Versuchsprotokoll zum Versuch P441: White Light Spectroscopy of Gold Nanostructures
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Contents

1 Theory

1.1 Plasmons

Plasmons are the quantized plasma oscillations of the free electron gas density which occur in solid matter. Quantum-mechanically they are considered to be quasi particles analogous to what photons represent for electromagnetic waves.

A distinction is made between surface plasmons and localized surface plasmons. Surface plasmons can be observed in larger metal structures and are able to propagate within the structure. Localized surface plasmons on the other hand result from confining the plasmon in a structure which has a size smaller that half of the wave-length of the plasmon itself. In this experiment such a confinement is achieved with gold structures in the nanometer dimension. The most simply structure are gold discs of a few nanometers size which are periodically distributed on an insulator.

1.2 Material requirements

To excite localized surface plasmons in such a gold structure, an external electro-magnetic field is used. To achieve the excitement of plasmons, some more conditions have to be fulfilled. The internal field within a sphere in a vacuum is

$$\vec{E}_{\mathrm{int}} = \vec{E}_0 \frac{3\epsilon_{\mathrm{d}}}{\epsilon_{\mathrm{m}} + 2\epsilon_{\mathrm{d}}}. \tag{1}$$

Since $\vec{E}_{\mathrm{int}}$ depends on the dielectrical function of the material the resonance frequency of the plasma oscillation in a sphere depends on the dielectric function as well. This can be simplified to the requirement of

$$\epsilon'_{\mathrm{m}} = -2\epsilon_{\mathrm{d}}. \tag{2}$$

Gold and silver fulfill this material requirement.

1.3 Semi-classical model

By applying an external electro-magnetic field, the charge carriers within a gold sphere are separated as shown in figure 1. Thus, using an oscillating external field results in a oscillation of the charge carrier distribution, which leads to an emission of electro-magnetic radiation. These electro-magnetic waves are superposed with the external field. To excite plasmons the oscillation of the external field needs to be close to the resonance frequency. In this case the phase shift between the external waves and the waves emitted by the charge carriers is 180°. This resonance frequency depends on parameters like the sphere size and polarizability of the medium.

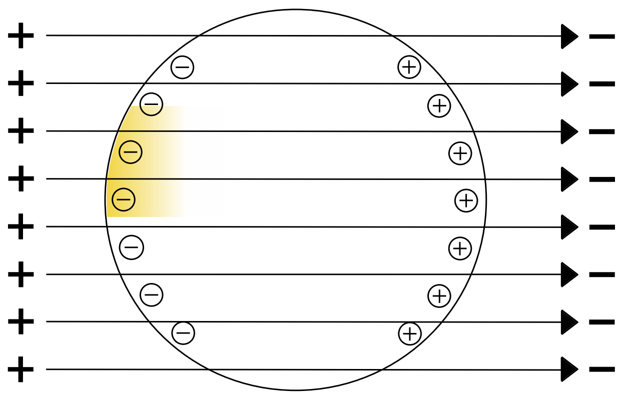

Figure 1: Distribution of charge carriers within the gold sphere with an external electro-magnetic field (Source: [1], page 5).

1.4 Size dependence and behavior of ellipsoids

Increasing the sphere size changes the resonance frequency. Since a resonance occurs when the the oscillating particles within the sphere form a standing wave. For a larger sphere radius, this wave length is larger and hence the transmission minimum has to shift to a longer wave length as well.

When looking at ellipsoids, two effects have to be considered. Assuming the stimulating radiation is polarized along the major axis of the ellipsoid, increasing the length of that axis will shift the transmission minimum to a longer wave length. In case of a polarization perpendicular to the major axis, the transmission minimum moves to a shorter wave length. This behavior is a result of the polarizability of an ellipsoid:

$$\alpha_{\mathrm{i}} = \frac{V_{\epsilon_0}}{Li} \frac{1 - \epsilon \mathrm{m}}{L_{\mathrm{i}}^{-1} + \epsilon_{\mathrm{m}}}, \mathrm{i} \in \{x, y, z\} \tag{3}$$

with $L_x + L_y + L_z = 1$ and L_{i} being the length of one side of the ellipsoid. Increasing the length of the major axis results in a decrease of the length of the other axes.

1.5 Coupling of localized surface plasmons

In figure2 two neighboring gold disks with interacting electric fields and polarization along the major and the minor axis are displayed. The polarization along the major axis results in a decrease of the force between the positive and the negative charges of the disks. This is proportional to r^{-2} (where r is the distance between the disks). This decrease shifts the transmission minimum to a longer wave length. For a polarization along the

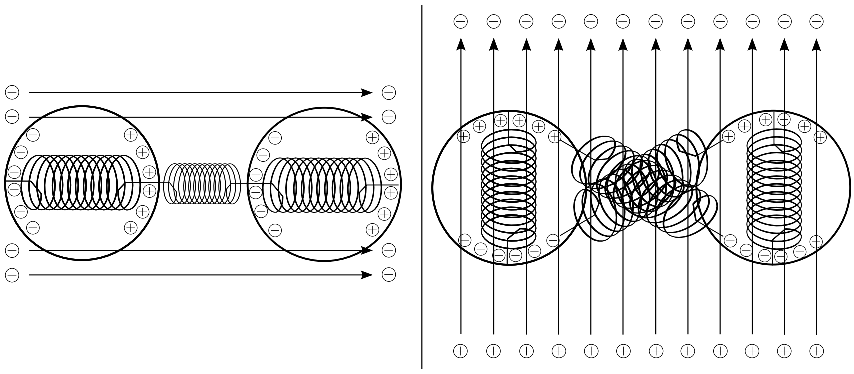

Figure 2: Visualization of particle plasmon coupling with polarization along the major axis (left) resp. along the minor axis (right). (Source: [1], page 8).

minor axis, the forece between the charges is increased, and therefore the transmission minimum moves to a shorter wave length.

