or emission from the input and distal nanowire tips as shown in Figure 2.

The orientation of the wires on the sample, the polarization direction of the incident light, and the position of the focal spot on the nanowire axes are crucial for the well-defined excitation of surface plasmons in silver nanowires. Only for nanowires oriented parallel to the incidence plane of the excitation light beam and for p-polarized light (vector of electric field in the incidence plane) were we able to observe a high-contrast interference fringes from both input and distal tips of the nanowires. This striking polarization dependence is in agreement with previously reported results on surface-plasmon-mediated interference effects in subwavelength double-slit structures in noble metal films[15] and silver nanowires[11,12] and confirms the control of direct SP excitation in our experiment.

Figure 3a reports an example of spectra taken at both nanowire tips of a wire excited with a coherent white light with p polarization. The pronounced periodic interference fringes are observed for both input and distal tips of a nanowire. Such spectral modulations are observed on many nanowires of different length and size and consistent with previously reported results interpreted in terms of Fabry−Perot cavity modes for surface plasmons.[11] To rule out the alternative explanation that the observed interference fringes originate from the interference of light directly scattered from both tips, several tests have been performed. First, the use of a spatially coherent white light source allowed us to focus the light on the input tip down to a diffraction limit, excluding the direct excitation of the distal tip. Second, the interference was also observed when illuminating the whole sample with the unfocused, but spatially incoherent light of a halogen lamp. Furthermore, light scattered by lithographically produced metal dots spatially separated from each other by 1−30 μm and aligned in the same way as silver nanowires, was measured in the same experimental configuration, giving no evidence of interference. The fact that the metallic point-like scatterers do not show the interference fringes under the same excitation conditions represents another evidence of the intrinsic plasmonic origin of the observed interference phenomena in silver nanowires.

Thus, silver nanowires act as Fabry−Perot cavities for surface plasmons and the interference fringes in the spectra are formed by many broad overlapping peaks corresponding to the longitudinal cavity modes for surface plasmons, bouncing back and forth between the input and distal tips of the nanowire (cavity mirrors). A large linewidth of the cavity modes can be explained by a very low *Q*-factor in such

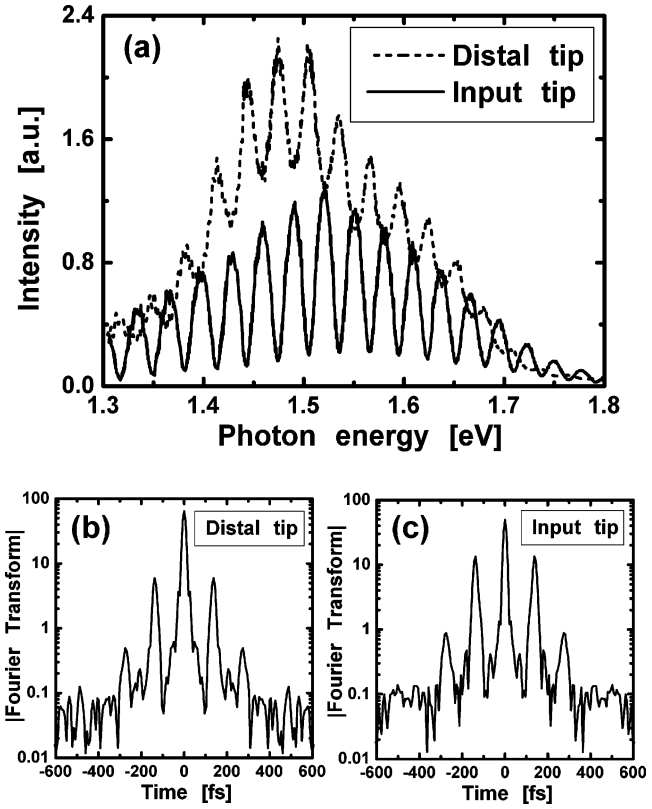

Figure 3. (a) Emission spectra from the two tips of a single 12 μm long silver nanowire. Both spectra were taken using a focused coherent white light source for the excitation of the input tip. (b), (c) Absolute values of the Fourier transforms of the two spectra presented in (a). Note that the horizontal axes in the Fourier transform domain are in time units and the sidebands mimic propagation of ultrashort surface plasmon pulses in such nanocavities (see text for details).

