# Plasmon dispersion relation of Au and Ag nanowires

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We have studied surface plasmon modes on silver and gold nanowires of a fixed cross section and different lengths, produced by electron beam lithography. The optically excited modes are determined by extinction spectroscopy and can be interpreted in terms of standing plasmon polariton waves. The eigenfrequencies are found to follow a dispersion relation similar to that for a planar metal/dielectric interface.

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## I. INTRODUCTION

An extended dielectric/metal interface can sustain propagating electromagnetic waves that are coupled to collective oscillations of the conduction electrons in the metal, so called surface plasmon polaritons (SPPs). Exciting SPPs with light, guiding them along the interface, and coupling them back into freely propagating light are processes of great current interest for the manipulation and transmission of light on the nanoscale. However, highly miniaturized integrated optical devices demand a lateral confinement of the light guiding structure.[1] Several concepts have been investigated for this purpose. Novikov and Maradudin proposed channel polaritons,[2] i.e., SPPs that are confined in the narrow groove of an otherwise planar surface. Ebbesen *et al.*[3] initiated an intensive discussion about the transmission of light through subwavelength apertures in metal films, and demonstrated the emission of a light beam with small angular divergence from a nanoscopic slit or cylindrical hole.[4] The guiding of light fields via a linear chain of metal nanoparticles was proposed,[5,6] and non-diffraction-limited light transport by gold nanowires has been shown.[7] Since for all these SPP systems the downscaling of the cross section is not limited by the light wavelength, they represent a promising alternative to dielectric optical waveguides. Thus, there is a substantial interest in the fundamental properties of SPP propagation in nanoscale structured matter, which is determined by the respective dispersion relations.

In contrast to the dispersion relation for a SPP at a planar metal/dielectric interface, which is well investigated theoretically and experimentally,[8,9] the dispersion of SPP modes in laterally confined metal films has to date only been investigated theoretically.[10–12] The experimental determination of the dispersion relation in such confined metal films with nanoscopic cross sections (nanowires) is a challenging task, since methods like, e.g., attenuated total internal reflection spectroscopy[8] cannot readily be applied due to the small size of the nanowires. We propose an alternate experimental technique: conventional extinction spectroscopy[13] enables the measurement of plasmon resonances in metal nanowires of finite length. Absorption and scattering within a nanowire give rise to an extinction band, the maximum of which serves to define the resonance frequency of the SPP mode.

In this paper, we report on the experimental determination of the dispersion relation for Ag and Au nanowires. We show that the multipolar plasmon resonances of metal nanowires can be described in terms of standing plasmon waves, allowing one to deduce the dispersion relation from optical extinction measurements. The proposed model is supported by additional investigations with a modified experimental setup.

## II. EXPERIMENTAL TECHNIQUES

We determined the extinction of gold and silver nanowire samples by measuring the optical transmission. To obtain a reasonable far field signal, one must use an (ordered) array rather than a single nanowire. The individual nanowires within an array should be highly uniform in shape so that inhomogeneous effects on the optical properties can be neglected.[14] This is possible via standard electron-beam lithography (EBL).[15]

Two different substrates ($1\times10\times10$ mm$^3$) have been chosen depending on the investigated spectral range. Transparency in the visible and the near infrared ($\lambda_0<5$ $\mu$m) is given by a fused quartz substrate ($n=1.45$), covered with a thin ITO (indium tin oxide) layer (thickness 3 nm) to provide a weak conductivity which is necessary for the EBL process. A glass substrate ($n=1.53$) doped with ITO through a 30 nm layer allows transmission measurements for wavelengths below 1.1 $\mu$m. In the first step of the EBL process a polymethylmetacrylat (PMMA) film with a typical thickness of 100 nm is spin coated on the substrate. A computer generated pattern is transferred in the PMMA film by the electron beam of an electron microscope (Jeol 6400). A wet chemical process removes the modified parts of the PMMA such that the residual PMMA film forms a negative mask. In a further step a gold (silver) film of desired thickness is deposited onto the mask by evaporation. Removing the mask with acetone re-

 

sults in gold (silver) structures of tailored shape and height that are arranged regularly on the substrate. Since we did not cover the nanowire arrays they are located at the air/substrate interface.