One pair of plasmons is called a *dimer*. An object consisting of five plasmons is called a *pentamer*. Figure 3 shows two different normal modes

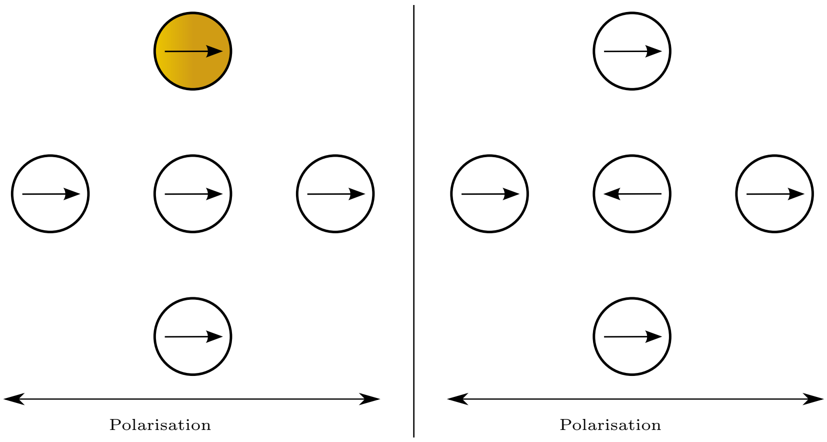

Figure 3: Pentameters with bright mode (left) and dark mode (right). (Source: [1], page 10).

of vibration. The interfering of these modes results in a *Fano resonance* (see figure 4.

1.6 Lattice effects

Since the a periodically arrangement of the gold disks is used, diffraction effects have to be considered as well. Bragg's law says that radiation of the

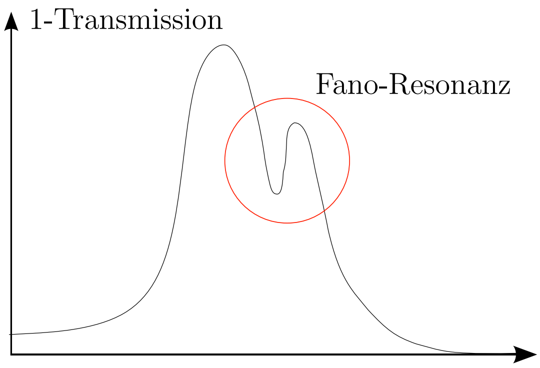

Figure 4: Fano resonance from two interfering modes. (Source: [1], page 10).

wave length

$$\lambda = n \cdot a \tag{4}$$

is suppressed due to diffraction effects. Here the material is glass, therefore we have: $n = 1.5$.

2 Setup

The setup is illustrated in figure 5.

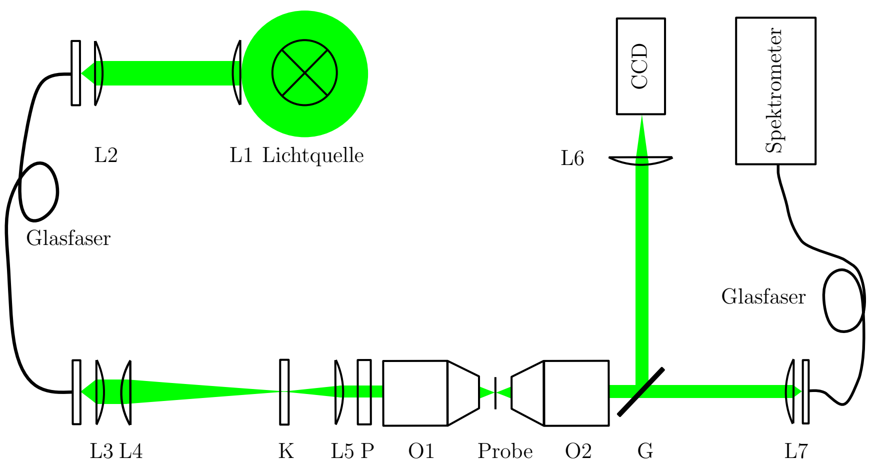

Figure 5: Setup (Source: [1], page 12).

It took a long time to arrange all parts as needed. We had mainly problems finding the focal plane of the lenses and adjusting the lenses to get a near-parallel stream of light.

3 Measurement

During the measurement, it happened multiple times, that a recorded spectrum was in some parts significantly above 100 percent of the reference spectrum. This happened, at least once, after bumping into the table the experiment was on. This was corrected with a new reference measurement through glass alone.

4 Analysis

The difference between the recorded transmission spectra seen through the nano structures and trough regular glass are illustrated in figure 6. The spectra through the nano structures are slightly darker everywhere in the spectrum. Apart from that, a further difference between the spectra is observed, that is concentrated around some wavelength (in figure 6 around 700 nm or 800 nm).

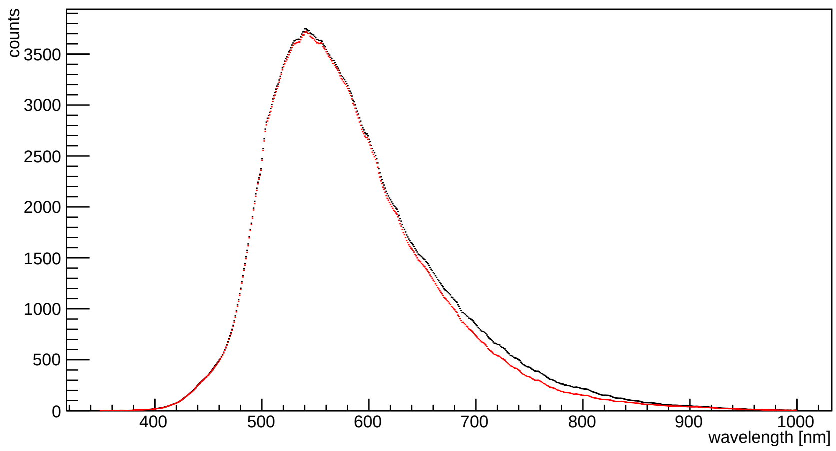

Figure 6: Comparison of a spectrum through glass and through gold nano structures (A1, 0 deg).