plasmonic nanocavity due to the short propagation length of surface plasmons at optical wavelengths (strong damping in the metal) and a small reflectivity of nanowire tips. To characterize the losses in such low-Q cavities, we analyze the Fourier transforms of the spectra according to the method theoretically proposed by Hofstetter and Thornton.[16,17] Parts b and c of Figure 3 show in a logartithmic scale the absolute value of Fourier transforms (FT) of the spectra presented in Figure 3a. The Fourier transforms of the optical spectra mimic the time evolution of ultrashort light pulses in such Fabry−Perot systems[17] with the horizontal axes in the time units. The clearly resolved first and much smaller second sidebands in the Fourier spectra correspond to single and double roundtrips of light in the Fabry−Perot cavity and contain information about surface plasmon propagation speed and cavity losses. From the ratio of the amplitudes of the first and the second sidebands (about factor of 10 for both Fourier transforms of the input and distal tips spectra) cavity losses during one roundtrip can be deduced. The currently still very large cavity losses of about 99% during one cavity roundtrip correspond to a very low Q-factor of such cavities. The cavity losses defined are the percentage of surface plasmon energy dissipated during one cavity roudtrip, originate from SP damping in the metal and SP emission/scattering into free-space radiation at nanowire tips. It should

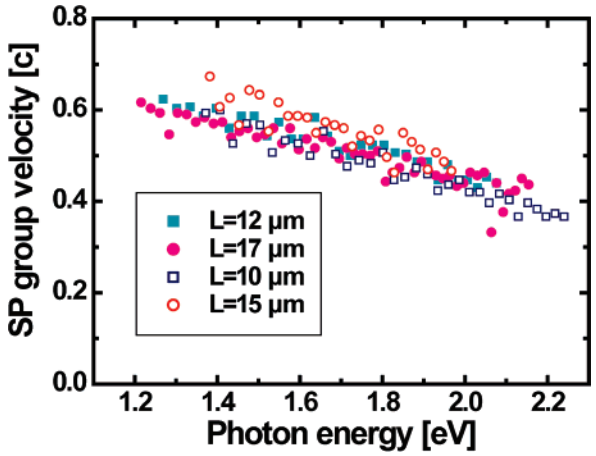

Figure 4. Spectral dependence of SP group velocity obtained by applying formula 1 to the spectra collected with the different excitation sources. Filled symbols: data collected with a spatially coherent broadband excitation source. Empty symbols: data collected under excitation with a halogen lamp. Different symbols correspond to different nanowires. The group velocities obtained for the two different excitation sources on different nanowires agree within the experimental error.

be noticed that in the case of large cavity losses the concept of the Q-factor itself becomes problematic or even obsolete. The obtained value for the cavity losses confirms the previously reported estimations made by Ditlbacher and coworkers on the basis of the contrast of spectral interference fringes in the emission spectra only from the distal tip.[11] Our analysis of the amplitudes of subsequent sidebands in the Fourier transform provides identical results for the spectra of both input and distal nanowire tips emission. Despite the very large losses in our silver nanowire cavities there is a great potential to reduce the losses in many different ways. First of all, a variation of the nanowire radius can help to increase the SP reflectivity by the nanowire tips. Second, working at longer wavelengths will help to reduce SP damping due to ohmic losses in the metal. Third, placing the nanowires inside a homogeneous dielectric medium could help to suppress SP radiative losses.

From the spectral dependence of the period of interference fringes in Figure 3a it is also possible to deduce the group velocity of surface plasmons. Using the same approach reported in literature for the dielectric photonic crystal cavities[18] and slit-groove pairs on metal films[19] the following expression can be derived for the group velocity v_{gr} of surface electromagnetic waves forming Fabry−Perot cavity modes:

$$v_{gr} = 2L\frac{\Delta\omega}{2\pi} = 2Lc\frac{\Delta\lambda}{\lambda^2} \qquad (1)$$

where L is the cavity (nanowire) length, c and λ stand for light speed and optical wavelength in vacuum, and $\Delta\omega = 2\pi c\Delta\lambda/\lambda^2$ is the frequency interval between two neighboring peaks in Fabry−Perot spectra.