The extinction properties of such gold and silver nanowire arrays are measured over a wide spectral range utilizing two experimental setups. For light wavelengths $\lambda_0 = 500-1050$ nm we used a Carl Zeiss MMS1 microspectrometer coupled to an optical microscope.[16] In this spectral range the polarization of the exciting light is of crucial importance. Depending on the polarization different plasmon modes of similar energies are sustained by the nanowire. In this paper we are interested in plasmon modes that can be excited by the electric field component of the incident light that is parallel to the long axis $w_y$ of the wire. Another plasmon mode can be excited by visible light that is polarized parallel to the *short* axis $w_z$ as has been shown recently for gold and silver nanowires.[17] To avoid this short axis mode (which is not discussed in the following) we keep for all measurements reported here the electric polarization in the plane of incidence formed by the surface normal and the long axis of the nanowires. This requires particular care if the incident light wave vector is not perpendicular to the sample plane.

The measurements in the near infrared (NIR) ($\lambda_0 = 1-5\ \mu$m) are made with a Fourier transform infrared spectrometer (Perkin Elmer Spectrum 2001) and use unpolarized light. This is adequate in the NIR because resonances associated with plasmon modes along the short dimension $w_z$ only occur at higher energies. In both setups we measured the transmission of light incident perpendicularly to the sample plane. Supplementary measurements with tilted sample plane have been performed with the microspectrometer.

### III. RESULTS AND DISCUSSION

To start from the dispersion relation of SPPs propagating along a flat dielectric/metal interface, we recall that the SPP frequency depends almost linearly on the surface wave vector in the near infrared spectral range.[8] For visible light the dispersion curve increasingly bends to the right side of the light line and the frequency approaches the limiting value $\omega_{sp}$ given by $\varepsilon_0 = -\varepsilon_1(\omega_{sp})$, where $\varepsilon_0$ is the dielectric constant of the dielectric and $\varepsilon_1(\omega)$ is the real part of the frequency dependent dielectric function of the metal. In this spectral region a small variation in frequency leads to a significant change of surface wave vector. As an example, the SPP dispersion relation for an interface between semi-infinite glass and Ag (Ref. 18) is shown in Fig. 1.

Turning now to laterally confined structures, how should one interpret the plasmon modes that can be excited in such metal nanowires? Recall the excitations of a linear antenna of length $w_y$, illuminated by light polarized along its length. In the limit that the antenna material responds as a perfect conductor, its resonances in vacuum are set by the simple geometrical condition of standing waves: $w_y = j(\lambda/2)$, where $j$ is an integer and $\lambda$ is the wavelength. This can be re-expressed as

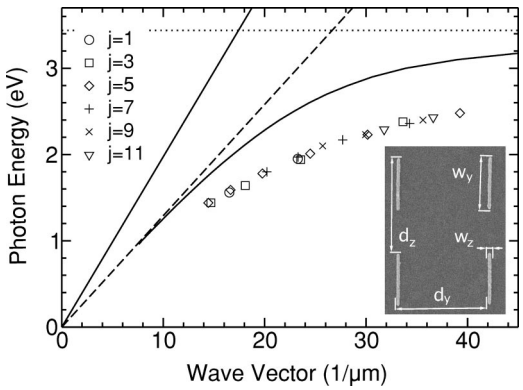


FIG. 1. SPP dispersion relations for Ag. Solid line: light line in vacuum. Dashed line: light line in glass. Solid curve: SPP on a flat silver/glass interface. Dotted line: limiting frequency $\omega_{sp}$. Symbols: photon energy vs $j\pi/w_y$ for Ag nanowires ($w_z = 85$ nm, $h = 75$ nm); the $j$ values are defined in the legend. The inset shows a SEM image with the sample geometry.

$$\omega = \frac{2\pi c}{\lambda} = c\left(\frac{j\pi}{w_y}\right) = cQ, \tag{1}$$

with $c$ the speed of light, $\omega$ the excitation frequency, and $Q$ the (standing) wave vector. We demonstrate now that an analogous dispersion relation underlies the optical response of nanowires. We do this by plotting the data as the excitation energy $\hbar\omega$ versus the surface wave vector $Q = j(\pi/w_y)$.