To further analyse these differences, the recorded transmission spectra through the nano structures are recorded in percent of the regular spectrum through glass. To create figure 6, we recorded the dark spectrum and the reference spectrum through ordinary glass. We then substracted the dark spectrum from the reference spectrum (black) and calculated the same curve wheighted with the transmission-percentage of one measured set (A1, 0 deg).

4.1 Disks with Variable Diameter (Row A)

This row contains four different structures, all with a lattice constant of 400 nm. In figure 8 and figure 9 we see these recorded spectra, fitted with a negative gaussian function to estimate where the minima are.

$$Fit = 100 - \alpha \exp\left(-\frac{1}{2}\left(\frac{x-m}{\sigma}\right)^2\right) \tag{5}$$

The perturbations at the beginning and the end of the spectra are probably due to the fact, that the accuracy of one count in the spectrum with respect to the percentage of the transmission is different for different wavelengths. This may be explained with figure 6. It is clear, that in the regions below 425 nm and above 925 nm a difference of one count in the reference spectrum and in the measured spectrum has a much greater effect on the percentage of transmission, than around, for example, 550 nm. So the error in the recorded spectrum is dependend on the overall counts for the current wavelength.

Due to this fact, not all values of the spectra were taken for the fit. This point where the last value to the right was taken into consideration for the fit, was estimated by the closeness of the fitting curve to the spectrum, where the spectrum seems to have minimal perturbations.

If all points up until and including the one for 1000 nm would have been taken into consideration for the fit, the minima would shift to slightly greater wavelengths.

In figure 7 we see the position of these estimated minima as a function of the disk size. As expected in the semi-classical model, the wavelength of the minima increases as the size of the disk increases. The slightly higher slope in the spectra for the 90 deg polarization (red curve), may be in the range of error, since we would expect these curves to be the same, due to the symmetry of the disk sizes an arrangement in both directions.

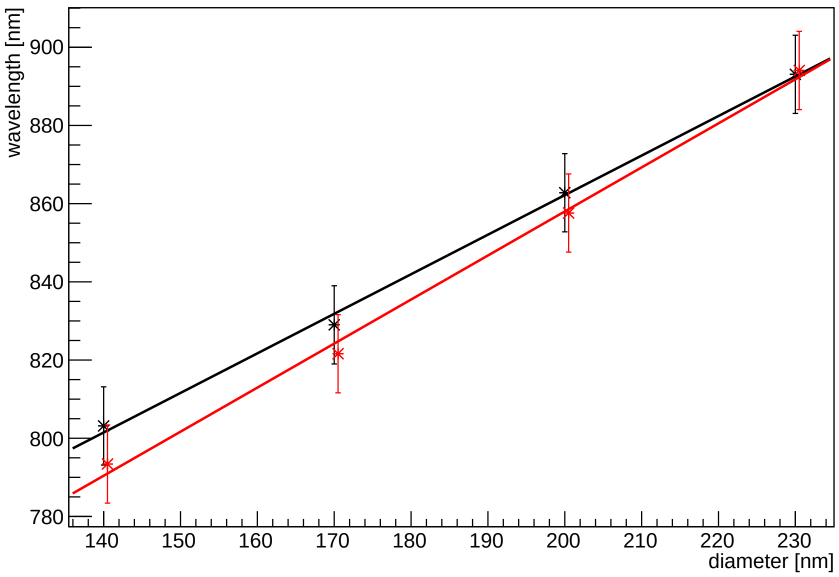

Figure 7: Position of transmission minima as a function of the disk size.

It should be noted, that the maximum percentage of blackout for the transmission are different in both polatizatin directions. This must be due to the setup of the experiment, again for symmetry reasons.

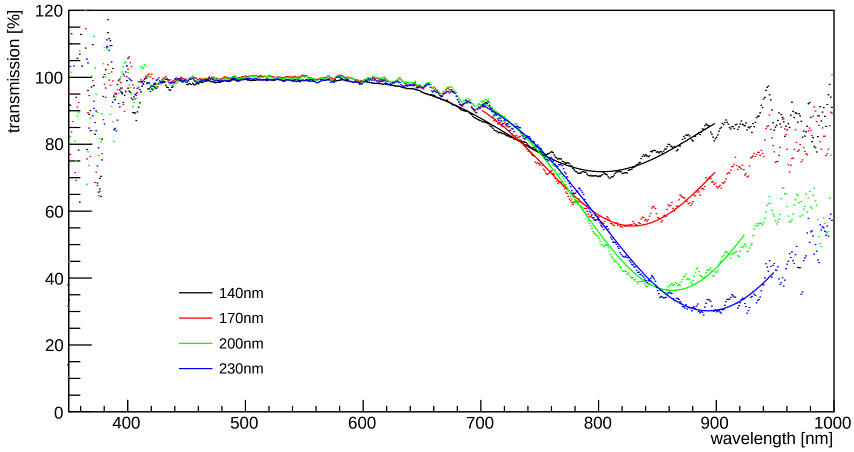

Figure 8: Transmission spectra of row A with a polarization angle of 0 deg.