Figure 4 shows the spectral dependence of the group velocity $v_{gr}(\omega)$ of surface plasmons in silver nanowires obtained using formula (1) from the analysis of interference

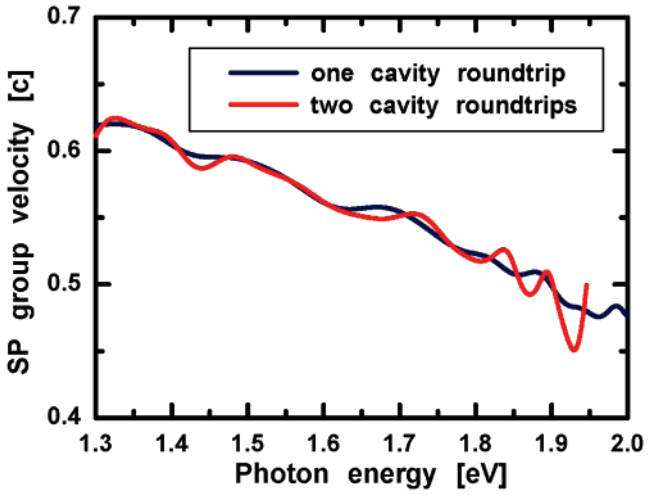

Figure 5. Spectral dependence of SP group velocity obtained by applying the Fourier-transform-based algorithm[19] to recover the phase of interference fringes presented in Figure 3a. The two curves were obtained from the analysis of the first and second sidebands in the Fourier transform domain shown in Figure 3b, corresponding to single and double roundtrips of surface plasmons in the silver nanowire cavity.

fringes. Spectra were obtained by excitation of silver nanowires with two light sources: spatially coherent laser-like white light source and spatially incoherent light of a halogen lamp. All curves obtained for many nanowires of different length ranging from ca. 10 to 30 μm coincide within the measurement accuracy. The group velocity of surface plasmons decreases monotonously from the value of 0.6*c* at 1.2 eV to 0.4*c* at 2 eV, which is typical for surface plasmon group velocity at flat metal−dielectric interfaces.[19]

The discussed spectral dependence of the group velocity can be alternatively obtained even with a better accuracy by applying the Fourier-transform-based algorithm to recover the phase of interference fringes in the whole spectral range.[19] Figure 5 shows the result of such reconstruction, where we have reconstructed the spectral dependence of the group velocity from the input tip emission spectrum in Figure 3a and applying the Fourier-transform algorithm to the Fourier transform shown in Figure 3b. We were able to obtain the correct group velocity not only using the strongest sideband in the Fourier transform (corresponding to the single roundtrip of surface plasmons in a nanowire cavity) but also using much smaller second sidebands (corresponding to two roundtrips in a cavity). Except for the small periodic modulations representing the artifacts of the Fourier transform reconstruction algorithm,[19] both curves coincide within the experimental accuracy.

The Fourier-transform-based analysis appears to be useful not only to characterize the losses and dispersion properties of low-Q cavities but also to reveal defects or imperfections in the cavities.[17] Figure 6a shows an example of a spectrum of light emitted by a tip of 20 μm long silver nanowire containing two different modulation periods. Both modulations were observed only when the wire was excited in *p* polarization, a fact that hints toward a plasmonic origin of both modulations. The application of formula (1) demonstrates that the modulation with a smaller period provides the same spectral dependence of the group velocity as shown in Figures 4 and 5. However, for the large modulation period in Figure 6a the calculated group velocity appears to exceed the light velocity in vacuum, which is obviously impossible. This large modulation period was occasionally observed for different nanowires, suggesting an explanation by a scattering center or defect inside the nanowire cavity. Indeed, a scattering defect in a cavity would lead to the modulation with a larger spectral period. In our case the presence of a scattering defect attached to a silver nanowire like a small metal nanoparticle or dust particle, which partially backscatters the propagating surface plasmons could explain the formation of a second Fabry−Perot subcavity with a shorter cavity length. The Fourier transform will contain sidebands of comparable strength as shown in Figure 6b corresponding to the two modulation periods discussed above.