For the first illustration of such an analysis we use the extinction data from a previously published study of Ag nanowires.[13] The array geometry is shown in the inset in Fig. 1. The periods are $d_y = d_z = 2000$ nm and the total array fills a 100-$\mu$m square patch on an ITO doped glass substrate. The Ag nanowires have fixed width $w_z = 85$ nm and height $h = 75$ nm while their length $w_y$ is varied for different samples from about 100 to 1000 nm. The optical extinction measurements were performed with a microspectrometer, using light at normal incidence with its electric field parallel to the long nanowire dimension $w_y$. In Ref. 13 the data were plotted as resonance wavelength versus nanowire length $w_y$. This yields a set of curves which are distinguished by mode index.[19]

Here we plot the same data as photon energy versus $Q = j\pi/w_y$ to obtain the dispersion relation defined by the individual symbols in Fig. 1. The trend of the dispersion agrees well with that of a SPP on a flat Ag/glass interface, although we find a larger $Q$ for each $\omega$. Thus, for a given frequency $\omega$, plasmon propagation is slower in such Ag nanowires compared to a planar Ag/glass interface. We also find a smaller upper limit for the SPP frequencies on nanowires compared to their behavior on an extended metal surface. This shift of the dispersion relation of the nanowires with respect to that of a flat silver/dielectric interface is characteristic of curved geometries. It stems partially from an increased radiation damping of the plasmon modes. Note that only odd values of $j$ occur in Fig. 1. This selection rule holds exactly at normal incidence since the electric field $E_y$ then has even parity about the center of each nanowire. Modes

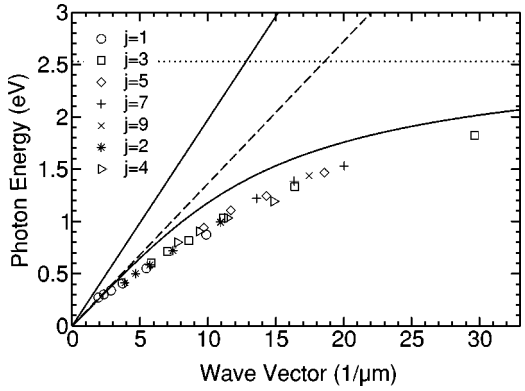


FIG. 2. SPP dispersion relations for Au. Solid line: light line in vacuum. Dashed line: light line in quartz glass. Solid curve: SPP of a thin gold layer on a flat quartz surface. Dotted line: limiting frequency $\omega_{sp}$. Symbols: photon energy vs $j\pi/w_y$ for Au nanowires ($w_z=91$ nm, $h=17$ nm), the $j$ values are defined in the legend.

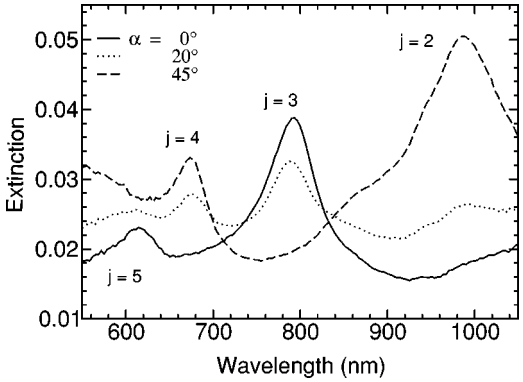


FIG. 3. Extinction spectra of Au nanowires ($h=50$ nm, $w_z=91$ nm, $w_y=575$ nm) for three angles of incidence $\alpha$.

with even $j$ have the opposite parity and can only be excited off normal incidence, as we illustrate below. It is remarkable in Fig. 1 that, independent of the nanowire length, all data points appear to follow a single dispersion. This behavior supports our standing wave picture. However, the interaction of an array of nanowires can influence the shape and spectral position of the extinction spectra. We infer from the smoothness of the dispersion curve that grating effects as reported in Ref. 20 can be neglected in this discussion. Furthermore, measurements in the visible spectral range revealed that a variation of the grating constant ($d_y=d_z=2,3$, and 4 $\mu$m) does not modify the dispersion relation significantly. The interaction of the individual nanowires in the NIR, where the wavelengths are larger than the distance between individual elements, deserves further investigation.

To examine whether this interpretation also works with other materials and over a wider frequency range, we have made an analogous study of Au nanowire arrays. The configuration is the same as in Fig. 1 but with $d_y=2100$ nm, $d_z=535$ nm, $w_z=91$ nm, and $h=17$ nm, while $w_y$ ranges from 90 to 1600 nm. For the substrate we chose fused quartz to provide optical transparency in both the visible and the NIR spectral range.