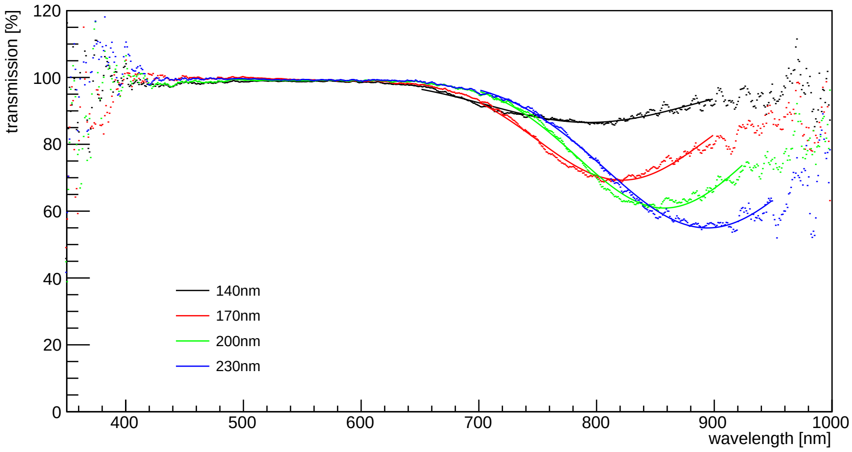

Figure 9: Transmission spectra of row A with a polarization angle of 90 deg.

4.2 Dimers with Variable Mid-to-Mid Distance (Row B)

The row B consists of dimer structures with different mid-to-mid distances, varying from 250 nm to 450 nm in steps of 25 nm.

Just like for row A, the transmission minima were determined via a gaussian fit, as seen in figure 11 and figure 12. The wavelength of those extracted minima as a function of the mid-to-mid distance of the dimers can be seen in figure 10 (red for 90 deg).

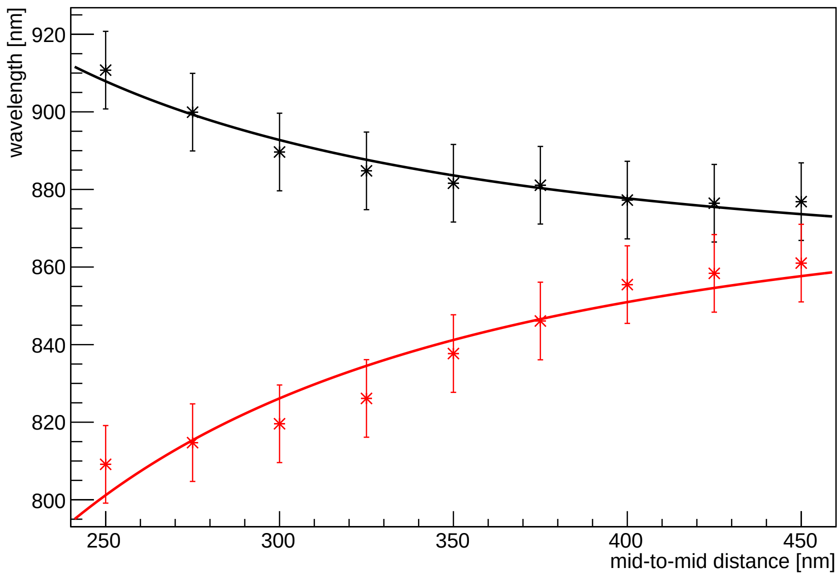

Figure 10: Position of transmission minima as a function of the mid-to-mid distance of the dimers.

This depencence is fitted via a $1/\Delta y^2$ curve, to see if it meets the theory, as follows.

$$Fit = \frac{\alpha}{\Delta y^2} + c \tag{6}$$

The fit curve for the 0 deg polarization (black line) fits quite nicely to an $1/\Delta y^2$ fit. The errors on the minima of the wavelength are a rough estimate from taking a look at the transmission curves in figure 11 and figure 12, ± 10 nm.

The fit curve for the 90 deg polarization (red line) on the other hand is rather bad in comparison. Without the fit it looks more like a straight line. The reason for this is probably some other influence in the spectra in higher wavelengths above 850 nm or 900 nm, which can be seen in figure 12. The gaussian fit does not quite work here, the curve does not return to a height somewhere near 100 percent. This might be due to some other absorbtion of the white light in gold. This yields in a higher shift to a greater wavelength of those minima, which would be at a higher wavelength without this influence anyway. This might explain the difference between the quality of the fit curves.

There is nevertheless a clear decrease for the 0 deg polarization and an increase for the 90 deg polarization.

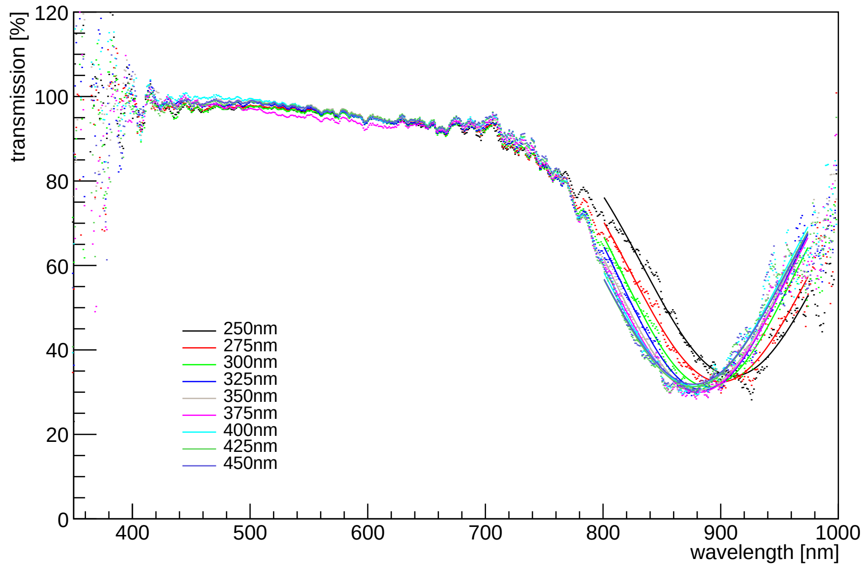

Figure 11: Transmission spectra of row B with a polarization angle of 0 deg.