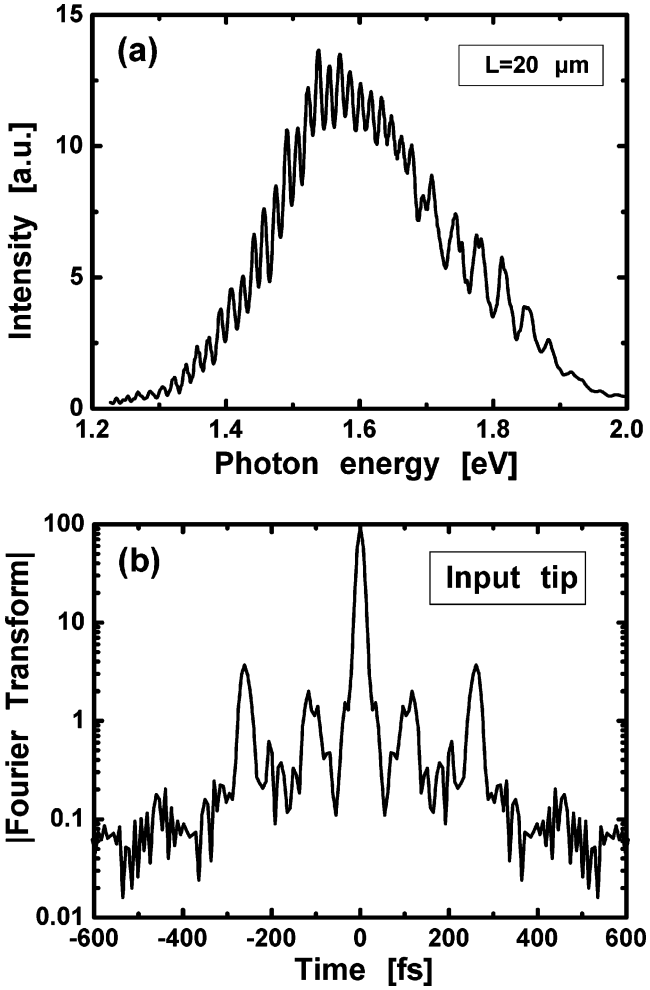

Figure 6. (a) Spectrum of the input tip emission of a 20 μm long silver nanowire contains two modulations with different periods corresponding to two sidebands of comparable amplitudes in its Fourier transform (b).

By applying the Fourier-transform-based algorithm[19] to recover the phase of interference fringes the spectral phase of both oscillations in the spectra could be recovered over the whole spectral range. Assuming that the large spectral oscillation period in Figure 6a (corresponding to smaller sidebands in the Fourier transform located at 120fs in Figure

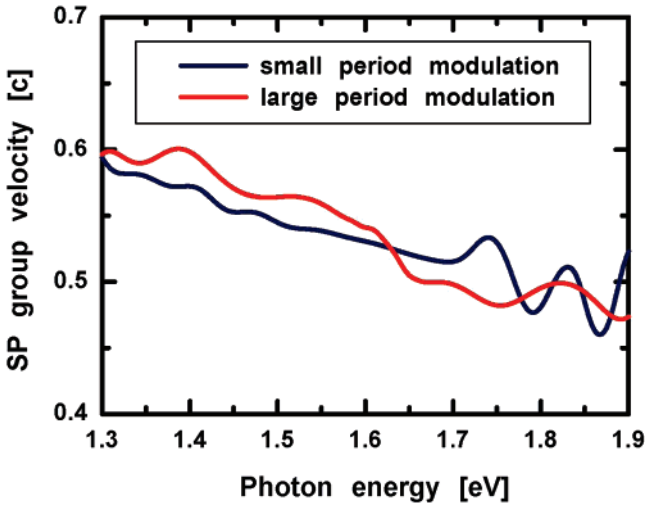

Figure 7. Spectral dependence of SP group velocity obtained by applying the Fourier-transform-based algorithm[19] to recover the phase of interference fringes presented in Figure 6a. The two curves were obtained from the analysis of the first and second sidebands in the Fourier transform domain shown in Figure 6b, corresponding to Fabry−Perot cavity mode in a 20 μm long cavity and 8 μm long subcavity (see text for details).

6b) originated from surface plasmon propagation in a shorter subcavity with the length of 8 μm the correct spectral dependence of the group velocity was obtained, as demonstrated in Figure 7.

In conclusion, we have analyzed SP-mediated optical interference phenomena in monocrystalline silver nanowires excited by broadband spatially coherent and incoherent light sources in the Kretschmann−Raether experimental configuration. Light scattered/emitted from both tips of the nanowire was collected and spectrally analyzed. Reproducible high-contrast periodic modulations in the spectra are found and explained as Fabry−Perot cavity modes in silver nanowires. The application of Fourier transform based algorithm allows for accurate determination of cavity losses and surface plasmon group velocity in these low-Q plasmonic nanocavities. The Fourier transform based analysis also allowed us to identify the formation of shorter subcavities by scattering defects inside the main plasmonic nanocavity.

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