In Fig. 2 the data are plotted in the same fashion as in Fig. 1, and again there appears to be a single dispersion that underlies the measurements. In the NIR this dispersion relation is nearly linear and close to the substrate light line. At higher $Q$ the dispersion bends to the right and stays well below the limiting frequency of the SPP at a planar Au/quartz interface. Since the Au nanowire thickness is somewhat smaller than the optical skin depth, the reference SPP dispersion (solid line) is calculated for a uniform Au layer of thickness $h=17$ nm on a flat quartz surface.[21] This curve lies everywhere below the result for an interface between semi-infinite Au and quartz, but still above the results for the nanowires.

Building on the theoretical model introduced in Refs. 22 and 23, we have been able to simulate reasonably well the new extinction data.[21] The model describes the plasmon resonances in metal nanowires as surface current distributions in rectangular metal patches. For these calculations to succeed quantitatively one must account for all the geometric parameters ($d_y$, $d_z$, $w_z$, $h$, and $w_y$) and for the optical response of both the Au and quartz glass. Consequently, we do not have a simple formula for the resulting dispersion relation evident in Fig. 2, although we can numerically reproduce the points that define it.

An unexpected phenomenon occurs in the NIR measurements that deserves further comment: there are extra (weak) extinction peaks in between successive odd-$j$ modes.[21] Assigning these an appropriate even $j$ index (either $j=2$ or 4 in Fig. 2), the additional peaks also fit into the common dispersion relation. We attribute the appearance of these supposedly forbidden modes to the fact that for our measurements the incident light is not strictly incident along the normal. For both spectrometers a lens is used to focus the light onto the nanowire array. In the NIR the lens of the FTIR spectrometer brings in rays up to 9° away from the normal, while a maximum angle of 4.3° contributes to the measurements with the microspectrometer. We claim that this difference in the range of incident angles accounts for the weak extra peaks in the NIR and their absence in the visible.

To support this explanation we determined extinction spectra of nanowire samples in the visible for both normal and oblique angles of incidence. The investigated Au nanowires have a height of $h=50$ nm, but otherwise the same geometrical parameters as the Au samples of Fig. 2. The substrate is ITO doped glass. For oblique incidence we maintained the optical pathway of the microspectrometer and tilted the sample to various angles $\alpha$ between the long axis $w_y$ and the polarization of the incident beam, taking care to allow no light polarization along the $w_z$ axis. Indeed we then observe new extinction bands that can be assigned to even-$j$ modes ($j=2,4,6\ldots$). In Fig. 3 three exemplary extinction curves for $w_y=575$ nm are shown. While for perpendicular incidence only modes with odd ($j=3$ or 5) index are excited (solid line), additional extinction bands appear for oblique incidence ($\alpha=20°$, dotted line). These bands are attributed to SPP modes with an even ($j=2$ or 4) index and together with the modes of odd $j$ form a single dispersion curve (not shown here). If the sample is further inclined to ($\alpha=45°$) only the even modes are significantly excited. The $j=3$ mode disappears in this case since it is not excited favorably at this angle of light incidence. To understand this behavior

consider a plane wave incident on a nanowire. If the wave vector of the incident light is perpendicular to the long axis of the wire the electric field vector can be chosen parallel to the long axis. For this case the incident electric light field is constant along the entire length of the nanowire. Conversely, the strength of the electric field vector varies along the length of a nanowire for oblique light incidence. The electric field vectors can even be antiparallel for different sections of the nanowire. Therefore, the angle of light incidence allows or forbids plasmon modes of distinct $j$ values due to retardation along the long axis. Our findings that plasmon modes with even index $j$ can be excited by obliquely incident light and that their eigenfrequencies agree very well with the dispersion curve determined by the odd $j$ modes represent a strong corroboration of the standing wave interpretation.

In conclusion, we investigated the properties of SPP modes in short Ag and Au nanowires by optical extinction spectroscopy. The optically excitable modes can be described as standing waves, with the plasmon wavelength $\lambda_p$ set by the length $w_y$ of the nanowire: $w_y = j\lambda_p/2$. Changing the angle of light incidence changes the excitation efficiency for modes of different symmetry. However, modes of either symmetry follow the same dispersion relation for a metal nanowire with a fixed cross section and environment. The limiting frequency for SPP excitation is smaller than that on a flat metal/dielectric interface.

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