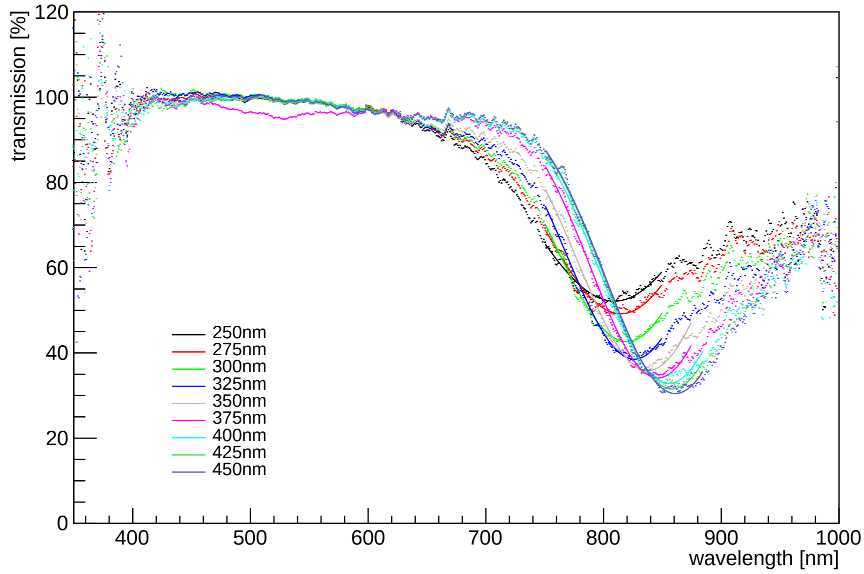

Figure 12: Transmission spectra of row B with a polarization angle of 90 deg.

4.3 Disks with Variable Period (Row C)

The disks in this sample all have a diameter of 200 nm with a variable mid-to-mid period from 300 nm to 500 nm in steps of 25 nm. As with the other rows, we fitted gaussian funcions on the spectra to determine the minima. When plotted against the mid-to-mid distance (figure 11), there seems to be a distance for which the wavelength is at a minimum. This might be due to the superposition of coupling alongside and perpendicular to the major axis (both $1/d^2$). Here fitted with a polynome of second degree, just to illustrate the minima.

Due to symmetry, the spectra seem similar (figure 14 and figure 15).

90 deg 150 nm figure 12

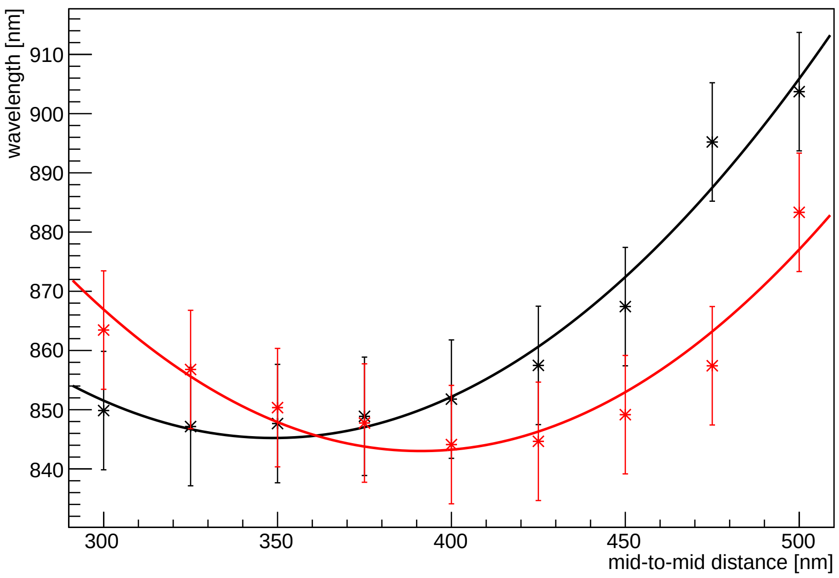

Figure 13: Position of transmission minima as a function of the mid-to-mid distance of the dimers.

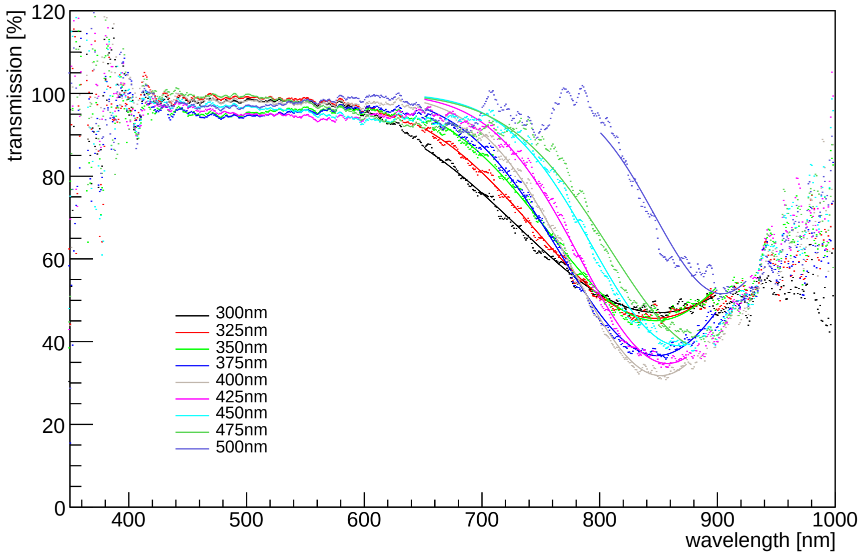

Figure 14: Transmission spectra of row C with a polarization angle of 0 deg.

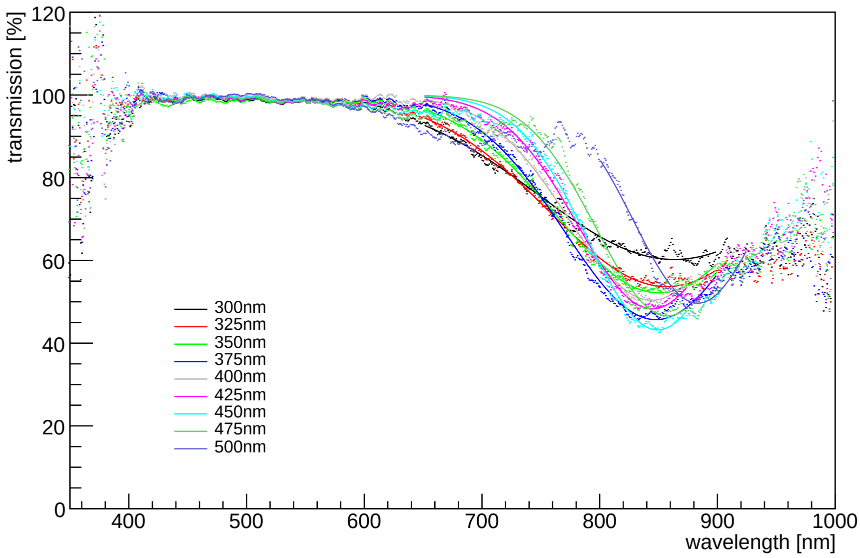

Figure 15: Transmission spectra of row C with a polarization angle of 90 deg.

4.4 Pentameters (Row D)

This row consists of pentameters, divided by a lattice constant of 900 nm and the mid-disk-to-mid-disk distance (d) varying from 150 nm all through 190 deg. The disk size itself is fixed with 140 nm.

The minima are all relatively close together, as seen in figure 17 and figure 18. The wavelength of the minima as a function of the distance d is displayed in figure 16 (90 deg in red). They agglomerate around 790 nm. This would be exactly the expected minimum for a structure of row A with a disk diameter of 140 nm (see figure 7). This tells us, that these minima are probably not from Fano resonance, as one might expect, but from the single disks itself. The spectra seem too perturbed to make out any other minima, that might resemble fano resonance. There is, however, a slight increase of the wavelength of the minima as the disk distance changes.

As expected, due to symmetry reasons, both spectra look similar.

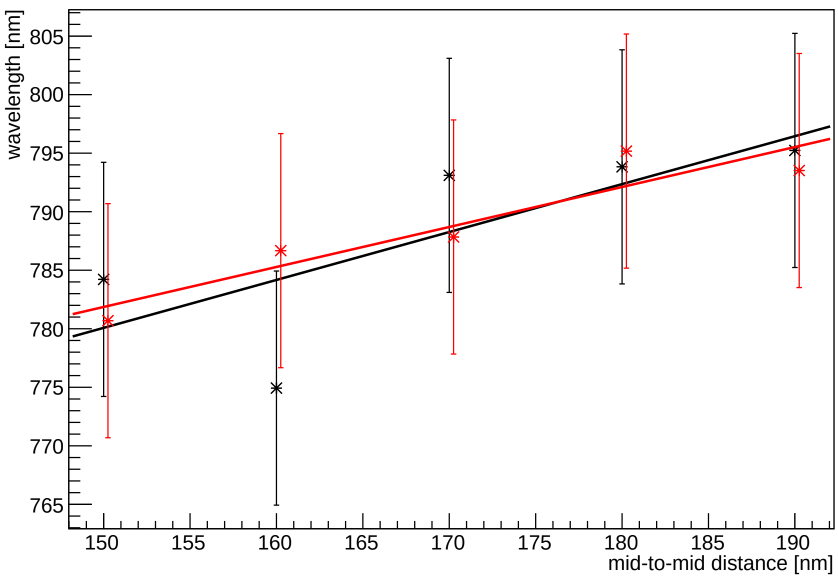

Figure 16: Position of transmission minima as a function of the mid-to-mid distance of the disks within a pentameter.

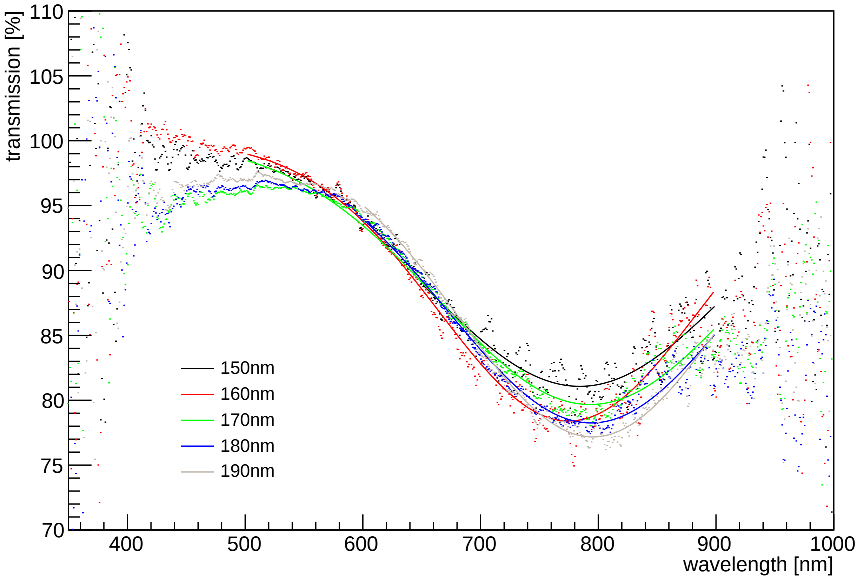

Figure 17: Transmission spectra of row D with a polarization angle of 0 deg.

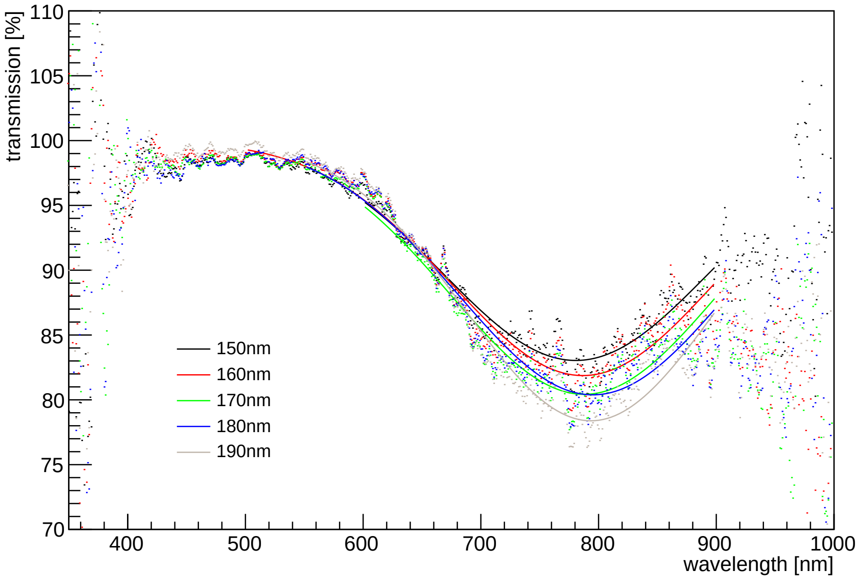

Figure 18: Transmission spectra of row D with a polarization angle of 90 deg.

4.5 Ellipses (Row E)

Row E consists of ellipses with a variable length of the major axis, ranging from 100 nm to 240 nm in steps of 20 nm and a fixed minor axis of 0 nm. The spectra are again fitted with a gaussian curve like before, to determine the minima as seen in figure 20 and figure 21. Structures E7 and E8 are for a polarization of 0 deg above 1000 nm, and thus left out.

As seen in figure 19, the minima of light polarized along the major axis (0 deg, black fit line) increase as the size of the major axis increases. This is in harmony with the theory, similarly to row A.

For light polarized perpendicular to the major axis (90 deg, red fit line) the wavelength seems to slightly decrease with the size of the major axis. This is also expected, since the relatively shorter minor axis should yield shorter wavelengths.

It should be noted that the effect for the polarization of 90 deg seems to be significantly lower - the minima are not as deep.

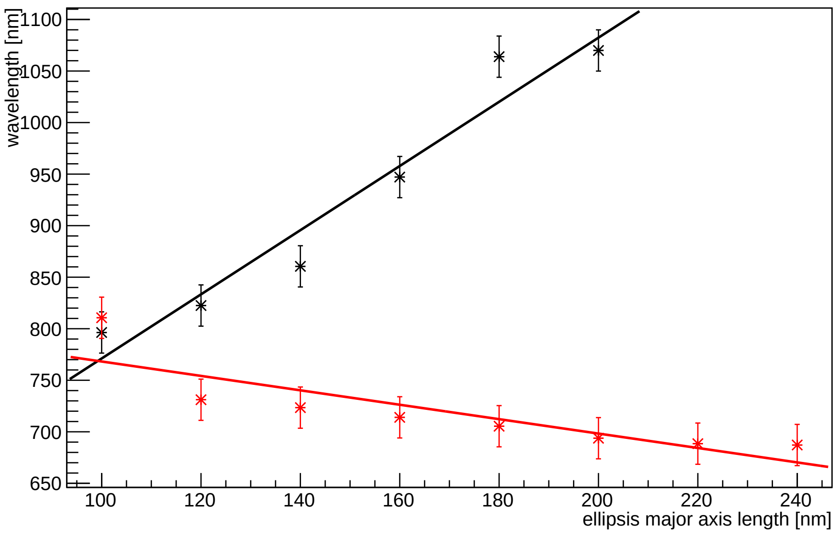

Figure 19: Position of transmission minima as a function of the major axis of the elliptical disks.

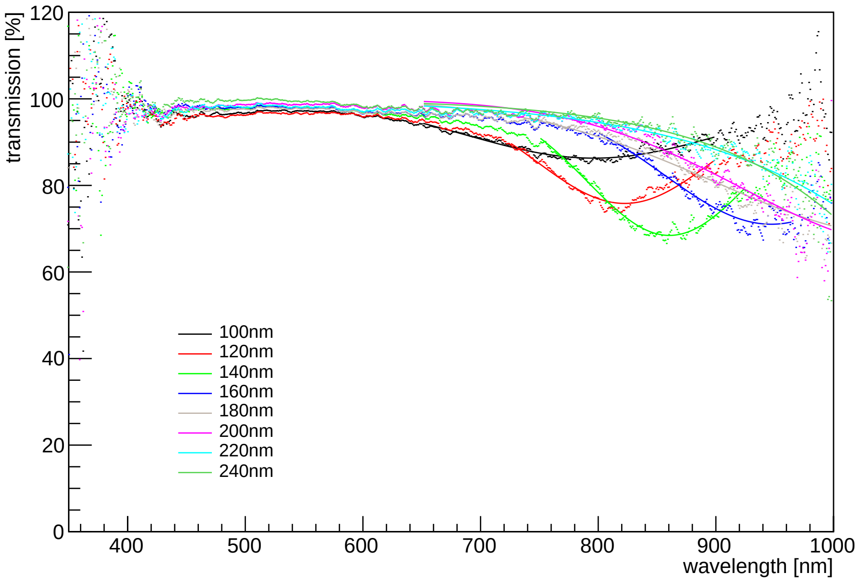

Figure 20: Transmission spectra of row E with a polarization angle of 0 deg.

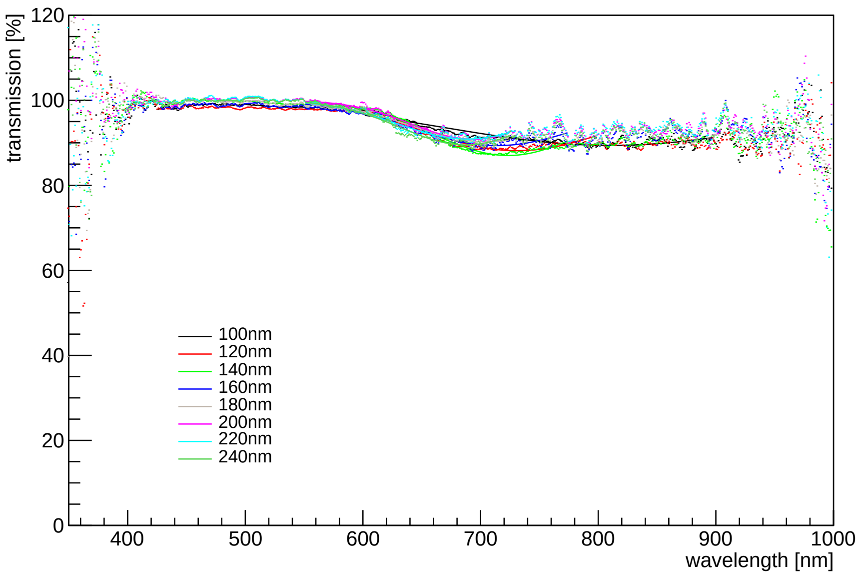

Figure 21: Transmission spectra of row E with a polarization angle of 90 deg.

5 Summary

Most of the structures behave as expected.

6 Appendix

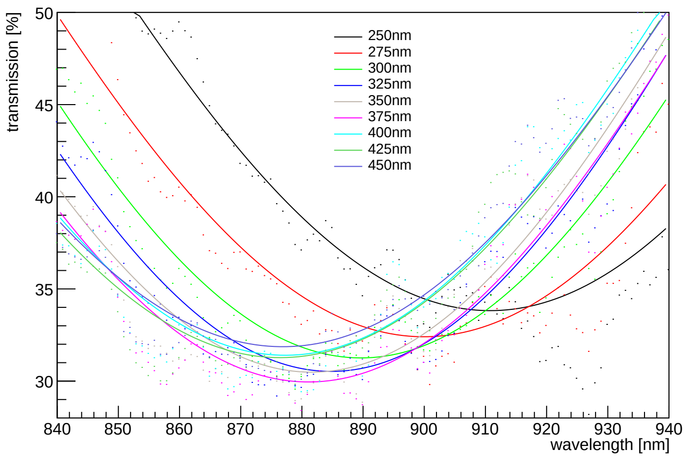

Figure 22: Zoomed transmission spectra of row B with a polarization angle of 0 deg.

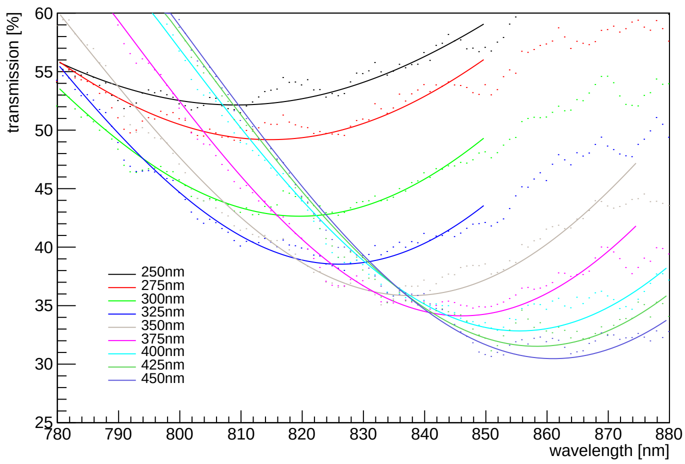

Figure 23: Zoomed transmission spectra of row B with a polarization angle of 90 deg.

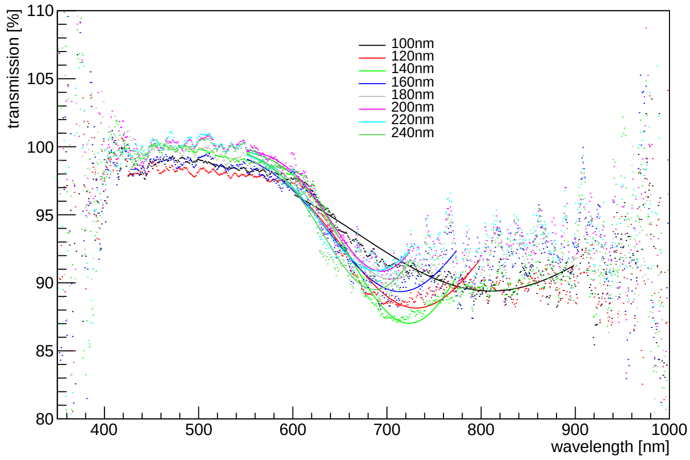

Figure 24: Zoomed transmission spectra of row E with a polarization angle of 90 deg.

References

[1] Röll, Roberto, *Weißlichtspektroskopie an metallischen Nanostrukturen* (Bachelorarbeit in Physik, Rheinische Friedrich-Wilhelms-Universität Bonn, August 2013)

[2] Source: Röll, Roberto, *Weißlichtspektroskopie an metallischen Nanostrukturen*, 2013, page 5

[3] Website: http://en.wikipedia.org/wiki/Plasmon (2014-04-30, 6:45 pm)

[4] Website: http://de.wikipedia.org/wiki/Plasmon_(2014-04-30, 6:48 pm)